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Research article

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Synthesis of bimetallic iron ferrite and its applications in alcohol fuel cell Qurat-ul-Ain¹, Suqqyana Fazal¹, Fawad Ahmad^{1*}

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Abstract

Fuel cell is a clean, safe, eco-friendly source of energy as an alternative to already existing energy resources like incineration of fossil fuel. Efficiency of fuel cell is high when platinum is used as an electrode material for both anode and cathode. However, it is very expensive metal. Bimetallic Iron Ferrite (BMIF) has shown better EOR activity considering onset potential, mass activity when compared with noble metal catalyst but it is economical as compared to Pt. XRD reveals the conformation of BMIF and its purity. FTIR before and after electrochemical analysis has confirmed the retainment of its structure. However, it hasn't shown good activity for MOR in any parameter i-e Tafel slope value, mass activity and onset potential comparatively.

Keywords: EOR, MOR, Tafel slope, Onset potential, Electrocatalyst



1.Introduction

One of the major issues that humanity is facing today is related to energy crises. Currently, incineration of fossil fuel is the major resource to meet the energy demands. However, this approach is not an environment friendly approach as it results in emission of harmful greenhouse gases and many other environmental perturbations [1]. Hence, there is a need of some alternative of already existing energy resources i-e electric batteries, fuel cell etc. The need of recharging, short life span due to charging and discharging cycles, draining dead batteries in open atmosphere, cost of electric batteries limit their use. As far as fuel cell is concerned, it is clean, reliable, efficient, sustainable, eco-friendly source of energy. Unlike batteries are thrown away, fuel cell is able to perform its function as long as fuel is provided. In hydrogen fuel cell (HFCs)

electricity up to 39.39 kWh/Kg⁻¹ can be produced which super cede the energy density of many batteries [2]. Combustion engine convert fuel's chemical energy into mechanical energy which when pass through generator convert into electrical energy. In fuel cell chemical energy is converted into electrical energy precisely but without any harmful gas emission. The efficiency of fuel cell is high almost 60-65% in comparison to combustion engine i.e. 25-30%. In comparison to HFCs, DEFCs are more preferable because of less toxicity of ethanol, its immense production from biomass fermentation [3], its energy density is high 6.34 kWhL⁻¹ as compared to hydrogen 0.53 kWhL⁻¹ [4]. DAFCs use alcohol as a fuel i-e ethanol, methanol etc. Combinely, AFCs (Alkaline fuel cells) have higher current density, low corrosion rate, low cost [5]. The energy density of ethanol is very less (24 MJdm⁻³) as compared to gasoline (34.2 MJdm⁻³). However, efficiency factor of ethanol can be mitigated by its low cost and efficient production from biomass fermentation as compared to gasoline[6]. When Platinum or palladium is used as a catalyst for both the electrodes in fuel cell, its efficiency is very high. However, platinum is a very expensive metal and according to DOE 56% cost of fuel cell is just because of platinum based catalyst [7] .Numerous studies have been done by researchers to find some catalyst that is less expensive than platinum but its efficiency should be comparative to it [8]. In this context bimetallic and trimetallic oxides have shown better activity.

In present work, considering platinum free approach Bimetallic Iron Ferrite (BMIF) material or Cobalt Zinc Iron Ferrite material has been tested for both EOR and MOR. For EOR it has shown good activity comparative to platinum however not a very good catalyst considering MOR. The catalytic activity is determined using parameters i.e. Tafel slope value, onset potential, current density and mass activity.

2. Chemicals and methods:

2.1. Synthesis of catalyst:

Bimetallic Iron Ferrite (BMIF) or Cobalt zinc ferrite $(CoZnFe_2O_4)$ particles were prepared using sol-Gel Combustion methodology. The reactants used were Fe $(NO_3)_3.9H_2O$, $Z(NO_3)_3.6H_2O$, $Co(NO_3)_3.6H_2O$. The concentration and amount of these reactants required is given in (Table 1).

All the above solutions are mixed in a proper stoichiometric amount followed by stirring for about half an hour and heating at 100°C until a dark viscous gel like thick liquid is formed. This viscous liquid is then kept in furnace to further raise the temperature up to 440°C for about half an hour. At this point, complete ignition of gel occurred. Temperature was further raised up to 800°C for 2hrs and now proper incorporation of transition metals inside spinel ferrite crystalline structure takes place [9]. After that, burnt gel was ground into fine powder using pestle and mortar. Washing of prepared material was done using ethanol and water. Finally, the drying of product takes place at 100°C in oven and then it was kept in dry place to study its electrochemical properties.

2.2. Catalyst Ink preparation:

After the synthesis of catalyst, in order to check its electrochemical activity we have to prepare the working electrode. First of all, we have prepared slurry or ink comprising Nafion membrane (as a binder), (isopropanol and ethanol 1:3) as a solvent, CoZnFe₂O₄ as a catalyst. The ratio among these three components is 1:1:1000 respectively [10]. After sonication for about 15-20 minutes a homogenous slurry will be formed. An ink drop was pasted on glassy carbon electrode (geometric surface area 0.07 cm⁻²) followed by drying in open air. After complete drying, working electrode is now ready for electrochemical analysis.

3. Catalyst characterization:

3.1: SEM:

Fig 1 (A, B) shows particles are neither exactly spherical nor of any other definite shape when observed at scale of $1\mu m$ and $5\mu m$. The relative distribution curves shows that the particle's size lies in the range of 0.08 to $0.3\pm0.02 \ \mu m$.

Table	Table 1. List of Chemicals for BMIF Synthesis				
Sr. No	Chemical	Concentration (M)	Molecular Formula	% Purity	
1	Iron(III) nitrate Nano hydrate	2	Fe(NO ₃) ₃ .9H ₂ O	98	
2	Cobaltous (II) nitrate Hex hydrate	0.5	Co(NO ₃) ₂ .6H ₂ O	98	
3	Zinc(II) nitrate Hex hydrate	0.5	Zn(NO ₃) ₂ .6H ₂ O	95	
4	Urea	6.67	NH ₂ CONH ₂	98	

Table 2: Current density of different anodic catalyst reported in literature [11].

Anodic catalyst	Electrolyte	Current density(mAcm ⁻²)
Pd/G	1M KOH+1M Ethanol	0.8
Pd-Sn/C	same	1.4
Pd-Sn-Ni/C	same	2.25
Pt-vulcan	0.1M NaOH+1M Ethanol	0.5
Pt ₃ -Sn/vulcan	same	1
Pt-Sn Vulcan	same	2.25
Pd/MnO ₂ /vulcan	0.2M KOH +1M Ethanol	0.91
Pd-Ni/MnO ₂ /vulcan	same	1.46
Pd-Ni-Fe/MnO ₂ /vulcan	same	3.03
Our material	0.5M NaOH+1M Ethanol	1.1757
PdCo/C	Same	48
Pd/C (commercial)		27

However, when analyzed at more magnified 5 μ m scale, particles were found to be of spherical shape but they were in agglomerated state due to magnetic interactions among them [12, 13]. As far as surface is concerned, it does not appear homogenous due to the polydisperse system (nonuniform size distribution). At some areas, pores are also observed. This might be due to liberation of gases at high temperature which have loosen the crystalline structure a little bit [14].

3.2. XRD:

Our sample material have shown cubic spinel structure (Figure 2) in accordance with literature reported data [15]. Spineal structure has been confirmed through the strongest or the intense peak obtained for (311) plane at $2\theta = 35^{\circ}$ [16, 17]. No extra peaks were observed in XRD plot showing high purity of our sample material [18].

Crystallite size has also been calculated using sherrer equation (0.315 μ m), which is in accordance with result obtained from SEM analysis (0.08-0.3 μ m). A crystallite consist of many particles, hence crystallite size is greater than particle size [19].

3.3. FTIR:

FTIR spectra (Figure 3, 1.4) have shown how the cations are scattered in octahedral and tetrahedral sites? Spectra existing in finger print region (400 to 600 cm⁻¹) due to metal-oxygen stretching vibrations has confirmed the spinel structure of BMIF [20]. The bands at high frequency are attributed to stretching vibration of (M_{tet} -O) while at low frequency is due to stretching vibration of (M_{oct} -O) [21]. As the bond length of tetrahedral complexes is shorter and hence their mode of vibration is high as compared to octahedral complexes [12]. The weak broader bands appear near 3400 cm⁻¹ and

peaks near 1600 cm⁻¹ (Fig1.3) is due to adsorbed moisture on ferrite surface[22, 23]. H-O-H bending vibration of water show band near 3400 cm⁻¹. The peak near 1600 cm⁻¹ is due to OH⁻ stretching vibrations [24, 25].

We have concluded from FTIR spectrum of BMIF that before and after electrochemical analysis (Figure 4), spinel structure remains persistent. All peaks are obtained in the same frequency range (400-600cm⁻¹) even after electrochemical analysis confirming the high structural stability of BMIF.

4. Electrochemical activity:

Cyclic voltammetry, linear sweep voltammetry are used to check electrochemical properties (EOR and MOR) of sample material.

Table 3: Mass	activity	of different	Pd based	electrocatalyst
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Metal catalyst	Mass activity(mAmg ⁻¹)	References
Pd/C	95 vs Hg/HgO	[26]
Pd/Bi-C	279	[27]
PdCo/C	105	[26]
Pd ₂ Ni ₃ /C	1.71	[28]

reported in literature



Figure 1: (A) BMIF SEM images at bar scale of $1\mu m$ and its relative distribution curve (B) BMIF SEM images at

bar scale of $5\mu m$ and its relative distribution curve

4.1. Ethanol Oxidation Reaction (EOR):

Mechanism of EOR is a dual pathway C_1 and C_2 pathway [29],

C₁ (complete oxidation)

$$CH_3CH_2OH \rightarrow CO + CH_X \rightarrow CO_2 + 12e^-$$

C₂ (incomplete oxidation)

 $CH_3CH_2OH \rightarrow CH_3COOH + 4e^-$



Figure 2: XRD plot for BMIF with maximum peak obtained at $2\theta=35^{\circ}$



Figure 3: FTIR spectrum of BMIF before and after electrochemical analysis in range of 4000-400 cm⁻¹



Figure 4: FTIR Spectrum of BMIF before and after electrochemical analysis in finger print region (800-400 cm⁻¹).

At high pH (alkaline medium) there is great possibility of C_1 pathway [30] as it is suggested that aldol condensation at alkaline medium supports C_1 pathway. Because the α hydrogen in CH₃ of acetaldehyde is slightly acidic, it is more prone to be attacked by (OH⁻) [31]. Consequently, C-C bond is now slightly hindered and now it is facile to break this bond. This suggestion towards selectivity of C_1 pathway is further reinforced by the fact that the intermediates of this route i-e CH_{x.ads} [32] and CO_{ads} [33] can easily be oxidized at low over potential in alkaline medium as compared to acidic one. We will determine the EOR catalytic activity of our sample material on the basis of following parameters.

Current density.

The current density calculated from the (Figure 5) at 1.5 V is $(0.0823/0.07=1.1757 \text{ mAcm}^{-2})$.when we compared the current density for different anodic catalyst reported in literature , this value is found to be in accordance as shown in (Table 2).



Figure 5: CV for BMIF at scan rate of 50 mVs⁻¹ *Mass* activity:

The mass activity of our material is calculated from (Figure 5) at 1.5V (0.0823/0.001=82.3 mAmg⁻¹) and at 0.9V (0.003517/0.001=3.517 mAmg⁻¹). The mass activity value reported in literature for other noble metal based catalyst is given in (Table1.3). The mass activity of BMIF is in good accordance with the reported values in literature for other noble catalyst.



Figure 6: LSV curves for BMIF at different scan rate.



Figure 7: Tafel plot of BMIF for EOR at different scan rate.

Onset potential:

Onset potential is the difference between equilibrium potential and the applied potential [34]. Low value of onset potential is an indication of efficient metal for EOR [35, 36]. Table 5 shows the comparison of onset potential for BMIF with other catalyst containing noble metals.

Tafel slope value:



Figure 8: Tafel slope value of two electrocatalysts (BMIF and

NZC, NiZnCuO) for EOR in different electrolyte.

(Figure 8, Table 7) shows that NZC (NiZn CuO) posses

greater tafel slope value in comparison to BMIF showing its less activity as compared to BMIF.

We have seen that (Figure 6, Table 4), with increase in scan rate the current response increases in accordance with Randles Sevick equation.

$$i_p = 0.446 nFAC^0 \left(\frac{nF\nu D_o}{RT}\right)^{1/2}$$
 eq - 1

All the observations from (Figure 6) are summarized in (Table 4).

Scan rate(mVs ⁻	Onset potential(v)	Over-potential(V)	Current response(mA)	Current density(mAcm ⁻²)
¹)				
10	0.907	1.677	0.0033	0.046
20	0.916	1.686	0.00296	0.0416
25	0.919	1.689	0.00304	0.0428
30	0.921	1.691	0.0032	0.0450
40	0.922	1.692	0.0038	0.0535

Journal of Chemistry and Environment **Table 4:** Numerical data showing current density of BMIF for EOR at different scan rate

Table 5: Onset potential for EOR of some other electro catalyst reported in literature:

Sr No;	Electrocatalyst	Onset potential(V vs RHE)	References	Over-potential(V)
1	Ni-Pd/ PVA	1.27	[37]	2.04
2	Pt _{2.3} -Ni/C	0.6	[38]	1.37
3	Ni-MnO ₂	1.32	[39]	2.09
4	Pt	0	[40]	0
5	Cu ₂ O/PPy	1.45	[41]	2.22
6	Pt/MoS ₂	0.67	[42]	1.44
7	Pt/C	1.36	[43]	2.13
8	Pd	0.9	[44]	1.67
9	Pt-CeO ₂	1	[45]	1.77
10	Co-Bi@rGO	1.28	[46]	2.05
	Our work	0.9		1.67

Table 6: BMIF tafel slope value at different scan rate

Scan rate (mVs ⁻¹)	Tafel slope value (Vdec ⁻¹)	
20	6.408 ± 0.10522	
25	6.961±0.1182	
30	6.702±0.10082	
40	6.907 ± 0.077	

At low scan rate (Figure 7) Tafel slope value is less showing best activity of catalyst (Table 6).

Table 7: Tafel slope for BMIF and NZC from (Figure 8)

Sample material	Electrolyte	Tafel slope value
BMIF	0.5M NaOH+1M Ethanol	7.748 ± 0.1334
BMIF	1M NaOH+1M Ethanol	7.127 ± 0.1080
NZC	same	8.465 ± 0.13128

Catalyst	Mass Activity (mAmg ⁻¹)[47]	Tafel slope (Vdec ⁻¹)
Pt/C at 0.45 V	4	0.619 [48]
Pd/C at 0.45V	25.4	0.182-0.195 [49, 50]
Pd based catalyst	-	0.12-0.17 [27, 51]
BMIF at 0.9V	3.517	6.9-7.7
BMIF at 1.5V	82.3	-

Table 8: comparison of BMIF EOR activity with noble metal catalyst reported in literature.

In a nutshell, BMIF is showing good mass activity comparative to Pt and Pd but at the expense of high potential. In terms of Tafel slope value our material is showing high value comparatively.

Scan rate	Onset potential	Over potential	Current response(mA)	Current density(mAcm ⁻²)
(mVs ⁻¹)	(v)	(V)		
20	0.9153	1.725	0.003259	0.04590
30	0.91094	1.720	0.002964	0.04174
40	0.9492	1.719	0.004302	0.06059
50	0.9547	1.7647	0.004971	0.07001

Table 9: Numerical data from BMIF LSV for MOR at different scan rate

4.2. Methanol oxidation reaction (MOR):

The MOR mechanism suggested is as follows[52],

 $CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$

The formal reduction potential for MOR reported in literature is -0.81 [53].



Figure 9: LSV curves of BMIF for MOR at different scan rate *Tafel slope value*:

Smaller the Tafel slope value , greater will be the over potential and hence catalyst under study would be poor [54]with increasing scan rate anodic Tafel slope value and corrosion rate also increases [55]. (Figure 10, Table 10) gives information about Tafel slope value for MOR at different scan rate. Low scan rate is again the best option to obtain good activity of BMIF for MOR.

Onset potential:

Figure 9 shows LSV curves for MOR from where we can get useful information about current density and onset potential. BMIF has shown greater value of onset potential i-e 0.8 V (Table 9) in comparison to Pt i-e 0.4 V (Table 11)

Mass activity:

The value of limiting current obtained at 0.9 V from (Figure 9) is i_1 = 0.005096 mA. The mass activity calculated is 5.095 mAmg⁻¹.(Table 9) much less than mass activity of Pt as mentioned in (Table 11).



Figure 10 : BMIF Tafel slope value at different scan rate In a nutshell, BMIF is showing good mass activity comparative to Pt and Pd but at the expense of high potential. In terms of Tafel slope value our material is showing high value comparatively.

 Table 10: BMIF tafel slope value for MOR at different scan

 rate

Scan rate mVs ⁻¹	Tafel slope value
20	6.725 ± 0.09
30	6.880 ± 0.602
40	6.980 ± 0.078
50	7.119 ±0.07

Table 11: comparison of BMIF MOR activity with noble

 metal catalyst reported in literature

Catalyst	Tafel slope (Vdec ⁻	Onset potential (V)	Mass activity(mAmg ⁻¹)
	¹)		
Pt/C	0.166[5	0.448[57]	56[58]
	6]		
BMIF	6.7-	0.8	5.095
	7.11		

BMIF haven't shown good activity for MOR in any parameter (Table 11).

5. Conclusion:

We have determined the catalytic activity of BMIF for EOR and MOR on the basis of different parameters. Spinel structure of BMIF was analyzed from XRD and retainment of this crystalline structure even after electrochemical analysis was confirmed through FTIR analysis. In terms of EOR, Onset potential and mass activity values were found in accordance with the one reported for noble metal catalyst reported in literature. However, BMIF cannot be suggested as good catalyst for MOR in comparison to noble metal catalyst.

6. Future perspective:

- Effect of temperature on activity of catalyst
- Combination of BMIF with any carbonaceous material might enhance its activity for MOR
- Poisoning of electrode due to oxides of carbon produced as a result of EOR and MOR needs further study.

Authors Contribution

QA and FA has the main idea of the manuscript. QA and SF wrote the the manuscript. FA revised the manuscript and provide suggestions.

.Conflicts of Interest

The authors reported no potential conflict of interest.

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Data Availability statement

The data presented in this study are available on request from the corresponding author.

REFERENCES

 Kannan, M., Current status, key challenges and its solutions in the design and development of graphene based ORR catalysts for the microbial fuel cell applications. Biosensors and Bioelectronics, 2016. 77: p. 1208-1220.

- Manoharan, Y., et al., Hydrogen fuel cell 11. vehicles; current status and future prospect. Applied Sciences, 2019. 9(11): p. 2296.
- Vigier, F., et al., On the mechanism of ethanol electro-oxidation on Pt and PtSn catalysts: electrochemical and in situ IR reflectance 1 spectroscopy studies. Journal of Electroanalytical Chemistry, 2004. 563(1): p. 81-89.
- Lamy, C., et al., Recent advances in the 13. development of direct alcohol fuel cells (DAFC). Journal of Power Sources, 2002. 105(2): p. 283-296.
- Kamarudin, M., et al., Direct ethanol fuel cells. 14. International journal of hydrogen energy, 2013.
 38(22): p. 9438-9453.
- Akhairi, M. and S.K. Kamarudin, Catalysts in direct ethanol fuel cell (DEFC): An overview. International Journal of Hydrogen Energy, 2016. 41(7): p. 4214-4228.
- Saedi, L., et al., Oxygen Activation on Four-Atom Metal Clusters and Alloys. Journal of Structural Chemistry, 2020. 61(4): p. 515-522.
- Nie, Y., L. Li, and Z. Wei, Recent advancements in Pt and Pt-free catalysts for 16. oxygen reduction reaction. Chemical Society Reviews, 2015. 44(8): p. 2168-2201.
- Das, I., et al., Synthesis of bimetallic iron ferrite CoO. 5ZnO. 5Fe₂O₄ as a superior catalyst for oxygen reduction reaction to replace noble metal catalysts in microbial fuel cell. International Journal of Hydrogen Energy, 2018.
 43(41): p. 19196-19205.
- 10. Ahmad, F., et al., Boosting fuel cell catalysis by surface doping of W on Pd nanocubes. Chinese 18. Journal of Catalysis, 2018. 39(7): p. 1202-1209.

- Kazan, E.S. and M. Bayramoğlu, Molybdenum
 compound cocatalyzed Ni-based anode
 electrocatalysts for EOR in alkaline media.
 International Journal of Energy Research, 2021.
 45(9): p. 12806-12824.
- Tatarchuk, T., et al., Structural characterization and antistructure modeling of cobalt-substituted zinc ferrites. Journal of Alloys and Compounds, 2017. 694: p. 777-791.
 - Borhan, A.I., et al., Cr³⁺ and Al³⁺ co-substituted zinc ferrite: Structural analysis, magnetic and electrical properties. Polyhedron, 2014. 70: p. 110-118.
 - 4. Tatarchuk, T., et al., Spinel cobalt (II) ferritechromites as catalysts for H_2O_2 decomposition: Synthesis, morphology, cation distribution and antistructure model of active centers formation. Ceramics International, 2020. **46**(17): p. 27517-27530.
- 15. Vaidyanathan, G. and S. Sendhilnathan, Characterization of Co_{1-x}Zn_xFe₂O₄ nanoparticles synthesized by co-precipitation method. Physica B: Condensed Matter, 2008. 403(13-16): p. 2157-2167.
 - Betancourt-Galindo, R., O. Rodríguez-Fernández, and E. Medina-Rodríguez, Obtención de látex magnético mediante la técnica de polimerización en miniemulsión. Superficies y Vacío, 2004. 17(1): p. 38-41.
- 17. Kim, Y.I., D. Kim, and C.S. Lee, Synthesis and characterization of CoFe₂O₄ magnetic nanoparticles prepared by temperature-controlled coprecipitation method. Physica B: Condensed Matter, 2003. 337(1-4): p. 42-51.
 - Bohara, R., et al., Synthesis of functionalized CoO. 5ZnO. 5Fe₂O₄ nanoparticles for biomedical

applications. Journal of Magnetism and Magnetic Materials, 2015. **378**: p. 397-401.

- Sumari, S., A. Roesyadi, and S. Sumarno, Effects of ultrasound on the morphology, 26. particle size, crystallinity, and crystallite size of cellulose. Scientific Study & Research. Chemistry & Chemical Engineering, Biotechnology, Food Industry, 2013. 14(4): p. 229.
- 20. Kaur, H., et al., Structural, thermal and 27. magnetic investigations of cobalt ferrite doped with Zn^{2+} and Cd^{2+} synthesized by auto combustion method. Journal of Magnetism and Magnetic Materials, 2019. **474**: p. 505-511. 28.
- Slatineanu, T., et al., Synthesis and characterization of nanocrystalline Zn ferrites substituted with Ni. Materials Research Bulletin, 2011. 46(9): p. 1455-1460.
- Kannan, K., et al., Structural and biological properties with enhanced photocatalytic behaviour of CdO-MgO nanocomposite by microwave-assisted method. Optik, 2020. 204: p. 164221.
- Revathi, V. and K. Karthik, Physico-chemical properties and antibacterial activity of Hexakis (Thiocarbamide) Nickel (II) nitrate single crystal. Chemical Data Collections, 2019. 21: p. 100229.
- 24. Suresh, S., et al., Green synthesis of copper oxide nanostructures using Cynodon dactylon and Cyperus rotundus grass extracts for antibacterial applications. Ceramics 32. International, 2020. 46(8): p. 12525-12537.
- 25. Harris, R.I., Discussion of "The annual rate of independent events for the analysis of extreme wind speed" by Alessio Torrielli, Maria Pia

Repetto & Giovanni Solari. Journal of Wind Engineering and Industrial Aerodynamics, 2017. **100**(164): p. 174-178.

- 26. Sankar, S., et al., Cobalt-Modified Palladium Bimetallic Catalyst: A Multifunctional Electrocatalyst with Enhanced Efficiency and Stability toward the Oxidation of Ethanol and Formate in Alkaline Medium. ACS Applied Energy Materials, 2018. 1(8): p. 4140-4149.
 - . Cai, J., Y. Huang, and Y. Guo, Bi-modified Pd/C catalyst via irreversible adsorption and its catalytic activity for ethanol oxidation in alkaline medium. Electrochimica Acta, 2013. **99**: p. 22-29.
- Zhang, Z., et al., Pd–Ni electrocatalysts for efficient ethanol oxidation reaction in alkaline electrolyte. International Journal of Hydrogen Energy, 2011. 36(20): p. 12686-12697.
- 29. Lan, B., et al., Ethanol Electrooxidation on Rhodium–Lead Catalysts in Alkaline Media: High Mass Activity, Long-Term Durability, and Considerable CO₂ Selectivity. Small, 2020. 16(40): p. 2004380.
- Rao, V., C. Cremers, and U. Stimming, Investigation of the ethanol electro-oxidation in alkaline membrane electrode assembly by differential electrochemical mass spectrometry. Fuel Cells, 2007. 7(5): p. 417-423.
- Guthrie, J.P., Rate-equilibrium correlations for the aldol condensation: an analysis in terms of Marcus theory. Journal of the American Chemical Society, 1991. 113(19): p. 7249-7255.
 - . Lai, S.C. and M.T. Koper, Ethanol electrooxidation on platinum in alkaline media. Physical Chemistry Chemical Physics, 2009. **11**(44): p. 10446-10456.

- 33. García, G. and M.T. Koper, Stripping 40. voltammetry of carbon monoxide oxidation on stepped platinum single-crystal electrodes in alkaline solution. Physical Chemistry Chemical Physics, 2008. 10(25): p. 3802-3811.
- 34. Pegis, M.L., et al., Standard reduction potentials
 for oxygen and carbon dioxide couples in acetonitrile and N, N-dimethylformamide.
 Inorganic Chemistry, 2015. 54(24): p. 11883-11888.
- Rostami, H., A.A. Rostami, and A. Omrani, An electrochemical method to prepare of 42. Pd/Cu₂O/MWCNT nanostructure as an anode electrocatalyst for alkaline direct ethanol fuel cells. Electrochimica Acta, 2016. 194: p. 431-440.
- Gu, Y., et al., A ternary nanocatalyst of 43. Ni/Cr/Co oxides with high activity and stability for alkaline glucose electrooxidation. Electrochimica Acta, 2016. 192: p. 296-302.
- 37. Mohamed, I.M., et al., Electrocatalytic behavior of a nanocomposite of Ni/Pd supported by 44. carbonized PVA nanofibers towards formic acid, ethanol and urea oxidation: A physicochemical and electro-analysis study. Applied Surface Science, 2018. 435: p. 122-129.
- Sulaiman, J.E., et al., Pt–Ni octahedra as electrocatalysts for the ethanol electro-oxidation 4 reaction. ACS Catalysis, 2017. 7(8): p. 5134-5141.
- 39. Nakayama, M., K. Suzuki, and K. Fujii, Singleion catalyst of Ni²⁺ anchored in the interlayer space of layered MnO₂ for electro-oxidation of ethanol in alkaline electrolyte. Electrochemistry 46. Communications, 2019. **105**: p. 106492.

- Wang, B., et al., Electrocatalytic oxidation of small molecule alcohols over Pt, Pd, and Au catalysts: The effect of alcohol's hydrogen bond donation ability and molecular structure properties. Catalysts, 2019. **9**(4): p. 387.
- A., El Attar. et al., Preparation and 41. characterization of copper oxide particles/polypyrrole (Cu_2O/PPv) via electrochemical method: Application in direct ethanol fuel cell. International Journal of Hydrogen Energy, 2020. 45(15): p. 8887-8898.
 - Wang, J., et al., MoS₂ nanoflower supported Pt nanoparticle as an efficient electrocatalyst for ethanol oxidation reaction. International Journal of Hydrogen Energy, 2019. 44(31): p. 16411-16423.
 - Ma, K.-B., et al., Direct ethanol fuel cells with superior ethanol-tolerant nonprecious metal cathode catalysts for oxygen reduction reaction. ACS Sustainable Chemistry & Engineering, 2018.
 6(6): p. 7609-7618.
 - Zhang, R.-L., et al., One-step aqueous synthesis of hierarchically multi-branched PdRuCu nanoassemblies with highly boosted catalytic activity for ethanol and ethylene glycol oxidation reactions. Applied Surface Science, 2020. **506**: p. 144791.
- 45. Murphin Kumar, P.S., et al., Pt nanoparticles supported on mesoporous CeO₂ nanostructures obtained through green approach for efficient catalytic performance toward ethanol electrooxidation. ACS Sustainable Chemistry & Engineering, 2017. 5(12): p. 11290-11299.
 - Munde, A.V., et al., Electrocatalytic ethanol oxidation on cobalt-bismuth nanoparticledecorated reduced graphene oxide (Co-Bi@

rGO): reaction pathway investigation toward direct ethanol fuel cells. The Journal of Physical Chemistry C, 2021. **125**(4): p. 2345-2356.

- 47. Ma, L., D. Chu, and R. Chen, Comparison of 55. ethanol electro-oxidation on Pt/C and Pd/C catalysts in alkaline media. International Journal of Hydrogen Energy, 2012. 37(15): p. 11185-11194.
- 48. Pushkarev, A.S., et al., Pt/C and Pt/SnOx/C 56. catalysts for ethanol electrooxidation: Rotating disk electrode study. Catalysts, 2019. 9(3): p. 271. 57.
- 49. Tripković, A., K.D. Popović, and J. Lović, The influence of the oxygen-containing species on the electrooxidation of the C1–C4 alcohols at some platinum single crystal surfaces in alkaline solution. Electrochimica Acta, 2001. 46(20-21): p. 3163-3173.
- Shen, S., T. Zhao, and J. Xu, Carbon supported PtRh catalysts for ethanol oxidation in alkaline direct ethanol fuel cell. international journal of hydrogen energy, 2010. 35(23): p. 12911-12917.
- Wang, M., W. Liu, and C. Huang, Investigation of PdNiO/C catalyst for methanol electrooxidation. International Journal of Hydrogen Energy, 2009. 34(6): p. 2758-2764.
- 52. Yuda, A., A. Ashok, and A. Kumar, A comprehensive and critical review on recent progress in anode catalyst for methanol oxidation reaction. Catalysis Reviews, 2022. 64(1): p. 126-228.
- Yu, E.H., U. Krewer, and K. Scott, Principles and materials aspects of direct alkaline alcohol fuel cells. Energies, 2010. 3(8): p. 1499-1528.
- 54. Qin, Y.-H., et al., Effect of carbon nanofibers microstructure on electrocatalytic activities of

Pd electrocatalysts for ethanol oxidation in alkaline medium. International Journal of Hydrogen Energy, 2010. **35**(15): p. 7667-7674.

- Prajitno, D.H. Effects of scan rate on the corrosion behavior SS-304 stainless steel in the nanofluid measured by Tafel polarization methods. in AIP Conference Proceedings. 2015. AIP Publishing LLC.
- Fang, Y.-H. and Z.-P. Liu, First principles Tafel kinetics of methanol oxidation on Pt (111). Surface Science, 2015. 631: p. 42-47.
 - . Zhang, Z., et al., Single-atom catalyst for highperformance methanol oxidation. Nature communications, 2021. **12**(1): p. 1-9.
- 58. Wang, Y., et al., Promoting effect of nickel hydroxide on the electrocatalytic performance of Pt in alkaline solution. Dalton Transactions, 2018.
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Research article

Identification of Sources and Mobilization of Trace Elements in Shallow Groundwater of the Upper Ganges River Basin Md Sheigdul Islam^{1*} M. C. Mastafa², Muhammad Tausaaf³⁴

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Abstract

The concentration of trace metals in groundwater is still not within the usual standards established by the national and international monitoring authorities. This study aims to evaluate the sources and distribution of trace metals in the shallow aquifer water of the Ganges River basin in the Bangladesh area. A total of 40 groundwater samples were collected and investigated for 11 trace elements and some selected water parameters followed by sophisticated methods. The results presented that three metals, viz. Fe, Mn, and Pb crossed the limit of WHO standard in most of the samples (70-100%) representing severe human health hazards. Besides, the samples are slightly acidic to basic and highly mineralized by divalent cations and bicarbonate because total hardness was found very high. To assess factors affecting the trace metal loads in groundwater samples and determine their possible sources and mobility, multivariate statistical techniques, including Pearson's correlation coefficient, principal components analysis, and dendrogram cluster analysis are performed. Results revealed that sources of trace elements were identified to be geologic and little from human activities, i.e., application of agrochemicals, excess water mining, and industrial wastewater. It was recognized that the elevated concentration of trace elements in samples was caused by geogenic factors rather than manmade activities. Groundwater in this area poses a large threat due to high levels of trace metals, without any purification, it is essential to avoid this water for drinking. It advised that the groundwater quality should be constantly monitored for sustainable water quality management in the study zone.

Keywords: Aquifer basement, Geogenic process, Groundwater, Multivariate analysis, Rock weathering, Toxicity

1.Introduction

Recently, groundwater quality and quantity are drastically deteriorating in Bangladesh due to over-exploitation of water, excessive use of agrochemicals, urbanization, and vast industrialization [1]. Moreover, frequent changes in geogenic processes and some anthropogenic causes deteriorated massively the groundwater quality concerning trace and heavy metal pollution in some parts of the country during the last 3-4 decades [2, 3]. Thus, the proper evaluation of sources and mobilization mechanisms of harmful trace metals such as Fe, Mn, Co, Cd, Pd, Cr, Hg, As, Zn, Cu, etc. (at a certain concentration) in aquifer basements is very important to ensure safe water for all-purpose uses. Groundwater contamination through trace elements is a global problem and a serious threat to public health, the natural ecosystem, food resources, and facilities [4]. Due to the consumption of groundwater, the

presence of toxic elements in human physiology can cause numerous problems. These elements in small amounts in the body may preserve cells. Though, the presence of more than the threshold limit of these elements may cause damage to the biotic organisms [5]. Trace metal analysis, distribution, and source identification in groundwater samples of the Bengal delta (Ganges basin) are the major aim of this study.

Trace metals have the property of ecosystem perseverance and bioaccumulation, and these metals pass in the aquatic system through several routes. These elements can be found on the earth's crust in their regular form. Some of them are very toxic and they not only harm the quality of the aquatic environment but also human well-being [6]. These metals are so hazardous that they cannot be degraded or decomposed in ecosystems and they have the arability to bioaccumulate [7]. Trace elements once get into the environment through the air, drinking water, or numerous chemicals and products that are manmade. The toxicity of these elements in the human body system decreases energy levels; disturbs brain functioning; disrupts the operation of numerous other organs such as the kidney, lungs, brain, and liver; and hampers blood composition.

Trace metals have two major sources in groundwater: (a) natural or geogenic and (b) anthropogenic or manmade sources. Natural sources include the dissolution of parent rocks at the aquifer level [8]. At first, these metals or their minerals accumulate in the soil layer, which is leached with rain or flood water and finally reaches the sub-surface water layer. The sources of trace metals in groundwater through human activities are well defined but the natural or geogenic activities are not easy to identify. These metals are found in high concentrations in the environment, they are formed by natural courses such as volcanic eruptions, dissolution of rocks/minerals in the water phase, and discharge into rivers, lakes, and oceans owing to the action of water [9]. Loads of trace metal in groundwater depend on the groundwater's local lithology or geology, hydrogeology, and geochemistry [10]. One of the chief geogenic sources of metal contamination is the dissolution of metal-laden rocks in groundwater. The

dissolution of sedimentary rocks such as calcite, dolomite, shale, or mixed rock makes the water polluted through the high level of toxic metals. When the interaction of water with rock elements occurs, it leads to the addition of these metals into the water phase; thus, pollution arises. Examples of such rocks are basalt, gabbro, granite, siderite, calcite, cuprite, calamine, azurite, smithsonite, malachite, chromite, arsenic trioxide, orpiment, kaolinite, montmorillonite, arsenopyrite, pyrolusite, nepheline, andesite, etc. [11, 12, 13]. The sulfide ore deposition also rises as it is connected with the mineralization of the gold and hydrous iron oxide (Fe_xO_y.nH₂O) rocks [14]. In this investigation, to assess factors affecting the level of trace metals in groundwater and identification their possible sources and mineralization processes, multivariate statistical techniques, including Pearson's correlation coefficient, principal and robust components analysis, and dendrogram cluster analysis are used.

2. Methods and Materials

2.1 Study area

The investigated area is part of Kushtia District, which is positioned at 23°41' and 24°11' north latitudes and 89°22' east longitudes. The total study zone is 1620.5 sq km and is bounded by the Padma River (Ganges River) and the other three branched rivers making a big deltaic flood plain (Fig. 1). The populace of that area is about 2.5 million and the majority of the inhabitant involved in farming activities [15]. The soil characteristics in this zone are very fertile with nutrient-rich sediments as the area lies in the floodplain of the Ganges River. The top-soil characterizes plain geomorphology which appears to level landscape with a raise of around 9 m above sea level, but in some parts, it contains shallow depression and slightly higher edges [16]. This area is enclosed by subtropic humid weather with warm and rainy in the monsoon and marked dry periods in the winter season. The maximum temperature is mostly detected in May-June and the lowest in December-January. The study area received a total rainfall of 1165 mm per year. About 95% of groundwater is utilized for irrigation events and the remaining for ingesting as drinking water.

The primary aquifer of the study area contains unconsolidated

alluvial sediment which is spread over the top surface by the porous sand, silt, and clayey soil. The geology of the study area comprises young alluvial deposits, deltaic silt deposits, stream, and flood-plain deposits, calcareous sandstone, and conglomerate.



Figure 1: Study area and sampling sites.

According to sub-surface hydrogeological information, it seems that the most important good aquifer in this zone occurs between 20 to 150 m depth from the surface layer. The deepness of the local aquifer varies because of the influences of basement rock thickness and the crosswise extent of the aquifer. The course of aquifer water flow in the study zone is usually from east-north to west-south.

2.2 Sampling strategy

The selection of sampling locations, collection, transportation, type of parameters, and analytical methods of the groundwater samples are the important factors for the present study's rational sampling and analytical strategy. The sampling area is rural and peri-urban. The sampling strategy is based on the identification of trace metal sources and justifies the water quality for drinking purposes. The nonpoint metal pollution sources (diffused sources) are the most common compared to the point sources (single source) in sampling areas. Nonpoint source pollution is the leading cause of water pollution in Bangladesh because it is challenging as there is no single identifiable source. In the study area, runoff and overflooding that has accumulated contaminants can sweep sediment, surface pollutants, nutrients, pesticides, fertilizer, inorganic pollutants, livestock wastes, human excreta, etc., into water bodies. Most of the

portions of these matters are leached into the subsoil and finally reach the ground aquifers. With other causes, the overall water quality of the study area is deviated by the above external sources. Table 1 represents the sampling descriptions and probable pollution sources of the group of sampling stations.

For physical and chemical analysis of groundwater, three sampling periods viz. April-May (Pre-monsoon), July-August (Monsoon), and October-November (Post-monsoon) were selected. Groundwater was collected from the shallow aquifer of both residential and agricultural areas, which was up to approximately 100 m below the surface, less than 100 years old, and continuous recharge by rainwater and river streams. Samples were collected randomly from the selected hand pump well to cover the topographical extension of the study area and the key geologic sceneries. It was collected from two different zones viz., residential and agricultural areas, and the depth of sampling wells ranged from 22 to 110 m.

2.3. Analytical procedure

A 40 groundwater sampling sites in the middle-western area of Bangladesh (Fig. 1) were selected for this study throughout the pre-monsoon (PRM), monsoon (MON), and post-monsoon (POM) periods in 2019-2020 and 2020-2021. Samples were collected from each administrative sub-zone of the 4 Upazilas of Kushtia district. Water samples were taken out in washed high-density polyethylene (HDP) plastic flasks as stated by the usual procedure [17]. After 3-5 min. of pumping, the water samples were collected to avoid any debris. For trace metal investigation, the samples were well-preserved with AR grade HNO₃ and kept at 4°C for further analysis. The study measured a total of 11 trace metal parameters such as iron (Fe), manganese (Mn), nickel (Ni), chromium (Cr), cadmium (Cd), lead (Pb), cobalt (Co), arsenic (As), boron (B), copper (Cu), and zinc (Zn) with some associated physicochemical water parameters such as pH, total hardness (TH), electrical conductivity (EC), and total dissolved solids (TDS). Instantly pH, EC, and TDS were measured in the sampling field by the portable multimeter, and TH was estimated by the general titrimetric method. Trace elements were analyzed by the well-

Sampling field	Sample ID	Point sources	Nonpoint sources
Residential area	1, 2, 3, 4, 5, 6, 7, 8, 11, 18, 19, 23,	- On-site septic systems, leaking	- Atmospheric deposition and hydrologic modification
• Shallow well (22-65 m)	24, 26, 32, 35, 36, 37, 38, and 39.	septic tanks - Landfill - Livestock wastes	- Microbes and nutrients coming from pet washes, livestock, and damaged septic systems
• Relatively high land			- Drainage, seepage - Flooding or overflow
 Mostly in river valley area 			 land runoff Soil erosion and sediment runoff
Agricultural area	9 10 12 13 14	- Livestock wastes	- Land runoff flooding waterlogging
	15, 16, 17, 20, 21,	- Landfill	- Chemical pesticides and fertilizers that
• Shallow/Semi-deep well (40-110 m)	22, 25, 27, 28, 29, 30, 31, 33, 34, and 40.		infiltrate the soil and make their way into an aquifer - Soil washed and erosion from heavy
• Mostly in deltaic basin area			farming - Contaminants in rainwater Atmorpheric deposition and
• Relatively low land			Annospierie deposition and hydromodificationOrganic wastes from farmlands

 Table 1: Sampling descriptions and probable metal and other pollution sources of the sampling stations.

accepted method through Atomic Absorption Spectrophotometer (AAS: Perkin-Elmer Model 3110). Quality control of investigation was kept in all metal analyses as stated by distinct instruction manuals and method accuracy was more than 95% in confidence interval (*CI*) with the correlation coefficient, $r = \sim 1$ of individual calibration curves.

2.4. Statistical and geostatistical analysis

Several statistical techniques such as Pearson's correlation matrix, robust and principal component analysis (PCA), Hierarchical cluster analysis (HCA), bivariate plot, etc. were used to evaluate the source of solutes in the groundwater solution. All the statistical computations were accomplished using IBM-Excel Worksheet, IBM-SPSS v-26 programs, and geostat v-2. Data screening exhibited that the data are normally skewed. Consequently, the data sets were log-transformed and resembled more closely to normally distributed data. At that time, all variables were standardized by computing their standard scores (z-scores). The PCA and the factor analysis are different types of

her Model 3110). processes that are the primary methods to recognize the geochemical weathering that designates the aquifer mineralization. These are discriminating the factors like manmade and geogenic processes that impact groundwater fficient, $r = \sim 1$ of chemistry [18, 19, 20]. The factors are self-determining, and varimax rotation was exploited to recognize factors encompassing the highest (normally distributed) variability; the variability is implied as an eigenvalue [21, 22]. Factors are considered with eigenvalues greater than one, thus limiting the number of factors used in the PC analysis. Cluster analysis (CA) is a valuable tool to organize samples into classified collections. The Q- and R- modes HCAs of

into classified collections. The Q- and R- modes HCAs of the water samples were presented to the outline groups of samples with the content of geochemical parameters and provided helpful statistics from the component analysis.

analysis. While these analyses are ordination statistical

4. Results and Discussion

4.1. Trace metal distribution in groundwater samples

Trace metals are a widespread limit of contaminations (mg/L) and steady a human health concern owing to their toxicity

dimensions even in low concentrations and can show an opposite impact on living existences with whole ecosystems and a tendency to biomagnification and bioaccumulate in lipids, fat, or tissues of organisms over time being [23, 24]. The metals such as Cr. Co, Cd, Pb, Hg, and As have no essential function in human physiology. Furthermore, long-term exposure may cause acute disruptions in the normal operations of the human organ systems where those metals are accumulated [6]. Several trace metals, like Fe, Mn, Cu, and Zn, play as micronutrients and are required in the human body in limited quantities for metabolic actions, but, at a higher level can cause opposite health effects [4]. The main manmade sources of trace elements in groundwater are natural substances percolated into the soil system or rocks, the residue of agrochemicals, precise release from the industrial run-off and sewage treatment plant, and uncontrolled escape from landfill spots and chemical accidents or disasters [25]. The groundwater is contaminated with excessive trace metals, particularly arsenic, and has become an alarming situation in Bangladesh. A total of 11 trace metals were investigated during three sampling seasons and the obtained results are stated in Table 2. On the other hand, Fig. 2 shows the average concentration of these metals in three sampling periods. The result showed that the metal concentrations usually obtained in the order were of the PRM<MON<POM sampling periods. The standard deviation (±SD) of all data is found to be very poor, and a low standard deviation means data are clustered around the mean concentrations. Besides, the skewness values showed that the data is normally distributed [26].

The study results revealed that an average of 100% of water samples carried an excess level of Fe and Mn in all sampling periods. The mean Fe and Mn concentrations of the three sampling periods were 8.435 and 2.848 mg/L, which are much greater than the permissible limit (Table 3). So, Fe and Mn contaminated water could seriously threaten public health and irrigation in the study area. On the other

hand, same Table 3 illustrated that analyzed results showed that around 50% of samples contained overloaded As (0.009 mg/L), Co (0.045 mg/L), Ni (0.320 mg/L), Cr (0.047 mg/L), and Cd (0.008 mg/L) than threshold limits. But the average concentration of Zn and Cu in groundwater in the study area was found 4.027 and 1.693 mg/L, of which 70.9 and 34.1% of samples cross the tolerance level, respectively (Table 3).

4.2. Source rock of metals in an aquifer

The bioavailability of metals in groundwater depends on various physical, lithological, chemical, and bacteriological factors in sedimentary aquifers. The availability of metals at the sediment level is closely tied to the quantity of sedimentladen trace metal dissolved in neighboring pore water. In oxic sediments, many metals may be adsorbed on the surface of clay particles; and Fe, Mn, and Ni oxides are coated on clay or organic particles [27]. As the level of O_2 in sediment reduces, typically due to bacterial degradation, the metaloxide coatings begin to dissolve, liberating adsorbed metals. In anoxic sediments, several metals react with sulfides produced by microbial actions to form unsolvable metal sulfides [28]. Metals may be unconfined from sorbet into sediment pore water in ionic forms during changes in pH and oxidation-reduction potential (Eh). For example, in oxicsediment, Cu and Ni are adsorbed on the surface of organic matter (OM) with Fe/MnO and only Fe/MnO respectively. In anoxic sediment, these two metals (Cu and Ni) are adsorbed on the surface of sulfide rocks of Cu and Fe (Cu₂S, CuS, FeCuS, etc.) and OM/NiS respectively [29]. Also, adsorbed metals may release into pore water by microbial degradation of organic matter. Certain microbes can methylate some metals, such as mercury, arsenic, and lead, into organic types that are more available than inorganic forms [30]. Except for the geogenic mechanism of metal dissolution in groundwater, metal concentrations can increase by anthropogenic causes. Based on the average metal concentration of different sampling seasons, some statistical methods are used here to find out the corresponding source of each trace metal.

4.3. Sources and dissolution of trace metals

Table 2: Statist	cal analysis of	trace metals	in the g	groundwater	samples o	of the	Pre-monsoon	(PRM),	Monsoon	(MON),	and
Post-monsoon (1	OM) sampling	seasons.									

	Pre-mon	soon (PR	M)								
	В	Fe	Mn	Cr	Pb	Co	Ni	Cd	As	Cu	Zn
Min.	0	1.14	0.66	0	0	0	0	0	0	0.03	0.79
Max.	1.25	12.62	4.84	0.088	0.096	0.088	1.095	0.051	0.019	3.11	6.63
Mean	0.631	7.997	2.725	0.043	0.035	0.043	0.304	0.008	0.009	1.592	3.940
SD (±)	0.394	3.156	1.227	0.024	0.034	0.023	0.351	0.011	0.006	0.831	1.618
Skewness	-0.416	-0.438	0.115	-0.397	0.482	-0.476	1.132	2.131	0.077	-0.108	-0.273
	Monsoon	(MON)									
Min.	0	1.87	0.46	0	0	0	0	0	0	0.14	0.79
Max.	1.235	13.73	5.66	0.088	0.092	0.097	1.185	0.042	0.019	3.32	6.72
Mean	0.661	8.521	2.872	0.048	0.038	0.045	0.324	0.008	0.009	1.732	4.047
SD (±)	0.395	3.273	1.373	0.023	0.031	0.025	0.358	0.011	0.007	0.865	1.584
Skewness	-0.374	-0.308	0.143	-0.665	0.328	-0.362	1.168	1.979	-0.089	-0.091	-0.365
	Post-mor	isoon (PC	M)								
Min.	0	1.985	0.540	0	0	0	0	0	0	0.090	0.670
Max.	1.450	14.440	5.605	0.095	0.099	0.093	1.190	0.045	0.022	3.370	6.770
Mean	0.692	8.783	2.944	0.051	0.040	0.047	0.332	0.008	0.009	1.755	4.085
SD (±)	0.419	3.3503	1.360	0.023	0.031	0.024	0.355	0.012	0.007	0.880	1.607
Skewness	-0.170	-0.443	0.09	-0.550	0.269	-0.570	1.145	2.008	0	-0.110	-0.410



Fig. 2. Average metal concentrations (mg/L) of three sampling seasons. The concentrations of Fe, Mn, Cu, Zn, B, and Ni are denoted by $100 \times mg/L$.

The presence of trace metals in the groundwater can be due to geochemical, geogenic, or human activities. In natural or geogenic activities, the dissolution of minerals or rocks that contain these metals, soil-water interaction, an explosion from volcanos, deposition of atmospheric salts, and geological occurring processes of dissolution can be comprised [31]. From these happenings, trace metals enter dissimilar units of the environment. Trace metals can be found in the forms of sulfates, sulfides, oxides, hydroxides, phosphates, and silicates or mixed types [32]. Although the rapid increase in industrialization and urbanization is an example of manmade sources through which water gets polluted by trace metals. The local geology, agrochemicals leaching, overexploitation of groundwater, etc., were the major causes of toxic metals in drinking water [33, 34, 35]. The metal concentration in groundwater sometime depends

Metal	Pre- PRN	monsoon, $4 (n = 40)$	Monsoo (MO	Monsoon, Post- (MON) (n=40) POM		Post-monsoon, POM (n = 40)		Average %Samples crossed the WHO std.	The	e MLC val Irinking wa	ue for ater
	Mean value	%Samples exceed the	Mean value	%Samples exceed the	Mean value	%Samples exceed the	-		WHO [45]	USEPA [17]	DPHE ^a [16]
		WHO std.		WHO std.		WHO std.					
В	0.631	0	0.661	0	0.692	0	0.661	0.0	2.4	None	1.0
Fe	7.997	100	8.521	100	8.783	100	8.434	100.0	0.3	0.3	0.3-1.0
Mn	2.725	100	2.872	100	2.944	100	2.847	100.0	0.1	0.05	0.1
Cr	0.043	52.5	0.048	47.5	0.051	37.5	0.047	48.7	0.05	0.1	0.05
Pb	0.035	60	0.038	70	0.040	80	0.038	70.0	0.01	0.015	0.05
Co	0.043	42.5	0.045	47.5	0.047	55	0.045	48.2	0.05	None	None
Ni	0.304	50	0.324	55	0.332	55	0.320	53.2	0.1	0.1	0.1
Cd	0.008	47.5	0.008	50	0.008	47.5	0.008	48.4	0.003	0.005	0.003
Cu	1.592	32.5	1.732	35	1.755	35	1.693	34.1	2.0	1.3	1.0
Zn	3.940	72.5	4.047	72.5	4.085	67.5	4.025	70.9	3.0	5.0	5.0
As	0.009	47.5	0.009	50	0.009	52.5	0.009	50.0	0.01	0.01	0.05

Table 3: Statistics of trace metal compositions in groundwater during the PRM, MON, and POM with the respective standard values.

Table 4: pH, EC (µS/cm), TDS (mg/L), and TH (mg/L) values in different 3 sample seasons.

Period	pH range (mean)	EC range (mean)	TDS range (mean)	TH range (mean)
Pre-monsoon (PRM)	6.63-8.04 (7.03)	367.5-1043.5 (670.0)	220.0-667.5 (413.4)	121.5-564.0 (362.8)
Monsoon (MON)	7.06-8.41 (7.43)	560.5-1237.0 (867.5)	369.0-815.9 (558.2)	157.1-594.4 (396.1)
Post-monsoon (POM)	7.14-8.91 (7.80)	663.0-1710.0 (947.1)	449.0-1108 (600.6)	225.7-613.3 (404.8)

Table 5: The average concentration (mg/L) of analyzed trace metals and some selected parameters in the groundwater samples of the three sampling seasons with basic statistics.

	Depth	pН	EC	TDS	тн	В	Fe	Mn	Cr	Pb	Co	Ni	Cd	As	Cu	Zn
Min.	22	7.03	530.3	351.8	216.6	0	1.71	0.55	0	0	0	0	0	0	0.09	0.75
Max.	125	8.22	1305.3	866.8	576.5	1.3	13.3	5.25	0.089	0.095	0.09	1.137	0.045	0.019	3.27	6.71
Mean	50	7.43	831.3	528.2	387.9	0.66	8.43	2.85	0.047	0.038	0.045	0.320	0.008	0.008	1.69	4.03
SD(±)	31.9	0.23	172.8	110.4	84.04	0.40	3.23	1.30	0.023	0.032	0.024	0.353	0.011	0.006	0.85	1.60
Skewness	0.96	0.76	0.82	1.05	0.33	-0.34	-0.41	0.12	-0.51	0.38	-0.45	1.15	2.04	-0.08	-0.12	-0.35

on the several physiochemical parameters of water samples such as pH, EC, TDS, and TH. Besides, water depth is another factor that regulates the mineralization of aquifer and solute concentration. The values pH, EC, TDS, and TH in different 3 sample seasons viz. pre-monsoon (PRM), monsoon (MON), and post-monsoon (POM) periods are presented in Table 4. Also, the average concentration of trace metals and some relevant physicochemical parameters, including water depth, pH, EC, TDS, and total hardness (TH) of the three seasons are stated in Table 5. The dataset indicated that the maximum parameter values in the MON and POM seasons were higher than in the PRM season, which may cause percolation leaching during the rainy season in the study areas (Tables 4 and 5). In this section, the identification of metal pollution sources is performed through the source rocks in the aquifer and using multivariate statistical techniques.

4.4. Multivariate statistical analysis

Various statistical and computer programs were used to source

and dissolve trace metals in local aquifer groundwater. In this connection, multivariate analysis such as R and Q mode Cluster analysis, Pearson's correlation matrix, and principal component analysis, numerous biplots, diagrams, and programs are used for this purpose and are stated below:

(i) Pearson's correlation matrix

Pearson's correlation matrix was utilized to realize possible correlations between these trace metals to determine whether either the presence of specific trace metals in a sample facilitates the occurrence of other metals, or if they coexist owing to anthropogenic or geogenic activity in the study areas. Table 6 summarizes the inter-parameters correlation coefficient in groundwater. The inter-metal and metal with other relevant parameter relationships deliver useful information on metal sources and flow paths [36]. The correlation analysis displayed strong and significant positive correlations (r>0.7) in some trace element pairs, such as Fe with Mn, Co, Pb, and Zn; Mn with Fe, Pb, Co, Cu, and Zn; Pb with Fe, Mn, Cd, Cu, and Zn; Co with Fe and Mn; Cu with Fe, Mn, Pb, and Zn; and Zn with Fe, Mn, Pb, and Cu. Other metals are not strongly correlated with others. It was seen that maximum metals are strongly correlated with Fe and Mn. In the case of other physical parameters, all most allmetal concentrations are negatively correlated with water depth, i.e., the concentration of trace metals decreases with the aquifer depth. The total hardness (TH) does not correlate with any trace metal, such a result indicated that Fe or any other trace metal is not responsible for water hardness. The EC and TDS are strongly positively associated with the Fe, Mn, Cd, Cu, and Zn concentrations. So, these metal concentrations depend on salinity and the mineralization rate of the groundwater [37]. The pH is slightly negatively correlated with all metals, which indicates that in lower pH (acidic medium) the metal concentrations are increased by a higher dissolution rate [38]. The dissolution of metal ions in aquifers mostly depends on water pH. At a low pH value, the trace metals tend to be more dissolution due to more solubility in an acidic water solution [39, 40]. Another study by these authors [41] showed that the pH values were acidic in the maximum water samples in the PRM season, indicating fewer metal ions present in higher concentrations compared to the POM season (Tables 2 and 4). But dataset showed that the average metal concentration of the PRM was lower than the MON and POM sampling seasons indicating other geogenic causes are responsible rather than the water pH (Table 2).

Based on the lithology of the study zone, the coarse sandy alluvial geologic form, and the deltaic floodplain land are thought to be porous and penetrable enough to allow the passage of the trace metal-laden water into the aquifer basement [42]. The correlation matrix showed that most of the trace elements have substantial relations with each other, indicating the similarity of sources [43]. It illustrated that Fe and Mn significantly correlate with all the trace metals and that the presence of extra Fe and Mn in the samples can be attributed to geogenic and manmade processes. The geogenic processes that could release Fe and Mn in groundwater include the redox condition of the aquifer systems and the rusting properties of water supply pipes [44].

Among the eleven (11) analyzed heavy metals, the Fe, Mn, Ni, Pb, Cu, and Zn levels of more than 50% of samples exceeded the WHO standard permissible level for drinking purposes (Table 3) and they are strongly correlated with each other. The Cd and Pb may be coming from the same contamination source due to their strong positive correlation. Cd occurs naturally with Pb in the same sulfide ores [45]. B, Cd, Cr, As, and Co have weak correlations with each other, and the dissolution processes occurred from different sources. The absence of correlation between the metal elements proposes that the contents of these elements are not measured by a unique factor, but rather by an amalgamation of hydro-geological support phases [46]. Loading association and cluster characteristics of the metal concentration are discussed in the PCA and cluster analysis

(ii) Principal component analysis (PCA)

Principle component analysis (PCA) and robust PCA were utilized to compare the compositional and spatial outlines between the investigated water samples and the recognized latent factors and find the probable sources of the trace. Table 6: Person's correlation matrix for trace metals and physicochemical parameters (from SPSS software).

	Depth	pН	EC	TDS	ТН	В	Fe	Mn	Cr	Pb	Со	Ni	Cd	As	Cu	Zn
Depth	1.00															
pН	-0.22	1.00														
EC	-0.08	-0.40	1.00													
TDS	-0.10	-0.44	0.98	1.00												
тн	0.11	-0.35	0.70	0.70	1.00											
В	0.24	-0.15	0.12	0.14	0.18	1.00										
Fe	-0.05	-0.31	0.57	0.53	0.29	0.17	1.00									
Mn	-0.03	-0.25	0.67	0.55	0.25	0.15	0.89	1.00								
Cr	0.13	-0.24	0.34	0.35	0.20	0.15	0.40	0.32	1.00							
Dh	0.13	-0.24	0.34	0.35	0.29	0.51	0.40	0.52	0.20	1.00						
ru	-0.11	-0.23	0.40	0.45	0.00	0.10	0.04	0.70	0.39	0.27	1.00					
	-0.07	-0.02	0.25	0.19	0.08	0.26	0.64	0.75	0.20	0.37	1.00	1.00				
Ni	-0.11	-0.23	0.41	0.40	0.24	0.25	0.35	0.47	0.05	0.46	0.18	1.00				
Cd	-0.05	-0.35	0.50	0.51	0.32	0.32	0.41	0.46	0.35	0.50	0.25	0.24	1.00			
As	0.17	-0.14	0.42	0.38	0.56	0.31	0.41	0.41	0.29	0.25	0.23	0.34	0.26	1.00		
Cu	0.02	-0.30	0.58	0.56	0.16	0.04	0.72	0.72	0.28	0.78	0.34	0.44	0.38	0.29	1.00	
Zn	0.17	-0.28	0.66	0.63	0.37	0.17	0.77	0.75	0.47	0.57	0.41	0.29	0.44	0.33	0.76	1
Table 7:	Principa	l comp	onent a	nalysis o	f detect	ed water	r param	eters (sc	orted by	size). T	he table	got from	m SPSS	softwa	e.	
				PC1			<u>PC</u>	22			PC3			<u>PC4</u>		
Mn Fo				0.869			-0.3	570			0.081			0.093	1	
ге Zn				0.835			-0.2	01			0.139			-0.032	+)	
EC				0.832			0.2	83		-	0.365			0.020	-	
TDS				0.807			0.3	19		-	0.390			-0.007	7	
Cu				0.792			-0.3	320		-	0.112			-0.262	2	
Pb				0.721			-0.4	410		-	0.051			-0.146	5	
Cd				0.612			0.1	32			0.008			0.026		
As				0.539			0.3	37			0.208			0.388		
N1 Ca				0.529			-0.0	153		-	0.181			0.342		
Co Cr				0.527			-0.4	60 60			0.333			0.340		
nH				-0.454	L		-0.3	372			0.338			0 425	L	
TH				0.540	r I		0.7	01		-	0.166			0.186		
Depth				-0.041			0.3	43			0.647			-0.429)	
B				0.297			0.2	83			0.610			0.355		
Variance	(%)			42.174	1		11.	501			9.123			6.969		
Cumulativ	ve (%)			42.174	1		53.0	575		6	52.798			69.76	7	
Eigenvalu	ie			6.748			1.8	40			1.460			1.115		

Note: Bold values indicate strong loading with component number.

elements in the groundwater PCA is extensively applied to classify anthropogenic contributions and geogenic pollution sources. Factor analysis (Table 7 and Fig. 3) gives four PCs of R-mode factors that have eigenvalues greater than one. These four factors have a percentage variance of 42.174, 11.501, 9.123, and 6.969% with Eigenvalue >1. FC1 shows Mn(0.869), Fe(0.853), Zn(0.838), Cu(0.792), and Pb(0.721) have high positive factor values (>0.7) indicating those metals are strongly associated with each other and dissolute from a similar type of source that is possibly exogenous discharge [47]. Though the origin of Fe and Mn is partially attributed to geogenic processes in the correlation analysis, this class is made up of parameters unusual to manmade sources rather than mineral dissolution. Based on the geological situation of the study area, there have been reports of mineral or soil deposits rich in trace metals that could release these potentially toxic elements into the aquifer systems [48, 49]. It was assumed that the above-mentioned highly associated metals are dissolute with water in aquifer sediment levels from the mixed rock such as (FeNi)O(OH), (CoFe)AsS, ZnCrO₄,

CuFeS₂, (FeZn)6Sb₂S₉, etc. [50]. The Cd, As, Ni, Co, and Cr have moderate factor values in PC1, which indicates they are moderately associated with each other. In PC2 and PC3, the factor value of the maximum metals is near zero or negative. Only boron (B) has a significant factor value in PC3 (0.610). The negative factor value of water depth and pH indicates the negatively associated with all the metal concentrations, which were supported by Pearson's correlation matrix.



Figure 3: Robust PC of metals and other selected water parameters in the water samples (Fig. plotted with the help of Microsoft excel and Aqua-Chem software).

The values with positive and negative in PCA explained that the water samples were affected or unaffected by the occurrence of extracted loads on an exact component. The moderately strong association or correlation among EC, TDS, and TH indicates the presence of a huge ionic form of the metal component which is gathered by aquifer rock-water interaction and manmade sources, like agrochemicals from agricultural run-off [51]. The results of the PCA were observed by statistical cluster analysis and TDS vs metals plot, which is discussed in the next sub-sections.

(iii) Cluster analysis

The hierarchical cluster analysis method gives 3 (three) major cluster groups based on an R- and Q-mode dendrogram with Ward's method for the trace metals with some physical parameters in the study area (Fig. 4). Parameters that fit in a similar cluster are probable to have been leached from the same mineral/rock source [52]. Like PCA, cluster analysis places parameters into groups based on illustrious same

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features and relations with each other. In an agglomerative schedule cluster study, the most alike variables are mentioned in one single cluster group and related to a closely associated cluster(s) and further from clusters with fewer comparative, all of which are related to form one big cluster group [21].



Figure 4: Hierarchical cluster analysis (HCA) of 40 sampling sites for the average value (mg/L) of trace metals and other selected parameters in three sampling seasons (PRM, MON, and POM). Dendrogram of Q-mode HCA presenting associations between samples from different portions of hydrologic systems. Figure constructed from SPSS software.

Cluster 1 is formed by only three variables TDS, EC, and TH. While all measured metals and well depth constructed cluster II. Like the findings from PC and correlation analysis, all-metal concentrations depend on pH and water depth (Cluster II). Low pH and shallow depth are responsible for higher concentrations of metals (mainly Fe, Mn, Pb, Cu, and Zn). The first cluster illustrates an analogous association between total hardness (TH) and total dissolved solids (TDS) and suggests the domination of groundwater by precipitation and associated contact with air CO_2 [36]. Figure 4 shows that EC, TDS, and TH are not in the same cluster as metals indicating the metal loadings are not dependent on other general cations and anions (e.g., Na, K, Ca, Mg, HCO₃⁻, SO₄²⁻, NO₃⁻ etc.) of groundwater.

It may be assumed that those metals are dissolute from rock



Figure 5: Bivariate diagram of TDS vs trace metals.

water independently and some portion comes from anthropogenic sources such as agrochemicals leaching.

4.5 Mineralization process

The rock/mineral-water interaction and drive of solutes in aquifers systems are the important factors controlling the groundwater mineralization courses. A diagram (Fig. 5) of measured trace metals associated with total dissolved solids (TDS) shows that the geochemical facies took part in the groundwater mineralization [53]. This Fig. 5 establishes that the analyzed trace metal ions, Fe (r=0.53), Mn (r=0.55), Cd (r=0.51), Cu (r=0.56), and Zn (r=0.63) of groundwater are strongly positively correlated with TDS. This result represents the leading trace metals that donate to the groundwater through metal-laden sediment in the aquifer. Water chemistry indicated that Fe, Mn, Pb, Cu, and Zn are the most abundant trace metals in the study zone's groundwater samples. These results endorse the constant addition of these metal ions along the aquifer water flow path also suggestively contributes to groundwater mineralization. The Fe and Mn concentrations crossed the guideline value in the 100% samples (Table 2). These two ions may be invented from similar sources. Thus, dissolution or weathering is the geogenic geochemical process controlled by the salt load along the groundwater

flow path [54].

The four statistical methods mentioned above, viz, correlation matrix, PCA, cluster analysis, and bivariate regression correlation, are used to identify trace metal pollution sources. Pearson's matrix revealed that all the metals are moderately or weakly correlated in the acidic medium of water samples. The study area is an agricultural zone and deeply irrigated using shallow groundwater. No, an industrial plant is situated in the study area or neighboring among the anthropogenic source, only area. So. agrochemical leaching is the cause of metal sources in groundwater. Besides, several studies assumed that the trace metal loading in aquifers occurred by local geogenic activities which are positively influenced by heavy water mining [55, 56, 57]. Therefore, except for some anthropogenic sources, the geogenic source is the key factor in increasing the trace metal concentration in aquifers and was supported by above mentioned statistical analysis.

5. Recommendations

The chemical features of groundwater in the study area were dependent on the water-rocks interaction, carbonate-based mineral dissolution, and most neighboring river morphology. The study findings may be used for sustainable water

resources management on a regional scale and may be put in another area with similar topography. Accordingly, it is expected that the results of this investigation would deliver useful understandings for future groundwater monitoring and management of the study area. Also, the findings of this investigation deliver a guideline for agricultural activists, policymakers, public health departments, and water managers of a shallow aquifer. In addition, the study suggests that the groundwater should be drunk after proper treatment for removing the trace heavy metal contaminant from the potable water. Besides, deep wells should be drilled near river valleys and avoid thick clay-layer areas.

This study measured higher levels of some trace metals in samples that make the water very harmful for every purpose. Elevated concentrations of iron, manganese, and lead seriously impacted the drinking water quality. Further study would be considered using modern and sophisticated investigative approaches with extensive parameters over a wide area. The study found that the lack of public awareness of water quality, inadequate modern water treatment practices, absence of water quality monitoring, as well reluctance of law implementation are the main challenges to safe water supply in the study area. Moreover, public awareness building and publicity programs towards groundwater contamination are imperative to ensure safe water for all. Further, advanced research and survey-based works in the areas needed to be enhanced to explore the safe water status and water-related problems.

According to the research findings, some recommendations to manage the sustainability and purposes of groundwater resources are proposed as follows:

- The water from the deeper aquifer is more suitable than the shallow aquifer for both irrigation and domestic purposes and should be used in deeper water instead of shallow water.
- A field study confirmed that the hardness and trace metal level of single-owner water-well is generally higher than those of community users. So, this study suggests the local government should ensure a

community-based water supply system instead of a single-owner system.

- The groundwater should be drunk after 24 hrs. of extraction.
- The low-cost and indigenous materials made for filtration with solar disinfection processes could be used to reduce the temporary hardness, some toxic metals, and microbes.
- Obsessive extraction of groundwater needs to control.
- It should be frequently monitored the chemical and trace metal characteristics of groundwater.

6. Conclusion

Trace elements in groundwater can have both natural and manmade sources due to industry, industrial effluents, and agrochemicals. In this study, the concentration of trace metals was determined from 40 groundwater samples within three seasons in the study area of the middle west part of Bangladesh. The analysis result showed that the maximum metal concentration exceeds the guideline values of the respective component. Three metals ion, viz. Fe, Mn, and Pb crossed the limit of WHO standards in the maximum of the water samples representing severe human health hazards. The levels of Fe (8.43 mg/L) and Mn (2.85 mg/L) were found 28 fold greater than the standard value of 0.3 and 0.1 mg/L, respectively for drinking purposes. Another finding is the trace metal concentration in MON and POM seasons are found to be somewhat higher than PRM. The investigation results exposed that mainly the natural processes and little manmade activities impacted the trace metal loads in the groundwater system of the area. To assess factors affecting the level of trace metals in groundwater samples and determine their probable sources and mobility, multivariate statistical techniques, including Pearson's correlation coefficient, principal components analysis, and dendrogram cluster analysis are utilized. Results revealed that sources of trace elements were identified to be geogenic and slightly from human actions, i.e., application of agrochemicals, excess water mining, and industrial wastewater. In addition, it was found that the level of trace elements in samples

somewhat depends on water pH and salinity. Groundwater in this area poses a huge threat due to high levels of trace metals, and without any purification, it is necessary to avoid this water for drinking.

Authors Contribution

MSI and MGM has the main idea of the manuscript and wrote the the manuscript. MT revised the manuscript and provide suggestions.

Conflicts of Interest

The authors reported no potential conflict of interest.

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Data Availability statement

The data presented in this study are available on request from the corresponding author.

REFERENCES

- Islam, M.S. and M.G. Mostafa, Groundwater Status and Challenges in Bangladesh. Eric Lichtfouse (Eds.), Sustainable Agriculture Reviews, Springer Nature, Switzerland AG. Chapter 4, Volume 52, 2021. pp. 79-146.
- Ullah, R., M., Suleman, H., Fazal, Z., AliShah, M.N., Ahmad, Y., Ahmed, N., Nawaz, A., Niaz, K., Ahmed and K. Basha, Evaluation of Heavy Metals in Drinking Water of Tribal Districts Ex FATA Pakistan. Journal of Chemistry and Environment 2022. 1(01): p. 74-79.
- WB Group, Multi-Hazard Groundwater Risks to the Drinking Water Supply in Bangladesh. Water Global Practice 8922, 2019.
- Soltani-Gerdefaramarzi, S. and M. Morovati, The most important physical, chemical and mineralogical properties of atmospheric dust deposited on Yazd city (Central Iran). Phys Geog Res 2021. 53: p. 21-36.
- Zhu, Y.C., L.J. Wang, X.Y., Zhao, J. Lian and Z.H. Zhang, Accumulation and potential sources of heavy metals in soils of the Hetao area, Inner Mongolia, China. Pedosphere 2020. 30: p. 244-52.
- 6. Qu, M.K., W.D. Li, C.R. Zhang et al. Source www.jspae.com

apportionment of heavy metals in soils using multivariate statistics and geostatistics. Pedosphere 2013. 23: p. 437-44.

- Shangguan, Y.X., B. Cheng, L. Zhao et al. Distribution assessment and source identification using multivariate statistical analyses and artificial neutral networks for trace elements in agricultural soils in Xinzhou of Shanxi Province, China. Pedosphere 2018. 28: p. 542-554.
- Soltani-Gerdefaramarzi, S., M. Ghasemi, and B. Ghanbarian, Geogenic and anthropogenic sources identification and ecological risk assessment of heavy metals in the urban soil of Yazd, central Iran. PLoS ONE 2021. 16(11): p. e0260418.
- McLennan, S.M. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochem Geophys. 2001. 2: p. 1-24.
- Wang, R., X. Zou, H. Cheng et al. Spatial distribution and source apportionment of atmospheric dust fall at Beijing during spring of 2008-2009. Environ Sci Pollut Res 2015.22: p. 3547-57.
- Gue'guen, F., P. Stille, M.L. Geagea, and R. Boutin, Atmospheric pollution in an urban environment by tree bark biomonitoring-Part I: Trace element analysis. Chemosphere 2012. 86: p. 1013-1019.
- Qiang, L., W. Yang, L. Jingshuang et al. Grain-size distribution and heavy metal contamination of road dusts in urban parks and squares in Changchun, China. Environ Geochem Health 2015. 37: p. 71-82.
- Singh, A., A. Sharma, R.K. Verma et al. Heavy Metal Contamination of Water and Their Toxic Effect on Living Organisms (Ch. The Toxicity of Environmental Pollutants). Intech open 2020. 1: p. 1-19.
- Shi, Z., W. Zhang, Y. Liu et al. PTEs pollution and the ecological risk assessment of urban street dust in Kunming, China. In: IEEE International Geoscience and Remote Sensing Symposium. 2011, Vancouver, BC, Canada.
- 15. BBS, Bangladesh burrow of the statistics yearbook.

Ministry of planning, people's republic of Bangladesh, 2021.

- DPHE, Bangladesh national drinking water quality survey. Department of Public Health and Engineering, Govt. of Bangladesh, 2009.
- US-APHA, Standard methods for the examination of the water and wastewater, 21st edn. APHA (American Public Health Association), AWWA, WPCF, Washington, DC, 2005. p.1134.
- Bouzourra, H., R. Bouhlila, L. Elango et al. Characterization of mechanisms and processes of groundwater salinization in irrigated coastal area using statistics, GIS, and hydrogeochemical investigations. Environ Sci Pollut Res 2015. 22: p. 2643-2660.
- Kalaivanan, K., B. Gurugnanam, H.R. Pourghasemi, et al. Spatial assessment of groundwater quality using water quality index and hydrochemical indices in the Kodavanar sub-basin, Tamil Nadu, India. Sustain. Water Resour Manag 2018. 4: p. 627-641.
- Gozzi, C., P. Filzmoser, A. Buccianti et al. Statistical methods for the geochemical Characterization of surface waters: The case study of the Tiber River basin (Central Italy). Computers & Geoscience 2019. 131: p. 80-88.
- Chegbeleh, L.P., B. Akurugu and S. Yidana, Assessment of Groundwater Quality in the Talensi District, Northern Ghana. The Scientific World Journal 2020. Article ID 8450860: p. 1-24.
- Nasher, N.M.R. and M.H. Ahmed, Groundwater geochemistry and hydrogeochemical processes in the Lower Ganges-Brahmaputra-Meghna River Basin areas, Bangladesh. Journal of Asian Earth Sciences 2021. X6(1).
- Ikejimba, C.C. and S. Sakpa, Comparative study of some heavy metals' concentrations in water and Tympanotonus fuscatus var radula samples of Egbokodo River, Nigeria. Int J Mod Biol Res 2014. 2: p. 7-15.

- 24. Malik, L.A., A. Bashir, A. Qureashi, et al. Detection and removal of heavy metal ions: a review. Environ Chem Lett 2019. 17: p. 1495-1521.
- Chen, T.-B., Y.-M. Zheng, M. Lei et al. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. Chemosphere 2005. 60: p. 542-551.
- 26. Narany, T.S., M.F. Ramli, A.Z. Aris et al. Identification of the Hydrogeochemical Processes in Groundwater Using Classic Integrated Geochemical Methods and Geostatistical Techniques, in Amol-Babol Plain, Iran. The Scientific World Journal 2014. 419058: p. 1-15.
- Islam, M.S. and M.G. Mostafa, Groundwater Quality and Risk Assessment of Heavy Metal Pollution in Middle-West Part of Bangladesh. Journal of Earth and Environmental Science Research 2021. 3(2): p. 1-15.
- 28. US-EPA, Final Guide for Incorporating Bioavailability Adjustments into Human Health and Ecological Risk Assessments at U. S. Department of Defense Facilities Part 1: Overview of Metals Bioavailability, 2003.
- Islam, M.S. and M.G. Mostafa, Influence of chemical fertilizers on arsenic mobilization in the alluvial Bengal delta plain: a critical review. Journal of Water Supply: Research and Technology-Aqua 2021. 70(7): p. 948-970. http://doi: 10.2166/aqua.2021.043.
- US-EPA, Risk Assessment Guidance for Superfund: Volume III: Part A, process for conducting probabilistic risk assessment. EPA 540-R-02-002. Office of Emergency and Remedial Response. U.S. Environmental Protection Agency, Washington, DC, 2001.
- Priti, P. and B. Paul, Assessment of heavy metal pollution in water resources and their impacts: A review. Journal of Basic and Applied Engineering Research 2016. 3(8): p. 671-675.
- Salgarello, M., G. Visconti, L. Barone-Adesi, Interlocking circumareolar suture with undyedpolyamide thread: A personal experience. Aesthetic Plastic Surgery 2013. 37(5): p. 1061 1062.

- Vetrimurugan, E., K. Brindha, L. Elango et al. Human exposure risk to heavy metals through groundwater used for drinking in an intensively irrigated river delta. Appl Water Sci 2017. 7: p. 3267-3280.
- 34. Serelis, K.G., I. Kafkala, K. Parpodis, et al. Anthropogenic and geogenic contamination due to heavy metals in the vast area of Vari, Attica. Bulletin of the Geological Society of Greece 2017. 43:2390.
- 35. Islam, M.S. and M.G. Mostafa, Trends of Chemical Pesticide Consumption and its Contamination Feature of Natural Waters in Especial Reference to Bangladesh: A Review. American-Eurasian J Agric & Environ Sci 2021. 21(3): p. 151-167. http://doi:10.5829/idosi.aejaes.2021.151.167
- 36. Islam, M.S. and M.G. Mostafa, Evaluation of hydrogeochemical processes in groundwater using geochemical approaches and geostatistical models in the upper Bengal basin. Geofluid 2022. P. 1-21.
- Vetrimurugan, E., K. Brindha, L. Elango et al. Human exposure risk to heavy metals through groundwater used for drinking in an intensively irrigated river delta. Appl Water Sci 2017. 7: p. 3267-3280.
- Barzegar, R., A.A. Moghaddam, J. Adamowski et al. Assessing the potential origins and human health risks of trace elements in groundwater: a case study in the Khoy plain, Iran. Environ Geochem Health 2019. 41: p. 981-1002.
- Islam, M.S. and M.G. Mostafa, Meta-analysis and risk assessment of fluoride contamination in groundwater. Water Environment Research 2021. 93(8): p. 1194-1216.
- 40. Islam, M.S. and M.G. Mostafa, Health risk assessment of trace metals from groundwater in the deltaic plain of Bangladesh. Int J Water Res Environ Sci 2022. 10(1): p. 1-13.
- Islam, M.S. and Mostafa M.G. Selection of water quality index models for the evaluation of groundwater quality: A case study in river basin, Kushtia,

Bangladesh. H2Open 2022. 5(2).

- 42. Egbueri, J.C., C.N. Mgbenu and C.N. Chukwu, Investigating the hydrogeochemical processes and quality of water resources in Ojoto and environs using integrated classical methods. Modeling Earth Systems and Environment 2019. 5: p. 1443-1461.
- Islam, M.S. and M.G. Mostafa, Groundwater suitability for irrigated agriculture in Alluvial Bengal delta plain: A review. International Journal of Advances in Applied Sciences 2021. 10(2): p. 156-170.
- 44. Barzegar, R., A.A. Moghaddam, J. Adamowski et al. Assessing the potential origins and human health risks of trace elements in groundwater: a case study in the Khoy plain, Iran. Environ Geochem Health 2019. 41: p. 981-1002.
- WHO, Guidelines for drinking-water quality, 4th edn. World Health Organization, Geneva, 2011.
- 46. Suresh, S., M. Chandrasekar and P. Selvakumar, Experimental studies on heat transfer and friction factor characteristics of CuO/water nanofluid under laminar flow in a helically dimpled tube. Heat Mass Transfer 2012. 48: p. 683-694.
- 47. Huang, Z., C. Liu, X. Zhao, et al. Risk assessment of heavy metals in the surface sediment at the drinking water source of the Xiangjiang River in South China. Environ Sci Eur 2020. 32: p. 1 23.
- MICS-B, Water quality thematic report: 2012-2013, Multiple Indicator Cluster Survey, UNICEF, and BBS, Bangladesh, 2018.
- Reddy, M., Basha, S., V.G.S. Kumar et al. Distribution, enrichment and accumulation of heavy metals in coastal sediments of the Alang- Sosiya ship scrapping yard, India. Mar Pollut Bull 2004. 48: p. 1055-59.
- 50. Xiao, Q., Y. Zong, Z. Malik et al. Source identification and risk assessment of heavy metals in road dust of steel industrial city (Anshan), Liaoning, Northeast China. Hum Ecol Risk Assess 2019. P. 1-20.
- 51. Bodrud-Doza, M., A.R.M.T. Islam, F. Ahmed et al.

Characterization of groundwater quality using water evaluation indices, multivariate statistics and geostatistics in central Bangladesh.Water Science 2016. 30: p. 19-40.

- Ahmed, N., M. Bodrud-Doza, S.M. Didar et al. Hydrogeochemical evaluation and statistical analysis of groundwater of Sylhet, north-eastern Bangladesh. Acta Geochimica 2018. 38: p. 440-455.
- Selvakumara, S., N. Chandrasekara and G. Kumar, Hydrogeochemical characteristics and groundwater contamination in the rapid urban development areas of Coimbatore, India. Water Resources and Industry 2017. 17: p. 26-33.
- Islam, M.S. and M.G. Mostafa, Development of an integrated irrigation water quality index (IIWQIndex) model. Journal of Water Supply 2021. 22(2): p. 2322-2337.
- 55. Hasan, M.A., K.M. Ahmed and O. Sracek, Arsenic in shallow groundwater of Bangladesh:investigations from three different physiographic settings. Hydrological Journal 2007. 15: p. 1507-1522.
- Hasan, M.K., A. Shabbir and K.U. Jim, Water pollution in Bangladesh and its impact on public health. Heliyon 2019. 5: p. 1-23.
- Zahid, A. Groundwater management aspects in Bangladesh. Technical Report, Center for Water and Environment, Bangladesh Water Development Board, 2015.

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Research Article

Evaluation of the Physical Properties of Various Biomass Materials for the Production of Activated Carbon

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Abstract

This study aims to produce activated carbon (AC) from different biomass sources using chemical activation; characterize the AC using Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM), proximate and ultimate analysis; and compare the results from the AC produced. The biomass blends of rice husk & groundnut shell (RH-GS), cocoa nut shell & saw dust (CS-SD) and sugar cane bagasse & banana peel (SB-BP) were used for the preparation of AC. The samples were first characterized using proximate and ultimate analysis, SEM, and FTIR spectroscopy. The results of the BG-SD sample characterization showed that the blend produced the best results in terms of adsorptive capacity. It is suggested that surface area difficulties with the ACs be investigated in order to improve their porosity and adsorption capacities.

Keywords: Activated carbon, Carbonization, Biomass sources, Waste characterization, Chemical activation, SEM analysis, FTIR Spectroscopy

1. Introduction

Carbon atoms bound by structural disorder and discontinuity that permit porosity are known as activated carbons (ACs) [1]. Besides, surface functionality as well as porosity might affect how specific an AC is [2]. On a global level, AC usage and prospective applications are constantly growing. Many resources, including coal and lignocellulose biomaterials containing carbon, including industrial waste fractions (such as bark and sawdust), can be used as raw materials to create ACs [3]. The basic materials are transformed through a thermochemical process to produce materials with a lot of carbon. Moreover, by adding activating agents during chemical or physical activation, carbon compounds can be further transformed into ACs [4]. Specific surface area (SSA), porous volume (PV), and porous size distribution (PSD), among other AC features, are dependent on a number of factors, including the raw material, the activation technique, and the process variables applied during the carbonization and activation processes [5].

Biodegradable materials, biologically derived wastes, and residues from agriculture, forestry, and aquaculture are used to create biomass. A variety of raw materials, such as wood, agricultural crops, waste from the processing of wood, manure, and the organic portion of waste products are used to create biomass. When used with variable loads and applications at the location and time of energy need, biomass offers the advantages of being conveniently stored, transported, and used

as a renewable energy source. This distinguishes biomass from other sources of renewable energy even though they can also be nonrenewable. Biomass resources currently available for producing energy can be classified into woody biomass, agricultural sources, and bio wastes [6].

Demand for AC has been steadily rising ever since Raphael von Ostrejko, known as the "father of activated carbon," got it for the first time in 1900 [7]. Market for AC is anticipated to develop at a compound yearly growth rate of 6.31% from 2019 to 2024 [8]. In addition to air and gas filtration, AC is now the method of choice for treating wastewater, aquariums, swimming pools, and potable water [9]. Because of rising environmental contamination, growing health issues, and strict governmental laws, these applications are the most crucial. Besides from that, AC is employed in the pharmaceutical sector to purify vitamins, antibiotics, and other substances as well as the food sector to decolonize and deodorize food and drinks [10]. The monitoring of gas emissions in automobiles, personal safety in the military industry, the recovery of resources like gold and precious metals, and as a catalyst in the removal of mercaptans in oil refineries are some further uses for AC [11]. In electrochemistry, where capacitors and Li-ion batteries are made and used for energy storage, ACs are also growing in popularity [12]. Due to a lack of resources and growing supply chain worries, the AC industry is currently experiencing price problems. Yet, the market is expanding as a result of AC's widespread use in applications for the liquid and gas phases [13].

Thus, the AC industry eventually had to look for less

expensive alternative precursors that would still meet environmental regulations due to escalating costs for traditional feedstock and severe penalties for environmental damage. Lignocellulose-derived biomass has proven to be a desirable solution to these problems from an economic and ecological perspective [14]. There are various forms of AC available with various physical characteristics, including pore size distributions, surface features, and morphologies (e.g., pelletized, granular, powdered, spherical, or beads, etc.) [15]. Porosity architectures and surface functional groups of AC vary depending on the precursor material, activation technique and conditions (such as temperature and oxygen), and posttreatment reactions. For example, the powdered and granular versions of AC are the most widely used kind [16]. Consequently, the objectives of this study are to produce AC from different biomass sources using chemical activation. characterize the AC using FTIR, SEM, proximate and ultimate analysis and compare the results from the AC produced.

2. Materials and Methods

2.1 Materials

Carbonaceous precursors use for the preparation of AC were biomass blends of rice husk & groundnut shell (RH-GS), cocoa nut shell & saw dust (CS-SD) and sugar cane bagasse & banana peel (SB-BP). They were collected separately from Maiduguri Monday Market, Borno State-Nigeria. Samples were washed greatly with deionize water to remove mud and other impurities present on the surface and then sun-dried for a week. An activating agent was used, in this case. Materials which include the samples, equipment, glass wares and reagents used in this work are listed in Tables 1 and Table 2.

S/No	Reagents	Manufacturer	Description	Source
1.	Deionized Water	Kaduna Polytechnic Lab	Analytical Grade	Spectral Laboratory
2.	Samples	Food wastes	Biodegradable biomass	Maiduguri Monday Market

Table 1: List of Reagents Used.

Table 2. List of Equipment and Glassware Used

S/No	Glass ware	Manufacturer	Description	Source
1.	Conical flask	Pyrex, England	Borosilicate	Spectral Laboratory
2.	Beaker	Approxboro, England	Borosilicate	Spectral Laboratory
3.	Measuring Cylinder	Bomex, Germany	Borosilicate	Spectral Laboratory
4.	Crucibles	LSP Industrial Ceramics	Ceramic	Spectral Laboratory
5.	Laboratory Spatula	Bürkle Nigeria	Stainless	Spectral Laboratory
6.	Weigh Balance	Apex Scientific	0 - 200 mg	Spectral Laboratory
7.	Desiccator	Normax-Fabrica de Vidro Cientifico	10 liters	Spectral Laboratory
8.	Drying Oven	The Grieve Corporation	150 liters	Spectral Laboratory
9.	Muffle Furnace	Bionics Scientific	4 liters	Spectral Laboratory
10.	Crucible with Cover	Shanghai Gongtao Ceramics Co., Ltd.	15 mL and 30 mL	Spectral Laboratory
11.	Laboratory Test Sieve	ENDECOTTS	425 μm	-

Combustible parts of the samples were separated from noncombustible ones before they were used for the experiment. The three experiments carried out were described.

2.2. Experimental Section

2.2.1 Preparation of Sample

Sugarcane bagasse, rice husks, peanut shells, coconut shells, banana peels and sawdust pose a lot of challenges in handling and disposal. Bagasse and co. could serve as an additive in the manufacture of sludge-based adsorbents to increase their adsorption capacity. After crushing and pressing sugarcane to get juice, bagasse was collected and dried. To create different particle sizes, it was ground and sieved. The chars were then activated.

2.2.2 Synthesis of Activated Carbon from Biomass Blend

After collecting the biomass from Maiduguri Monday Market, Borno State, Nigeria, various blends were formed (i.e., RH-BS, CS-SD and SB-OP). A typical process that involves initial cleaning to remove dust, dirt and other impurities was carried out. The cleaned waste biomass was then dried under sunlight for 1 week. The dried waste biomasses were precarbonized in a muffle oven at 700 °C for 3h under nitrogen atmosphere to obtain carbon black before grinding and its subsequent activation. The carbonized waste biomass particles were then blended and mixed in the ratio of 1:1 (RH:GS, CS:SD and SB:OP). Then separate blends were activated using chemical activation method. Finally, the prepared ACs were washed with distilled water, dried and kept in a closed container until further use. The ACs were named RG-ACs, CS-ACs and OS-ACs using initial alphabets in the 3 blends.

2.2.3 Characterization of Activated Carbon

In general, the selection of a characterization methodology must be based on the type of information that is important for the specific use of the materials in question. As already mentioned, the characterization of adsorbents from biomass materials should be performed not only on the final product but also on the precursor of the AC. Analysis of the raw material is required to determine moisture, percentage of main polymer structure, as well as density and the presence of other compounds [17].

Proximate analysis was conducted prior to carbonization phase and ultimate analysis after that, to provide important

information about the properties of the final product [18]. Techniques applied for the characterization of the samples are Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and ultimate analysis.

3. Results and Discussion

3.1. Physiochemical Properties of Activated Carbon Produced

3.1.1. Bulk Density

Bulk densities measured, ranged from 0.5417 to 0.7183 mg/L, with BG-SD having the lowest bulk density and OS-CS the highest. There was no remarkable difference in the mean bulk densities of the powdered blends varieties as shown in Table 3. The bulk density of a material affects how easily it may be transported, notably in terms of container space. However, more advanced correlations have shown bulk density as a key predictive indicator in determining the suitability of a material for absorption purposes in water treatment systems, with materials of lower bulk densities reported to have a higher adsorptive capacity. Compared with bulk densities reported by other researchers, the bulk densities of blends varieties can be harnessed for synthesis of adsorbents.

3.1.2. Moisture Content

Dry basis moisture content of the biomass blend varieties ranges from 4.12-7.15%. Values obtained are in the acceptable range that has been reported in the literature. However, other scholars have reported values out of this range. This could be attributed to the difference in the drying conditions such as higher temperature and longer drying times whereas, the average particle size difference could also have led to differing moisture content.

3.2. Proximate and Ultimate Analysis of the AC3.2.1 Proximate Analysis

Proximate analysis of the selected biomass-sourced ACs provided various fixed carbon content depending on the moisture content, ash content and volatile matter content present. While ultimate analysis gave sulphur, hydrogen, oxygen, nitrogen and carbon (C) contents present in each precursor raw material. Results from the proximate analysis and ultimate values are reported for these selected materials, even though the values obtained for other samples with different carbonization time was not significantly different for the selected samples. CS-OP, BG-SD and RH-GS had a fixed carbon content of ~27.24, ~32.33 and ~32.82 wt% respectively. This is comparable to earlier studies reported on AC from similar biomass raw materials. A detailed summary of the entire proximate results for the selected samples are shown in Table 3.

Table 3: Proximate Analysis.

S/N	Parameter	Unit	RH-GS	OP-CS	BG-SD
	Feedstock	g	5	5	5
1.	Moisture content	%	4.12	4.74	7.15
2.	Ash content	%	61.33	0.72	1.79
3.	Volatile matter	%	5.86	71.54	65.88
4.	Fixed carbon	%	32.82	27.24	32.33
5.	Bulk density	mg/L	0.6322	0.7183	0.5417

3.2.2 Ultimate Analysis

The carbon, hydrogen, nitrogen, oxygen and sulphur contents in the 3 biomass blends are shown in Table 4.

Table 4: Ultimate Analysis Results.

S/No	Parameter	Unit	RH-GS	OP-CS	BG-SD
	Feed stock	%	100	100	100
1	Carbon	%	51.76	56.48	68.13
2	Hydrogen	%	11.01	11.97	9.49
3	Oxygen	%	36.69	31.21	21.90
4	Sulphur	%	0.21	0.05	0.17
5	Nitrogen	%	0.33	0.29	0.31
This ultimate composition is close to those of other biomasses summarized and reported by Pathak et al. (2016) and in the same range with other biomass blends varieties. Carbon content in all the peels renders them viable for AC production. Normally, the higher the C content, the more viable a material is for AC precursor. Moreover, there are relatively higher C in some blend's varieties. Based on the composition, the suitability for AC production for the biomass blends varieties is in the order: BG-SD > OP-CS > RH-GS.

Oxygen composition in all the blends suits them for better reactivity during AC production. Presence of oxygen influences the reactivity of biomass during pyrolysis, which consequently affects the final products yield and quality. Studies have suggested that the more the presence of oxygen in the biomass, the more will be the reactivity. The oxygen and hydrogen compositions for all the varieties suit them for chemical activation. Oxygen and hydrogen compositions (Table 4) above 25% and 5% respectively, predictably imply better activation chemically. After activation, the $\overline{\text{ACs}}$ were characterized using FTIR and SEM, where the results obtained were vividly explained.

3.3.1 FTIR Analysis

To study the surface functional groups present in ACs, FTIR analysis was performed. From the chart of Figure 1, the FTIR spectroscopy of AC shows the peaks for OP-CS, RH-GS, and BG-SD, which are 3850.04, 3850.04 and 3842 cm⁻¹ respectively. They are ascribed to –OH stretching of hydroxyl group which decreased considerably in AC. It shows a reduced intensities in AC FTIR spectroscopy due to decomposition during the carbonization process. The band for OP-CS, RH-GS, and BG-SD are 2353.23, 2438.1 and 2337.8 cm⁻¹ corresponding with C–H symmetric and asymmetric vibrations of the methoxyl groups. Sharp peak at 1543.1,1519.96 and 1527.67 cm⁻¹, which are attributed to C-O vibrations in the ACs; OP-CS, RH-GS, and BG-SD respectively are shown in Figures 1-3.



3.3 Activated Carbon Characterization

Figure 1: FTIR Spectroscopy of Activated Carbon: OP-CS.



Figure 2: FTIR Spectroscopy of Activated Carbon: BG-SD.



Figure 3: FTIR Spectroscopy of Activated Carbon: RH-GS.

3.3.2 SEM Analysis

Surface roughness of AC made from biomass, comprising CS-OP, BG-SD, and RH-GS, is depicted in Figures 4, 5, and 6. The dehydrating agent will be the activating agent; sodium hydroxide (NaOH), which was combined with the precursor before being subjected to activation. During chemical activation, the activating agent penetrates the biomass blend's surface texture to aid in the development of a porous structure. It is evident that AC has a porous microstructure with numerous irregular pores and broken edges. Similar morphology was observed in the AC made from empty banana fruit [20]. The evaporation and gasification of the activating agent (in this case, NaOH) during the activation process by leaving the area it occupies during the impregnation step causes the formation of holes and cavities.



Figure 4: SEM Microstructures of the Activated Carbons: (a) BG-SD.



Figure 5: SEM Microstructures of the Activated Carbons: (b) OS-CS.



Figure 6: SEM Microstructures of the Activated Carbons: (c) RG-GS.

4. Conclusion

This work examines FTIR, Proximate, Ultimate and SEM of biomass mixtures namely, CS-OP, BG-SD and RH-GS to evaluate their applicability for AC production. Almost all varieties have AC yield potential, specifically due to their ash content, which is below 5% (except in the case of RH/GS). The increase in volatile matter upon treatment with NaOH implies a larger surface area for the AC, but could also be suitable for synthesis gas production.

The conclusion that biomass blend use can serve as an affordable raw material for the manufacturing of AC in the near future can be drawn from the findings of experimental examination of the ACs generated in the current study, thereby minimizing their presence in the environment as waste material. The synthesis of AC from biomass blend works best when utilizing a chemical activation process with NAOH as the activating agent. According to the results of the SEM study, AC has an amorphous crystalline structure and a microporous surface structure, respectively. A good adsorbent must have a porous surface and an amorphous crystalline structure.

Thus, adsorption and filtration applications can make use of AC in powder form. Using FTIR spectroscopy research, it can be seen that water and hydroxyl groups in the AC powder vanished after the precursor and AC were both activated. After activation, the C material also exhibits an increase in aromaticity and the creation of new surface groups. All of the blend types' elemental compositions make them suitable for the generation of AC, with C contents high enough to produce chars and oxygen and hydrogen contents predictable enough to be reactive during torrefaction operations. Based on the results of the BG-SD sample characterization, it can be concluded that the blend produced the best results in terms of absorptive capacity. Therefore, it is advised that issues with the ACs' surface area be looked upon in order to enhance their porosity and adsorption capabilities.

Authors Contribution

Based on <u>CRediT</u> standards, authors description can be described as follows: Mr. Saka is credited with the project

conceptualization and funds acquisition; Mrs. San-Pedro does the formal analysis, data curation and edit the review; Mr. A. M. Abubakar provides the resources as well as the needed administration and supervision of the work; Dr. T. Sylvain conducts data validation and software use; Mr. Budianto visualize, investigates and wrote the methodology; and Dégninou Houndedjihou wrote the original draft and also participates in the editing of the review by anonymous reviewers.

Conflicts of Interest

There are no conflicts of interest reported by the writers.

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Data Availability Statement

Data presented in this study are available on request from Mr. Tahiru Saka (send mail to tahirusaka23@gmail.com).

REFERENCES

- H. Marsh and F. R. Reinoso, Activated carbon, 1st ed. Physical Sciences and Engineering: Elsevier Science Limited, 2006.
- Y. Zhao and Y. Wang, "Surface chemistry of activated carbons and its characterization," in Activated Carbon Surfaces in Environmental Remediation, 1st ed., T. J. Bandosz, Ed. Elsevier, 2015, pp. 27–47.
- P. Kumar, D. M. Barrett, M. J. Delwiche, and P. Stroeve, "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production," Ind. Eng. Chem. Res., vol. 48, no. 8, pp. 3713–3729, 2009, doi: 10.1021/ie801542g.
- S. Wang, Y. Boyjoo, A. Choueib, and Z. H. Zhu, "Removal of dyes from aqueous solution using fly ash and red mud," Water Res., vol. 39, no. 1, pp. 129–138, 2005, doi: 10.1016/j.watres.2004.09.011.
- 5. H. Y. Choi, J. S. Ryu, S. J. Park, Y. J. Kim, and J. H. Kim,

"Effects of preparation conditions on the characteristics of activated carbon," Environ. Eng. Res., vol. 26, no. 2, 2021.

- H. Yang, B. Huang, S. Wu, Y. Xu, and Y. Liu, "Overview of biomass energy development in China," Bioresour. Bioprocess., vol. 8, no. 1, pp. 1–14, 2021.
- V. K. Gupta and A. Nayak, "History of activated carbon and its present status as a powerful adsorbent," in Handbook of Environmental Materials Management, Springer, 2020, pp. 1–23.
- MarketsandMarkets, "Activated carbon market by type (powdered, granular, others (pelletized, bead)), application (liquid phase (water treatment, foods & beverages, pharmaceutical & medical), gas phase (industrial, automotive)), region - global forecast to 2026," Marketsandmarkets Research Private Ltd, 2023. https://www.marketsandmarkets.com/Market-

Reports/activated-carbon-362.html (accessed Mar. 07, 2023).

- J. K. Nduka, J. N. Nwakaire, A. Chukwu, and M. A. Nwachukwu, "Emerging trends in the application of activated carbon for wastewater treatment," Environ. Sci. Pollut. Res., vol. 28, no. 6, pp. 6616–6632, 2021.
- Y. Wang, L. Li, X. Li, H. Sun, and H. Wu, "A review of the applications of activated carbon in the food industry," Food Sci. Hum. Wellness, vol. 9, no. 2, pp. 87–95, 2020.
- Y. Liu, X. Liu, X. Wang, and Y. Zhang, "Recent advances in the preparation and application of activated carbon," J. Chem. Technol. Biotechnol., vol. 96, no. 5, pp. 1265–1277, 2021.
- Y. Shao, J. Wang, H. Wu, M. Liu, I. A. Aksay, and Y. Lin, "Graphene based electrochemical sensors and biosensors: A review," Electroanalysis, vol. 22, no. 10, pp. 1027–1036, 2013.
- 13. GVR, "Activated carbon market size, share & trends analysis report by product (powdered, granular), by application (liquid phase, gas phase), by end use (water treatment, food & beverage), and segment Forecasts, 2020-2027," Grand View Research, Inc, 2021.

https://www.grandviewresearch.com/industry-

analysis/activated-carbon-market (accessed Mar. 07, 2023).

- Y. Zhang et al., "Biomass-derived porous carbon materials for water treatment: A review of preparation strategies, performance, and mechanisms," Front. Chem., 2021, doi: 10.3389/fchem.2021.797534.
- B. Lesbayev et al., "Recent advances: Biomass-derived porous carbon materials," South African J. Chem. Eng., vol. 43, pp. 327–336, 2023,
- S. Wong, N. Ngadi, I. M. Inuwa, and O. Hassan, "Recent advances in the applications of activated carbon from biowaste for wastewater treatment: A short review," J. Clean. Prod., vol. 175, pp. 361–375, 2018, doi: 10.1016/j.jclepro.2017.12.059.
- M. O. Prakash, G. Raghavendra, S. Ojha, and M. Panchal, "Characterization of porous activated carbon prepared from arhar stalks by single step chemical activation method," in Materials Today: Proceedings 39-Materials Journal of Worldwide, 2021, pp. 22–27, doi: 10.1016/j.matpr.2020.05.370.
- J. A. Duke, Handbook of proximate analysis tables of higher plants, 1st ed. Boca Raton: CRC Press, 2018.
- P. D. Pathak, S. A. Mandavgane, and B. D. Kulkarni, "Characterizing fruit and vegetable peels as bioadsorbents," Curr. Sci., vol. 110, no. 11, pp. 2114–2123, 2016, [Online]. Available:
- N. Juntarachat and U. Onthong, "Removal of hydrogen sulfide from biogas using banana peel and banana empty fruit bunch biochars as alternative adsorbents," Biomass Convers. Biorefinery, 2022, doi: 10.1007/s13399-022-03430-z.

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Review article

Unraveling the Challenges of Oxidative Stability: Methods for Assessing Oxidative Stability of Commercial Oils: A Review

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Abstract

Edible oils are among the most crucial nutritional constituents as these are utilized for frying or cuisine. Though, these oils are prone towards oxidative deterioration from manufacturing to transportation due to environmental exposure as well as storage conditions which result in generation of different types of oxidation products. The generation of primary and secondary products result in harmful impacts on human health and may also result in cardiovascular diseases in consumers. The mechanism of oxidative deterioration cannot be assessed easily due to complexity of the reaction under which it may take place. Different types of approaches have been proposed to determine the products generated as a result of oxidation so that safety for their user can be assured. Different types of analytical techniques can be employed in addition to chemical methods so that analysis of oxidative deterioration can be done completely. The proposed study is aimed to assess the oxidative stability of oils in addition to the factors which can influence oxidation of these oils under different conditions. This review also summarize the classical and advanced state of the art analytical techniques which has recently been developed in different possible ways and effectively can be employed for analysis of oxidative deterioration of edible oils. This article possibly will oblige as a reference in the assortment, establishing, and enhancement of approaches for investigating the oxidative stability of edible oil.

Keywords: Edible oils, oxidative stability, shelf-life, factors effecting oxidation, analytical techniques, oxidation products etc.

1.Introduction

The rate of food consumption is rising enormously as the population of world is increasing day by day [1]. Because of this fact the demand of edible oils also has been increased much more compared to the past [2]. Edible oils are among the major constituents of food products along with carbohydrates, proteins, minerals etc. Edible oils provide essential fatty acids and fat-soluble vitamins to our body and also give flavor to our food [3, 4]. As the demand of edible oils has been increased the maintenance of the quality has become a major concern for the manufacturing industry which

is mainly dependent upon their oxidation [5].

One of the most important and largest classes of naturally present molecules is lipids which comprises of fatty acids, glycerol, glycolipids, phospholipids, sterol esters, waxes etc. [6]. Lipids containing food products are usually insoluble in polar solvents like H₂O and CH₃OH and become easily soluble in non-polar solvents like CHCl₃ and ethers etc. Fats are major kinds of lipids which could be defined as, esters of triglycerides. Both oils and fats are subsets of lipids and are composed of fatty acids, most of the oils befall in liquid state at room temperature and almost all fats are solid at room conditions [7].

Fats regulate many significant tasks which may involve, to meet high energy demand of body, impart delicious taste to our food, serve as a courier for many of the biological active compounds, serve as a medium for absorption of fat soluble enzymes like A, D, E & K, important part of body fluids and cell membranes, and serve as insulator for body [8].

In our everyday life one of the most ingested or consumed constituents around the world for cooking purposes are edible oils. Oils play a crucial role in everyday life of mankind besides of edible applications. Besides their nutritional value fatty acids find applications in many industries such as production of soaps, washing powder, cosmetics, and detergents, oleo-chemical industry and bio-fuels etc. [9, 10]. Major source of edible oils in terms of production in the whole world are from soybean and palm oil which together account for over 65%. Production of the edible oils has been enhanced abruptly during the last few years due to high consumption demand. Maximum level of production was about 126.02 million metric tons (MMT) of major edible oils in year 2010-11 which now has been reached up to 152.29 MMT by the year 2014-15. The production of palm oil has been increased from 48.84 to 63.29 MMT and soybean oil from 41.29 to 46.95 MMT which are major edible oils produced as compare to that of canola oil (23.46 to 26.76 MMT) and sunflower oil (12.43 to 15.29 MMT) [11].

Based upon fatty acids profiling edible oils are classified into saturated and unsaturated oils. In saturated fatty acids (SFAs) there is no double bond, while monounsaturated fatty acids (MUFAs) have only one double bond and polyunsaturated fatty acids (PUFAs) comprises of multiple double bonds present along the carbon chain [12]. Recently many researchers have elaborated that foodstuffs enriched in SFAs cause an increased level of cholesterol and low-density lipoprotein (LDL) which could promote the risks of many heart diseases. Furthermore a lot of research has been done which reveals the effects of these SFAs on the cancer or tumor development, obesity and other disorders [13-15]. In Asian countries, the majorities of SFAs are obtained from ghee, Vanaspati (hydrogenated fat), cheese and also from

some cooking oils which includes coconut oil, palm kernel oils [16].

In contrast to SFAs intake of food products enriched in MUFAs as well as PUFAs are helpful in lowering the level of cholesterol and increased the level of high density lipoprotein and decrease the low density lipoprotein, which will resolve the health risk of coronary heart diseases [17-19]. Canola, rice bran, olive, mustard and groundnut are among those oils which are enriched with MUFAs. Likewise, sunflower, corn, sovbean, linseed oils are enriched with many of essential dietary PUFAs which are vital for our health assurance. There is another type which is known as Trans fatty acids (TFAs) are generated during the production process of hydrogenated vegetable oils and might also be present in fats. This type of fat mostly includes UFAs that exhibit isolated double bonds (one or more) in the Trans form of configuration [20, 21]. Research work in clinical field reveals that a high intake of TFAs containing food products is directly linked with development of cardiovascular disease (CVD) by enhancing serum LDL cholesterol relative to SFA [22, 23].

According to the American Heart Association (AHA) the accepted or recommended limit of fats containing foodstuffs consumption should always be lower than 30 -35% of total calories required for energy demand, In this extreme limit, the consumption of SFAs should always be confined to 10%, MUFAs to about 15% and PUFAs to about 10% of total calories required for energy demand [24]. Likewise, TFAs level of consumption should be limited to 1% only of total energy. Therefore, maximum consumption limits of all types of fatty acids should be in the ratio of SFA: MUFA: PUFA, 1:1.5:1. But, consumption or use of only single type of edible oil alone cannot fulfill the intimate regulations, blending of two or more oils are generally advised for betterment of human health [25, 26].

1.1. Aims and objectives

This article is proposed by keeping some important points in mind which are as following;

• To analyze the oxidation challenges which occur from manufacturing to storage as well as utilization for

betterment of human beings.

- To analyze different factors which prone these oils towards oxidative deterioration after proper manufacturing.
- To analyze the potential of natural antioxidants which can be applied for the enhancement of oxidative stability and shelf life of these oils
- An overview of different chemical and state of the art analytical techniques which can be applied for analyzing oxidation products at different stages of oxidation assessment.
- Also overviewing of the advanced biosensor type approaches which can be applied for the analysis of oxidation.

2. Methodology

This review provide a comprehensive overview of analysis of oxidative stability of commercial edible oils which face the challenges of oxidative deterioration due to different environmental factors as well as storage conditions. This review was designed to elaborate these challenges of oxidative deterioration as well as its proper determination by applying different advanced techniques which has recently been developed. This review entails comprehensive data available on oxidative stability of edible oils mostly from 2000 and onward period also include some studies which has been conducted before 2000. This review was designed by overviewing a huge number of articles which provide detail study about oxidative stability analysis. The data collected for this study was mostly from different sites which include Google Scholar, Semantic Scholar, PubMed and Research Gate which has been published during the specified period of the time. So, as a whole this review article entails the comprehensive and complete overview regarding this problem of oxidative stability which occurred in edible oils during different storage conditions as well as their shelf-life analysis due to these factors.

3. Relationship between oxidative stability and shelf life of oils

Most of edible oils are unsaturated and are susceptible

towards deterioration which in turn causes quality loss of these oils because maintenance of oils quality is mainly dependent on rate of oxidation [27]. The oxidative stability in case of edible oils is the resistance towards oxidation process from processing to storage [28]. The resistance towards oxidation is mostly expressed as time period taken by oil samples to reach the critical point; this oxidation may be abrupt acceleration of oxidation process or may be a change in sensor response [29]. As the rate of oxidation increases deterioration of oil occur at faster rate and cause generation of rancid odor and off-flavor which is prohibited for consumers [30]. The generation of rancid odor and bad smell is due to formation of some short chain molecules and polymers. As a result of oxidation loss of nutritional value occur consequently this will be of no importance for health or possibly may impose some negative effects on human health. Rate of oxidation also results in decline of shelf life or storage period of lipid containing food products [31].

The process of lipid oxidation is thought to be a major process or reaction which cause decline in vitality of food products. It merely provide bad smell and off-flavor to fat containing products but also cause generation of highly reactive O₂ species which is directly associated with highly dangerous carcinogenic, aging, and many other diseases like inflammation [32-34]. The phenomenon of oxidation may effect acceptability of sensors of human, and loss of nutritional values of fat containing foods and thus play pivotal role in assessing oxidation process, their uses and also predicting their shelf life [35, 36].

Furthermore the rate of increased lipid oxidation is responsible for the formation of oxides of cholesterols which will cause the formation of plaque in blood vessels, consequently risk of cardiovascular diseases increases [37]. During the whole process from the manufacturing to storage it is quite important to monitor the lipid oxidation rate and extent to which it may occur so that concerns towards acceptability of sensors and health hazards in case of human consumption may be resolved. Edible oils are mostly consisted of PUFAs which are susceptible towards any type of oxidation like auto-oxidation, thermal oxidation and photosensitized oxidation [38]. The

degree or extent of oxidation can be determined by using different types of methodologies which will determine the quantity of intermediates or products formed during specific stage of reaction [39].

Storage of edible oils is important factor after manufacturing properly because storage conditionings affect the rate of oxidation which directly alters quality of lipid containing food. Storage of edible oils under harsh conditions or improper environmental conditions may cause deterioration of lipid containing foods, these may include high temperature, presence of light, or direct contact with oxygen which readily increase the rate of oxidation and deterioration of oil samples [40, 41]. Primary products formed during oxidation of oils are hydro-peroxides which on further oxidation may cause formation of secondary products which include aldehydes, ketones and other small molecules which may cause food poisoning [42, 43]. The process of oxidation directly affects quality of oil containing food samples which in turn cause decrease in the shelf life of lipid containing products. As the rate of oxidation increases stability decreases as a result of which shelf life of edible oils also decreases. The oxidative stability index also determines the period or storage time during which our lipids containing food could be remain safe and after this period it will be of no use and could be harmful [44, 45].

There are many kinds of variable which could be helpful in predicting the shelf life of different edible oils or fat containing foodstuff. These may include type of processing, conditions at which samples are stored, sunlight exposure, type of material used for packing, presence or absence of oxygen, and presence of antioxidants which could affect the vitality and quality of edible oils and lipid containing food products [46]. However, research on shelf-life prediction or storage conditioning of edible fat/oils at room conditions, which are nearly the real storage conditions, but are not enough when compared with accelerated oxidative conditions or at harsh conditions [47].

4. Oxidation products of oils

Assessment of oxidation of lipids in foodstuff is a pertinent

consideration because products formed during the process of oxidation are affiliated to distasteful sensorial and may cause biological impacts. Adequate assessment of products formed during lipid oxidation persist an insisting work because the phenomenon of oxidation is guite difficult and depends upon kind of lipid, the catalyst which promote oxidation, and ambient conditions [48]. Different methodologies have been adopted to evaluate the extent of oxidation in oils. Free fatty acids (FFAs) and peroxides are among the oxidation products formed at early stage. To monitor these products, acid value and peroxide value have been determined by performing chemical titration methods which act as primary indicators of oxidation products formation [49]. But if the conditions are favorable for oxidation of lipid containing samples then these product will further react and will be converted into secondary products like aldehydes, ketones and other small molecules which could be harmful for health. Thus storage of oil containing food products at specific conditions is necessary to protect them from environmental conditions and safe for human health [50].

There are two major reactions that may cause oil deterioration. Most of rancidity is caused by the reaction when oil reacts with oxygen and is known as oxidative rancidity. On the other hand oxidation may occur due to presence of moisture or enzymes [51]. For example presence of lipase enzyme cause liberation of fatty acids from the triglycerides and result in the formation of diglycerides and monoglycerides. As a result of this reaction FFAs are produced. Hydrolysis may be caused by a chemical action due to the presence of moisture and heat energy, this type of rancidity is known as hydrolytic rancidity [52]. The oxidative rancidity is main reaction of interest as it cause generation of off-flavor molecules and can be detected early as process of oxidation start to develop but not possible in hydrolytic rancidity [53, 54].

Rancidity of edible oil determine its extent of oxidation, different types of product are formed at different stage of oxidation. Primary oxidation product are produced as a result of reaction between alkyl radical which is formed due to presence of heat energy and light (initiation step) with O₂ as a result of

which peroxy radical is formed which attack UFA and peroxides in addition to free radicals are generated (propagation step) [55]. This type of reaction continues until there is no further O_2 present. On the other hand this reaction ends up when radical combine with a stable antioxidant or when two reactive and unstable species react with each other to form stable molecule (termination step) [56, 57].

4.1 Primary oxidation products

At early stage rate of reaction is slow and compounds generated during this period are peroxides, mostly hydroperoxides are known as primary products. These oxidation products are also known as intermediate of lipid oxidation; these products are stable to some extent depending upon structure of lipid and in the absence of heat, light radiation, heavy metals or other radicals. Environmental conditions should be under control to prevent further deterioration; sometime antioxidants may be added to prevent oxidation [48]. Mechanism of hydro-peroxide formation as a result of oxidation is as following;



Figure 1: Mechanism of primary oxidation products formation during early stage of storage or oxidation [42].

4.2 Secondary oxidation products

Primary oxidation products are stable to some extent but in the presence of heat or radiation energy and radicals the primary products further take part in chemical reaction and are converted into secondary oxidation products. These products result by peroxide reaction alone or due to some chain reaction and lead to the formation of short chain molecules such as ketones, aldehydes or some volatile alcohols or acids, which result in the generation of rancid odor due to formation of these products [43]. The presence of antioxidants may cause the interruption of the chain reaction and slow down chain propagation step of oxidation. On the other hand some synthetic antioxidant may be added from outside to prevent oxidation such as phenols [52].

Mechanism of secondary oxidation product formation is given below;



Figure 2: Mechanism of secondary products formation during later stage of oxidation [42]

5. Factors affecting oxidation of oils

To assure the extended shelf-life achievable for edible oils it is significant for us to be cautious of such factors which could impact oxidative stability of oils. These factors mutually influence the rate of oxidation of edible oils and this is not

fluent to distinguish the peculiar impact of each factor.



Figure 3: Description of the factors which effect oxidative stability of edible oils

5.1 Fatty acid composition

The composition of fatty acids tells us significant findings while glancing at relative stability of edible oils. For such oils which possess higher unsaturation in their chemical structure are more prone towards oxidation as compare to those having less unsaturation [58, 59]. The increment of double bond or unsaturation in composition of edible oil results in enhanced rate of oxidation of oil sample which in turn cause increased formation of clustered primary products at the apex of induction time period [40, 47].



Linolenic Acid



UFAs containing oils are more prone towards oxidation as compare to SFAs or MUFAs containing oils. For example oils having oleic, linoleic and linolenic acid are at higher risk of oxidation [60, 61]. In these unsaturated fatty acids Linoleic acid has already been examined comprehensively and results have been concluded which shows that oil samples containing linolenic acid are about 10 to 100 folds more deceivable to phenomenon of oxidation in contrast to SFAs containing oils and monoenes [62, 63].

For instance, when comparison was made among oxidative stability of regular canola and soybean oil with modified oils having lower linoleic acid in their composition then there was lesser percentage of polar components in modified oils after frying [64]. Likewise, resistance towards oxidation of corn oils with enhanced degree of saturation in composition was estimated. After storage corn oil which possess elevated saturation was more resistance towards oxidation in contrast to regular corn oil [65]. Moreover, edible oils which possess iodine value greater than 130 are less stable toward oxidation and deteriorate early. While, those which possess iodine value less than 20 are more resistant toward oxidation [66, 67]. By enhancing concentration of oleic and stearic acid, by genetic modification in seeds and by hydrogenation in soybean oil resistance towards autoxidation could be enhanced [68-70].

5.2 Processing of oil

The method applied for processing of oil also influence stability of oil towards oxidation. Unrefined oil possess higher resistance towards oxidation as compare to refined bleached deodorized (RBD) oil. The stability towards oxidation of unrefined oil is always higher in comparison to RBD oil to some extent because unrefined oil possesses greater concentration of naturally occurring antioxidant [72-74]. Similarly oxidative stability of walnut and macauba kernel oil extracted with supercritical CO₂ was considerably lesser than walnut and macauba kernel oil obtained by just pressed method [75]. The process of roasting of seeds of sesame before extraction of oil also increased resistance of oils towards oxidation, which simply may occur due to products formed as a result of Maillard reactions which act as antioxidants. The stability of oil also increases when temperature rises during roasting as well as expeller pressing of seeds [76, 77].



Figure 5: Fatty acid composition of some of the mostly used oils which has already been reported in the literature [71]



Figure 6: Structures of tocopherols which are present in edible oils and play role as an antioxidants during oxidative stability

5.3 Temperature

Temperature is also a factor which impacts at induction period of edible oils and causes decrease in shelf-life of edible oil, because reaction rate of fatty acid molecule with oxygen approximately becomes twice for each 10°C rise in temperature [78]. In the experimental storage study performed by Crapiste et al. it was cleared that peroxide and acid value rises at faster rate when was obtained at elevated temperature of 40 °C, 47 °C and 67 °C. In case of storage of shortening blends obtained by (hydrogenation or solidifying fats) at 50 °C and 58

60 °C, the results indicate that peroxide values rises at much faster rate at 60°C temperature as compare to 50 °C. The results were also confirmed by performing sensory tests [79]. The process of autoxidation as well as degradation of peroxides formed at initial stages also rises as temperature for storage of oils is increased. For instance, hydro-peroxides degrade at faster rate at elevated temperature [80]. The formation of products as a result of autoxidation reaction is slower at lower temperature throughout the induction period terminal after which a sudden rise in oxidation reaction occur [81, 82]. The percentage of peroxides rises up to a certain level after which alternative increment of oxidation reaction occur. The concentration of polymerized contents also rises considerably after end up of induction time of autoxidation [83].

5.4 Light

Like process of autoxidation another type of oxidation occurs which also cause deterioration of edible oils is known as photo-oxidation. Presence of light at storage place of oils has a fostering impact on oxidation of oils [84]. The process of oxidation by exposure of light takes place in a different way in contrast to free radical mechanism of oxidation. The process of oxidation in the presence of light comprises stimulation of substrate that afterward reacts with fatty acids having unsaturation. For instance, riboflavin reacts with unsaturated fatty acids double bonds in the presence of light [85]. As Frankel (1985) illustrated another type of mechanism which involves oxidation of oils in the presence of light is by excited state of molecular oxygen. Effect of light is most significant factor as compare to temperature in case of singlet oxygen oxidation process. Form of light having short wavelength range has most adverse impact on oxidation of oil as contrast to those having longer wavelength [86]. Perhaps, the impact of light exposure on oxidation of oil alters fewer changes in composition as temperature rises during storage [81, 87].

5.5 Packing material

Type of packing material also affects vitality of edible oil. Selection of most proficient form of packing

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material for the storage of oil also cause resistance towards oxidation and make a huge difference of shelf-life. The process of oxidation occurs at faster rate in transparent glass as well as polyethylene tetra-phthalate (PET) bottles while slower in brown amber bottles [88]. Purified oil of sunflower seeds stays reliable for about 24 months while kept in container of polyethylene having higher density as well as closed cans without evolving obvious taste and smell [89]. For example, impact of different type of packing materials on oxidation of fatty acids in potato crunch was evaluated by exposure to fluorescent lighting and was noticed that light of visible region having wavelength higher than 380 nm cause deterioration of fatty acids containing crunches [90].

5.6 Oxygen concentration

The process of oxidation mostly occurs in the presence of oxygen as well as catalyst. Form of oxygen and amount present in oil also influence rate of oxidation [41]. Amount of oxygen dissolved in oil is associated with its partial pressure in sealed container of edible oil. For instance 1 g soybean can dissolve about 55 ŭg of oxygen at ambient condition [91]. Amount of dissolved oxygen in oil sample rises when pressure exerted by oxygen in the closed container is higher. Also rate of oxidation of lipids enhanced when concentration of oxygen dissolved in oil increases [41]. The impact of dissolved amount of oxygen on deterioration of edible oil become more prominent at harsh conditions such as elevated temperature, presence of light and traces of metals etc. At elevated temperature dependence of oxidation of oil on amount of dissolved oxygen become less due to decrease in solubility of oxygen in oil. But when percentage of oxygen is lower, then rate of oxidation depends only on amount of oxygen dissolved and becomes independent of concentration of lipid [54, 91].

5.7 Minor components

Major components of edible oils are triacylglycerol, in addition to these components they may also entail some minute constituents like, phospholipids, tocopherols, phenolic compounds, carotenoids etc. They may also entail traces of metals, peroxides, free fatty acids, mono- and di-glycerides.



Figure 7: Different impacts of lipid oxidation on the food as well as human health.

Some of these minor constituents promote oxidation rate of fatty acids which results in deterioration of edible oil, some of these retard oxidation rate of edible oil and make them suitable for our health [48].

5.7.1 Antioxidants

Antioxidants are present in oils in minor concentration are among the important constituents which play vital role in enhancing oxidative stability and nutritional importance of edible oils [92]. Edible oils naturally entail some antioxidants which includes phenolic compounds, tocopherols as well as tocotrienols, some carotenoids etc. These naturally occurring antioxidant play pivotal role in maintaining vitality of edible oil for human by neutralizing free radicals formed as a result of chain reaction [93]. There are about eight isomeric forms of vitamin E which are naturally present in edible oils, four of these isomeric form are tocopherols (α -, β -, γ -, and δ -) and other four are tocotrienols (α -, β -, γ -, and δ -). Each isomeric form of vitamin E has its unique biological capability and plausible impact on human health [94, 95]. These naturally occurring components anticipate deterioration of edible oils and enhance their stability toward oxidation which results in longer shelf-life of oil. The percentages of these antioxidants also play vital role in prohibition of some diseases like Parkinson disease and ataxia which results due to deficiency of vitamin E [96].

5.7.2 Tocopherols

In analyzing capacity of tocopherols behaving as an antioxidant

it is necessary to accommodate the conditioning for oxidation reaction which could impact their functioning as hindrance in the way of oxidation of lipids like, temperature, presence of oxygen or its concentration, light, state of lipids and percentage of tocopherols contents [97-99]. Most of percentage of these antioxidants degrades or lost during oil processing such as, extraction, purification, bleaching and deodorization. For instance in case of olive oil about 18%, rapeseed and soybean about 25% removal of tocopherols occur. Moreover in case of cottonseed, sunflower and peanut oil this percentage is quite high, which is about 36%, 37% and 40% respectively. But the percentage of naturally occurring tocopherols remaining behind is also enough to preserve these edible oils from deterioration as a result of oxidation under environmental conditions [100-102].

5.7.3 Synthetic Antioxidants

There are some artificial antioxidants which are intentionally dissolved in samples containing fats or oils to make them intact during different stages of refining. For instance tertiarybutyl hydroquinone (TBHQ) is an artificial antioxidant which is dissolved in oils to protect them from oxidation reaction occurred during purification and deodorization [103]. TBHQ possess brilliant resistance against secondary products which is determined by para-anisidine value and possess stabilizing effect on tocols. On the other hand TBHQ is also reported to be efficient in protecting unrefined oil from deterioration under storage conditions, which is quite usable for countries like Malaysia where transportation of crude oil is very far away and extended storage period is required before reaching to destinations [104].

5.7.4 Other type of antioxidants

The phenolic compounds are also present in composition of edible oil which possess multiple substitutions at benzene ring and could donate hydrogen atom to free radicals [105, 106]. For instance mono- and poly-hydroxyl phenolics are among the main constituents which could donate hydrogen atom. So any species which possess lesser reduction potential as compare to free radical will be able to transfer his hydrogen to free radical until reaction will become opposing [107]. Similarly chelating agents like EDTA, ascorbic acid, and phosphoric acid also cause resistance against oxidation in another way. They cause production of metal complexes which are insoluble or convert ions into insoluble complexes or can cause spatial hindrance in the generation of complexes among metals and oxidation products [108].

5.7.5 Free fatty acid and mono- and diacylglycerols

Oil samples in crude form entail some percent of FFAs, but during processing of oils like, refining percentage of these types of components decreases. For instance, oil obtained from sesame seeds entail about 0.72% FFA, but in case of oil obtained after bleaching by acid clay cause reduction of FFA to about 0.56% [109]. These contents present in edible oil behave as pro-oxidant and promote deterioration of oils. It is also concluded that FFA cause reduction of surface tension which result in more diffusion of oxygen into oil and decrease towards oxidation [110]. In addition resistance to triacylglycerol mono- and diacylglycerols are also entailed by oils in different ranges. These acylglecerols behave as promoter for oxidation of oil in the absence of light. These must be separated from oil during purification of oil to enhance stability of oil against oxidation [109, 111].

5.7.6 Metals

Traces of metals may also present in extracts of oils in their crude form like iron or copper. But on purification concentration of these metal traces decreases. Presences of these metals cause further oxidation of oils which is due to lower activation energy required for initiation of autoxidation to about 64~103 kJ/mol [112]. Metals present in oils react abruptly with fatty acids and generate free radicals of alkyl group. These could also generate reactive singlet oxygen which result in the formation of primary oxidation products [113]. Presence of ferric ion also results in degradation of phenolic compounds which acts as antioxidant, for instance, ferric ion cause degradation of olive oil and resistance towards oxidation decreases [114].

Table 1: Applications	of plant based mate	rials which has bee	en applied for enhancing oxidativ	e stability of oils
Plant materials	Conc. of	Oils analyzed	Effect of extracts	References
	extract			
Leaves of olive tree	200 mg	Sunflower oil	Increase in total phenolic	[124]
(Olea Europaea	extract/kg of oil		content and oxidative	
<i>L</i> .)			stability	
Leaves of olive tree	1000-1500 mg	Corn oil	Increase in total phenolic	[125]
(Olea Europaea	extract/kg of oil		and carotenoid contents and	
<i>L.</i>)			antioxidant potential	
Leaves of olive tree	3% of extract	Olive oil	Increase in Total phenolic	[126]
(Olea Europaea			content and antioxidant	
<i>L.</i>)			potential	
Leaves of rosemary	400 mg/kg of	Soybean,	Increase in oxidative	[127]
(Rosmarinus	011	cottonseed and	stability especially reduction	
Officinalis L.)	0102 1	rice bran oil	in peroxide value	[120]
Leaves of oregano	0.1, 0.3 and $0.70(-0.5)$	Soybean oil	Enhanced oxidative stability	[120]
(Origanum	0.7% of extract			
Vuigare L.)	400 mg/lsg of	Sunflower oil	Enhancement of antioxident	[120]
(Origanum	400 mg/kg of	Sumower on	potential	[120]
(Origanum Vulgare I.)	OII		potential	
Essential oil of	0.01% /volume	Extra virgin	Enhancement of oxidative	[129]
laurel <i>(Laurus</i>	of oil	olive oil	stability	
Nobilis L.)	01 011		Successf	
Leaves and flower	0.1 and 0.2%	Sovbean oil	Increment in induction	[130]
of thyme (Thymus	extract		period of oil	[]
Schimperi R.)			1	
Leaves of basil	3000 mg/kg of	Soybean oil	Enhancement of oxidative	[131]
(Ocimum	oil		stability	
Basilicum L.)				
Leaves of basil	100 and 300	Sunflower oil	Increment in antioxidant	[128]
(Ocimum	mg/kg of oil		potential	
Basilicum L.)				
Pepper powder	10, 20, and 40	Extra virgin	Enhanced oxidative stability	[119]
(Capsicum	g/kg of oil	olive oil		
Annuum L.)	2 0 2 0 1 40			51103
Garlic powder	20, 30, and 40	Extra virgin	Enhanced oxidative stability	[119]
(Allium	g/kg of oll	olive oli		
Sativum L.)	200, 400, and	Canala ail	Enhanced evidetive stability	[120]
Carum Contigum	200, 400, and	Caliola oli	and antioxidant potential	[132]
Essential oil of	100, 200, and	Canola oil	Enhanced antioxidant	[133]
Carum Conticum	400 mg/kg of	Canola oli	notential	[155]
fruit	oil		potential	
Sea buckthorn	3000 mg/kg of	Canola oil	Enhanced antioxidant	[134]
pomace and seed	oil		potential	r1
extracts			r	
Thyme and ginger	200 and 300	Sunflower oil	Reduction in oxidation and	[135]
extract	mg/kg of oil		increment in antioxidant	_
			potential	
Leaves extract of	25, 50, and 75	Sunflower oil	Enhanced antioxidant	[136]

olive oil	μg/mL of oil		potential and reduction of primary and secondary oxidation parameters value	
vitamin E, phytic acid, antioxidant of bamboo leaves, rosemary extract, tea polyphenols, ascorbyl palmitate and tea polyphenol palmitate composites	Different conc. of these mixed antioxidants up to different proportion	High oleic acid sunflower oil	Enhanced shelf-life with addition of these antioxidants	[137]
Extracts of rosemary, sage, and savory, summer	0.1% of by volume of oil	Moringa oil	Enhanced antioxidant potential	[138]
Essential oil of rosemary	0.05. 0.1, 0.2 and 5.0% by volume	Sunflower, soybean oil and tallow fat	Enhanced shelf-life	[139]

6. Enhancement of oxidative stability of oils by using plant extracts

In addition to the naturally occurring antioxidant that are found in oils utilizing synthetic antioxidant complexes is one way to enhance the oxidative stability and overall quality of oil. Despite this, there are questions regarding their impacts on health of consumers, and there is evidence to suggest that these synthetic compounds may cause cancer [115, 116]. Because of this, a number of other potential approaches for improving oxidative stability of oils have been suggested. Specifically, the exploitation of natural antioxidants derived from subordinate torrents, foodstuff by-products, and other agro-food residues. Above all, considering that remaining from foodstuff processing accounts for 30.6 million tons per year, with 35% of that coming from fresh fruits and vegetables [117]

In spite of this, these by-products need to be processed, which involves the inclusion of chemicals (solvents). This is necessary not only for the extraction of phenolic compounds which behave as antioxidants, but also for other reasons. Because it is highly prospective that the extraction practice will also consequence in the release of other unwanted mixtures. But for betterment it is essential to search for natural sources of antioxidants in greater quantity. Alternatively, medicinal and aromatic plants (MAPs) appear to be an excellent candidate for the extraction of naturally occurring antioxidant compounds. Their exploitation, dating back to prehistoric times, by a variety of developments due to the numerous health and therapeutic properties they possessed [118]. There have been a number of studies that have focused on the addition of antioxidants derived from MAPs to oils to enhance their stability [119-123].

7. Oxidative stability of some selected oils

7.1 Soybean oil

Soybean is a type of plant which belongs to legume family and seeds of this plant are mostly utilized in soft food products like tofu and sauce. Seeds of this plant exhibit approximately 20% oil content [140]. The major constituents of soybean includes proteins and fatty acids. Among these fatty acids alpha linolenic acid, docosahexaenoic acid and eicosapentaenoic acid are of prime importance which control transfer of triglycerides into the blood [141]. On the other hand proteins present in seeds of soybean also have a vital role in reducing nourishing inadequacies and inhibiting the diseases associated with hormones like prostate cancer [142]. Soybean possess some potential applications which involve maintaining temperature of body, Source for essential fatty acids, behave as medium for vitamins which are soluble in fats and source for omega-3 and vitamin E [143]. Seeds of soybean entail higher percentage of fats which are at the risks of deterioration and exhibit shorter shelf-life and may result in the development of offensive smell and taste because of decomposition of fatty acids during storage time, due to this reason quality maintenance is necessary [144]. During storage period of the oil, the rate of reaction among the UFAs and molecule of oxygen rises which result in enhanced deterioration of this oil and quality of food products for which it is used [145].

7.1.1 Composition of soybean oil

The major constituents present in soybean oil includes linoleic, linolenic and oleic acids which entail about 55%, 13% and 18% orderly of total composition of soybean oil. Other fatty acids are also present which include palmitic and stearic acid which cover about 10% and 4% of total oil composition. Due to presence of more unsaturation in composition soybean oil is more prone towards oxidative deterioration by oxygen present in the oil entailing container [142, 146]. As a result of oxidation FFAs are generated which can result in affliction of mitochondria. Due to damage of this organelle generation of energy decreased as mitochondria is power house for cells [147]. FFAs produced as a result of oxidation of lipids also facilitate further oxidation which could cause generation of offensive smell or taste in foodstuff [148].

7.1.2 Oxidation of soybean oil

There are different kinds of oxidation which could take place in fat containing products, these may include autoxidation, photo-oxidation, or may be due to enzymes known as enzymatic oxidation [149]. Among these reactions of deterioration of edible oil, autoxidation is major oxidation reaction which occurs due to auto-catalytic activity among UFAs and oxygen. As the unsaturation increases oxidation reaction occur quite easily, same in the case of soybean oil which possess higher percentage of unsaturation in its composition and can be attacked by oxygen quite easily [150]. Soybean oil possesses higher percentage of unsaturation in the form of linolenic and linoleic acids which exhibit more

threat for oxygen attack [151, 152]. Fatty acids having two double bonds in its structure possess higher oxidation ability of about 10 to 40 folds as compare to the fatty acids which possess only one double bond [153]. In most of unsaturated fatty acids autoxidation takes place which consisted of three stages of initiation, propagation and termination. As a result of this type of oxidation hydro-peroxides are generated which assemble as primary products, also free radicals are generated which trigger further reaction. At last stage two radicals merge with each other which result in the formation of stable non-radical species [154]. Peroxides are the main products generated at early stages are degraded further into other products if conditions are favorable for further oxidation. Secondary oxidation products includes aldehydes as well as ketones which are carbonyl compounds and give offensive odor to the oil and cause deterioration of oil sample [155]. So fatty acid composition of this oil conclude that this oil will be less stable and deteriorated more easily as compared to the oil which possess lesser percentage of unsaturation.

7.2 Palm oil

Palm oil is obtained from palm tree fruit which resembles with fruit of date tree. Fruit of this tree composed of two parts, outer portion of the fruit is known as mesocarp and inner portion of the fruit is palm kernel. The fruit of palm tree is collected quite carefully before extreme ripening so that to avoid some damage. These collected fruit clusters are processed instantly so that percentage of free fatty acids could be reduced by enzymatic action [156, 157]. There are two major constituents which are obtained from fruits of palm tree. One is palm oil which is obtained from upper layer of fruit bunches while other is known as kernel oil which is produced from the inner portion of fruit [158]. Both these two oil products possess different physical and chemical features. Palm oil possesses palmitic acid as a major constituent and occurs in solid form at environmental conditions in cooler areas and in the form of fluid in tropical regions [159]. On the other hand kernel oil is most stable oil as compare to other oils or fats because this oil entails lauric acid in higher percentage and also possesses very lower percentage of

Journal of Chemistry and Environment **Table 2:** Applications of FTIR spectroscopy based techniques for the oxidative stability analysis of oils

Oils analyzed	Conditions	Major activity	References
Colza, corn, frying,	Heat at 170° C each 3 h	Oxidative stability and	[231].
and sunflower oil	for 36-h	kinetics	
Canola oil	Heating and frying potatoes	Oxidative products identification	[232].
Olive, corn and sunflower oil	Heating up to boiling	Oxidative degradation analysis	[233].
Sunflower oil	Heating of potatoes for 40h	Total polar compounds analysis	[234].
Soybean, rapeseed, sunflower and peanut oil	Heating from 50 to 260 °C	Acid value and peroxide value	[235].
Soybean, flaxseed, coconut, cottonseed, peanut, rapeseed, corn, rice bran, and camellia oil	4 °C from 1 month to 1 year	Free fatty acid value	[236].
Colombian crude oils	220 to 440 °C	Total acid no determination (TAN)	[237].
Palm and mustard oil	170-230 °C heating range	Compositional analysis after heating samples	[238].
Hazelnut and extra virgin olive oil	Heating at 180 °C for 24 h	Thermal stability	[239].
Walnut oil	Heating at 110 °C	Induction period determination	[240].

Oils analyzed	Type of technique	Major activity	References
Sunflower oil	¹ H NMR	thermo-oxidation, and hydrolytic processes	[265].
Fish oil	¹ H NMR	Oxidative deterioration	[266].
Blends of raspberry with sunflower and corn oil	Low field NMR and ¹ H NMR	Thermal and oxidative stability	[267].
Cold-pressed and commercially refined camellia oil	¹ H NMR and ³¹ P NMR	Oxidative stability	[268].
Sunflower, soybean, peanut, and corn oil	Low field NMR and ¹ H NMR	Primary and secondary oxidation products	[269].
Linseed and fish oil	1D and 2D Low field NMR	Thermal oxidation stability	[270].
Palm oil	¹ H NMR	hydrolytic and oxidative degradation	[271].
Blends of vegetable fish and fungal oils	¹ H NMR	Primary and secondary oxidation products	[272].
Virgin olive oil	¹ H NMR	Stability and shelf-life prediction	[273].
Edible oils	¹ H NMR	Cis Trans fatty acids	[274].

Table 3: Applications of NMR	spectroscopy based techniq	ues in analyzing	2 oxidation of oils
			<u> </u>

UFAs [160].

In most cases this oil is converted into fractions, to serve in variable form in the widespread markets. Palm oil is mostly fractionated into two products like palm-olein which is present in liquid form and other is known as stearin which is present in harder or solid form under normal conditions [161]. Like other oils there are also some minor constituents which are present in palm oil composition when obtained from palm tree fruits. When palm oil is fractionated into palm-olein and palm stearin the minor components like, FFAs, mono-, and diglycerides, antioxidant tocopherols, carotenoids, and products formed by oxidation are remained in olein fraction, some other components like metal traces and phospholipids are migrated with other fraction known as palm stearin [162].

7.2.1 Composition of palm oil

The major constituents of palm-olein oil are SFAs and

MUFAs. PUFAs are present in very small percentage as compare to other oils. Palm oil is enriched with SFAs which include palmitic acid and stearic acid which make about 44% of total composition of palm oil. Other major components are MUFAs which includes oleic acid and contribute to about 42% of composition of palm-olein oil. PUFAs occupy only 12% of total composition of palm-olein oil which includes linoleic acid [158]. There are some other oils which contain higher percentage of MUFAs than palm oil but their oxidative stability is less than palm-olein oil because they entail lower percentage of saturated fatty acids which ranges from 6 to 11.8%. For instance, olive oil contain about 80% of MUFAs, sunflower with higher oleic content possess about 81.3% MUFAs, canola entail about 61% of oleic contents, but these are less stable than palm olein oil due to lesser percentage of SFAs [163, 164].

7.2.2 Oxidation of palm-olein oil

Different types of chemical reaction are effective in determining the oxidative deterioration of oils [42, 165]. In comparison to PUFAs containing edible oils palm-olein oil is most stable oil against oxidative deterioration. This is because of fatty acids composition of this oil which possesses balanced percentage of SFAs and MUFAs and very lower percentage of PUFAs which cause resistance towards oxidation of this oil in comparison to soybean, corn or other UFAs containing edible oils [164]. Minor constituents present in palm-olein oil are also responsible for quality assessment of palm oil. Among these constituents tocols are of prime importance which show resistance against oxidation of palm oil [166, 167].

In spite of the fact that palm oil is most stable oil against oxidation reaction but there are some factors which oppose the application of palm-olein oil for food cooking purposes. Diet rich in SFAs results in obesity which may also result in cardiovascular diseases [168]. Consumption of oil having higher percentage of SFAs also result in enhanced level of cholesterol in blood which may trigger heart diseases [169]. This type of oil is also associated with overweight which in turn cause loss of sensitivity of insulin thus is also associated with diabetes [170, 171]. So oxidative analysis of this oil conclude that this oil is more stable as compare to mostly unsaturated oils which is due to balanced composition of SFAs and MUFAs and lesser percentage of PUFAs

7.3 Canola and rapeseed oil

In Canada canola oil is acquired from the seeds of Brassica species such as, Rapa and Napes. The oil obtained from these varieties of Brassica possesses lower percentage of erucic acid and glucosinolates which are quite different from the composition of rapeseed oil [172]. Oil acquired from rapeseed possesses higher concentration of glucosinolates and erucic acid, because of this reason both of these oils inhibit different physicochemical properties and nutritional values [173]. Triglycerides are major constituents of all edible oils and fats, which are esters of glycerol with fatty acids molecules. But percentage contents of these glycerides may vary from one to other oil [174]. Analysis of canola oil expresses higher percentage of triglycerides to some extent in contrast to rapeseed and soybean oil. Canola possesses higher percentage of triglycerides which ranges from 94.5 to 99.2% of total composition of lipids, on the other hand rapeseed possess 91 to 99 % and soybean has 93 to 99% of total lipid composition [175, 176].

7.3.1 Effect of glucosinolates

In various studies it has been elaborated that higher level of glucosinolates may exert adverse effect especially when fed to red meat, brute and ruminative [177]. As a result of hydrolysis different products are generated these includes some compounds of sulfur and isothiocyanates. These products thus generated intrude with iodine absorption from thyroid glands, result in diseases related to liver, disturb growth rate in the consumers and loss of body weight [173]. Due to these facts plant breeders ascertain that such type of varieties should be developed which possess low contents of glucosinolates. In 1950 Dr. Krzymanski discovered a perfect breed of rapeseed which possess very lower concentration of glucosinolates in its composition and could be used for foodstuff baking purposes [172].

7.3.2 Fatty acid composition of canola oil

To minimize the adverse effect of erucic acid which is present in rapeseed oil different modification has been done in seeds. As a result of modifications in breeds of rapeseed reduction in the percentage contents of erucic acid occured which result in enhanced percentage of octadecanoic acids [172]. Actually octadecanoic acid makes approximately 95% of total fatty acid composition of canola oil. Other breeds of canola has been established which possess about 2.1% of linolenic acid content in fatty acid composition [178]. As a result of low percentage of linolenic acid this oil possesses resistance against oxidation and show enhanced storage time as compare to the regular form of canola. Canola having lower percentage of linolenic acid also expresses enhanced frying performance and prolonged storage ability of fried foodstuff like potato chips. Similarly canola is modified which exhibit enhanced oleic acid contents from 60% to 85%. This oil also possesses better frying performance and excellent quality [64, 179].

By keeping in mind health prospect as well as flavor both form of canola oil show better results. In both high oleic acid containing canola and low linolenic acid containing canola possess better taste and health impact in the absence of Trans form of isomers [180]. Latterly, canola oil has been evolved which possess higher percentage of lauric acid and mostly utilized for candy wafers, whiting of coffee, whipped cream toppings, and fat filling [181]. Canola is the only edible oil which possesses fatty acids with sulfur as constitution of molecule. The structures of these types of fatty acid molecules imply the generation or proximity of these isomers [182, 183].

7.3.3 Stability of canola oil

Canola oil entails about 7 to 11% linolenic acid in fatty acid composition. Presence of this type of fatty acid prone canola oil in the same trouble as soybean and other PUFAs containing oils. Canola oil is also susceptible towards oxidation as well as flavor reversion and face storage problems. The reversion of flavor occurs mostly due to autoxidation and photo-oxidation of UFAs in oils which is known as oxidative deterioration. Oxidative stability of this oil is restricted due to UFAs, chlorophyll and it's degradation products, and also due to presence of traces of reactive species like as minor concentration of fatty acids which possess higher number of double bonds or more than three at least [184]. So canola oil face same problem of oxidative deterioration as soybean or other UFAs containing oils.

7.3.4 High-erucic acid rapeseed (HEAR) oil

In those countries where mostly canola is grown, rapeseed having higher percentage of erucic acid is utilized only for specific food purposes and mostly non-food applications. Its major application is as completely hydrogenated oil which blended with peanut butter in approximately 1 to 2 % to avoid oiling in western countries [185]. Commercially available rapeseed oil which possesses highest percentage of erucic acid is oil having 45 to 50% to erucic acid in its composition. As the melting point of oil which contain fully hydrogenated erucic acid is quite higher, so this fully hydrogenated oil is very useful in fixing oily liquid in array of crystal. Use of this type of oil is quite useful in inter-esterification stearin fraction of palm oil to generate compact fat margarine having zero or no Tran's isomer [186, 187]. Many examples for other applications of completely hydrogenated HEAR oil has been elaborated in 1960s and 1970s. Major purpose of these applications was to elaborate crystallization properties, either as hard stock for the preparation of shortenings in small quantity or as base stock for monoacylglycerols conversion [188].

7.4 Cottonseed oil

In Turkey agricultural production cotton is most consequential marketable crop and biggest congenital source of natural fibers. In addition to source of fibers seeds of cotton possess eloquent percentage of oil which may vary from breed to breed of cottonseed. But in most breeds of cottonseed percentage contents of oil vary from 12 to 25% [189-191]. The amount of oil acquired from seeds of cotton as by-product was utilized to compensate demand of edible oil in Turkey and was utilized for different cooking purposes. After sunflower oil consumption, cottonseed is the most prevailing oil being utilized.

Journal of Chemistry and Environment **Table 4:** Applications of gas chromatog

Oils analyzed	Techniques for	Detector	Major activity	References
	extraction			
Rapeseed oil	HS-Trap-GC-MS	Mass selective	Volatile products	[286].
n-3 PUFA-rich oils	HS-SPME-GC-MS	Mass selective	Volatile products	[287].
Blends of cold- pressed black cumin oil and sunflower oil	HS-SPME-GC-MS	Mass selective	Volatile products	[288].
Soybean, sunflower, and olive oils	MDES-UALLME-GC- FID	FID	Heptanal and hexanal	[289].
Corn oil	DI-SPME-GC-MS	Mass selective	Minor oxidative products	[290].
Olive, Pomace, sunflower and palm olein	GD-ME-DLL-ME	Mass spectrometer	Secondary oxidation products	[291].
Soybean, palm sunflower, coconut, mustard, and rice bran oil	SHS-GC-FID	FID	Hexanal	[292].
Soybean, rapeseed, peanut, sunflower, olive and camellia	TGA-GC-MS	Mass spectrometer	Volatile oxidation products	[293].
Rapeseed oil	HS-SPME–GC × GC– TOF-MS	Mass spectrometer	Volatile products	[294].
Marine and edible oils	GC-TQ/MS	Mass spectrometer	Furan fatty acid identification	[295].

Table 5: Applications of high performance liquid chromatography (HPLC) based techniques for the analysis of oxidation of oil.

Oils analyzed	Techniques	Major activity	References
Rapeseed oil	RP-HPLC	Malondialdehyde, 4-hydroxy-	[302].
		hexenal, and 4-hydroxy-2-	
		nonenal	
Sunflower with varied	NP-HPLC-DAD	hydroperoxy-, keto- and	[83].
fatty acid composition		hydroxy-dienes	
Canola oil	HPLC-MS/MS	Isomeric hydro-peroxides	[298].
Olive, soybean, sesame and sunflower oil	HPLC-UV-FLD	Malondialdehyde	[303].
palm olein, soybean,	HPLC-RID	Total polar components	[304].
canola and sunflower oil			
Sunflower and corn oil	RP-HPLC	2,4-decadienal as major	[305].
Olive oil	HPLC-SFD	Malondialdehyde	[306].
Canola oil	HPLC-UV	Carbonyl compound	[307].
palm, soybean and olive	HPLC, PU	Total polar components and	[308].
oil		polycyclic aromatic	
		hydrocarbons	
Edible oils	HPL-UV	Oxidation of 2-tert-butyl-1,4 benzoquinone	[309].

In most commonly used edible oils in Turkey, sunflower standing first with approximately 1.38 million tons, and cottonseed oil comes second with approximately 1.28 million tons average demand followed by soybean, peanut and rapeseed oil with some less percentage [192].

Cottonseed oil in its unrefined form possess odor which strongly resemble with odor of walnut and peanut oil but appearance is faint to some extent or having pale color. The color of unrefined oil of cottonseed may fluctuate from brownish yellow to dark reddish which is due to presence of sufficient percentage of pigments transfer to oil extract during extraction process of this oil [193, 194]. In addition to the essential fatty there are also some other constituents which are present in oil of cottonseed which includes, phospholipids, pigments, gossypol, sterol etc. which account for approximately 2% of total fatty acid composition [195]. In addition to essential fatty acid cottonseed oil is also enriched in minerals which are also necessary for proper health. It entails vitamin B and other vitamins which are readily soluble in fats and oils for instance, vitamin A, E, D and vitamin K [196].

7.4.1 Fatty acid composition and oxidative stability

Composition of fatty acids play a pivotal role in determining oxidative stability of edible oils, similarly fatty acid profile of cottonseed oil is one of the unique characteristics which influence vitality of this oil [192]. This oil contain both saturated as well as unsaturated fatty acid in 1:2 ratio. It is elaborated as hydrogenated oil which occur naturally in this oil due to higher concentration of PUFAs. In all breeds of cottonseed most percentage of UFAs ranges up to 70% of total composition. In this percentage about 52% are PUFAs which include linolenic acid, while 18% are MUFAs which includes oleic acid. On the other hand approximately 26% are SFAs which includes palmitic acid and stearic acid. This profile of fatty acid composition enhances oxidative stability during frying performance without performing any additional processing [197]. In contrast to other edible oils vitality and stability of cottonseed oil is dependent upon composition of fatty acid as well as unsaponifiable substances remaining in the oil [198]. The presences and percentage of these components fluctuate due to some factors which include environmental conditions, variety or breed of cottonseed, processing and also storage conditions [199, 200]. These facts conclude that cottonseed oil is stable as compare to soybean but more easily prone towards oxidation as compare to palm oil which is due to higher percentage of UFAs as compared to palm oil.

8. Impact of lipid oxidation on food quality and human health

Degradation of fatty acid as a result of oxidation is a customary issue and possess long term frugality concernment in most of food industries because it influences most of foodstuff regardless of fatty acid tenor. Therefore detection of oxidative degradation of majority of foodstuff could be done with the help of sensory organ if food products contain 0.5% or lesser fat contents in them [49, 201]. As elaborated earlier proneness of oxidative degradation of fatty acids in foodstuff

mainly based upon some factors such as, fatty acid profile, environmental conditions, methods used for processing of oil, presence or absence of antioxidants and other minor components like traces of metals etc. [202, 203]. Oxidative deterioration of fatty acids always contribute dilemma during oil processing as well as storage conditioning [204]. There are some major impacts of lipid oxidation which are as following;

8.1 Reversion of flavor

As a result of oxidation primary oxidation products are formed which on further reaction are converted into secondary products. For instance carbonyl compounds are formed which exhibit negative impact and decline taste of foodstuff because of these secondary products. Due to oxidative deterioration of PUFAs varieties of volatile components are generated which possess specifically offensive smell and taste [205, 206]. For instance, soybean oil which is unsaturated in nature could easily experience reversion of taste as a result of photo-oxidation on exposure to visible or ultraviolet light as well as on heating [207, 208]. It has already been proposed that oxidation of alpha linolenic acid in oil is impeccable for the generation of 2-pentylfuran and its isomeric forms, which may generate objectionable flavor or taste in the food product containing this [45, 209, 210]. Similarly in case of butter which possesses unsaturated carbons and linolenic acids in composition is also at the risk of oxidative deterioration and may prone towards oxidation and generate such products which are responsible for the production of such compounds which give offensive odor to the butter. For example oxidation of butter can result in formation of Pantanal, heptanal, and butanoic acid which give off-flavor to foodstuff [211].

8.2 Nutritional implications

The process of oxidation may also result in loss of nutritional constituents which are helpful for proper growth of body. The process of oxidative deterioration of lipids may cause reduction of nutritional importance by decomposition of compulsory fatty acids as well as vitamins which are soluble in lipids such as vitamin A, D, E, and K and also by reducing



Figure 8: List of classic and advanced analytical techniques which can be applied for the oxidative stability of edible oils during different stages of oxidation.

Oils analyzed	Heating conditions	Major activity	References
Sesame oil	0–400 °C	Thermal and oxidative stability	[315].
Favela oil	110-250 °C	Thermal and oxidative stability	[316].
palm, rapeseed, sunflower, linseed oil	1, 5, 7.5, 10, 15, 20 °C/min	Thermo-oxidative stability	[314].
Olive, sunflower and crease oil	10 °C /min	Oxidative stability and thermal profile	[317].
Blends of sesame and sunflower oil	100, 110, 120, and 130 °C	Thermal and oxidative stability	[318].
Sunflower Soybean Jatropha and Waste oil	10 °C /min	Thermal stability determination	[319].
Nectarine and Kernel oil	261 °C	Oxidative stability and thermal behavior	[320].
Blackberry, Chokeberry and Raspberry	50–700 °C	Thermal stability analysis	[321].
Sunflower oil	100 °C	Oxidative stability evaluation	[322].
Rice bran and Karajan oil	5 °C min ⁻¹	Oxidative stability	[323].

Table 6: A	Applications o	f Thermogravimetric	analysis techniques	(TGA) based	approaches for	the analysis of o	xidation of oils
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energy caloric percentage [212]. During process of oxidation some free radicals and metabolites are also generated which remain in oil and transfer into foodstuff and may abuse unsympathetic impacts on heath of mankind [213, 214].

8.3 Health hazards

When rancid oil is used for frying or cooking purposes it imparts toxic effect to food and our body, on the bases of consumption of this type of foodstuff different kind of nutritional ramification may occur. There are some common diagnostics which appear due to toxic deteriorated fat containing foodstuff like unfavorable development of body, diarrhea, muscle weakness due to scar muscle fibers, liver enlargement, yellow fat disease which occur due to lower level of vitamin E or antioxidants and higher level of unsaturation in fats, and consequent scarcity of vitamins like A and E [215].

There are also some validations which indicate that foodstuff enriched in products of lipid oxidation are entailed in injuries of blood vessels, narrowing of blood vessels due to formation of plaque and blood clots in vessels which are highly risky for health. In an experiment it also has been explained that cyclic molecules generated as a result of oil heating at high temperature could cause toxicity in the rats even at lower percentage of about 0.01 % in diet [216, 217].

9. Methods for the analysis of oxidative stability

Oils and fats are among major constituents of foodstuff along with proteins, carbohydrates as well as minerals [9]. Assessment of quality and stability of edible oils are two factors which are interrelated to each other. Evaluation of vitality of edible oils is quite necessary, but both the sellers and consumers are withstanding the issue regarding evaluation of quality that they prefer for baking or frying their food products. They should be aware of satisfactory quality of edible oil when purchasing either it is safe to use or not and for how much time period it will remain safe [218, 219]. To keep vitality or stability of edible oil satisfactory both dealer of raw material and buyer should proficiently subscribe to the protocols needed for analysis in industry [220].

9.1 Volumetric methods

These methods are applied to determine the primary oxidation products of edible oils produced as a result of oxidation at early stage of storage. These methods include free fatty acid value and peroxide value by performing acid base and iodometric titrations respectively.

9.1.1 Free fatty acid value by titration

The determination of FFA based on the principle of acid base titration in which ethanolic potassium hydroxide solution is applied as a titrant against free fatty acids present in the oil sample as a result of deterioration occurred. Acid value is measured and each unit of acid value is approximately equal to 0.503% of free fatty acid so, acid value of oil is approximately double of FFA value [221]. Determination of free fatty acid value is of primarily significance because firstly it gives information regarding decomposition or deterioration of oil, secondly presence of free fatty acid could exhibit pro-oxidant impact which is associated with percentage of FFA [110, 222].

9.1.2 Peroxide value by titration

The determination of peroxide value is among the most widely used procedure for elaborating the deterioration of edible oil as a result of oxidation reaction at early stages [223]. The PV is mostly described as, mille-equivalents of peroxide oxygen contents as a result of oxidation per one kilogram of oil. Number of different analytical procedures has been developed for the determination of peroxide values. One of the most commonly applied methods for PV value determination is based upon oxidation ability of peroxides of lipid molecules to produce iodine molecule after reaction with potassium iodide salt. Furthermore it was reported that value of peroxide greater than 7.5 suggested enough deterioration of edible oil and generation of carbonyl compounds which cause induction of offensive smell in fried chips [224]. The range of PV exhibit quite better relationship with aroma log but this is true only at early stages of storage period because oxidation yields only primary products but on further oxidation reaction then these unstable primary products are converted into secondary products [225, 226].

9.2 Spectroscopic methods

9.2.1 Analysis by FTIR spectrophotometer

FTIR spectroscopic method has successfully been applied in order to overcome the limitations of analysis time, accuracy and precision as faced by using classical volumetric methods for determining oxidative deterioration of edible oils [227]. As in other sample analysis by this approach particular peaks appeared when deteriorated oil is analyzed. Hu et al. applied FTIR spectrophotometer in combination with quartz cuvette for infrared wavelength to determine free fatty acids by measuring acid value of various oils which occurred due to oxidation of fatty acids at early stage as primary oxidation products [228]. Shang et al. also used the same configuration to determine peroxide value of various commercial oils as hydro-peroxides are primary indicator of lipid oxidation and quite helpful in predicting shelf-life of edible oils [229].

In addition to primary oxidation products analysis this techniques was also applied for analyzing secondary oxidation products which are generated due to deterioration of soybean and corn oil when the sample of these oils were subjected to different heating effect. Like primary products the enhanced deterioration was determined due to peak shift in spectra of these oils when were compared with fresh oil samples [230]. In addition to this type of FTIR arrangement, attenuated total reflectance with FTIR (ATR-FTIR) has also effectively been applied for analysis of simple corn, sunflower, and colza and a mixture of different oils after high temperature treatment [231].

9.2.2 Analysis by using UV-Visible Spectrophotometer9.2.2.1 Iodide oxidation method

The primary oxidation products such as, the percentage of hydro-peroxide contents have also been evaluated by using a spectrophotometric iodide based approach. The lipid or fatty acid containing sample is dissolved in an acidic solution before being combined with iodide in this uncommon procedure [241]. Iodide is converted to iodine via the lipid hydro-peroxide. The produced tri-iodide anion is distinguished spectrophotometrically at 350 nm which is produced as a result of an excess reaction between the developed iodine and iodide. Fe (II) was utilized by Bloomfield as a catalyst in this process. The short response time reduces interference from side reactions, while the closed conditions eliminate intervention from ambient oxygen [242, 243].

9.2.2.2 Conjugated dienes and trienes value

As a result of oxidation at early stages peroxides are formed from deterioration of fatty acids which are unstable to some extent and may be stabilized due to displacement of double bonds delocalized electrons, and converted into conjugated molecules known as dienes and trienes [244]. These structures are stable to some extent as compare to peroxides and show absorbance in ultraviolet region at wavelength of about 235 nm and 270 nm orderly which can be determined by using spectrophotometer [245].

The value of conjugated dienes is usually described from the prospect of dienoic acid present in the edible oil which also represents percentage of primary oxidation. This dienoic acid mostly shows absorbance limit in UV region ranging from 232 to 234 nm. For the determination of CV values mostly iso-octane is used as a solvent and absorbance is measured [34]. These conjugated molecules proliferate to a specific level in edible oil and then are stabilized as these molecules are subjected to further decomposition and are converted into further products. Major products generated at this level are trienes. The detection of such type of secondary products is also possible with the help of spectrophotometer. Mostly the absorbance region of these products lie at wavelength of about 268 nm, but this should be minded that in this region of wavelength, overlapping of many compounds may take place [39, 246].

9.2.2.3 Anisidine value

The major products generated as a result of secondary oxidation are carbonyl compounds such as, aldehydes. These products are mainly responsible for the generation of rancid odor [247]. This methodology for oxidation products determination utilized reaction of generated carbonyl compounds with anisidine solution in the proximity of acetic acid.

Oils analyzed	Heating conditions	Major activity	References
Linseed oil	(90, 100, 110, 120, 130, 140 °C)	Oxidative stability was determined by activation energy and induction period	[331].
Virgin coconut oil A mixture including virgin coconut and refined soybean/ refined safflower oils	25 °C and 10 °C/min	Determination of thermodynamic nature	[327].
Cold-pressed linseed, rapeseed, camelina black cumin evening primrose hempseed milk thistle poppy, pumpkin and sunflower oil.	5 °C/min	Oxidative stability in comparison with Rancimat test	[329].
Soybean and sunflower oils enriched with herbal extracts	(4, 7.5, 10, 12.5 and 15.0°C/min)	Oxidation kinetics parameters	[204].
Echium oil	(50, 60, 70, 80, 90, 100 and 110°C	effect of hydroxytyrosol and rosemary extract on oxidation	[330].
Blackberry, Chokeberry Raspberry Seeds and Oils	2 °C/min to 160 °C temp.	To analyze thermal properties	[321].
Olive corn and sunflower oil	(110, 120, 130, 140 °C)	Oxidative stability determination	[332].
Different cultivars of flaxseed oil	2 and 5 °C/min	Thermo-oxidative analysis	[333].
Amaranth and Quinoa Oils	(100, 110, 120, 130, 140 °C)	kinetic parameters of oxidation process	[334].
Different cultivars of Camelina sativa L.	(1, 2, 5, 10, 15 °C min ⁻¹)	Thermo-oxidative stability analysis	[335].

Journal of Chemistry and Environment **Table 8:** Applications of sensor based approaches for the analysis of oxidation of oils.

Detection system	Major activity	References	
Reagent kit based on spectrophotometer	Acid value and peroxide value	[352].	
Wavelength-shift-based Colorimetric Sensor	Peroxide value	[353].	
Perovskite nanomaterial based multiplex-mode Fluorescence Sensor	Acid value, moisture content and 3- chloro-1,2-propanediol	[354].	
High-performance fluorescent sensor based on CsPbBr ₃ quantum dots	Total polar compounds	[355].	
Chitin based calorimetric sensor	Aldehyde detection	[356].	
Paper based colorimetric sensor soaked with eutectic solvents	Malondialdehyde analysis	[357].	
Nanofiber mat prepared from polyvinyl alcohol and Schiff's reagent	Aldehyde detection	[351].	
Composite films based sensor	Aldehyde detection	[358].	
Electronic nose coupled with artificial neural network	Shelf-life prediction	[359].	
4-hydrazinyl-7-nitrobenzofurazan fluorogenic probe	Malondialdehyde analysis	[360].	
Screen-printed electrode Gold nanocluster based fluorometric biosensor	Free fatty acid value Prooxidant activity analysis	[361]. [362].	
Digital Image Colorimetry	Peroxide value determination	[363].	
Paper based analytical device	Peroxide value determination	[364].	

This result in the formation of Schiff bases and yellowish coloration is appeared in the reaction mixture which shows absorbance at about 350 nm. The value of absorbance rises about 4 to 5 times if aldehydes possess conjugated double bond along with double bond of carbonyl group [248].

This procedure of secondary oxidation determination is supposed to be quite easy and rapid. Para-anisidine value along with peroxide value helps us to measure total percentage of oxidation or oil deterioration. This totox value give confirmation regarding history as well as present quality of edible oil, thus allow observer to evaluate total extremity of oxidation or deterioration in foodstuff [249]. The anisidine value has been conferred as better characteristic for determination of secondary products because it is associated with peroxide value, Thiobarbituric acid value and other analytical method quite nicely [250].

9.2.2.4 Thiobarbituric acid (TBA) assay

Malondialdehyde is major product formed as a result of oxidation of primary products and this is also most widely utilized marker to elaborate oxidation process of edible oils. TBA forms a complex molecule with MDA whose value could be expressed by applying spectrophotometer. The reaction between MDA and TBA takes place mostly at elevated temperature and lower pH which result in the formation of complex molecule which behave as chromophore and possess highest absorbance at about 532 nm [251].

There are different types of protocols which could be applied in analysis of foodstuff. For instance, there exist some protocols which could be applied like, heating sample directly, distillation of sample, and extraction of lipids by using organic or aqueous acid, accompanied by reaction of acid with TBA [252]. The most commonly applied protocol includes homogenization as well as centrifugation in acidic median for example, tricholoacetic acid and ensuring reaction with TBA at elevated temperature [253]. This method has been recommended as most reliable and perceptive procedure for the evaluation of rancidity or deterioration of edible oil as compare to other test like determination of hexanal and anisidine value [254, 255].

9.2.3 Analysis by nuclear magnetic resonance (NMR)

Many of the research groups' practiced the ¹H and ¹³C NMR spectroscopy for food products analysis especially edible oils [256, 257]. They have proven that this approach is extremely helpful in determining the degree of oxidation of the lipid fraction and in giving details on the types of major functional groups and concentration of the primary and secondary oxidation products identified in oils [258-261]. In addition to identification, this technique is also proven a valuable approach in quantification of oxidation products of fatty acid produced as a result of oxidation during different storage periods [262]. Also this method possesses decent relationship with conservative analysis approaches for instance TBA has already been described [263]. In recent years, a number of multidimensional NMR approaches have been fabricated, including diffusion ordered spectroscopy, nuclear overhauser effect spectroscopy, and correlational spectroscopy. The uses of these instruments needs a lot of time owing to the procurement procedure even if they offer an improved consignment than one-dimensional spectra, which enhances the categorization of dietary lipid samples [261, 264].

9.2.4 Analysis by chromatographic techniques9.2.4.1 Analysis by gas chromatography

The determination of volatile products which are generated as a result of further oxidation of primary oxidation products can be efficiently done by performing gas chromatographic analysis. Most of these products involved hexanal and pentanal determination as these are among most commonly produced oxidation products [275, 276]. This analytical technique also provides useful evidences regarding fundamental pathway of reaction through which oxidative deterioration has been occurred [277]. Appropriate GC techniques have been devised for direct oil injection onto the column but there are some drawbacks of this method as it results in reduction of column life as well as unstable chromatographic baseline which results in inaccurate results [278, 279]. As a result, the separation of

volatile products produced by oxidation was instigated by means of a U-tube that is coupled to the GC [280]. Vacuum distilling the volatiles keen on a cold trap before GC exploration is alternative preference for on-column injection [281].

In addition to these approaches, another method was developed by utilizing solid phase microextraction (SPME) and GC for analyzing oxidation of lipid containing food products. Aforementioned abstraction of volatile components by using SPME has been deemed an eco-friendly approach for analysis as this development involved exclusion of harmful solvents. Additionally, the outcomes were well correlated with the anisidine value [282-284]. Xia & Budge (2018) developed a GC-MS technique in combination with solid phase extraction and trimethylsilyl derivatization process for illustration of hydroxy fatty acid which are produced as a result of oxidative deterioration of edible oils. This approach also facilitates imminent quantifications of these oxidative products. Additionally, the usage of EI and PCI spectra enabled the interpretation of both saturated as well as unsaturated hydroxy FA which in turn can provide information of specific fatty acid oxidation [285].

9.2.4.2 Analysis by liquid chromatography

In addition to volatile components there are also nonvolatile components which can be generated as a result of oxidative damage of lipid containing food products. These types of products can be identified and quantified by using liquid chromatographic techniques in combination with UV or MS detecting systems [296, 297]. Kato et al. (2018) utilized the liquid chromatography tandem mass spectrometry for the determination of different form of isomeric hydro-peroxides which not only influence quality of edible oil but also are not analyzed by peroxide value. In addition to this, this approach was quite helpful in determining mechanism of oxidative deterioration of edible oils [298]. In addition to primary oxidation products analysis, it is also possible to analyze secondary oxidation products and their differentiation from hydro-peroxides which are produced at later stage of oxidation by using liquid chromatography [299].

In addition to normal phase chromatography reverse phase HPLC can be applied for the analysis of oxidation products. This approach can be applied for the analysis and differentiation of conjugated dienes and peroxides isomers which is based upon geometrical isomerism [300]. Gotoh et al established an approach for the determination of peroxide values for edible oil quality check in the colored samples of lipid containing food samples. The working of this approach was based upon the reaction of lipids with triphenylphosphine which result in the formation of a complex which exhibit absorbance at 260 nm. When these samples are analyzed by using HPLC having UV detector then the peroxides were identified and quantified by this method [301].

9.2.5 Thermal techniques

9.2.5.1 Thermogravimetric analysis

Thermogravimetric analysis may also be used to investigate the thermal degradation of oils caused by oxidation of lipids. Weight variation in response to oxygen uptake and thermal degradation are two methods used to analyze the oxidative deterioration in the oil containing food product [310-312]. Gao & Birch proposed that TGA is comparatively simple, easy and lesser time taking technique and can be applied for the estimation of beginning of oxidation in different edible oils (i.e., flaxseed, hemp, and canola oil) [313]. Hoki oil's shelf life was determined by using TGA and Arrhenius extrapolation equation to be 0.56 years, although DSC projected it to be 1.39 years [312]. Li et al. (2018) employed TGA to make comparison among the oxidative stability of numerous edible oils for instance, sunflower, palm, linseed, and rapeseed oils [314].

9.2.5.2 Differential scanning calorimetry

DSC has been developed to assess the oxidation resistance of fat-containing food products. It is a thermal analytical approach that advantages such as high sensitivity, quickness, and small amount of sample [324]. In comparison to previous approaches, this accelerated technique enables the continuous tracking of thermal activity in the oxidative deterioration process [325]. In comparison to the Rancimat approach, this technique also required shorter stability assessment duration. Ramezan et al.

performed this technique for the analysis of various commercial oils at varied temperature conditions and compared the results with the Rancimat results and suggested the DSC as a better option because of its advantages over Rancimat method [326].

According to the results of DSC, Srivastava et al. revealed the thermodynamic configuration of virgin coconut oil amalgamated with other refined oils such as soybean and safflower oil [327]. Belayneh et al studied Camelina seed oil to determine the influence of different extraction techniques such as, cold press, soxhlet, and supercritical CO₂ extractions on the oil's oxidative stability [328]. Symoniuk et al observed the thermal oxidative stability of various selected cold-pressed oils by applying this technique [329]. Lately, Echium oil has been investigated to perceive the influence of extract of rosemary and hydroxytyrosol on the oxidative stability of this oil [330].

9.2.7 Determination of oxidation by using Sensors

American oil chemists' society (AOCS) has industrialized numerous methods to measure and evaluate the level of oxidative deterioration of edible oils, for instance the Paraanisidine value, acid value or free fatty acid value, peroxide value, and others. These methods of analysis are easy, but these methods are mostly time taking and disparaging. They moreover cause prospective risks to the surroundings and human healthiness owing to higher amount of solvent waste [201]. To overcome these issues there is need to develop other methods. The most obvious development of action is to depend on an automated system like an E-Nose, which not merely simulate human olfaction but as well has the ability to find and categorize harmful vapors using a complex process. A device called an E-Nose can quickly identify some of the dangerous products which are produced as a result of oxidation [336]. The stability or durability of numerous food products has been determined by applying olfactory device which include tomatoes [337], apples [338, 339], meat products and raw milk samples [340], valerianella [341], deep-fried potatoes [342], Rice [343], and cultivated foodstuffs [344-347]. Pattern recognition techniques and facts

examination are compulsory to distinguish the indicators or their patterns to categorize the data. The E-Nose detected signal pattern can be examined by exploiting artificial neutral network (ANN) and statistical software like discriminant factorial analysis (DFA) and principle component analysis (PCA) [336]. Visual detection by the color variation of gauge strips or films is a supreme scheme to enable excellence evidence about foodstuffs analysis. The approach is mainly based upon computer visualization which has been successfully applied for analyzing the oxidative deterioration of edible oils of foodstuffs which possess oil contents [348]; on the other hand, rare other assessment approaches have been developed which depend on human visualization and not rely on apparatuses and computers. Robins and his colleagues developed Schiff reagent (colorless solution) which is comprised of pararosaniline hydrochloride and sodium sulfite and can be applied for analysis of oil containing foodstuffs. After exposure to secondary oxidation products especially aldehyde, this colorless solution turned into reddish purple or bluish purple [349]. On the basis of this reaction, polyvinyl alcohol (PVA) and Schiff's reagent based amalgamated films have been developed with the help of solution casting process. These films can be applied to identify the existence of aldehyde which is the foremost secondary product produced as a result of extensive deterioration of lipids. The purpose of the PVA/reagent Schiff's based films was to monitor lipid oxidation in foodstuffs. But, these films' response interval to oxidation products (i.e., aldehydes) was too extended, approximately 1 hour, and these fabricated films were not proven so effective for the estimation of oxidative deterioration of foodstuffs [350, 351].

10. Conclusion

Edible oils are among major constituents of food so their proper quality assurance is quite necessary for human use. The maintenance of the quality is a major concern after proper manufacturing which is mainly dependent upon the oxidation. There are different factors which prone these oils towards oxidative deterioration which includes fatty acid composition, storage conditions and presence of minor components. On the other hand there some other minor components present in

edible oils and prevent them from oxidative deterioration and extent their shelf-life. Similarly there is another approach which include the addition of plant based extracts which can be added to these oils which also prove helpful in enhancing the oxidative stability of these edible oils. The proper analysis of the oils after extraction and manufacturing is required after time to time interval so that we can protect them from oxidation and usefulness for human health. There are number of different approaches which can be employed for the analysis of different oxidation products during different stages of the storage. These approaches are quite helpful in the analysis of different oils and their oxidation products which provide useful information regarding their usefulness for the human and their adverse effect on health. However, these techniques are quite useful but there are some factors which limit their applications for analysis of large number of samples. So, there is need of proper analysis of these oils after specific time intervals by developing new methods which are precise, accurate and less time taking.

11. Future Perspectives

There are number of protocols which are proposed by AOCS for their proper analysis. These methods have no limitations but these methods required large volume of solvents and more time to conduct. Moreover, these methods required proper laboratory for performance which is not possible for all the consumers to analyze these edible oils. In order to overcome such types of issues analytical techniques has been developed and successfully applied for the analysis of these oils. These include spectroscopic, chromatographic as well as thermal techniques which have been applied in recent past for the oxidative study of these oils. These techniques also provides results with quite accuracy and timely as compared to the conventional chemical methods. But these techniques are quite expensive and also required highly pure solvents for analysis which is also a major issue regarding analysis of deteriorated oils. On the other hand these analytical instruments required highly trained persons who can perform these analysis, everyone cannot conduct these analysis. In addition to these analytical techniques electronic noses have

been fabricated based upon sensory evaluation method which can also provide information about the oxidation products of the edible oils. These types of methods have been proven helpful in analyzing the oxidative stability of these edible oils.

In addition of these methods there is another emerging field which is proving quite helpful in every field of life which is known as biosensor. There are different types of sensors which could be applied for the analysis of different food products and make assurance about their usefulness for human and other consumers. Different types of sensors has been developed which could also analyzed oxidation products quite easily and within short frame of time. But the already developed sensors are not quite enough to analyze oxidation products of edible oils. As the process of oxidation of edible oil is complicated process which could proceed differently under different conditions and result in different types of products which could impose negative health impacts.

There is need to develop biosensors which could be applied for analysis of different kinds of oxidation products. As there are different types of products could be generated as a result of oxidation so different types of biosensors should be developed which could analyze different products produced under different conditions. There is need to develop biosensor according to the type of products produced so that accuracy could be enhanced. In addition to this simple type of biosensor should be developed so that everyone can use it easily and accurately. Like lactometer simple type of instrument should be developed so that quality of oil could be analyzed at the cooking areas such as restaurants and bakeries.

Declaration

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Conflicts of Interest

The authors declare that they have no conflict of interest.

Authors Contribution

Iqbal Ahmed convinced the main idea and wrote the manuscript. Muhammad Furqan Farooq, Iqra Rani, Ijaz Hussain, Hunain Zulfiqar revised manuscript and prepared figures and other improvements. Hira Zulfiqar and Abid Jan

helps in scientific writing of paper. **Data Availability statement**

The data presented in this study are available on request

from the corresponding author.

REFERENCES:

- 1. Davis, K.F., et al., Meeting future food demand with current agricultural resources. Global Environmental Change, 2016. **39**: p. 125-132.
- Food and A.O.o.t.U. Nations, Technical Platform on the Measurement and Reduction of Food Loss and Waste. 2020.
- Cui, Y., et al., Effect of traditional Chinese cooking methods on fatty acid profiles of vegetable oils. Food Chemistry, 2017. 233: p. 77-84.
- 4. Li, Q., et al., Application of Fourier transform infrared spectroscopy for the quality and safety analysis of fats and oils: A review. Critical reviews in food science and nutrition, 2019. **59**(22): p. 3597-3611.
- da Costa, G.B., et al., Using near infrared spectroscopy to classify soybean oil according to expiration date. Food Chemistry, 2016. 196: p. 539-543.
- Casimir, C. and B. David, Food Lipoids: nutrition and biotechnology. 1997, England: Sheffield Academic Press Ltd.
- 7. Fahy, E., et al., A comprehensive classification system for lipids. 2018.
- Kiran, C.R. and A. Sundresan, Thermal degradation studies on Edible Oil during Deep Fat Frying Process. 2015, Cochin University of Science and Technology.
- 9. Kumar, A., A. Sharma, and K. C Upadhyaya, Vegetable oil: nutritional and industrial perspective. Current genomics, 2016. **17**(3): p. 230-240.
- Colombo, C.A., et al., Macauba: a promising tropical palm for the production of vegetable oil. OCL, 2018.
 25(1): p. D108.
- Mahlia, T.M.I., et al., Palm oil and its wastes as bioenergy sources: a comprehensive review. Environmental Science and Pollution Research, 2019.
 26(15): p. 14849-14866.
- 12. Covaciu, F.-D., et al., Edible oils differentiation based on the determination of fatty acids profile and

Raman spectroscopy—a case study. Applied Sciences, 2020. **10**(23): p. 8347.

- Kris-Etherton, P.M. and S. Yu, Individual fatty acid effects on plasma lipids and lipoproteins: human studies. The American journal of clinical nutrition, 1997. 65(5): p. 1628S-1644S.
- Hu, F.B., et al., Dietary saturated fats and their food sources in relation to the risk of coronary heart disease in women. The American journal of clinical nutrition, 1999. **70**(6): p. 1001-1008.
- 15. de Oliveira Otto, M.C., et al., Biomarkers of dairy fatty acids and risk of cardiovascular disease in the multi-ethnic study of atherosclerosis. Journal of the American Heart Association, 2013. **2**(4): p. e000092.
- Jeyarani, T. and S.Y. Reddy, Physicochemical evaluation of vanaspati marketed in India. Journal of food lipids, 2005. 12(3): p. 232-242.
- Mensink, R.P. and M.B. Katan, Effect of dietary fatty acids on serum lipids and lipoproteins. A metaanalysis of 27 trials. Arteriosclerosis and thrombosis: a journal of vascular biology, 1992. 12(8): p. 911-919.
- Denke, M.A., Dietary fats, fatty acids, and their effects on lipoproteins. Current atherosclerosis reports, 2006. 8(6): p. 466-471.
- Leaf, A., Historical overview of n- 3 fatty acids and coronary heart disease. The American journal of clinical nutrition, 2008. 87(6): p. 1978S-1980S.
- 20. Phillips, C.M., et al., Leptin receptor polymorphisms interact with polyunsaturated fatty acids to augment risk of insulin resistance and metabolic syndrome in adults. The Journal of nutrition, 2010. **140**(2): p. 238-244.
- 21. Calder, P.C., Functional roles of fatty acids and their effects on human health. Journal of parenteral and enteral nutrition, 2015. **39**: p. 18S-32S.
- 22. Food and H. Drug Administration, Food labeling: trans fatty acids in nutrition labeling, nutrient content claims, and health claims. Final rule. Federal Register, 2003. **68**(133): p. 41433-41506.
 - Remig, V., et al., Trans fats in America: a review of their use, consumption, health implications, and regulation. Journal of the American Dietetic Association, 2010. **110**(4): p. 585-592.
- Organization, W.H., Diet, nutrition, and the 35.
 prevention of chronic diseases: report of a joint WHO/FAO expert consultation. Vol. 916. 2003: World Health Organization.
- Slawson, D.L., N. Fitzgerald, and K.T. Morgan, Position of the Academy of Nutrition and Dietetics: the role of nutrition in health promotion and chronic disease prevention. Journal of the Academy of Nutrition and Dietetics, 2013. 113(7): p. 972-979.
- Kimokoti, R.W. and B.E. Millen, Nutrition for the prevention of chronic diseases. Medical Clinics, 2016. 100(6): p. 1185-1198.
- 27. Galano, J.-M., et al., Special Issue on "Analytical Methods for Oxidized Biomolecules and Antioxidants" The use of isoprostanoids as biomarkers of oxidative damage, and their role in human dietary intervention studies. Free Radical Research, 2015. 49(5): p. 583-598.
- Guillén, M.a.D. and N. Cabo, Fourier transform infrared spectra data versus peroxide and anisidine values to determine oxidative stability of edible oils. Food chemistry, 2002. 77(4): p. 503-510.
- 29. Silva, F.A., F. Borges, and M.A. Ferreira, Effects of phenolic propyl esters on the oxidative stability of refined sunflower oil. Journal of Agricultural and Food Chemistry, 2001. **49**(8): p. 3936-3941.
- 30. Morales, M.T. and R. Przybylski, Olive oil oxidation, in Handbook of olive oil. 2013, Springer. p. 479-522.
- Falowo, A.B., P.O. Fayemi, and V. Muchenje, Natural antioxidants against lipid–protein oxidative deterioration in meat and meat products: A review. Food Research International, 2014. 64: p. 171-181.
- Min, D. and H. Lee, Lipid Oxidation of Edible Oil, Food Lipid: Chemistry, Nutrition and Biochemistry, Akoh CC and and Min DB (Eds.), 283-296. 1998, Marcel Dekker, New York.
- Pezzuto, J.M., et al., Characterization of natural product chemopreventive agents, in Cancer chemoprevention. 2005, Springer. p. 3-37.
- 34. Li, C., X. Wang, and Q. Zeng, Research progress of the process and mechanism, determination and influential factors of vegetable lipid oxidation. Food and Fermentation industries, 2016. **42**(9): p. 277-284.

- Dobarganes, C. and G. Márquez-Ruiz, Oxidized fats in foods. Current Opinion in Clinical Nutrition & Metabolic Care, 2003. **6**(2): p. 157-163.
- Anwar, F., M. Bhanger, and S. Yasmeen, Antioxidant activity of some natural extracts in corn oil, in Advanced Research on Plant Lipids. 2003, Springer. p. 27-30.
- Ansorena, D., et al., Thermo-oxidation of cholesterol: effect of the unsaturation degree of the lipid matrix. Food Chemistry, 2013. 141(3): p. 2757-2764.
- Akoh, C.C., Food lipids: chemistry, nutrition, and biotechnology. 2017: CRC press.
- Gunstone, F.D. and F.A. Norris, Lipids in foods: chemistry, biochemistry and technology. 2013: Elsevier.
- 40. Roman, O., et al., Oxidative reactivity of unsaturated fatty acids from sunflower, high oleic sunflower and rapeseed oils subjected to heat treatment, under controlled conditions. LWT-Food Science and Technology, 2013. **52**(1): p. 49-59.
- 41. Johnson, D.R. and E.A. Decker, The role of oxygen in lipid oxidation reactions: a review. Annual review of food science and technology, 2015. **6**: p. 171-190.
- 42. Choe, E. and D.B. Min, Mechanisms and factors for edible oil oxidation. Comprehensive reviews in food science and food safety, 2006. **5**(4): p. 169-186.
- 43. Pratt, D.A., K.A. Tallman, and N.A. Porter, Free radical oxidation of polyunsaturated lipids: New mechanistic insights and the development of peroxyl radical clocks. Accounts of chemical research, 2011.
 44(6): p. 458-467.
- 44. Yang, Y., et al., A novel method for determining peroxide value of edible oils using electrical conductivity. Food Control, 2014. **39**: p. 198-203.
- 45. Wang, Y., et al., Comparison of furans formation and volatile aldehydes profiles of four different vegetable oils during thermal oxidation. Journal of food science, 2019. 84(7): p. 1966-1978.
- Guiotto, E.N., et al., Effect of storage conditions and antioxidants on the oxidative stability of sunflower– chia oil blends. Journal of the American Oil Chemists' Society, 2014. 91(5): p. 767-776.
- 47. Martín-Polvillo, M., G. Márquez-Ruiz, and M.C. Dobarganes, Oxidative stability of sunflower oils

differing in unsaturation degree during long-term 60. storage at room temperature. Journal of the American Oil Chemists' Society, 2004. **81**(6): p. 577-583.

- Barriuso, B., I. Astiasarán, and D. Ansorena, A review of analytical methods measuring lipid 61. oxidation status in foods: a challenging task. European food research and technology, 2013. 236(1): p. 1-15.
- 49. Xu, L., et al., A novel method for qualitative analysis of edible oil oxidation using an electronic nose. Food 62. chemistry, 2016. 202: p. 229-235.
- Olanrewaju, A.S. and O.E. Moriyike, Physicochemical Characteristics and the effect of packaging materials on the storage stability of selected Cucurbits oils. Am. J. Food Nutr, 2013. 1: p. 63. 34-37.
- 51. Ajith, S., et al., Effect of storage temperatures and humidity on proximate composition, peroxide value and iodine value of raw cashew nuts. Journal of food science and technology, 2015. **52**(7): p. 4631-4636.
- Hamilton, R.J., et al., Chemistry of free radicals in lipids. Food Chemistry, 1997. 60(2): p. 193-199.
- 53. Przybylski, R., Methods to measure volatile compounds and the flavor significance of volatile compounds. Methods to assess quality and stability of oils and fat-containing foods, 1995.
- 54. Zhang, Y., et al., Mechanism, indexes, methods, challenges, and perspectives of edible oil oxidation analysis. Critical Reviews in Food Science and Nutrition, 2021: p. 1-15.
- 55. Frankel, E.N., Lipid oxidation. 2014: Elsevier.
- 56. Schaich, K.M., Lipid oxidation: theoretical aspects. Bailey's industrial oil and fat products, 2005.
- 57. Waraho, T., D.J. McClements, and E.A. Decker, 68. Mechanisms of lipid oxidation in food dispersions. Trends in food science & technology, 2011. 22(1): p. 3-13.
- Parker, T.D., et al., Fatty acid composition and oxidative stability of cold-pressed edible seed oils. 69. Journal of food science, 2003. 68(4): p. 1240-1243.
- Ayyildiz, H.F., et al., Evaluation of fatty acid composition, tocols profile, and oxidative stability of some fully refined edible oils. International Journal of Food Properties, 2015. 18(9): p. 2064-2076.

- Jeong, M., et al., Correlation of volatiles and fatty acids in thermally oxidized fatty acid model systems using statistical approaches. Food Science and Biotechnology, 2010. **19**(5): p. 1233-1239.
- Koh, E., D. Ryu, and J. Surh, Ratio of malondialdehyde to hydroperoxides and color change as an index of thermal oxidation of linoleic acid and linolenic acid. Journal of Food Processing and Preservation, 2015. **39**(3): p. 318-326.
- Seppanen, C. and A.S. Csallany, Incorporation of the toxic aldehyde 4-hydroxy-2-trans-nonenal into food fried in thermally oxidized soybean oil. Journal of the American Oil Chemists' Society, 2004. **81**(12): p. 1137-1141.
- Velasco, J., et al., Quantitation of short-chain glycerolbound compounds in thermoxidized and used frying oils. A monitoring study during thermoxidation of olive and sunflower oils. Journal of agricultural and food chemistry, 2005. **53**(10): p. 4006-4011.
- Przybylski, R., E. Gruczynska, and F. Aladedunye, Performance of regular and modified canola and soybean oils in rotational frying. Journal of the American Oil Chemists' Society, 2013. 90(9): p. 1271-1280.
- Shen, N., et al., Oxidative stability and AromaScan analyses of corn oils with altered fatty acid content. Journal of the American Oil Chemists' Society, 1999.
 76(12): p. 1425-1429.
 - Tan, C., et al., Comparative studies of oxidative stability of edible oils by differential scanning calorimetry and oxidative stability index methods. Food chemistry, 2002. **76**(3): p. 385-389.
- 67. Maszewska, M., et al., Oxidative stability of selected edible oils. Molecules, 2018. **23**(7): p. 1746.
 - Liu, Q., S. Singh, and A. Green, High-oleic and highstearic cottonseed oils: nutritionally improved cooking oils developed using gene silencing. Journal of the American College of Nutrition, 2002. **21**(sup3): p. 2058-211S.
 - Wilson, R.F., The role of genomics and biotechnology in achieving global food security for high-oleic vegetable oil. Journal of oleo science, 2012. **61**(7): p. 357-367.
- 70. Horn, P.J., D. Sturtevant, and K.D. Chapman, Modified oleic cottonseeds show altered content,

composition and tissue-specific distribution of 82. triacylglycerol molecular species. Biochimie, 2014. **96**: p. 28-36.

- Parcell, J., et al., Global edible vegetable oil market trends. Biomedical Journal of Scientific & Technical 83. Research, 2018. 2(1): p. 2282-2291.
- Finley, J.W., et al., Antioxidants in foods: state of the science important to the food industry. Journal of agricultural and food chemistry, 2011. 59(13): p. 84. 6837-6846.
- Pavlović, N., et al., Recovery of tocopherols, amygdalin, and fatty acids from apricot kernel oil: Cold pressing versus supercritical carbon dioxide. European Journal of Lipid Science and Technology, 85. 2018. 120(11): p. 1800043.
- 74. Absalome, M.A., et al., Biochemical properties, nutritional values, health benefits and sustainability of palm oil. Biochimie, 2020. **178**: p. 81-95.
- 75. Trentini, C.P., et al., Extraction of macauba kernel oil using supercritical carbon dioxide and compressed propane. The Canadian Journal of Chemical Engineering, 2019. **97**(3): p. 785-792.
- 76. Lee, S.W., et al., Effects of roasting conditions of sesame seeds on the oxidative stability of pressed oil during thermal oxidation. Food chemistry, 2010. 88. 118(3): p. 681-685.
- Ji, J., et al., Effect of roasting treatment on the chemical composition of sesame oil. Lwt, 2019. 101: 89. p. 191-200.
- 78. Talbot, G., The stability and shelf life of fats and oils, in The stability and shelf life of food. 2016, Elsevier. p. 461-503.
- Crapiste, G.H., M.I. Brevedan, and A.A. Carelli, Oxidation of sunflower oil during storage. Journal of the American Oil Chemists' Society, 1999. 76(12): p. 1437.
- Karoui, I.J., et al., Thermal stability of corn oil flavoured with Thymus capitatus under heating and deep-frying conditions. Journal of the Science of Food and Agriculture, 2011. 91(5): p. 927-933.
- Velasco, J. and C. Dobarganes, Oxidative stability of virgin olive oil. European Journal of Lipid Science and Technology, 2002. **104**(9-10): p. 661-676.

Krichene, D., et al., Stability of virgin olive oil and behaviour of its natural antioxidants under medium temperature accelerated storage conditions. Food Chemistry, 2010. **121**(1): p. 171-177.

- Velasco, J., et al., Quantitative determination of major oxidation products in edible oils by direct NP-HPLC-DAD analysis. Journal of Chromatography A, 2018.
 1547: p. 62-70.
- Kiralan, M., et al., Monitoring stability and volatile oxidation compounds of cold-pressed flax seed, grape seed and black cumin seed oils upon photo-oxidation. Journal of Food Measurement and Characterization, 2018. 12(1): p. 616-621.
- Frankel, E., K. Warner, and K. Moulton Sr, Effects of hydrogenation and additives on cooking oil performance of soybean oil. Journal of the American Oil Chemists' Society, 1985. **62**(9): p. 1354-1358.
- Ayu, D., et al., Photo-oxidative changes of red palm oil as affected by light intensity. International Food Research Journal, 2017. 24(3).
- 87. Spatari, C., et al., A critical evaluation of the analytical techniques in the photodegradation monitoring of edible oils. LWT-Food Science and Technology, 2017. **76**: p. 147-155.
 - Dabbou, S., et al., Impact of packaging material and storage time on olive oil quality. African Journal of Biotechnology, 2011. **10**(74): p. 16929-16936.
 - Ramezani, R., The effect of packaging materials and storage condition on the oxidative stability of refined sunflower oil. Food Science and technology research, 2007. **10**(3): p. 350-354.
- 90. Silva, A.S., J.L. Hernández, and P.P. Losada, Modified atmosphere packaging and temperature effect on potato crisps oxidation during storage. Analytica chimica acta, 2004. **524**(1-2): p. 185-189.
- Andersson, K., Influence of reduced oxygen concentrations on lipid oxidation in food during storage. 1998: SIK Institutet för livsmedel och bioteknik, Göteborg, Sverige.
- 92. Dauqan, E., et al., Effect of different vegetable oils (red palm olein, palm olein, corn oil and coconut oil) on lipid profile in rat. Food and Nutrition Sciences, 2011. 2(4): p. 253.
- Evans, J., D.R. Kodali, and P. Addis, Optimal tocopherol concentrations to inhibit soybean oil 84

oxidation. Journal of the American Oil Chemists' 105. Society, 2002. **79**(1): p. 47-51.

- 94. Gąsior, R., M. Pieszka, and F. Brzóska, Validation of a method for simultaneous determination of tocopherols and tocotrienols in cereals using normal phase HPLC. Journal of Animal and Feed Sciences, 2009. 18(1): p. 173-192.
- 95. Smolarek, A.K. and N. Suh, Chemopreventive activity of vitamin E in breast cancer: a focus on γ and δ -tocopherol. Nutrients, 2011. **3**(11): p. 962-986.
- 96. Žilić, S., et al., Characterization of sunflower seed and kernel proteins. Helia, 2010. **33**(52): p. 103-114.
- 97. Seppanen, C.M., Q. Song, and A. Saari Csallany, The antioxidant functions of tocopherol and tocotrienol homologues in oils, fats, and food systems. Journal of the American Oil Chemists' Society, 2010. 87(5): p. 469-481.
- Choe, E., Interaction of light and temperature on tocopherols during oxidation of sunflower oil. Journal of the American Oil Chemists' Society, 2013.
 90(12): p. 1851-1857.
- 99. Kim, J.Y., et al., Effects of relative humidity on the antioxidant properties of α-tocopherol in stripped corn oil. Food chemistry, 2015. 167: p. 191-196.
- 100. Ergönül, P.G. and O. Köseoğlu, Changes in α -, β -, γ and δ -tocopherol contents of mostly consumed vegetable oils during refining process. CyTA-Journal of Food, 2014. **12**(2): p. 199-202.
- 101. Al Juhaimi, F. and M.M. Özcan, Effect of cold press and soxhlet extraction systems on fatty acid, tocopherol contents, and phenolic compounds of various grape seed oils. Journal of Food Processing and Preservation, 2018. 42(1): p. e13417.
- 102. Ahmed, I.A.M., et al., Effects of cold-press and soxhlet extraction systems on antioxidant activity, total phenol contents, fatty acids, and tocopherol contents of walnut kernel oils. Journal of oleo science, 2019: p. ess18141.
- Tapera, M., Towards greener preservation of edible oils: A mini-review. Asian Journal of Applied Chemistry Research, 2019. 4(1-2): p. 1-8.
- 104. Olajide, T.M., et al., Natural or Synthetic Antioxidants in Foods. Human Health Benefits of Plant Bioactive Compounds, 2019: p. 55-65.

Wang, X., et al., Profiling and quantification of phenolic compounds in Camellia seed oils: Natural tea polyphenols in vegetable oil. Food Research International, 2017. **102**: p. 184-194.

- 106. Zeb, A., A comprehensive review on different classes of polyphenolic compounds present in edible oils. Food Research International, 2021. 143: p. 110312.
- 107. Mishra, S.K., P.D. Belur, and R. Iyyaswami, Use of antioxidants for enhancing oxidative stability of bulk edible oils: A review. International Journal of Food Science & Technology, 2021. 56(1): p. 1-12.
- Admassu, S. and M. Kebede, Application of antioxidants in food processing industry: Options to improve the extraction yields and market value of natural products. Adv. Food Technol. Nutr. Sci, 2019.
 5: p. 38-49.
- 109. Choi, H., M.J. Kim, and J. Lee, Effect of Polar and Non-Polar Compounds from Oxidized Oils on Oxidative Stability in Corn Oil. European Journal of Lipid Science and Technology, 2018. **120**(3): p. 1700312.
- 110. Fuller, I.D., et al., Free fatty acids in commercial krill oils: concentrations, compositions, and implications for oxidative stability. Journal of the American Oil Chemists' Society, 2020. 97(8): p. 889-900.
- Gomes, T., et al., Effects of monoacylglycerols on the oxidative stability of olive oil. Journal of the Science of Food and Agriculture, 2010. **90**(13): p. 2228-2232.
- 112. Ghazani, S.M. and A.G. Marangoni, Minor components in canola oil and effects of refining on these constituents: A review. Journal of the American Oil Chemists' Society, 2013. **90**(7): p. 923-932.
- 113. Madhujith, T. and S. Sivakanthan, Oxidative stability of edible plants oils. 2019, Springer Nature.
- 114. Keceli, T. and M. Gordon, Ferric ions reduce the antioxidant activity of the phenolic fraction of virgin olive oil. Journal of Food Science, 2002. **67**(3): p. 943-947.
- 115. Fadda, A., et al., Innovative and sustainable technologies to enhance the oxidative stability of vegetable oils. 2022. **14**(2): p. 849.
- 116. Carocho, M., I.C.J.F. Ferreira, and c. toxicology, A review on antioxidants, prooxidants and related controversy: Natural and synthetic compounds,

screening and analysis methodologies and future 129. perspectives. 2013. **51**: p. 15-25.

- 117. Muik, B., et al., Direct monitoring of lipid oxidation in edible oils by Fourier transform Raman spectroscopy. 2005. 134(2): p. 173-182.
- 118. Xu, D.-P., et al., Natural antioxidants in foods and medicinal plants: Extraction, assessment and resources. 2017. **18**(1): p. 96.
- 119. Gambacorta, G., et al., Changes in the chemical and sensorial profile of extra virgin olive oils flavored with herbs and spices during storage. 2007. 14(2): p. 202-215.
- 120. Kozłowska, M. and E.J.C.P. Gruczyńska, Comparison of the oxidative stability of soybean and sunflower oils enriched with herbal plant extracts. 2018. **72**: p. 2607-2615.
- 121. Asensio, C.M., et al., Consumers' acceptance and quality stability of olive oil flavoured with essential oils of different oregano species. 2013. 48(11): p. 2417-2428.
- 122. Ayadi, M., et al., Physico-chemical change and heat stability of extra virgin olive oils flavoured by selected Tunisian aromatic plants. 2009. **47**(10): p. 2613-2619.
- 123. Aydeniz, B., E.J.E.j.o.l.s. Yilmaz, and technology, Enrichment of frying oils with plant phenolic extracts to extend the usage life. 2012. **114**(8): p. 933-941.
- 124. Salta, F., et al., Oxidative stability of edible vegetable oils enriched in polyphenols with olive leaf extract. 2007. **13**(6): p. 413-421.
- Şahin, S., et al., Effects of natural antioxidants in the improvement of corn oil quality: olive leaf vs. lemon balm. 2017. 52(2): p. 374-380.
- 126. Tarchoune, I., et al., Olive leaf addition increases olive oil nutraceutical properties. 2019. **24**(3): p. 545.
- 127. Yang, Y., et al., Rosemary extract can be used as a synthetic antioxidant to improve vegetable oil oxidative stability. 2016. **80**: p. 141-147.
- 128. Kozłowska, M. and K.J.C.P. Zawada, Evaluation of oxidative stability of vegetable oils enriched with herb extracts by EPR spectroscopy. 2015. **69**: p. 950-957.

- Taoudiat, A., et al., The effect of Laurus nobilis L. essential oil and different packaging systems on the photo-oxidative stability of Chemlal extra-virgin olive oil. 2018. **55**(10): p. 4212-4222.
- 130. Hailemariam, G.A. and S.A.J.B.J.A.S.T. Emire, Antioxidant activity and preservative effect of thyme (Thymus schimperi R.). 2013. **3**(4): p. 1311-1326.
- 131. Veronezi, C.M., et al., Basil (Ocimum Basilicum L.) as a Natural A ntioxidant. 2014. **38**(1): p. 255-261.
- 132. Tooryan, F., M.J.I.F.S. Azizkhani, and T.R. Journal, Improvement of the oxidative stability of canola oil using Carum copticum fruit extracts as a natural antioxidant. 2019. **15**(1): p. 13-24.
- 133. Tooryan, F. and M.J.J.o.V.R. Azizkhani, Evaluation of antioxidant properties of Carum copticum fruit essential oil (EOs) and its effect on the oxidative stability of canola oil. 2019. **74**(2).
- 134. Patra, B.R., V.B. Borugadda, and A.K.J.B.T.R. Dalai, Microwave-assisted extraction of sea buckthorn pomace and seed extracts as a proactive antioxidant to stabilize edible oils. 2022. **17**: p. 100970.
- Pezeshky, A., M. Khakbaz Heshmati, and Z.J.J.o.F.R. Abutalebi, Effect of thyme and ginger metanoic extraction on the oxidative stability of sunflower oil. 2020. 30(3): p. 107-121.
- Bahmaninia, S., M. Abbasvali, and S.S.J.I.J.o.N.S. Shekarforoush, Antioxidant Activity of Methanolic Extract of Olive Leaf on Oxidative Stability of Sunflower Oil. 2022. 7(4): p. 217-224.
- 137. Pei, X.-C., et al., Improving the oxidation stability of high-oleic sunflower oil with composite antioxidants. 2022. 18.
- Ghafoor, K., et al., Evaluation of the antioxidant activity of some plant extracts (rosemary, sage, and savory, summer) on stability of moringa oil. 2021.
 45(3): p. e15203.
- 139. Razavi MAjd, M., et al., Evaluation of the effect of essential oil of Rosemary on sunflower oil, soybean oil and tallow fat. 2021. **13**(4): p. 95-113.
- Patil, A., et al., Improvement of oil quality in soybean [Glycine max (L.) Merrill] by mutation breeding. Journal of the American Oil Chemists' Society, 2007. 84(12): p. 1117-1124.

- Han, K.H., Omega-3-fatty acid and triglyceride. The Korean Journal of Medicine, 2012. 83(6): p. 724-727.
- Prabakaran, M., et al., Changes in soybean (Glycine max L.) flour fatty-acid content based on storage temperature and duration. Molecules, 2018. 23(10): p. 2713.
- 143. Karasulu, H.Y., et al., Soybean oil: production process, benefits and uses in pharmaceutical dosage form, in Soybean and health. 2011, IntechOpen.
- 144. Isaac, O., et al., Effect of storage periods on seed quality characteristics of three soybean (Glycine max (L) Merrill) varieties. 2016.
- 145. Singh, J., S. Paroha, and R.P. Mishra, Factors affecting oilseed quality during storage with special reference to soybean (Glycine max) and Niger (Guizotia abyssinica) seeds. Int J Curr Microbiol App Sci, 2017. 6(10): p. 2215-2226.
- 146. Clemente, T.E. and E.B. Cahoon, Soybean oil: genetic approaches for modification of functionality and total content. Plant physiology, 2009. **151**(3): p. 1030-1040.
- 147. Ghassemi-Golezani, K., et al., Seed vigor and field performance of winter oilseed rape (Brassica napus L.) cultivars. Notulae Botanicae Horti Agrobotanici Cluj-Napoca, 2010. 38(3): p. 146-150.
- Saxena, N., S.S. Rani, and M. Deepika, Biodeterioration of Soybean (Glycine max L.) seeds during storage by Fungi. International Journal of Current Microbiology and Applied Sciences, 2015. 4(6): p. 1118-1126.
- 149. Taghvaei, M., et al., The effect of natural antioxidants extracted from plant and animal resources on the oxidative stability of soybean oil. LWT-Food Science and Technology, 2014. 56(1): p. 124-130.
- 150. Sarkar, A., et al., Increasing the oxidative stability of soybean oil through fortification with antioxidants. International Journal of Food Science & Technology, 2015. 50(3): p. 666-673.
- 151. Kim, J., et al., Correlation of fatty acid composition of vegetable oils with rheological behaviour and oil uptake. Food chemistry, 2010. **118**(2): p. 398-402.
- 152. Casarotti, S.N. and N. Jorge, Antioxidant activity of rosemary extract in soybean oil under thermoxidation.

Journal of Food Processing and Preservation, 2014. **38**(1): p. 136-145.

- 153. Szterk, A., et al., Chemical composition and oxidative stability of selected plant oils. Journal of the American Oil Chemists' Society, 2010. **87**(6): p. 637-645.
- 154. Ahmed, M., et al., Oxidation of Lipids in Foods. Sarhad Journal of Agriculture, 2016. **32**(3).
- Farhoosh, R., S. Einafshar, and P. Sharayei, The effect of commercial refining steps on the rancidity measures of soybean and canola oils. Food chemistry, 2009. 115(3): p. 933-938.
- 156. Verheye, W., Growth and production of oil palm, in Land use, land cover and soil sciences. 2010, UNESCO-EOLSS Publishers.
- 157. Rival, A. and P. Levang, Palms of controversies: Oil palm and development challenges. 2014: CIFOR.
- 158. Chong, C.L., Measurement and maintenance of palm oil quality, in Palm oil. 2012, Elsevier. p. 431-470.
- 159. Lesage, C., J.A. Cifuentes-Espinosa, and L. Feintrenie, Oil palm cultivation in the Americas: review of the social, economic and environmental conditions of its expansion. 2021.
- Ibrahim, N.A., Characteristics of Malaysian palm kernel and its products. Journal of Oil Palm Research, 2013. 25(2): p. 245-252.
- Achaw, O.-W. and E. Danso-Boateng, Manufacture of crude palm oil and refined palm oil, in Chemical and Process Industries. 2021, Springer. p. 195-211.
- 162. Tong, S.C., T.K. Tang, and Y.Y. Lee, A Review on the Fundamentals of Palm Oil Fractionation: Processing Conditions and Seeding Agents. European Journal of Lipid Science and Technology, 2021. 123(12): p. 2100132.
- 163. Norhaizan, M.E., et al., Palm oil: Features and applications. Lipid Technology, 2013. **25**(2): p. 39-42.
- Koushki, M., M. Nahidi, and F. Cheraghali, Physicochemical properties, fatty acid profile and nutrition in palm oil. Archives of Advances in Biosciences, 2015. 6(3): p. 117-134.
- 165. Adetola, O., O. Alabi, and I. Abdulrauf, Investigating storage duration and packaging materials on quality of fresh palm oil. FUTA Journal of Research in Sciences, 2016. 12(2): p. 252-259.

- 166. Daud, Z.A.M., D. Kaur, and P. Khosla, Health and nutritional properties of Palm oil and its components, in Palm oil. 2012, Elsevier. p. 545-560.
- 167. Sundram, K., Meeting the rising health awareness: The palm oil formula. Palm Oil Developments, 2005.43: p. 20-28.
- 168. Ponnampalam, E.N., et al., Differential effects of natural palm oil, chemically-and enzymaticallymodified palm oil on weight gain, blood lipid metabolites and fat deposition in a pediatric pig model. Nutrition Journal, 2011. 10(1): p. 1-7.
- 169. Fattore, E., et al., Palm oil and blood lipid-related markers of cardiovascular disease: a systematic review and meta-analysis of dietary intervention trials. The American journal of clinical nutrition, 2014. 99(6): p. 1331-1350.
- Riccardi, G., R. Giacco, and A. Rivellese, Dietary fat, insulin sensitivity and the metabolic syndrome. Clinical nutrition, 2004. 23(4): p. 447-456.
- 171. Yubero-Serrano, E.M., et al., Insulin resistance determines a differential response to changes in dietary fat modification on metabolic syndrome risk factors: the LIPGENE study. The American journal of clinical nutrition, 2015. **102**(6): p. 1509-1517.
- 172. Przybylski, R. and N.M. Eskin, Oil composition and properties, in Canola. 2011, Elsevier. p. 189-227.
- Przybylski, R. and T. Mag, Canola/rapeseed oil. Vegetable Oils in Food Technology: Composition, Properties and Uses. Blackwell Publishing Ltd., Hoboken, 2011: p. 107-136.
- 174. Thiyam-Holländer, U., N.M. Eskin, and B. Matthäus, Canola and rapeseed: production, processing, food quality, and nutrition. 2012: CRC Press.
- 175. Ratnayake, W. and J. Daun, Chemical composition of canola and rapeseed oils. Rapeseed and canola oil. Production, processing, properties and uses. CRC Press LLC, Boca Raton, 2004: p. 37-78.
- Goyal, A., et al., Rapeseed/Canola (Brassica napus) Seed, in Oilseeds: Health Attributes and Food Applications. 2021, Springer. p. 47-71.
- 177. Zhou, Q., et al., Distribution of glucosinolate and pungent odors in rapeseed oils from raw and microwaved seeds. International Journal of Food Properties, 2018. 21(1): p. 2296-2308.

- 178. Przybylski, R., et al., Canola oil. Bailey's industrial oil and fat products, 2005. **2**: p. 61-122.
- Petukhov, I., et al., Storage stability of potato chips fried in genetically modified canola oils. Journal of the American Oil Chemists' Society, 1999. 76(8): p. 889-896.
- Daun, J.K., M.N. Eskin, and D. Hickling, Canola: chemistry, production, processing, and utilization. 2015: Elsevier.
- Del Vecchio, A., High-laurate canola. inform, 1996. 7: p. 230-243.
- 182. Kenar, J.A., B.R. Moser, and G.R. List, Naturally occurring fatty acids: Source, chemistry, and uses, in Fatty acids. 2017, Elsevier. p. 23-82.
- 183. Beszterda, M. and M. Nogala-Kałucka, Current research developments on the processing and improvement of the nutritional quality of rapeseed (Brassica napus L.). European Journal of Lipid Science and Technology, 2019. 121(5): p. 1800045.
- 184. Cai, Z., et al., Recent progress in the thermal treatment of oilseeds and oil oxidative stability: a review. Fundamental Research, 2021.
- 185. Kramer, J.K., High and low erucic acid in Rapeseed Oils. 2012: Academic press.
- 186. Kowalski, B., et al., Chemical and enzymatic interesterification of a beef tallow and rapeseed oil equal-weight blend. European journal of lipid science and technology, 2004. **106**(10): p. 655-664.
- 187. Temple-Heald, C., High erucic oil: its production and uses. Rapeseed and Canola Oil, 2004: p. 111-130.
- Kadamne, J.V., Effect of High Intensity Ultrasound on the Crystallization Behavior of Interesterified Fats. 2018, Utah State University.
- Kohel, R., Evaluation of near infrared reflectance for oil content of cottonseed. Journal of cotton science, 1998.
- Mert, M., Y. Akışcan, and O. Gencer, Inheritance of oil and protein content in some cotton generations. Asian Journal of plant sciences, 2004. 3(2): p. 174-176.
- Bellaloui, N., R.B. Turley, and S.R. Stetina, Cottonseed protein, oil, and minerals in cotton (Gossypium hirsutum L.) lines differing in curly leaf morphology. Plants, 2021. 10(3): p. 525.

- 192. Konuşkan, D.B., et al., Physico-chemical characteristic and fatty acids compositions of cottonseed oils. Journal of Agricultural Sciences, 2017. 23(2): p. 253-259.
- Orhevba, B.A. and A. Efomah, Extraction and Characterization of Cottonseed (Gossypium) Oil. 2012.
- Shah, S., et al., FTIR characterization and physicochemical evaluation of cottonseed oil. Pakistan Journal of Analytical & Environmental Chemistry, 2017. 18(1): p. 46-53.
- O'Brien, R., Cottonseed oil In Vegetable Oils in Food Technology: Composition, Properties and Uses (Gunstone FD, ed). 2002, Oxford: Blackwell Publishing.[Google Scholar].
- 196. Sawan, Z.M., et al., Cottonseed, protein, oil yields and oil properties as affected by nitrogen fertilization and foliar application of potassium and a plant growth retardant. World J. Agric. Sci, 2006. **2**(1): p. 56-65.
- 197. Sekhar, S.C. and B. Rao, Cottonseed oil as health oil. Pertanika J. Trop. Agric. Sci, 2011. **34**(1): p. 17-24.
- 198. Mathur, P., Separation, identification and quantification of the unsaponifiables of cottonseed oil and its deodorizer distillate. 2011: Texas Woman's University.
- Reddy, B. and E. Aruna, Effect of irrigation levels through drip on growth, yield and quality of cotton. Journal of Cotton Research and Development, 2009.
 23(1): p. 56-59.
- 200. Asadi, R., et al., Effect of surface and subsurface drip irrigation systems on yield of cotton in orzoueyeh, Kerman province. Journal of Science and Technology of Agriculture and Natural Resources, 2013. 17(63): p. 11-21.
- 201. Karami, H., M. Rasekh, and E. Mirzaee-Ghaleh, Qualitative analysis of edible oil oxidation using an olfactory machine. Journal of Food Measurement and Characterization, 2020. 14(5): p. 2600-2610.
- 202. Poljsak, B., V. Kovač, and I. Milisav, Antioxidants, food processing and health. Antioxidants, 2021.
 10(3): p. 433.
- 203. Fernandes, R.d.P.P., M.A. Trindade, and M.P. de Melo, Natural antioxidants and food applications:

healthy perspectives, in Alternative and replacement foods. 2018, Elsevier. p. 31-64.

- 204. Kozłowska, M. and E. Gruczyńska, Comparison of the oxidative stability of soybean and sunflower oils enriched with herbal plant extracts. Chemical Papers, 2018. 72(10): p. 2607-2615.
- 205. Let, M.B., C. Jacobsen, and A.S. Meyer, Sensory stability and oxidation of fish oil enriched milk is affected by milk storage temperature and oil quality. International dairy journal, 2005. **15**(2): p. 173-182.
- 206. Horn, A.F., et al., Addition of fish oil to cream cheese affects lipid oxidation, sensory stability and microstructure. Agriculture, 2012. 2(4): p. 359-375.
- 207. KATAWAL, S.B., Technological and Nutritional Evaluation of Sel-Roti. 2013, Department of Food Technology, Institute of Science and Technology
- Liu, X., et al., Volatile profile and flavor characteristics of ten edible oils. Analytical Letters, 2021. 54(9): p. 1423-1438.
- 209. Min, D., A. Callison, and H. Lee, Singlet oxygen oxidation for 2-pentylfuran and 2-pentenyfuran formation in soybean oil. Journal of Food Science, 2003. 68(4): p. 1175-1178.
- Grebenteuch, S., et al., Formation of secondary and tertiary volatile compounds resulting from the lipid oxidation of rapeseed oil. Foods, 2021. 10(10): p. 2417.
- 211. Mallia, S., et al., Characterization and quantification of odor-active compounds in unsaturated fatty acid/conjugated linoleic acid (UFA/CLA)-enriched butter and in conventional butter during storage and induced oxidation. Journal of agricultural and food chemistry, 2009. 57(16): p. 7464-7472.
- 212. Arab-Tehrany, E., et al., Beneficial effects and oxidative stability of omega-3 long-chain polyunsaturated fatty acids. Trends in Food Science & Technology, 2012. **25**(1): p. 24-33.
- 213. Nogueira, M.S., et al., Oxidation products from omega-3 and omega-6 fatty acids during a simulated shelf life of edible oils. LWT, 2019. **101**: p. 113-122.
- 214. Tao, L., Oxidation of polyunsaturated fatty acids and its impact on food quality and human health. Adv. Food Technol. Nutr. Sci, 2015. 1: p. 135-142.

- 215. Shahidi, F. and P. Ambigaipalan, Omega-3 polyunsaturated fatty acids and their health benefits. Annual review of food science and technology, 2018.
 9: p. 345-381.
- 216. Ghnimi, S., E. Budilarto, and A. Kamal-Eldin, The new paradigm for lipid oxidation and insights to microencapsulation of omega-3 fatty acids. Comprehensive Reviews in Food Science and Food Safety, 2017. 16(6): p. 1206-1218.
- 217. Golanski, J., P. Szymanska, and M. Rozalski, Effects of omega-3 polyunsaturated fatty acids and their metabolites on haemostasis—current perspectives in cardiovascular disease. International journal of molecular sciences, 2021. 22(5): p. 2394.
- 218. Nondzor, H.E., Y.S. Tawiah, and A. Michael, Consumer knowledge, perception and preference of edible oil: Evidence from Ghana. Science Journal of Business and Management, 2015. 3(1): p. 17-23.
- Zargaraan, A., et al., Challenges of edible oils from farm to industry: views of stakeholders. Food and nutrition bulletin, 2019. 40(1): p. 99-110.
- 220. Pandey, R., S. Kumari, and K. Kumari, Consumers preference for edible oil in Patna city, Bihar. 2022.
- 221. Rukunudin, I., et al., A modified method for determining free fatty acids from small soybean oil sample sizes. Journal of the American Oil Chemists' Society, 1998. 75(5): p. 563-568.
- 222. Frega, N., M. Mozzon, and G. Lercker, Effects of free fatty acids on oxidative stability of vegetable oil. Journal of the American Oil Chemists' Society, 1999.
 76(3): p. 325-329.
- 223. Antolovich, M., et al., Methods for testing antioxidant activity. Analyst, 2002. **127**(1): p. 183-198.
- 224. Makhoul, H., T. Ghaddar, and I. Toufeili, Identification of some rancidity measures at the end of the shelf life of sunflower oil. European Journal of Lipid Science and Technology, 2006. 108(2): p. 143-148.
- 225. Gotoh, N. and S. Wada, The importance of peroxide value in assessing food quality and food safety. JAOCS, Journal of the American Oil Chemists' Society, 2006. 83(5): p. 473.
- 226. Velasco, J., C. Dobarganes, and G. Márquez-Ruiz, Oxidative rancidity in foods and food quality, in

Chemical deterioration and physical instability of food and beverages. 2010, Elsevier. p. 3-32.

- 227. Rohman, A. and Y.C. Man, Fourier transform infrared (FTIR) spectroscopy for analysis of extra virgin olive oil adulterated with palm oil. Food research international, 2010. **43**(3): p. 886-892.
- 228. Hu, K., et al., Rapid determination of acid value of edible oils via FTIR spectroscopy using infrared quartz cuvette. Journal of Oleo Science, 2019: p. ess18156.
- 229. Shang, J., et al., A simple and practical method to determine peroxide values in edible oils via infrared quartz cuvette-based Fourier transform infrared spectroscopy. Analytical Methods, 2018. 10(29): p. 3675-3679.
- 230. Saeed, R. and S. Naz, Effect of heating on the oxidative stability of corn oil and soybean oil. Grasas y Aceites, 2019. **70**(2): p. e303-e303.
- 231. Mahboubifar, M., et al., Evaluation of long-heating kinetic process of edible oils using ATR–FTIR and chemometrics tools. Journal of food science and technology, 2017. **54**(3): p. 659-668.
- 232. Naz, S. and R. Saeed, Oxidative Stability of Canola Oil by Physico-Chemical Analysis and FT-IR Spectroscopy. Asian Journal of Pharmaceutical Research and Development, 2018. **6**(1): p. 9-15.
- 233. Rexhepia, F., et al., Comprehensive Investigation of Thermal Degradation Characteristics and Properties Changes of Plant Edible Oils by FTIR-Spectroscopy. Acta Chem. IASI, 2019. 27(2): p. 263-286.
- 234. El-Naggar, E.A., The evaluation of deep frying oil quality with the spectrophotometric method for the rapid assessment of total polar compounds. Zagazig Journal of Agricultural Research, 2019. **46**(5): p. 1489-1502.
- 235. Liu, H., et al., FT-IR and Raman spectroscopy data fusion with chemometrics for simultaneous determination of chemical quality indices of edible oils during thermal oxidation. Lwt, 2020. **119**: p. 108906.
- 236. Dong, Y., et al., An indirect analytical approach based on ATR-FTIR spectroscopy for determining the FFA content in vegetable oils. RSC advances, 2020. 10(40): p. 24073-24078.

- 237. Rivera-Barrera, D., H. Rueda-Chacon, and D. Molina, Prediction of the total acid number (TAN) of colombian crude oils via ATR–FTIR spectroscopy and chemometric methods. Talanta, 2020. 206: p. 120186.
- Soni, A., et al., An assessment of thermal impact on chemical characteristics of edible oils by using FTIR spectroscopy. Materials Today: Proceedings, 2022.
 68: p. 710-716.
- 239. Cakmak-Arslan, G., Monitoring of Hazelnut oil quality during thermal processing in comparison with extra virgin olive oil by using ATR-FTIR spectroscopy combined with chemometrics. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2022. 266: p. 120461.
- 240. Wen, Y., et al., New Method for the Determination of the Induction Period of Walnut Oil by Fourier Transform Infrared Spectroscopy. Food Analytical Methods, 2022. 15(3): p. 833-843.
- 241. Watanabe, Y., et al., Suppressive ability of defatted rice bran against lipid oxidation in cookies containing iron. Bioscience, biotechnology, and biochemistry, 2010. **74**(2): p. 262-265.
- Steltzer, E.T., Evaluation of chemical assays for determining hydroperoxides levels in oxidized lipids.
 2012: Rutgers The State University of New Jersey-New Brunswick.
- 243. Bloomfield, M., The spectrophotometric determination of hydroperoxide and peroxide in a lipid pharmaceutical product by flow injection analysis. Analyst, 1999. 124(12): p. 1865-1871.
- 244. Elisia, I., et al., Association between tocopherol isoform composition and lipid oxidation in selected multiple edible oils. Food research international, 2013. 52(2): p. 508-514.
- 245. Shahidi, F. and Y. Zhong, Lipid oxidation: measurement methods. Bailey's industrial oil and fat products, 2005.
- 246. Redondo-Cuevas, L., G. Castellano, and V. Raikos, Natural antioxidants from herbs and spices improve the oxidative stability and frying performance of vegetable oils. International Journal of Food Science & Technology, 2017. 52(11): p. 2422-2428.
- 247. Liu, S., et al., Changes in fatty acids and formation of carbonyl compounds during frying of rice cakes

and hairtails. Journal of Food Composition and Analysis, 2021. **101**: p. 103937.

- 248. Moigradean, D., M.-A. Poiana, and I. Gogoasa, Quality characteristics and oxidative stability of coconut oil during storage. Journal of Agroalimentary Processes and Technologies, 2012. 18(4): p. 272-276.
- 249. Naghshineh, M., et al., Effect of saturated/unsaturated fatty acid ratio on physicochemical properties of palm olein–olive oil blend. Journal of the American Oil Chemists' Society, 2010. **87**(3): p. 255-262.
- 250. Nuchi, C., et al., Assessment of the levels of degradation in fat co-and byproducts for feed uses and their relationships with some lipid composition parameters. Journal of Agricultural and Food Chemistry, 2009. 57(5): p. 1952-1959.
- 251. Papastergiadis, A., et al., Malondialdehyde measurement in oxidized foods: evaluation of the spectrophotometric thiobarbituric acid reactive substances (TBARS) test in various foods. Journal of agricultural and food chemistry, 2012. 60(38): p. 9589-9594.
- Ulu, H., Evaluation of three 2-thiobarbituric acid methods for the measurement of lipid oxidation in various meats and meat products. Meat science, 2004. 67(4): p. 683-687.
- 253. Peiretti, P.G., et al., Determination of carnosine, anserine, homocarnosine, pentosidine and thiobarbituric acid reactive substances contents in meat from different animal species. Food Chemistry, 2011. 126(4): p. 1939-1947.
- 254. Pignoli, G., et al., Suitability of saturated aldehydes as lipid oxidation markers in washed turkey meat. Meat science, 2009. **83**(3): p. 412-416.
- 255. Soglia, F., G. Baldi, and M. Petracci, Effect of the exposure to oxidation and malondialdehyde on turkey and rabbit meat protein oxidative stability. Journal of Food Science, 2020. **85**(10): p. 3229-3236.
- 256. Tyl, C.E., L. Brecker, and K.H. Wagner, 1H NMR spectroscopy as tool to follow changes in the fatty acids of fish oils. European Journal of Lipid Science and Technology, 2008. **110**(2): p. 141-148.
- 257. Guillén, M.D. and A. Ruiz, Monitoring of heat-induced degradation of edible oils by proton NMR. European Journal of Lipid Science and Technology, 2008. 110(1): p. 52-60.

- Colzato, M., et al., 1h Nmr investigation of oil oxidation in macadamia nuts coated with zein-based films. Journal of Food Processing and Preservation, 2011. 35(6): p. 790-796.
- Alonso-Salces, R.M., M.V. Holland, and C. Guillou, 1H-NMR fingerprinting to evaluate the stability of olive oil. Food Control, 2011. 22(12): p. 2041-2046.
- 260. Guillén, M.D. and P.S. Uriarte, Monitoring by 1H nuclear magnetic resonance of the changes in the composition of virgin linseed oil heated at frying temperature. Comparison with the evolution of other edible oils. Food Control, 2012. 28(1): p. 59-68.
- 261. Scano, P., et al., 1H-and 13C-NMR characterization of the molecular components of the lipid fraction of pecorino sardo cheese. Journal of the American Oil Chemists' Society, 2011. 88(9): p. 1305-1316.
- 262. Namal Senanayake, S. and F. Shahidi, Measuring oxidative stability of structured lipids by proton nuclear magnetic resonance. Journal of Food Lipids, 2007. 14(3): p. 217-231.
- Silva, A.C.d.O., et al., Effect of gamma radiation on lipids by the TBARS and NMR. Brazilian Archives of Biology and Technology, 2011. 54: p. 1343-1348.
- 264. Hatzakis, E., et al., High-resolution NMR spectroscopy: an alternative fast tool for qualitative and quantitative analysis of diacylglycerol (DAG) oil. Journal of the American Oil Chemists' Society, 2011.
 88(11): p. 1695-1708.
- 265. Martínez-Yusta, A. and M.D. Guillén, Monitoring compositional changes in sunflower oil-derived deep-frying media by 1H Nuclear Magnetic Resonance. European Journal of Lipid Science and Technology, 2016. 118(7): p. 984-996.
- 266. Tan, Z., et al., Novel approach to study fish oil oxidation using 1H nuclear magnetic resonance spectroscopy. Journal of Functional Foods, 2017. 36: p. 310-316.
- 267. Han, Z., et al., The thermal oxidation evolution and relationship of unsaturated fatty acids and characteristic functional groups in blended oils with raspberry seed oil during deep-frying process by low field nuclear magnetic resonance and 1H nuclear magnetic resonance. LWT, 2020. **133**: p. 110055.
- 268. Zhu, M., et al., Comparative study of the oxidation of cold-pressed and commercial refined camellia oil

during storage with 1H and 31P NMR spectroscopy. Food chemistry, 2020. **321**: p. 126640.

- 269. Yang, X., et al., Monitoring the oxidation state evolution of unsaturated fatty acids in four microwave-treated edible oils by low-field nuclear magnetic resonance and 1H nuclear magnetic resonance. LWT, 2021. 138: p. 110740.
- 270. Resende, M.T., C. Linder, and Z. Wiesman, Low-Field Nuclear Magnetic Resonance Time Domain Characterization of Polyunsaturated Fatty Acid–Rich Linseed and Fish Oil Emulsions during Thermal Air Oxidation. Journal of the American Oil Chemists' Society, 2021. 98(5): p. 495-508.
- 271. Pinto, V.S., et al., Analysis of thermal degradation of Brazilian palm oil by quantitative 1H NMR and chemometrics. Food Control, 2021. **130**: p. 108406.
- 272. Hoppenreijs, L.J., et al., Evaluation of oxygen partial pressure, temperature and stripping of antioxidants for accelerated shelf-life testing of oil blends using 1H NMR. Food Research International, 2021. 147: p. 110555.
- 273. Alonso-Salces, R.M., et al., 1H–NMR fingerprinting and supervised pattern recognition to evaluate the stability of virgin olive oil during storage. Food Control, 2021. **123**: p. 107831.
- 274. Jiang, X., et al., Determination of cis/trans fatty acid contents in edible oils by 1H NMR spectroscopy in association with multivariate calibration. Journal of Food Composition and Analysis, 2022. 105: p. 104195.
- 275. Azarbad, M.H. and H. Jeleń, Determination of hexanal—an indicator of lipid oxidation by static headspace gas chromatography (SHS-GC) in fat-rich food matrices. Food analytical methods, 2015. 8(7): p. 1727-1733.
- 276. Xu, L., et al., Monitoring oxidative stability and changes in key volatile compounds in edible oils during ambient storage through HS-SPME/GC-MS. International Journal of Food Properties, 2017. 20(sup3): p. S2926-S2938.
- 277. Bogusz, B.A., Assessing presence of alternate lipid oxidation pathways from volatile products detected by gas chromatography. 2015: Rutgers The State University of New Jersey-New Brunswick.
- 278. Pignitter, M. and V. Somoza, Critical evaluation of methods for the measurement of oxidative rancidity in

vegetable oils. Journal of Food and Drug Analysis, 2012. **20**(4).

- 279. Lubes, G. and M. Goodarzi, Analysis of volatile compounds by advanced analytical techniques and multivariate chemometrics. Chemical reviews, 2017. 2117(9): p. 6399-6422.
- 280. Jennings, W., Qualitative analysis of flavor and fragrance volatiles by glass capillary gas chromatography. 2012: Elsevier.
- Blomberg, J., P. Schoenmakers, and U.T. Brinkman, Gas chromatographic methods for oil analysis. Journal of Chromatography A, 2002. 972(2): p. 137-173.
- Doleschall, F., et al., A new analytical method to monitor lipid peroxidation during bleaching. European journal of lipid science and technology, 2002. 104(1): p. 14-18.
- 283. Li, Y., et al., Comparison of SDE and SPME for the analysis of volatile compounds in butters. Food Science and Biotechnology, 2020. 29(1): p. 55-62.
- 284. Ma, C., et al., Headspace solid-phase microextraction coupled to gas chromatography for the analysis of aldehydes in edible oils. Talanta, 2014. **120**: p. 94-99.
- 285. Xia, W. and S.M. Budge, GC-MS Characterization of Hydroxy Fatty Acids Generated from Lipid Oxidation in Vegetable Oils. European Journal of Lipid Science and Technology, 2018. **120**(2): p. 1700313.
- 286. Sghaier, L., et al., Validation of a headspace trap gas chromatography and mass spectrometry method for the quantitative analysis of volatile compounds from degraded rapeseed oil. Journal of separation science, 2016. **39**(9): p. 1675-1683.
- 287. Yang, K.-M., et al., Characterization of volatile compounds with HS-SPME from oxidized n-3 PUFA rich oils via Rancimat tests. Journal of Oleo Science, 2017. 66(2): p. 113-122.
- 288. Kiralan, M., et al., Blends of cold pressed black cumin oil and sunflower oil with improved stability: A study based on changes in the levels of volatiles, tocopherols and thymoquinone during accelerated oxidation conditions. Journal of Food Biochemistry, 2017. **41**(1): p. e12272.
- 289. Babaee, S. and A. Daneshfar, Magnetic deep eutectic solvent-based ultrasound-assisted liquid–liquid

microextraction for determination of hexanal and heptanal in edible oils followed by gas chromatography–flame ionization detection. Analytical Methods, 2018. **10**(34): p. 4162-4169.

- 290. Alberdi-Cedeño, J., M.L. Ibargoitia, and M.D. Guillén, Monitoring of minor compounds in corn oil oxidation by direct immersion-solid phase microextraction-gas chromatography/mass spectrometry. New oil oxidation markers. Food chemistry, 2019. 290: p. 286-294.
- 291. Custodio-Mendoza, J., et al., Determination of malondialdehyde, acrolein and four other products of lipid peroxidation in edible oils by Gas-Diffusion Microextraction combined with Dispersive Liquid-Liquid Microextraction. Journal of Chromatography A, 2020. 1627: p. 461397.
- 292. Sharma, A., et al., Determination of Hexanal Using Static Headspace GC-FID Method and Its Correlation with Oxidative Rancidity in Edible Oils. Food Analytical Methods, 2022: p. 1-12.
- 293. Zhou, X., et al., Discriminant analysis of vegetable oils by thermogravimetric-gas chromatography/mass spectrometry combined with data fusion and chemometrics without sample pretreatment. LWT, 2022. 161: p. 113403.
- 294. Drabińska, N. and H.H. Jeleń, Optimisation of headspace solid-phase microextraction with comprehensive two-dimensional gas chromatography– time of flight mass spectrometry (HS-SPME–GC× GC–ToFMS) for quantitative analysis of volatile compounds in vegetable oils using statistical experimental design. Journal of Food Composition and Analysis, 2022. 110: p. 104595.
- 295. Xu, L., et al., Targeted quantitation of furan fatty acids in edible oils by gas chromatography/triple quadrupole tandem mass spectrometry (GC-TQ/MS). Food Chemistry, 2023. **404**: p. 134521.
- 296. Zeb, A., Chemistry and liquid chromatography methods for the analyses of primary oxidation products of triacylglycerols. Free Radical Research, 2015. **49**(5): p. 549-564.
- 297. Jerónimo, E. and S.P. Alves, Lipid-derived oxidation products, in Food Lipids. 2022, Elsevier. p. 231-253.
- 298. Kato, S., et al., Determination of triacylglycerol oxidation mechanisms in canola oil using liquid chromatography-tandem mass spectrometry. npj Science of Food, 2018. **2**(1): p. 1-11.

- Zhang, Q., et al., Application of chromatographic techniques in the detection and identification of constituents formed during food frying: A review. Comprehensive Reviews in Food Science and Food Safety, 2015. 14(5): p. 601-633.
- 300. Murru, E., et al., Reversed-phase HPLC analysis of conjugated linoleic acid and its metabolites, in Advances in conjugated linoleic acid research. 2020, AOCS Publishing. p. 94-100.
- 301. Gotoh, N., et al., Simple method for measuring the peroxide value in a colored lipid. Food analytical methods, 2011. **4**(4): p. 525-530.
- 302. Ma, L. and G. Liu, Simultaneous analysis of malondialdehyde, 4-hydroxy-2-hexenal, and 4hydroxy-2-nonenal in vegetable oil by reversedphase high-performance liquid chromatography. Journal of Agricultural and Food Chemistry, 2017. 65(51): p. 11320-11328.
- 303. Custodio-Mendoza, J., et al., Analysis of free malondialdehyde in edible oils using gas-diffusion microextraction. Journal of Food Composition and Analysis, 2019. 82: p. 103254.
- 304. Tarmizi, A.H.A., E. Hishamuddin, and R.A. Abd Razak, Impartial assessment of oil degradation through partitioning of polar compounds in vegetable oils under simulated frying practice of fast food restaurants. Food Control, 2019. 96: p. 445-455.
- 305. Sun, H., et al., Determination of 2, 4-decadienal in edible oils using reversed-phase liquid chromatography and its application as an alternative indicator of lipid oxidation. Journal of food science, 2020. 85(5): p. 1418-1426.
- 306. Merás, I.D., et al., Optimization of the thiobarbituric acid-malonaldehyde reaction in non-aqueous medium. Direct analysis of malonaldehyde in oil samples by HPLC with fluorimetric detection. Microchemical Journal, 2020. 159: p. 105318.
- 307. El-Maghrabey, А sensitive М., et al., chemiluminescence detection approach for 4-dinitrophenylhydrazine determination of 2, derivatized aldehydes using online UV irradiationluminol CL reaction. Application to the HPLC analysis of aldehydes in oil samples. Talanta, 2021. 233: p. 122522.
- 308. Chiang, K.-M., et al., Particulate matters, aldehydes, and polycyclic aromatic hydrocarbons produced

from deep-frying emissions: comparisons of three cooking oils with distinct fatty acid profiles. npj Science of Food, 2022. 6(1): p. 1-8.

- 309. Dong, B., et al., Colorimetric detection of 2-tert-butyl1, 4-benzoquinone in edible oils based on a chromogenic reaction with commercial chemicals.
 Food Chemistry, 2023. 400: p. 134037.
- 310. Van Aardt, M., et al., Effect of antioxidants on oxidative stability of edible fats and oils: thermogravimetric analysis. Journal of agricultural and food chemistry, 2004. 52(3): p. 587-591.
- 311. Reda, S.Y., Evaluation of antioxidants stability by thermal analysis and its protective effect in heated edible vegetable oil. Food Science and Technology, 2011. **31**: p. 475-480.
- 312. Tengku-Rozaina, T.M. and E.J. Birch, Thermal oxidative stability analysis of hoki and tuna oils by Differential Scanning Calorimetry and Thermogravimetry. European Journal of Lipid Science and Technology, 2016. 118(7): p. 1053-1061.
- 313. Gao, F. and J. Birch, Oxidative stability, thermal decomposition, and oxidation onset prediction of carrot, flax, hemp, and canola seed oils in relation to oil composition and positional distribution of fatty acids. European Journal of Lipid Science and Technology, 2016. 118(7): p. 1042-1052.
- 314. Li, J., et al., The mathematical prediction model for the oxidative stability of vegetable oils by the main fatty acids composition and thermogravimetric analysis. Lwt, 2018. 96: p. 51-57.
- 315. Nair, S.S., K.P. Nair, and P.K. Rajendrakumar, Evaluation of physicochemical, thermal and tribological properties of sesame oil (Sesamum indicum L.): a potential agricultural crop base stock for eco-friendly industrial lubricants. International Journal of Agricultural Resources, Governance and Ecology, 2017. 13(1): p. 77-90.
- 316. Santos, K.A., et al., Chemical composition, antioxidant activity and thermal analysis of oil extracted from favela (Cnidoscolus quercifolius) seeds. Industrial Crops and Products, 2017. 97: p. 368-373.
- 317. Nehdi, I.A., et al., Characterization of ternary blends of vegetable oils with optimal ω -6/ ω -3 fatty acid ratios. Journal of oleo science, 2019. **68**(11): p. 1041-1049.

- 318. Ghosh, M., et al., Thermal and oxidative stability assessment of synergistic blends of sunflower and sesame oils tailored for nutritionally stable composition of omega fatty acids. Journal of Thermal Analysis and Calorimetry, 2019. 135(4): p. 2389-2398.
- Attia, N., et al., Chemical and rheological assessment of produced biolubricants from different vegetable oils. Fuel, 2020. 271: p. 117578.
- 320. Sodeifian, G. and S.A. Sajadian, Antioxidant capacity, physicochemical properties, thermal behavior, and oxidative stability of nectarine (Prunus persica var. nucipersica) kernel oil. Journal of Food Processing and Preservation, 2021. 45(2): p. e15198.
- 321. Piasecka, I., et al., The Study of Thermal Properties of Blackberry, Chokeberry and Raspberry Seeds and Oils. Applied Sciences, 2021. **11**(16): p. 7704.
- 322. Valdés García, A., et al., Effect of frying and roasting processes on the oxidative stability of sunflower seeds (Helianthus annuus) under normal and accelerated storage conditions. Foods, 2021. 10(5): p. 944.
- 323. Edla, S., et al., Evaluation of physicochemical, tribological and oxidative stability properties of chemically modified rice bran and karanja oils as viable lubricant base stocks for industrial applications. Tribology International, 2022: p. 107631.
- 324. Pardauil, J.J., et al., Determination of the oxidative stability by DSC of vegetable oils from the Amazonian area. Bioresource technology, 2011.
 102(10): p. 5873-5877.
- 325. Grajzer, M., et al., Characteristics of rose hip (Rosa canina L.) cold-pressed oil and its oxidative stability studied by the differential scanning calorimetry method. Food chemistry, 2015. **188**: p. 459-466.
- 326. Ramezan, Y., et al., The application of differential scanning calorimetry as a mean to determine the oxidative stability of vegetable oils and its comparison with Rancimat. Orient J Phys Sciences, 2015. **31**(3): p. 1389-94.
- 327. Srivastava, Y., et al., Melting, crystallization and storage stability of virgin coconut oil and its blends by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR).

Journal of food science and technology, 2017. **54**(1): p. 45-54.

- 328. Belayneh, H.D., et al., Effect of extraction method on the oxidative stability of Camelina seed oil studied by differential scanning calorimetry. Journal of food science, 2017. **82**(3): p. 632-637.
- 329. Symoniuk, E., et al., Impact of selected chemical characteristics of cold-pressed oils on their oxidative stability determined using the rancimat and pressure differential scanning calorimetry method. Food Analytical Methods, 2018. **11**(4): p. 1095-1104.
- 330. Bañares, C., et al., Protective effect of hydroxytyrosol and rosemary extract in a comparative study of the oxidative stability of Echium oil. Food chemistry, 2019. 290: p. 316-323.
- 331. Symoniuk, E., K. Ratusz, and K. Krygier, Comparison of the oxidative stability of linseed (Linum usitatissimum L.) oil by pressure differential scanning calorimetry and Rancimat measurements. Journal of food science and technology, 2016. 53(11): p. 3986-3995.
- 332. Almoselhy, R., Comparative study of vegetable oils oxidative stability using DSC and Rancimat methods. Egyptian Journal of Chemistry, 2021. 64(1): p. 299-312.
- Tomaszewska-Gras, J., et al., Comprehensive thermal characteristics of different cultivars of flaxseed oil (Linum usittatissimum L.). Molecules, 2021. 26(7): p. 1958.
- 334. Wirkowska-Wojdyła, M., et al., Application of Chromatographic and Thermal Methods to Study Fatty Acids Composition and Positional Distribution, Oxidation Kinetic Parameters and Melting Profile as Important Factors Characterizing Amaranth and Quinoa Oils. Applied Sciences, 2022. 12(4): p. 2166.
- 335. Islam, M., et al., DSC isothermal and non-isothermal assessment of thermo-oxidative stability of different cultivars of Camelina sativa L. seed oils. Journal of Thermal Analysis and Calorimetry, 2022: p. 1-14.
- 336. Srivastava, S., G. Mishra, and H.N. Mishra, Probabilistic artificial neural network and E-nose based classification of Rhyzopertha dominica infestation in stored rice grains. Chemometrics and Intelligent Laboratory Systems, 2019. 186: p. 12-22.

- 337. Gómez, A.H., et al., Monitoring storage shelf life of 347. tomato using electronic nose technique. Journal of Food Engineering, 2008. 85(4): p. 625-631.
- 338. Brezmes, J., et al., Correlation between electronic nose signals and fruit quality indicators on shelf-life measurements with pinklady apples. Sensors and Actuators B: Chemical, 2001. **80**(1): p. 41-50.
- 339. Saevels, S., et al., An electronic nose and a mass spectrometry-based electronic nose for assessing apple quality during shelf life. Postharvest biology and technology, 2004. **31**(1): p. 9-19.
- 340. Amari, A., N. El Bari, and B. Bouchikhi, Conception and development of a portable electronic nose system for classification of raw milk using principal component analysis approach. Sensors & Transducers, 2009. 102(3): p. 33.
- 341. Cortellino, G., S. Gobbi, and A. Rizzolo, Shelf life of fresh-cut lamb's lettuce (Valerianella locusta L.) monitored by electronic nose and relationship with chlorophyll a fluorescence and mechanical-acoustic test. Postharvest biology and technology, 2018. 136: p. 178-186.
- 342. Chatterjee, D., P. Bhattacharjee, and N. Bhattacharyya, Development of methodology for assessment of shelf-life of fried potato wedges using electronic noses: Sensor screening by fuzzy logic analysis. Journal of Food Engineering, 2014. 133: p. 23-29.
- 343. Malegori, C., et al., A modified mid-level data fusion approach on electronic nose and FT-NIR data for evaluating the effect of different storage conditions on rice germ shelf life. Talanta, 2020. 206: p. 120208.
- 344. Marek, G., et al., Detection and differentiation of volatile compound profiles in roasted coffee arabica beans from different countries using an electronic nose and GC-MS. Sensors, 2020. **20**(7): p. 2124.
- 345. Baietto, M. and A.D. Wilson, Electronic-nose applications for fruit identification, ripeness and quality grading. Sensors, 2015. **15**(1): p. 899-931.
- 346. Gancarz, M., et al., Detection and measurement of aroma compounds with the electronic nose and a novel method for MOS sensor signal analysis during the wheat bread making process. Food and Bioproducts Processing, 2021. **127**: p. 90-98.

Wilson, A.D., Diverse applications of electronic-nose technologies in agriculture and forestry. Sensors, 2013.
 13(2): p. 2295-2348.

- 348. Sanaeifar, A. and A. Jafari, Determination of the oxidative stability of olive oil using an integrated system based on dielectric spectroscopy and computer vision. Information processing in agriculture, 2019. 6(1): p. 20-25.
- 349. Robins, J., G. Abrams, and J. Pincock, The structure of Schiff reagent aldehyde adducts and the mechanism of the Schiff reaction as determined by nuclear magnetic resonance spectroscopy. Canadian Journal of Chemistry, 1980. 58(4): p. 339-347.
- Xie, M., J. Wang, and H. Zhao, A PVA film for detecting lipid oxidation intended for food application. Sensors and Actuators B: Chemical, 2018. 273: p. 260-263.
- 351. Xie, M., et al., Visual determination of oxidation of edible oil by a nanofiber mat prepared from polyvinyl alcohol and Schiff's reagent. Microchimica Acta, 2020. 187(11): p. 1-9.
- 352. Kwon, C.W., et al., Rapid and sensitive determination of lipid oxidation using the reagent kit based on spectrophotometry (FOODLABfat System). Journal of Chemistry, 2016. 2016.
- 353. Zhu, Y., et al., Wavelength-shift-based colorimetric sensing for peroxide number of edible oil using CsPbBr3 perovskite nanocrystals. Analytical chemistry, 2019. 91(22): p. 14183-14187.
- 354. Zhao, Y., et al., Perovskite nanomaterial-engineered multiplex-mode fluorescence sensing of edible oil quality. Analytical chemistry, 2021. **93**(31): p. 11033-11042.
- 355. Huangfu, C. and L. Feng, High-performance fluorescent sensor based on CsPbBr3 quantum dots for rapid analysis of total polar materials in edible oils. Sensors and Actuators B: Chemical, 2021. 344: p. 130193.
- 356. Liu, X., et al., Visual detection of edible oil oxidation by using chitin-based colorimetric sensor for aldehydes. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2021. **628**: p. 127303.
- 357. Grazioli, C., et al., A colorimetric paper-based smart label soaked with a deep-eutectic solvent for the

detection of malondialdehyde. Sensors and Actuators B: Chemical, 2021. **329**: p. 129174.

- 358. Xie, M., et al., A novel method for detection of lipid oxidation in edible oil. LWT, 2020. **123**: p. 109068.
- 359. Karami, H., M. Rasekh, and E. Mirzaee-Ghaleh, Identification of olfactory characteristics of edible oil during storage period using metal oxide semiconductor sensor signals and ANN methods. Journal of Food Processing and Preservation, 2021. 45(10): p. e15749.
- 360. Wang, X., et al., Development of 4-hydrazinyl-7nitrobenzofurazan as a fluorogenic probe for detecting malondialdehyde in biological samples. Sensors and Actuators B: Chemical, 2018. 254: p. 248-254.
- Manoj, D. and S. Shanmugasundaram, Detection of FFA content of coconut milk by using screen-printed electrode. IJCS, 2020. 8(5): p. 420-422.
- Akyüz, E., et al., A novel gold nanocluster-based fluorometric biosensor for measuring prooxidant activity with a large Stokes shift. Talanta, 2020. 208: p. 120425.
- 363. Anconi, A.C.S.A., N.C.S. Brito, and C.A. Nunes, Determination of peroxide value in edible oils based on Digital Image Colorimetry. Journal of Food Composition and Analysis, 2022. 113: p. 104724.
- 364. Ghohestani, E., J. Tashkhourian, and B. Hemmateenejad, Colorimetric determination of peroxide value in vegetable oils using a paper based analytical device. Food Chemistry, 2023. 403: p. 134345.

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Research article

First Principles study of Silver Argyrodites-structured compounds A₈BC₆ (A=Ag; B=Si, Ge; C=Te) for Optoelectronic application

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Abstract

The structural and optical properties of a material are studied using Density Functional Theory. By the method of full potential linearized augmented plane wave (FP-LAPW) silver argyrodites Ag₈SiTe₆ and Ag₈GeTe₆ has been investigated. To obtain stable geometry of A₈BC₆ materials, the energy minimization approach is applied. The Generalized Gradient Approximation (GGA) approach is used to optimize the crystal structure of the Argyrodites materials. All these compounds crystalize in a cubic unit cell with lattice constant increasing from 12.13 Å (Si) to 12.28 Å (Ge). The mBJ-functional shows a semiconducting nature Ag₈SiTe₆ for and metallic nature for Ag₈GeTe₆ of these compounds with an indirect band gap lying at the L-X symmetry points with a band gap of 0.24 eV (Si) and 0.0068 eV (Ge) to obtain the optical properties such as refractive index, complex dielectric constant with real and imaginary part of dielectric function, and other optical properties are discussed. Effective mass of electrons is smaller than those of holes resulting in higher carrier mobility for electronic devices.

Keywords: Argyrodites, Optical properties, Effective mass.

1.Introduction

Energy is an essential component of society that contributes significantly to its growth by raising living standards and quality of life. The global energy crisis of today is a major concern for researchers due to the ongoing depletion of energy resources, which is also environmentally unsound. Our primary energy needs are met by fossil fuels, which are neither renewable nor abundant. They will be consumed within the next 50 years, according to some estimates [1]. The scientific community has been compelled to look for more environmentally friendly and sustainable options as a result of the rapid rise in energy demand. The right choice seems to be energy from the sun and waste heat. Solar and thermal energy can be extracted from argyrodites materials. Additionally, thermoelectric energy converters are very important because they can make use of the waste heat that is produced in factories, power plants, and heat engines [2, 3].In the literature on solid state sciences, a series of simple yet fairly efficient empirical models fully or partly based on the ionic radii was reported for predicting the cell parameters of scientifically and technologically important families of cubic crystalline materials such as perovskites ABX₃ [4, 5], defect halide perovskites A_2BX_6 [6,7], pyrochlores $A_2B_2X_7$ [8, 9], and spinel's AB_2X_4 [10, 11].The name "argyrodites" was first discovered. Subsequently, a series of synthetic compounds were reported with preparations made by substituting Ge for main groups III, IV and V other elements, partially substituting S for chalcogens or other halogens, or substitute Ag for Cu has been detected [12, 13]. The band structure and optical properties of the recently synthesized compounds Ag_8MX_6 (M = Si, Ge, Sn, X = S, Se, Te) have not been investigated enough. Studies of the crystal growth, crystallography and phase diagrams of Ag_8MX_6 and some results on the electric, photoelectric, and optical properties of argyrodites and canfieldite have been reported. Allots members of the argyrodites, a previously unknown of tetrahedrally closepacked structures families, have been synthesized and described using x-ray technologies. Their generally represented by formula:

 $A^{m+}_{(12-n-x)/m}B^{n+}X^{2-}_{(6-x)}Y^{-}_{x}(A: Cu, Ag, Cd, Hg; B: Ga, Si,$ Ge, Sn, P, As; X = S, Se, Te; Y = CI, Br, I; $0 \le x \le 1$). With a disordered A-cation sub-lattice. Transitions into other ordered structures occur at lower temperatures. An anion framework of interpenetrating, centered icosahedra provides ideal and deformed tetrahedral cation sites, which is a characteristic structural property. Some argyrodites work well as ionic conductors, while others work well as non-linear optical materials. Despite the fact that the argyrodites family's structurally similar structures may be observed to arise from a single high-temperature parent phase with (overall) cubic symmetry F43m [14]. Phosphorus-containing argyrodites Me_6PS_5X (Me = Cu+, Ag+, Li+, and X = Cl, Br, I) are now the most investigated compounds Me₆PS₅X and M₆PSe₅X (M=Ag, Cu and X=Halide) belong to a large class of solids collectively referred to as argyrodites. Phosphorus-containing argyrodites Me_6PS_5X (Me = Cu+, Ag+, Li+, and X = Cl, Br, I) are now the most investigated compounds Me₆PS₅X and M₆PSe₅X (M=Ag, Cu and X=Halide) belong to a large class of solids collectively referred to as argyrodites [15]. Thermoelectric materials can convert waste heat to usable electricity. The technology of energy conversions from waste heat into electrical energy is very important for developing alternative energy technologies to reduce our dependence on fossil fuels. The efficiency of a thermoelectric device depends on material properties, which in turn Depend on the thermoelectric figure of merit. Focused on thallium tellurides as advanced thermoelectric materials [16]. Having current

scientific interests in the structural family of argyrodites [17, 18]. The compounds Ag_8SiTe_6 and Ag_8GeTe_6 under our consideration form an important group of argyrodites their properties have not been fully investigated experimentally as well as theoretically. It is, therefore, imperative to perform a detailed theoretical investigation of these compounds to understand them and to judge their suitability towards optoelectronics and thermoelectric applications.

2: Computational Details

The structural, electronic, optical and elastics characteristics and properties of the argyrodites A₈BC₆ (A=Ag; B=SI, Ge; C=Te). were investigated by using the method of FP-LAPW [19] with in the DFT framework implemented in the Wien2K code using in material modeling [20] Wu-Cohen-Generalized Gradient Approximation (WC-GGA) [21] the modified Becke-Johnson potential (mBJ) were used to approximate the exchange-correlation potential [22]. To carry out electronic structure the FP-LAPW method is widely used in Wien2K calculation. This method is used to solve the Kohn-Sham's equation for many body systems by this method the unit cell is split into two regions i.e. Moffin Tin region and interstitial region. The potential is considered to be spherically symmetric in Moffin Tin region while in interstitial region considered constant. Plan wave solutions and radial solution of the Schrödinger wave equation are used in the Moffin Tin region and interstitial region respectively inside the sphere. For expansion of wave inside the spheres the maximum value of angular momentum $1_{max} = 10$ is considered. Similarly the plane wave cutoff value R_{MT} . $K_{max} = 7$ is chosen for interstitial region to separate the core and valance states the cutoff energy -6Ry is to be taken to perform Self-Consistent Field (SCF) calculation a k-mesh with 1000 k-points in the first Brillion zone was used.

3. Results and Discussion

3.1. Structural Properties

Compound structural properties are determined by looking at a variety of structural parameters. The structural parameters are the lattice constants a (Å), b (Å), and c (Å),

the bulk modulus B (GPa), and the bulk modulus (Bp) pressure derivative. The mention structural characteristics are obtained by maximizing the volume of the unit call of the substance. The total stable state energy was calculated using "Birch Murnaghan's equation of state. The technique of optimization produces the plot between the unit cell volume and the related energy. Ag₈SiTe₆ and Ag₈GeTe₆ are argyrodites with the general formula A₈BC₆ (A=Ag; B=SI, Ge; C=Te). Figure 3.1 shows the crystal structure of Ag₈SiTe₆, which is isostructural with Ag₈GeTe₆. The structure is a cubic crystal with the space group F.43m, and each unit cell contains more than 60 atoms. Ag₈SiTe₆, on the other hand, has the same crystal structure as Ag₈GeTe₆ [16].

3.2. Volume Optimization

The optimizing volume of unit cell and energy is satisfied by Brich Murnaghan relationship.

$$E(V) = E_0 = \frac{9V_0 B_0}{16} \{ [(\frac{V_0}{V})^{2/3} - 1]^3 - B'_0 + [(\frac{V_0}{V})^{2/3} - 1]^2 [(6 - 4\frac{V_0}{V})^{2/3}] \}$$

Ground state parameters are represented by Energy (E_0), volume (V_0) and modulus of (B_0) [23].The optimize graph of the two compounds Ag₈SiTe₆ and Ag₈GeTe₆ shown in figure 3.2 (a, b) parabolic curves show the optimize volume of unit cell which similar to ground state density, ground state volume and energy are indicated at the lowest point of parabolic curve the minimum energy state is called the steady state which is the most stable state corresponds to the experimental values. The lattice constant at stable state of both compounds Ag₈SiTe₆ and Ag₈GeT₆ were computed by the optimization of the structure that is 12.130 A^0 and 12.89 A^0 respectively with a very slight variation from experimental ones which is 11.515 A^0 and 11.566 A^0 for Ag₈SiTe₆ and Ag₈GeTe₆[23, 24].

3.3. Electronic Properties

The electronic properties are a set of factors and representations that comprehensively explain the state and

behavior of electrons in materials. The electronic properties of Argyrodites A_8BC_6 (A=Ag; B=Si, Ge; C=Te) compounds in cubic phase have been explored using electronic structure of bands and total as well as calculations of partial density of states.

3.4. Energy Band Structure

The energy bands are of two types of a material according to energy band theory the conduction band (CB) and valance band (VB) the area in which electrons are not fit is called prohibited energy band gap which in between the valance and conduction bands. The types of materials also distinguish from band structure whether it is conductors, insulators, or semiconductors. Material having direct band gap used in optical devices. Visible region band gap from 1.3eV to 1.8eV with a band gaps of 1.4eV and 6.0eV the material behaves semiconductor and insulator. The overlapping of conduction and valance band at Fermi level show the metal nature of material according to band gap theory. Wu-Cohen, GGA, PBE sol-GGA and modified Becke-Johnson method are used for the study of electronic band structure of argyrodites Ag₈SiTe₆ and Ag₈GeTe₆ in the energy ranges from -3eV to 3eV from the band structure of these compounds it is clear that the selected compounds have direct band gap. Ag₈SiTe₆ have semiconductor nature with a band gap of 0.24eV while Ag₈GeTe₆ have half metallic nature with a band gap of 0.0068eV. The Eigenvalues of VBM, CBM and Fermi energy for Ag₈SiTe₆ are 5.649 eV, 5.890 eV and 5.743 eV. The Eigenvalues of VBM, CBM and Fermi energy for Ag_8GeTe_6 are 5.214 eV, 5.209 eV and 5.209 eV.

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Figure 1: Ag₈SiTe₆ crystal structure. Ag, Si, and Te are represented by grey, blue, and red balls, respectively. Individual places of Ag and Te are indicated by (a) and (b), respectively. (c) Shows the locations of Ag, Si, and Te in the same crystal frame.



Figure 2: volume optimization of compounds (a) Ag₈SiTe₆ (b) Ag₈GeTe.

Compounds	Lattice constant (A ⁰)		$V_0(a.u^3)$	B(GPA)	Вр	$E_0(Ry)$
	A ⁰ _{comp}	A^0_{exp}				
Ag ₈ SiTe ₆	12.130	11.515	3011.332	33.697	5.148	- 145950.526
Ag ₈ GeTe ₆	12.289	11.566	3131.189	37.571	7.072	- 149568.559

Table 1: summarizes the lattice constants of stable compounds, as well as their related energies, equilibrium structures, bulk modulus, pressure derivative of bulk modulus, optimized volume, and experimental values.

3.6. Energy Band Structure

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3.7. Density Of States

In condense matter physics and solid state physics the accessible state per unit energy range occupy by electron is describe through density of state (DOS) different energy levels make the band structure of a substance the band structure consist of valance and conduction band the contribution of different orbitals in the valance and conduction band are explain by DOS plots which is a simple approach to the contribution of orbitals in the band structure for both compounds Ag₈SiTe₆ and Ag₈GeTe₆ the energies are distributed between -6eV and 6eVas illustrated below. For Ag₈SiTe₆ the total density of state (TDOS) is show in the figure 4 (a) the contribution of Ag atom maximum to the TDOS in the conduction band as well in valance band and Te atom also have maximum contribution and Si atom have least contribution .TDOS of the compound Ag_8GeTe_6 as show in the figure 4 (b) in which the maximum contribution came from the Ag atom to the total density of state (TDOS) while the other atoms have minimum contribution to the TDOS of the compound Ag₈GeTe₆

3.8. Partial Desity Of States

The partial density of state (PDOS) of the compound Ag_8SiTe_6 is shown in figure 5.1 (a, b, c). In the case of the

Ag atom, the partial density of state shown in figure 5.1 (a), the d_{xy} orbital has the maximum contribution to the total DOS of Ag atom in the valance band (V.B), while the s orbital has the maximum contribution in the conduction band (C.B), and the other orbitals have a small contribution to the total DOS of Ag atom. In case of Si atom the partial density of state shown in the figure 5.1 (b) in which p_v orbital have maximum contribution to the total density of states of Si atom in valance band (V.B) while in conduction band (C.B) the maximum contribution came from s and p_x orbital while the other have small contribution to total density of state of Si atom in conduction band in case of Te atom the partial density of state shown in the figure 5.1 (c) in which p_v orbital have maximum contribution to the total density of states of Si atom in valance band (V.B) while in conduction band (C.B) the maximum contribution also came p_x orbital while the other have small contribution to total density of state of Te atom in conduction band. figure 5.2 (d, e, f) show partial density of state (PDOS) of compound Ag8GeTe6.in case of Ag atom the partial density of state shown in the figure 5.2 (d) in which d_z^2 orbital have maximum contribution to the total density of states of Ag atom in valance band (V.B) the contribution of d_{xz} orbital also came maximum in valance band while in conduction band (C.B) the maximum contribution came from s orbital and the other have small contribution to total density of state of Ag atom.in case of Ge atom the partial density of state shown in the figure 5.2 (e) in which p_z and p_x orbital have maximum contribution to the total density of states of Ge atom in valance band while in conduction band from 0 to nearly 1.9eV the maximum contribution came from s orbital and from 2eV to 5eV the maximum contribution came from p_z orbital while the other have small contribution to total density of state of Ge atom in conduction band in case of Te atom the partial density of state shown in the figure 5.2 (f) in which p_z and p_x orbitals have maximum contribution to the total density of states of Ge atom in valance band (V.B) also in conduction band (C.B) the maximum contribution came from p_x and p_z orbitals while the other have small

contribution to total density of state of Te atom in conduction band.

4. Optical Properties

The response of materials to the electromagnetic radiation shows the optical properties of materials. Argyrodites Ag₈SiTe₆ is semiconductor and Ag₈GeTe₆ is half metallic so the optical parameters such that complex dielectric constant, refractive index, reflectivity, optical conductivity, absorption and extinction coefficient energy/frequency dependent optical properties determined with detail explanation when the material expose to electromagnetic radiation. For the study of optoelectronic applications, we need a detail information about material response to visible, infrared and ultra violet radiations.

4.1. Real And Imaginary Dielectric Functions

The dielectric function descried the response of materials when expose to electromagnetic radiation Dielectric function have two parts real and imaginary complex dielectric function can be written as : $\mathcal{E}(\omega) = \mathcal{E}1(\omega) + \mathcal{E}(\omega)$ $i\mathcal{E}2(\omega)$ real part $\mathcal{E}1(\omega)$ is responsible for the material how much material disperse light or how much the material polarizibility while the imaginary part $\mathcal{E}2(\omega)$ show the material absorption properties. In the band structure different transitions of orbitals the argyrodites compounds Ag₈SiTe₆ and Ag₈GeTe₆ shows different optical spectra's Ag₈SiTe₆ semiconductor in nature so the optical properties will different as compare Ag₈GeTe₆ to have half metallic nature illustrated in figure 6 (a) Static dielectric constant $\mathcal{E}1(0)$ is called zero frequency limit. Ag₈SiTe₆ has a static dielectric 13.0 in the energy ranges from 0 to 0.5 eV the polarizibility increasing when the photons energy increases the maximum spectra for Ag₈SiTe₆ compound will be occur at energy 1.81eV is 16.7 after reached to this maximum peak the disperse light now decreasing and reached to its minimum point below zero point in the negative region the

metallic nature of material indicated. Compound Ag₈GeTe₆ shows half metallic nature in band structure so spectral lines varies with the photon energies illustrated in the figure 6 (a) static dielectric function is in the energy ranges from 0 almost to 0.9eV the critical point is at 14.70 at energy 0.04eV the maximum dispersion of the Ag₈GeTe₆ at energy 1.44 eV is 16.80 after the maximum peak dispersion decrease with the increasing in energy and become negative at a specific energy.

Imaginary part $\mathcal{E}2(\omega)$ of the dielectric function for compounds Ag₈SiTe₆ and Ag₈GeTe₆ the figure illustrated in 6 (b) shows the absorption properties of silver based argyrodites materials the spectra threshold points of the materials related with the band gap energy beyond the threshold point different curves causes by inter band transitions critical point for Ag₈SiTe₆ occur at energy 0.0605 *eV* while maximum is at 2.82 *eV* is 15.7 for Ag₈GeTe₆ and for critical point is at 0.0355*eV* and that of maximum is at 2.59*eV* is 14.9

4.2. Absorption Coefficient $\alpha(\omega)$

The interaction between the incident photon on material surface and the absorption of photon in the material surface illustrated in figure 7 (a, b) of the absorption $\boldsymbol{\alpha}$ ($\boldsymbol{\omega}$) the critical points are at energies 0.280 eV and 0.157 eV for both compounds Ag₈SiTe₆ and Ag₈GeTe₆ the absorption coefficient increasing as the photon energy increasing the peak values of absorption coefficient $\boldsymbol{\alpha}$ ($\boldsymbol{\omega}$) for Ag₈SiTe₆ is 1.3×10^6 cm¹, at energy 7.84 eV and for Ag₈GeTe₆ is 1.3×10^6 cm⁻¹ at energy 7.3.

4.3. Extinction Coefficient $K(\omega)$.

Extinction coefficient indicate the absorption of photons by material. The extinction coefficient is a measure of the attenuation of an electromagnetic wave as it passes through a material. It is a measure of the rate of decrease in transmitted photons due to scattering and absorption for a medium.



Figure 3: Energy band structures (a) Ag₈SiTe₆ (b) Ag₈GeTe₆



Figure.5.1: Partial density of state (PDOS) of compounds Ag₈SiTe₆



Figure 6: (a) real part $\mathcal{E}1(\omega)$ and (b) imaginary part $\mathcal{E}2(\omega)$ of dielectric function for compounds Ag₈SiTe₆ and Ag₈GeTe₆



Figure 7: The absorption coefficient $\alpha(\omega)$ of compounds (a) Ag₈SiTe6 (b) Ag₈GeTe₆





Figure 8: shows the extinction coefficient $K(\omega)$ of compounds (a) Ag₈SiTe₆ (b) Ag₈GeTe₆

10

Figure 10: The Reflectivity $R(\omega)$ of compounds (a) Ag₈SiTe₆ (b) Ag₈GeTe₆

8

0.36

0.34

0

2

6

Energy(ev)

4

8

10

Compounds	Effective mass(me*) of electron Kg	Effective mass(mh*) of hole Kg
Ag ₈ SiTe ₆	0.65x10 ⁻³²	-3.78x10 ⁻³²
Ag ₈ GeTe ₆	1.39x10 ⁻³²	-2.15x10 ⁻³²

Table 2: Electron and hole effective mass of compounds Ag₈SiTe₆ and Ag₈GeTe₆

This is because the refractive index is complex and can be express as n-iK. Where n is the real part of the refractive index (which tells the velocity in the medium) and K is the extinction coefficient. The extinction coefficients of the Ag₈SiTe₆ and Ag₈GeTe₆ compounds are illustrated in

4 6 Energy(ev)

6

2

figure 8(a, b). The maximum value of $K(\omega)$ for the Ag₈SiTe₆ compound is 2.32 at energy of 3.56 eV, and for the Ag₈GeTe₆ compound an extinction coefficient of 2.32 at an energy of 4.41 eV, respectively, is observed. The extinction coefficient $K(\boldsymbol{\omega})$ is a measure of light loss due to

0.33

0.30

0

scattering and absorption per unit volume, so the value of

K (ω) is high

4.5. Refractive Index (n)

The propagation of light through material medium is explain by refractive index .Speed of light is represented by c and refractive index is by n The optical transparency of any material can be investigated through refractive index. extinction and absorption coefficient of electromagnetic radiation refractive index as show in the figure 9 (a, b) is 3.64 at zero frequency and at energy 0.026 eV for compound Ag₈SiTe₆ while maximum peak will be 4.26 at 2.12 eV due to energy increasing the refractive index fluctuation between 3.64 and 4.26 in the energy ranges from 0.026 eV to 2.12 eV. For compound Ag₈GeTe₆ in the energy range from 0.016 eV to 1.571 eV, the refractive index n fluctuates between 3.83 and 4.181 due to the various rates of the inner-band transitions the lower refractive index indicates less polarization in the higher energy range for both compounds the fall of refractive index (n) suggested the reduction of magnetization with increase in energy

4.6. Reflectivity $R(\omega)$

Ratio between incidents, reflected light called coefficient of reflectance or reflectivity behavior of electromagnetic radiation on the surface of material is described by the interaction of EM radiation to the material surface. Material surface properties and material surface information is described by this important property energy ranges is in between 0 to 10 eV for both compounds Ag₈SiTe₆ and Ag₈GeTe₆ show in the figure 10 (a, b) in figure (a) the lowest value at which just both compound Ag₈SiTe₆ start is called zero photon energy or critical point that is 0.342 at energy 0.0206 eV between the energy ranges reflectivity $R(\omega)$ increases at energy $1.04 \ eV$ is 0.336 and then decreases to 0.337 at $1.23 \, eV$ and then gain a spectacular peak of 0.445 at energy 3.03 eV can be detected and then reflectivity start decreasing with the increasing of energy in figure (b) for

compound Ag₈GeTe₆ zero photon energy or critical point start from 0.0057 at energy 0.034 eV and continue to increase up to 0.355 at energy 0.496 eV then decreases at energy 0.641 eV to 0.351 at energy 4.42 eV a remarkable peak of 0.493 seen in the reflectivity after thisstart decreasing to its minimum values a significant lower values is observe between 0.496 eV to 0.641 eV.

5. Effective Mass

To comprehend the concept of effective mass, we must first comprehend the band structure in solids, where energies are dispersed in two types of energy bands: valence band and conduction band. The curvature of E-K relationships determines the effective mass (m*) of curvature in a semiconductor. Energy (E) and wave vector K have a parabolic relationship. By comparing each electron's behavior to that of a free particle of the same mass, the effective mass (m*), energy (E), and wave vector (K) are computed. Effective mass is represented as by making an analogy with the behavior of a free particle of that mass. $m_e^* = \mathbf{h}^2 [\frac{d^2 E}{dk^2}]^{-1}$. By using the band structure of silver argyrodites compounds A8BC6 (A=Ag; B=Si, Ge; C=Te), the effective mass is determined by measuring the curvature of conduction band minima. The estimated hole impact mass mh* is negative due to valence band minima. The negative number indicates that if a force is applied in the -X direction, the electron will move in the +X direction like electrons in lattice as a result holes move in a semiconductor with an effective mass that is generally negative near the band's top, according to band-structure calculations. The hole effective mass is smaller than electron effective mass

6. Conclusions

Through the study of computational analysis, the structural, electronic and optical properties of A_8BC_6 (A=Ag, B=Si, Ge, C=Te) argyrodites compounds were generated using the FPLAPW method using the mBJ approximation implemented in the wien2k code. Structural optimization of A_8BC_6 argyrodites (A=Ag; B=Si, Ge; C=Te) shows that the lattice parameters and bulk modulus of the A_8BC_6 compound

are substantially close to the available experimental data. The electrical properties of the A₈BC₆ argyrodites compounds show a straight band gap behavior. Ag contributes the greatest to the overall density of states in the valence band in these compounds. The optical properties of the A_8BC_6 (A = Ag; B = Si, Ge; C = Te) argyrodites compound are determined from the results of the complex dielectric function, refractive index, extinction coefficient, photoconductivity, absorption coefficient, and reflectance. All peaks (maximum values) in the absorption spectrum of the A8BC6 compound are due to inter band transitions of electrons. The optical properties of these materials were calculated in the energy range from 0 to 10 eV. The absorption coefficient increases as the energy of the incident light (photons) increases. The coefficient of absorption increases as the energy of the incident light (photon) increases. The maximum value in the real and imaginary part of the complex dielectric function are found at energies of 1.81 eV for Ag₈SiTe₆ and 1.44 eV for Ag₈GeTe₆. The critical points of these substances are found in the visible spectrum on an absorption coefficient. For compound Ag₈SiTe₆ absorption start from 0.28 eV up to maximum point of 7.84 eV and for Ag₈GeTe₆ absorption start from 0.157 eV up to maximum point of 7.31 eV which shows the absorption of ultra violet spectrum which is from 3.1 eV to 30 eV

Authors Contribution

Muhammad Munsif, Matiullah Shah and G.Murtaza have the main idea of the manuscript and wrote the manuscript. Suliman Khan ,Asim Sajjad, Zakir Ullah, Hamid Ullah and Abdur Rashid revised the manuscript and provide suggestions.

Conflicts of Interest

The authors reported no potential conflict of interest.

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Data Availability statement

The data presented in this study are available on request

from the corresponding author.

REFERENCES:

- Kalkan, N.; Young, E.; Celiktas, A. Renewable and sustainable energy reviews, 2012,16 (8), 6352-6383.
- 2. Mirza, U.K.; Ahmad, N.; Majeed, T. Renewable and sustainable energy reviews, 2008, 12 (7), 1988-1996.
- Ali, S.; Anwar, S.; Nasreen, S. Forman Journal of Economic Studies, 2017, 13.
- C. Ye, J. Yang, L. Yao, N. Chen, Chin. Sci. Bull. 47 (2002) 458–460, https://doi.org/10.1360/02tb9105
- V. Sidey, J. Solid State Chem. 279 (2019) 120951, https://doi.org/10.1016/j.jssc.2019.120951.
- M.G. Brik, I.V. Kityk, J. Phys. Chem. Solid. 72 (2011) 1256–1260, https://doi.org/10.1016/j.jpcs.2011.07.016.
- V. Sidey, J. Phys. Chem. Solid. 126 (2019) 310–313, https://doi.org/10.1016/j.jpcs.2018.11.02
- B.C. Chakoumakos, J. Solid State Chem. 53 (1984) 120– 129, https://doi.org/10.1016/0022-4596(84)90234-2
- V. Sidey, Z. Kristallogr. 232 (2017) 729–731, https://doi.org/10.1515/zkri-2017-2057.
- R.J. Hill, J.R. Craig, G.V. Gibbs, Phys. Chem. Miner. 4 (1979) 317–339, https://doi.org/10.1007/BF00307535
- M.G. Brik, A. Suchocki, A. Kaminska, Inorg. Chem. 53 (2014) 5088 –5099, https://doi.org/10.1021/ic500200a
- S.T.Kong, H.J.Deiseroth, C.Reiner, O.Gün, E.Neumann, C.Ritter, & D.Zahn, (2010). "Lithium argyrodites with phosphorus and arsenic: order and disorder of lithium atoms, crystal chemistry, and phase transitions". Chemistry–A European Journal, 16(7), 2198-2206.
- X.Shen, C.C.Yang, Y.Liu, G.Wang, H.Tan, Y.H.Tung, & H.Zhou,(2018). "High-temperature structural and thermoelectric study of argyrodite Ag₈GeSe₆". ACS applied materials & interfaces, 11(2), 2168-2176
- W.F.Kuhs, R.Nitsche, & K.Scheunemann, (1979). "The argyrodites—A new family of tetrahedrally closepacked structures". Materials Research Bulletin, 14(2), 241-248.

- Beeken, R. B., Garbe, J. J., Gillis, J. M., Petersen, N. R., Podoll, B. W., & Stoneman, M. R. (2005). Electrical conductivities of the Ag₆PS₅X and the Cu6PSe5X (X= Br, I) argyrodites. Journal of Physics and Chemistry of Solids, 66(5), 882-886.
- A.Charoenphakdee, A., K.Kurosaki, K., H.Muta, H., M.Uno, M., & S.Yamanaka, (2009). "Ag8SiTe6: a new thermoelectric material with low thermal conductivity". Japanese Journal of Applied Physics, 48(1R), 011603.
- Studenyak, V.Y. Izai, A.I. Pogodin, O.P. Kokhan, V.I. Sidey, M.Y. Sabov, A. Kezionis, T. Salkus, J. Banys, Lith. J. Phys. 57 (2017) 24–251, https://doi.org/10.3952/physics.v57i4.3603
- A.I. Pogodin, M.J. Filep, T.O. Malakhovska, M.Y. Sabov, V.I. Sidey, O.P. Kokhan, I.P. Studenyak, Solid State Ionics 341 (2019) 115023, https://doi.org/10.1016/j.ssi.2019.115023.
- Petersen, M.;Wagner, F.;Hufnagel, L.;Scheffler, M.;Blaha, P. et al. Computer Physics Communications, 2000, 126 (3), 294-309.
- Blaha, P.;Schwarz, K.;Madsen, G.K.;Kvasnicka, D.; Luitz, J. An augmented plane wave+ local orbitals program for calculating crystal properties, 2001, 60.
- Wu, Z.; Cohen, R.E. Physical Review B, 2006, 73 (23), 235116.
- Tran, F.; Blaha, P. Physical review letters, 2009, 102 (22), 226401.
- 23. D.D.Koelling; B.N. J.Harmon, Phys. Com. 1977, 10, 3107.
- W.F.Kuhs, R.Nitsche, & K.Scheunemann, (1979). "The argyrodites—A new family of tetrahedrally closepacked structures". Materials Research Bulletin, 14(2), 241-248.

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Research Article

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Elemental Mercury Removal from Natural Gas Using Nano-Tio₂ Mohamed A. Mandor¹, F. I. El-Hosiny², Y. M. Moustafa¹, Mohamed A. Ebiad¹, Mohamed

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Abstract

The study focused on the utilization of titanium dioxide (TiO₂) as a photo-catalyst for the treatment of natural gas contaminated with elemental mercury (Hg^0). The catalyst was carefully characterized using various physical techniques, including transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDAX), UV-visible diffuse reflectance spectroscopy (DRS), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction analysis (XRD). The results clearly demonstrated that TiO_2 exhibited outstanding efficacy in oxidizing Hg⁰ when exposed to UV light. This phenomenon was ascribed to the excitation of photoelectrons within the valence band, leading to their transfer to the conduction band, generating photo-induced electrons that acted as reactive agents responsible for converting Hg⁰ into HgO. Notably, the activity of TiO₂ under UV-visible light was significantly lower compared to TiO₂ under UV light. The overall findings indicated that TiO₂ under UV light exhibited the highest removal capacity, measured at 31.74 μ g/g, followed by TiO₂ under UV-visible light at 25.91 μ g/g, and TiO₂ in the dark at 20.89 μ g/g. The study underscores the promising potential of TiO₂ photo-catalyst for effectively eliminating Hg⁰ contamination in natural gas.

Keywords: Elemental mercury (Hg⁰), Photo-catalysis, TiO₂, UV, UV-visible

1. Introduction

Natural gas utilization as a vital fossil fuel in various human activities can lead to the presence of heavy metal contaminants, such as Hg and As, which present a substantial threat to both the environment and human health, which occur naturally [1, 2]. Among these contaminants, the highly volatile form of mercury (Hg⁰) is of particular concern due to its volatility, neurotoxicity, tendency to bioaccumulate, and persistent nature. "The World Health Organization (WHO)" recognizes the significance of safeguarding organisms from the potential harm posed by it [3]. It has an unpleasant economic effect through natural gas processing plants [4, 5], even a small amount of mercury can cause significant damage to the heat exchangers with aluminum structure that are commonly utilized in cryogenic temperature processes used in LNG plants or naphtha crackers for olefin production [5, 6]. Also, mercury released to the environment through combustion of natural gas is constantly increasing from different sources in line with the Global Mercury Assessment of UNEP [7]. There are three types of mercury: elemental Hg⁰, oxidized Hg²⁺, and particulate Hg^p [8–11], Among these, elemental mercury (Hg⁰) is the most common form found in natural gas [5, 12]. Numerous techniques have been researched for eliminating Hg⁰, such as adsorption, conventional chemical oxidation, advanced oxidation, and catalytic oxidation, which

encompasses photocatalytic oxidation procedures [13-18]. Mercury's oxidized forms, commonly represented as Hg²⁺ species, have garnered significant attention due to their propensity to be efficiently captured by conventional control devices. This property leads to increased solubility in water and enhanced adsorption onto particles. Recognizing this characteristic, our study specifically targeted photocatalytic oxidation as a potential approach to address the issue.

TiO₂ is a widely favoured photocatalyst primarily due to its affordability, non-toxic nature, and advantageous band edge positions [19]. Its extensive use is attributed to its ability to harness the energy of light and convert it into chemical energy, thereby accelerating the reaction rate of various chemical processes [20]. Its exceptional properties render it an ideal choice for diverse applications, including water purification, air pollution control, and hydrogen production [36–38]. Additionally, its stability and durability under harsh conditions make it a reliable and efficient choice for industrial and environmental applications [19].

The majority of research in the field of photocatalytic removal of elemental mercury has primarily concentrated on flue gases. This preference stems from the fact that flue gases are more amenable to photocatalytic oxidation processes compared to natural gas. This is mainly due to the presence of components such as NOx, SO₂, H₂O, and HCl in flue gases, which facilitate the photooxidation process of Hg⁰[24, 25].

The study aims to investigate the effectiveness of TiO_2 as a photocatalyst for removing elemental mercury from natural gas under three different conditions: in the dark, in UV light, and in UV-visible light. The experiment will measure the removal efficiency of mercury using TiO_2 in each condition to determine which is the most effective. This information could be useful for optimizing the process of mercury removal in natural gas production. The study could also contribute to a better understanding of the mechanisms involved in photocatalytic reactions using TiO₂, and provide insights into the factors that affect their performance.

2. Materials and Methods

2.1 Materials

 TiO_2 nanoparticles were produced through the sol-gel technique using Titanium tetraisopropoxide as the starting material, HNO₃ bought from Merck and AR grade isopropanol procured from SD's Fine Chemicals (Pty) Ltd.

2.2 Synthesis of Catalyst

To prepare TiO₂ nanoparticles, a sol-gel method was used with 4 mL of Titanium tetraisopropoxide (TTIP) precursor in 10 mL of isopropanol. After undergoing agitation for 30 minutes at ambient temperature, the solution was subjected to forced hydrolysis through the addition of a solution containing isopropanol, deionized water, and HNO₃. The mixture stirred for two hours until a homogeneous and viscous solution was achieved. HNO₃ served as an acid catalyst to improve the hydrolysis and condensation rates [26]. Afterward, the solution was subsequently subjected to drying in an oven at 80°C for a duration of 2 hours, followed by a heat treatment process at 500°C for an additional 2 hours.

2.3 Characterization

The samples underwent characterization using various techniques, involving X-ray diffraction (Bruker XRD), transmission electron microscopy (JEOL 2100F TEM), and energy-dispersive X-ray spectroscopy (EDS), Surface area BET (NOVA2000) and UV/vis reflectance spectroscopy. The UV-visible diffuse reflectance spectra (DRS) were acquired using a Perkin Elmer Lambda 35 UV-visible spectrophotometer, which was equipped with an integrating sphere assembly. BaSO₄ was used as the reflectance standard for the measurements. K-ALPHA instrument for X-ray photoelectron spectroscopy (XPS) from (Thermo Fisher Scientific. USA) with monochromatic Al K-alpha radiation were used, which covered a range of 10 to 1350 eV. The spot size was 400 micrometers, and the pressure was maintained at 10-9 mbar. The full spectrum pass energy was set to 200 eV, and the

narrow spectrum was set to 50 eV.

2.4 Photocatalytic activity test

The objective of the experiment was to assess the efficacy of TiO₂ catalyst in photo-catalytically removing elemental mercury. A quartz tube bed filled with glass beads and photocatalyst was used for the experiment. The weight ratio of catalyst to glass beads was 0.1:0.7g, with the glass beads performing as support for the catalyst and ensuring an even distribution of catalyst particles within the bed. The bed was exposed to two different UV wavelengths, i.e., 253.7 nm and 365 nm, as well as a dark medium. The mercury concentration before and after the bed was measured using a Nippon WA-4 instrument (an atomic absorption spectroscopy technique). The experiment involved the preparation of the catalysts by packing them with glass beads in the quartz tube bed. To determine the least effective temperature for catalyst activity, the performance of TiO₂ was assessed at three different media conditions: Dark, UV, and UV-visible. The activity of elemental mercury removal was evaluated using the initial and final concentration of mercury passing through the catalyst bed using equation 1.

$$q = \frac{Q \int_0^t (C_{in} - C_{out}) dt}{m}$$
(1)

The formula provided is used to calculate the dynamic Hg^0 adsorption capacity, where q is in units of $\mu g \cdot g^{-1}$. Q represents the total gas flow rate, measured in m³·min⁻¹; t represents the time elapsed, measured in minutes; m represents the mass of sorbent used, measured in grams; C_{in} represents the real-time concentration of Hg^0 at the inlet, measured in $\mu g \cdot m^{-3}$; and C_{out} represents the real-time concentration of Hg^0 at the real-time concentration of Hg^0 at the outlet, also measured in $\mu g \cdot m^{-3}$.

3. Results and discussion

The results obtained from the physico-chemical characterization techniques are now being discussed.

3.1 X-ray diffraction analysis

X-ray diffraction (XRD) is a valuable technique for

analyzing the crystal structure and average size of nanoparticles. It provides insights into the atomic arrangement within a sample and captures the diffraction pattern resulting from the interaction of X-rays with the sample. The pattern of TiO_2 nanoparticles (XRD) was analyzed to determine its crystal structure.





The results showed that the nanoparticles have the crystalline features of anatase, as indicated by the peaks in the pattern matching to the anatase phase at specific 2θ values 25.43°, 38°, 48.01°, 54.08°, 55.36°, and 62.78°. The observed peaks in the X-ray diffraction pattern are identified by their corresponding hkl values enclosed in parentheses, such as (1 0 1), (1 1 2), (2 0 0), (1 0 5), (2 1 1), and (2 0 4). The main diffraction peak in the anatase XRD pattern is at $2\theta = 25.43^{\circ}$, matches with the (1 0 1) plane. The size of the nanoparticles was determined by calculating the full width at half maximum (FWHM) of the (1 0 1) diffraction peak and applying Scherrer's equation (number 2). The equation establishes a correlation between the average crystallite size (D), the wavelength of the Xray source (λ), the FWHM of the diffraction peak (β), and the diffraction angle (θ) . The result provides an average size estimate for the nanoparticles, but does not account for the size distribution or shape.

$$D = K\lambda/\beta \cos\theta (2)$$

In the equation, D represents the crystal size of the sample,



Figure 2: XRD patterns of undoped TiO₂ catalyst λ denotes the wavelength of the X-ray (1.54056 Å), β corresponds to the full width at half maximum (FWHM) of the diffraction peak in radians, K is a coefficient (0.89), and θ represents the diffraction angle at the peak maximum. The crystal size of TiO₂ is found to be 20.31 nm.

3.2 HR-TEM characterization and EDAX spectrum

The TEM image shown in figure 3a reveals the shape, structure, and range of sizes of the synthesized TiO_2 nanoparticles. The irregular spherical shape observed suggests that the nanoparticles are not perfectly round, but instead have variations in shape, likely due to the synthesis method used. The small particle size observed between 15 to 35 nm indicates that the nanoparticles are relatively small, which is important for achieving high surface area and reactivity in photocatalysis. The uniform size distribution observed suggests that the synthesis method used is efficient and reproducible.

The EDAX spectrum shown in figure 3b provides elemental information about the sample, indicating the presence of titanium and oxygen, which is expected for TiO_2 . This further confirms the successful synthesis of TiO_2 nanoparticles. Overall, the combination of TEM and EDAX analysis provides important evidence about the morphology and size distribution of the synthesized TiO_2 nanoparticles.

3.3 UV-visible diffuse reflectance spectra (DRS)

The (UV-vis DRS) was used to examine the optical

properties of the samples. Results, shown in Figure 4a, indicate that TiO₂ exhibits a pronounced absorption band in the ultraviolet (UV) region, ranging from 200 to 380 nm. However, there is little absorption in the visible light region (above 400 nm). This is mainly due to electrons transmission from valence to conduction band of TiO₂. Nevertheless, it is evident that the TiO2 samples exhibit a significant absence of absorption in the visible light region, which extends beyond 400 nm[27].





Figure 3: Images of a) TEM and b) EDAX Spectra of TiO_2 . To estimate the band gap energy (Eg) of the samples, the Kubelka-Munk equation (3) was used to determine band gap energy (Eg) and the equation assumes an infinitely thick sample, disregarding the effects of sample thickness and holder on reflectance (R) [28].

$$\frac{\kappa}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = F(R_{\infty})$$
(3)

where BaSO₄ was used as the reference material for white light. The equation involves two coefficients, K and S, and the remission or K-M function, $F(R_{\infty})$, where R_{∞} is the final reflectance, obtained by dividing the sample reflectance by the reference reflectance. The wavelength was exchanged to electron volts (eV) by dividing 1240 by the wavelength. R_{∞} is the square root of the product of energy and R. (Eg) was obtained from the slope of the F vs R_{∞} plot of the prepared TiO₂ as shown in Figure 4b was determined to be 3.3 eV [28].



Figure 4: a) UV–Vis-DRS and b) the band gap energy of TiO₂.

3.4 BET Characterization

A Type IV isotherm is typically observed in mesoporous materials and is commonly associated with materials that possess slit-shaped or cylindrical pores. The hysteresis loop indicates the presence of mesopores, which are formed when the particles that make up the material agglomerate during synthesis. The particles form voids or spaces between them, which are the meso-pores. The shape of the hysteresis loop gives information regarding the size and shape of the meso-pores. In the case of H3 loop, it suggests the observed hysteresis loop suggests the existence of slitshaped pores and/or panel-shaped particles, which means that the pores have a long and narrow shape.

The surface area of TiO₂, determined using the BET method, is 43.034 m²/g, which indicates that TiO₂ has a relatively low surface area. However, the presence of meso-pores in the material suggests that it may have good accessibility for reactants and products, which is beneficial for catalytic applications. The pore size distribution analysis revealed that TiO₂ exhibits a range of pore sizes

from 4 to 9 nm, an average pore diameter (3.650 nm) and a pore volume (0.098 cc/g). These findings confirm the mesoporous nature of the surface pores in TiO_2 [29, 30]



Figure 5: N₂-adsorption–desorption isotherm and Pore Size distributions of TiO₂.

As shown in figure 5. Where, in this type of adsorption isotherm, as the relative pressure increases, both the adsorption volume and the adsorption rate show a corresponding increase. Overall, the presence of a Type IV isotherm and the analysis of pore size distribution suggest that the TiO_2 material exhibits a mesoporous structure characterized by slit-shaped or cylindrical pores. Although it has a relatively low surface area, it offers favourable accessibility for reactants and products. These properties indicate its potential usefulness in catalytic applications.

3.5 XPS

XPS is commonly used, as shown in Figure 6, to investigate the chemical bonding and electronic structure of metal oxides, including TiO₂. Specifically, the Ti2p and O1s spectra were examined to gain insights into the bonding characteristics. Based on the provided data, 458.64 eV and 464.34 eV are the binding energies of Ti2P peaks that are recognized to titanium oxide lattice, corresponding to the binding energy of highest oxidation state of Ti atoms in TiO₂ nanoparticles (Ti⁴⁺ ions). TiO₂ nanoparticles did not reveal any peaks associated with reduced titanium Ti³⁺, indicating



Figure 6: XPS spectral of TiO₂ a) Ti2p and b) O1s spectra.

Overall, the XPS analysis suggests that the studied TiO_2 nanoparticles are of high purity and possess a well-defined crystalline structure. These characteristics make them suitable for potential applications in various fields, including photocatalysis, energy storage, and biomedical engineering.



Figure 7: Break through curves of Hg⁰ photo-oxidation and adsorption over TiO₂ in a) Dark, b) UV light and c) UV-visible light.



Figure 8: Impact of light source on the mercury removal efficiency of TiO₂.

the absence of defects in the material [31]. The O1s spectrum reveals two distinct peaks. The peak observed at a lower binding energy of approximately 530 eV is associated with lattice oxygen atoms (O^{2-}), indicating their presence within the TiO₂ structure. On the other hand, the peak observed at a higher binding energy of approximately 532 eV can be attributed to surface hydroxyl groups (OH⁻) or adsorbed water molecules. This information provides insights into the chemical environment and surface properties of the TiO₂ nanoparticles, highlighting the presence of both oxygen species within the material [32].

3.6 Photo-Catalytic Activity

The experimental setup for evaluating the photocatalytic activity of TiO_2 involved the passage of a gas stream containing elemental mercury through a quartz tube filled with the catalyst material. The concentration of elemental mercury was then measured after it passed through the catalyst. The experiments were conducted under various conditions, including darkness, UV light, and UV-visible light. The removal capacity of TiO_2 was found to be 20.894

 μ g. g⁻¹ in 12 hours in the dark shown in figure 7a, 25.913 μ g. g⁻¹ in 20 hours under UV-visible light shown in figure 7c, and 31.746 μ g. g⁻¹ in 27 hours under UV light displayed in figure 7b.

As shown in Figure 7b, the higher removal capacity under UV light can be explained by the movement of photoelectrons from the valence band to the conduction band of TiO₂, producing photo-generated electrons and holes [33]. This process generates highly reactive species, for example hydroxyl radicals, that have the ability to oxidize Hg⁰ to Hg²⁺. The Hg²⁺ ions that are formed can readily adsorb onto the surface of the TiO₂ particles, effectively removing them from the gas stream as shown in figure 8.

Changing from a UV lamp (253.7 nm) to a UV-visible lamp (365 nm) alters the emitted light wavelength and energy. The lower energy of the UV-visible lamp leads to a reduced capacity for Hg^0 removal compared to the UV lamp. This is attributed to insufficient generation of electrons and holes for efficient Hg^0 photo-oxidation [34].

 Table 1 The Brunauer–Emmett–Teller (BET) surface area result.

Sample	Pore volume (cm ³ .g ⁻¹)	Average pore size (nm) SBE	Γ (m ² . g ⁻¹)	
TiO ₂	0.098	3.650	43.034	
	Table 2: Capacity of F Radiation	able 2: Capacity of Hg^0 removal over TiO_2 in $\mu g/g$.RadiationQ (Adsorption)		
	Dark	20.89	_	
	UV	31.74		
	UV-visible	25.91		

4. CONCLUSION

The study aimed to investigate the photo-catalytic activity of TiO2 in the removal of elemental mercury from a gas stream under various light conditions. The results showed that TiO₂ exhibited higher removal capacity under UV light 31.74 μ g/g compared to UV-visible 25.91 μ g/g and dark 20.89 μ g/g conditions, owing to the presence of highly reactive species produced during the photocatalytic process

leads to the oxidation of elemental mercury (Hg⁰) to Hg²⁺. This highlights the potential of photocatalysts such as TiO₂ as an eco-friendly and economical solution for effectively removing elemental mercury from natural gas. However, further research is needed to optimize the photo-catalytic performance of TiO₂ and to develop effective methods for scaling up the process of industrial applications. Also, the efficiency of the photo-catalytic reaction is significantly influenced by the energy emitted by the light source employed in the process. Hence, selecting a light source that can generate an adequate amount of photo-generated electrons and holes is essential for ensuring efficient photocatalytic reactions.

Authors Contribution

M.A.E., A.A.E and M.B.M have the main idea of the manuscript. M.A.M and A.A.S wrote the the manuscript. Y.M.M. and F.I.E. revised the manuscript and provide suggestions.

Conflicts of Interest

There are no conflicts of interest reported by the writers.

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Data Availability statement

The data presented in this study are available on request from the corresponding author.

REFERENCES

- R. Khunphonoi, P. Khamdahsag, S. Chiarakorn, N. Grisdanurak, A. Paerungruang, and S. Predapitakkun, "Enhancement of elemental mercury adsorption by silver supported material," J. Environ. Sci. (China), vol. 32, pp. 207–216, 2015, doi: 10.1016/j.jes.2015.01.008.
- K. J. Irgolic and B. K. Puri, "Organic Arsenic Compounds in Petroleum and Natural Gas," in Metal Speciation in the Environment, Berlin,

Heidelberg: Springer Berlin Heidelberg, 1990, pp. 377–389. doi: 10.1007/978-3-642-74206-4_20.

- World Health Organization (WHO), "Elemental mercury and inorganic mercury compounds: human health aspects," 2003. [Online]. Available: http://www.who.int/ipcs/publications/cicad/en/cicad5 0.pdf?ua=1
- M. D. Bingham, "Field Detection and Implications of Mercury in Natural Gas," SPE Prod. Eng., vol. 5, no. 02, pp. 120–124, May 1990, doi: 10.2118/19357-PA.
- A. A. El-Feky, W. El-Azab, M. A. Ebiad, M. B. Masod, and S. Faramawy, "Monitoring of elemental mercury in ambient air around an Egyptian natural gas processing plant," J. Nat. Gas Sci. Eng., vol. 54, no. January, pp. 189–201, Jun. 2018, doi: 10.1016/j.jngse.2018.01.019.
- M. F. Ezzeldin, Z. Gajdosechova, M. B. Masod, T. Zaki, J. Feldmann, and E. M. Krupp, "Mercury Speciation and Distribution in an Egyptian Natural Gas Processing Plant," Energy & Fuels, vol. 30, no. 12, pp. 10236–10243, Dec. 2016, doi: 10.1021/acs.energyfuels.6b02035.
- UNEP, "Global Mercury Assessment," 2018. [Online]. Available: https://www.amap.no/documents/doc/global-mercuryassessment-2018/1757
- S. Zhao, D. Pudasainee, Y. Duan, R. Gupta, M. Liu, and J. Lu, "A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies," Progress in Energy and Combustion Science, vol. 73. Pergamon, pp. 26–64, Jul. 01, 2019. doi: 10.1016/j.pecs.2019.02.001.
- 9. D. STREETS et al., "Anthropogenic mercury emissions in China," Atmos. Environ., vol. 39, no. 40,
pp. 7789–7806, Dec. 2005, doi: 10.1016/j.atmosenv.2005.08.029.

- Y. Wang et al., "Experimental study on mercury transformation and removal in coal-fired boiler flue gases," Fuel Process. Technol., vol. 90, no. 5, pp. 643–651, May 2009, doi: 10.1016/j.fuproc.2008.10.013.
- G. Kos et al., "Evaluation of discrepancy between measured and modelled oxidized mercury species," Atmos. Chem. Phys., vol. 13, no. 9, pp. 4839–4863, May 2013, doi: 10.5194/acp-13-4839-2013.
- M. A. Ebiad, M. Bakry, and N. City, "Adsorption of Hg 2 + using modified sulfur-impregnated activated carbon from olive stone," Mansoura J. Chem., vol. 42, no. 2, p. 16, 2016.
- P. Wang et al., "Catalytic oxidation of Hg0 by MnOx-CeO₂/γ-Al₂O₃ catalyst at low temperatures," Chemosphere, vol. 101, pp. 49–54, 2014, doi: 10.1016/j.chemosphere.2013.11.034.
- J. Y. Lee, Y. Ju, T. C. Keener, and R. S. Varma, "Development of cost-effective noncarbon sorbents for Hg⁰ removal from coal-fired power plants," Environ. Sci. Technol., 2006, doi: 10.1021/es0519511.
- Z. Tan et al., "Gas-phase elemental mercury removal by novel carbon-based sorbents," Carbon N. Y., vol. 50, no. 2, pp. 362–371, 2012, doi: 10.1016/j.carbon.2011.08.036.
- N. Saman et al., "Enhanced elemental mercury removal by facile sulfurization of agrowaste chars," Chem. Eng. Res. Des., vol. 144, pp. 198–208, 2019, doi: 10.1016/j.cherd.2019.02.010.
- Z. Liu, W. Yang, W. Xu, and Y. Liu, "Removal of elemental mercury by bio-chars derived from seaweed impregnated with potassium iodine," Chem.

Eng. J., vol. 339, no. February, pp. 468–478, 2018, doi: 10.1016/j.cej.2018.01.148.

- W. Ji, Z. Shen, M. Fan, P. Su, Q. Tang, and C. Zou, "Adsorption mechanism of elemental mercury (Hg⁰) on the surface of MnCl₂ (1 1 0) studied by Density Functional Theory," Chem. Eng. J., vol. 283, pp. 58– 64, 2016, doi: 10.1016/j.cej.2015.06.033.
- E. Pitoniak, C. Y. Wu, D. W. Mazyck, K. W. Powers, and W. Sigmund, "Adsorption enhancement mechanisms of silica-titania nanocomposites for elemental mercury vapor removal," Environ. Sci. Technol., 2005, doi: 10.1021/es049202b.
- J. An et al., "Performance evaluation of non-thermal plasma injection for elemental mercury oxidation in a simulated flue gas," J. Hazard. Mater., vol. 268, pp. 237–245, 2014, doi: 10.1016/j.jhazmat.2014.01.022.
- P. Fang, C. P. Cen, X. M. Wang, Z. J. Tang, Z. X. Tang, and D. S. Chen, "Simultaneous removal of SO₂, NO and Hg⁰ by wet scrubbing using urea + KMnO4 solution," Fuel Process. Technol., vol. 106, 2013, doi: 10.1016/j.fuproc.2012.09.060.
- F. Ding, Y. Zhao, L. Mi, H. Li, Y. Li, and J. Zhang, "Removal of gas-phase elemental mercury in flue gas by inorganic chemically promoted natural mineral sorbents," Ind. Eng. Chem. Res., vol. 51, no. 7, pp. 3039–3047, 2012, doi: 10.1021/ie202231r.
- Y. Zhao, F. Xue, X. Zhao, T. Guo, and X. Li, "Experimental study on elemental mercury removal by diperiodatonickelate (IV) solution," J. Hazard. Mater., vol. 260, pp. 383–388, 2013, doi: 10.1016/j.jhazmat.2013.05.040.
- Z. Barnea, T. Sachs, M. Chidambaram, and Y. Sasson, "A novel oxidative method for the absorption of Hg⁰ from flue gas of coal fired power plants using task specific ionic liquid scrubber," J. Hazard. Mater., vol.

244–245, pp. 495–500, 2013, doi: 10.1016/j.jhazmat.2012.10.067.

- T. Abbas et al., "Mercury capture from natural gas by carbon supported ionic liquids: Synthesis, evaluation and molecular mechanism," Fuel, vol. 177, pp. 296–303, Aug. 2016, doi: 10.1016/j.fuel.2016.03.032.
- G. Cheng, Q. Zhang, and B. Bai, "Removal of Hg0 from flue gas using Fe-based ionic liquid," Chem. Eng. J., vol. 252, pp. 159–165, 2014, doi: 10.1016/j.cej.2014.05.007.
- B. Shen et al., "Simultaneous removal of NO and Hg0using Fe and Co co-doped Mn-Ce/TiO₂ catalysts," Fuel, 2018, doi: 10.1016/j.fuel.2018.03.080.
- Y. Cao et al., "Impacts of halogen additions on mercury oxidation, in a slipstream Selective Catalyst Reduction (SCR), reactor when burning subbituminous coal," Environ. Sci. Technol., vol. 42, no. 1, 2008, doi: 10.1021/es071281e.
- Y. Gao et al., "A Critical Review on the Heterogeneous Catalytic Oxidation of Elemental Mercury in Flue Gases," Environ. Sci. Technol., vol. 47, no. 19, pp. 10813–10823, Oct. 2013, doi: 10.1021/es402495h.
- Y. Xu, Q. Zhong, and X. Liu, "Elemental mercury oxidation and adsorption on magnesite powder modified by Mn at low temperature," J. Hazard. Mater., vol. 283, pp. 252–259, 2015, doi: 10.1016/j.jhazmat.2014.09.034.
- H. Wang, S. Zhou, L. Xiao, Y. Wang, Y. Liu, and Z. Wu, "Titania nanotubes-A unique photocatalyst and adsorbent for elemental mercury removal," Catal. Today, vol. 175, no. 1, pp. 202–208, 2011, doi: 10.1016/j.cattod.2011.03.006.

- Y. Yuan et al., "Electrospun metal oxide–TiO₂ nanofibers for elemental mercury removal from flue gas," J. Hazard. Mater., vol. 227–228, pp. 427–435, 2012, doi: 10.1016/j.jhazmat.2012.05.003.
- J. Yang, S. Ma, Y. Zhao, H. Li, J. Zhang, and C. Zheng, "Elemental Mercury Removal from Flue Gas over TiO₂ Catalyst in an Internal-Illuminated Honeycomb Photoreactor," Ind. Eng. Chem. Res., vol. 57, no. 51, pp. 17348–17355, 2018, doi: 10.1021/acs.iecr.8b04417.
- S. M. Gupta and M. Tripathi, "A review of TiO₂ nanoparticles," Chinese Sci. Bull., vol. 56, no. 16, pp. 1639–1657, 2011, doi: 10.1007/s11434-011-4476-1.
- A. L. Linsebigler, G. Lu, and J. T. Yates, "Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results," Chem. Rev., vol. 95, no. 3, pp. 735–758, 1995, doi: 10.1021/cr00035a013.
- Y. Wen et al., "Spectrophotometric determination of arsenic in environmental and biological samples," INDIAN J. CHEM. TECHNOL, vol. 5, no. 1, pp. 1–7, Dec. 2014, doi: 10.1016/j.molcata.2012.07.020.
- M. R. Pai et al., "A comprehensive study on sunlight driven photocatalytic hydrogen generation using low cost nanocrystalline Cu-Ti oxides," Sol. Energy Mater. Sol. Cells, vol. 154, pp. 104–120, 2016, doi: 10.1016/j.solmat.2016.04.036.
- P. Supphasrirongjaroen, P. Praserthdam, J. Panpranot, D. Na-Ranong, and O. Mekasuwandumrong, "Effect of quenching medium on photocatalytic activity of nano-TiO₂ prepared by solvothermal method," Chem. Eng. J., vol. 138, no. 1–3, pp. 622–627, 2008, doi: 10.1016/j.cej.2007.09.035.
- H. Li, C. Y. Wu, Y. Li, L. Li, Y. Zhao, and J. Zhang, "Role of flue gas components in mercury oxidation over TiO2 supported MnOx-CeO₂ mixed-oxide at low

temperature," J. Hazard. Mater., vol. 243, pp. 117–123, 2012, doi: 10.1016/j.jhazmat.2012.10.007.

- 40. S. Zhao, D. Pudasainee, Y. Duan, R. Gupta, M. Liu, and J. Lu, "A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies," Progress in Energy and Combustion Science, vol. 73. Pergamon, pp. 26–64, Jul. 2019. doi: 10.1016/j.pecs.2019.02.001.
- S. Ananth, T. Arumanayagam, P. Vivek, and P. Murugakoothan, "Direct synthesis of natural dye mixed titanium dioxide nano particles by sol-gel method for dye sensitized solar cell applications," Optik (Stuttg)., vol. 125, no. 1, pp. 495–498, Jan. 2014, doi: 10.1016/j.ijleo.2013.07.018.
- N. Sobana, M. Muruganadham, and M. Swaminathan, "Nano-Ag Particles Doped TiO₂ for Efficient Photodegradation of Direct Azo Dyes Nano-Ag particles doped TiO₂ for efficient," J. Mol. Catal. A Chem., vol. 258, no. November 2016, pp. 124–132, 2006, doi: 10.1016/j.molcata.2006.05.013.
- J. G. Wen, "X-ray diffraction and reflectivity," in Practical Materials Characterization, New York, NY: Springer New York, 2014, pp. 189–229. doi: 10.1007/978-1-4614-9281-8_5.
- W. Wang, P. Liu, M. Zhang, J. Hu, and F. Xing, "The Pore Structure of Phosphoaluminate Cement," Open J. Compos. Mater., vol. 02, no. 03, pp. 104– 112, 2012, doi: 10.4236/ojcm.2012.23012.
- 45. M. Thommes et al., "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)," Pure Appl. Chem., vol. 87, no. 9–10, 2015, doi: 10.1515/pac-2014-1117.
- D. Briggs, "Handbook of X Ray Photoelectron Spectroscopy: A Reference Book of Standard

Spectra for Identification and Interpretation of XPS Data," in Handbook of Adhesion, Chichester, UK: John Wiley & Sons, Ltd, 2005, pp. 621–622. doi: 10.1002/0470014229.ch22.

- K. Ubolchollakhat, L. Sikong, and W. Sangchay, "Effect of Ni-doped on surface of titaniumdioxide thin film," Dig. J. Nanomater. Biostructures, vol. 10, no. 4, pp. 1469–1473, 2015.
- T. N. Obee, "Photooxidation of sub-parts-per-million toluene and formaldehyde levels on titania using a glass-plate reactor," Environ. Sci. Technol., vol. 30, no. 12, pp. 3578–3584, 1996, doi: 10.1021/es9602713.Society, 89(11), pp.2669-2676.

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Research article

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Characterization of Paper Mill Effluent and Its Impacts on the Environment Md Shakilur Zaman Shakil and Md Golam Mostafa*

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Abstract

The study aimed to characterize paper mill effluents and determine the quality of surface water in the vicinity of the paper mills using a water quality index to understand the pollution level due to the discharge of untreated effluents. Physicochemical parameters and CCME (Canadian Council of Ministersof the Environment) Water Quality Index (WQI) were used to estimate the degree of pollution in the selected paper mills area in Bogura District of Bangladesh. Moreover, a public perception survey was conducted in the study area to illustrate the present scenario regarding paper mill effluent discharge. The analytical results revealed that the concentrations of TSS, EC, COD, BOD₅, phenols, K, and NO₃ – N were higher than the permissible limit, and the DO level was below the ECR 1997 standard. However, there was no concentrations of heavy metals exceeded the permissible level. The FTIR analysis showed the presence of several toxic pollutants, including lignin, phenol, and halo compound. The CCME WQI showed that sites S-1 and S-2 were ranked as marginal, while site S-3 was ranked as fair. The study observed that the discharge of untreated paper mill effluent has the potential to cause harm to aquatic life and the environment.

Keywords: Heavy metals, indexing, physicochemical parameters, pollutant, water quality

1. Introduction

There are 110 paper mills in Bangladesh with annually more than 1.5 million tons of paper productioncapacity [1]. As the country's demand is around 0.9 - 1.0 million metric tons, paper mills can use half of their production capacity. Therefore, nearly a decade ago, paper and paper product exporting was started, and the opportunity has become a boon for the industry. Industrial water use and effluent generation are global concerns. Most of the industries directly discharge poorly treated or untreated effluents into the nearby water body, which results in deterioration of water quality [2-6]. Among the major effluent-generating industries, the paper industry is among the most notorious industries around the globe [7-8]. The process of making paper uses a lot of freshwater. [8-10]. One ton of paper requires 273 - 455 m³ of freshwater. Therefore, it discharges approximately 300 m³ of effluent to produce one ton of paper [11]. The main steps of paper production are raw material preparation, digestion, pulping, bleaching, etc. [12]. Almost all steps generate different types of environmental pollutants like air emissions, solid waste, and toxic effluent [13]. The volume and physicochemical characteristics of the paper mill effluent depend on the different production methods and raw materials. Different types of chemicals are used as additives, fillers, dyes, whiteners, strengtheners, surfactants, and biocides in the paper manufacturing process. As a result, the effluent from paper mills comprises BOD, COD, TSS, TDS, different inorganic ions, and organic compounds at high level [14-19]. More than 250 chemicals are found in pulp and paper mill effluent [20]. Discharge of untreated or insufficiently treated effluent from pulp and paper mills or other industrial processes into nearby

surface water destroys the aquatic ecosystem [16, 21-23]. Usually, nontechnical politicians, policymakers. government officers, or the general public have no idea or scope to understand the water quality physicochemical data. In this case, the water quality index (WOI) plays an important role as a communication tool to transfer water quality data [24-26]. To reveal water quality data in an easily understood format, several water quality indices have been developed [27, 28]. The CCME (Canadian Council of Ministers of the Environment) summarizes data of water quality conventionally to design a water quality index. The CCME WOI, considering all water quality data, generates a single number between zero and 100 that indicates the water quality level [29-32]. The objective of this study was to characterize the paper mill effluents and assess the impacts of the untreated effluents on the environment around the mills' area.

2. Materials and Methods

2.1 Study Area

The study area is located at Kahaloo Upazila in Bogura district, Bangladesh (Figure 1). It lies between 24° 52' 0" north and 89° 11' 0" east. More than three private sector paper mills are located in this Upazila, which relies on imported pulp and recycles waste paper. Among those, a paper mill was selected for the study based on production capacity and location. The effluent of the paper mill discharges through a canal connected to the Nagar River at the location point S1 (Figure 1). In the rainy season, the water source of the canal was the Nagar River, but it becomes dry in the winter, and the water quality severely deteriorates and cannot be used for any purposes.

2.2 Questionnaire survey

A structured questionnaire survey was conducted to get the public's perception of the present scenario of the discharge of paper mill effluent into the surface water body in the study area. It was conducted based on different categories of questions, including personal and socioeconomic data, environmental impact data, health impact data, etc. A total of fifty (50) villagers were selected using the random sampling technique. The data were analyzed using statistical methods.

2.3 Sample Collection

Effluent samples were collected from the outlet of a paper mill, before mixing with the surface water body, in the years 2019 to 2020. In the same time, surface water samples were collected around the effluent discharging point, canal, and the Nagar River. All samples were collected at three times (Pre-monsoon, Monsoon, and Post-monsoon) in a calendar year during two years from the outlet, effluent discharge point(S-1), middle of the discharge point, and the river, which is 350 meters downstream of the canal (S-2), and 700 meters downstream where the canal falls into the river (S-3). All samples were collected in clean plastic pots and were preserved in refrigerator to avoid any chemical change before analysis.



Figure 1: Location Map of the study area.

2.4 Physicochemical Analysis

This study considered a total of 28 physicochemical parameters (i.e., Temperature, pH, EC, DO, turbidity, TDS, TSS, BOD₅, COD, TOC (Total Organic Carbon), Phenolic compounds, Total Hardness (TH), Cl⁻, SO4²⁻, PO4³⁻, NO3⁻⁻ N, HCO3⁻, Na, K, Ca, Mg, Cu, Fe, Mn, Zn, Pb, Cd, and Cr. Digital meters were used in the sites to monitor the temperature, pH, EC, DO, and turbidity directly. Using the standard methods other parameters were measured in laboratory [33, 34]. Moreover, an FTIR analysis of the paper mill effluent was conducted to identify functional groups of organic pollutants.

Fable 1: Description of The Canadian Council of Ministers of the Environment	(CCME) Water	Quality	Index	(WQI)	
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Score	Ranking	Description
95 100 Excellent		Water quality is protected with a virtual absence of threat, or impairment; conditions
95-100	Execution	very close to natural, or pristine levels
20.04	Card	Water quality is protected with only a minor degree of threat, or impairment;
80-94	Good	conditions rarely depart from natural, or desirable levels
65-79 Fair		Water quality is usually protected but occasionally threatened, or impaired; conditions
		sometimes depart from natural, or desirable levels
15 (1		Water quality is frequently threatened, or impaired; conditions often depart from
45-64	Marginal	natural, or desirable levels
0.44	D	Water quality is almost always threatened or impaired; conditions usually depart from
0-44 Poor		natural, or desirable levels

The calculated WQI score was then ranked into one of the following five categories (Excellent, good, fair, marginal, and poor) mentioned in Table 1.

Equtions:

Scope, F1 =
$$\left(\frac{Number \ of \ Failed \ Variables}{Total \ Number \ of \ Variables}\right) \times 100$$
 (i)
Frequency, F2 = $\left(\frac{Number \ of \ Failed \ Tests}{Total \ Number \ of \ Tests}\right) \times 100$ (ii)

Amplitude, $F_{\mathcal{F}}$ Amplitude is calculated based on the excursion of each failed test relative to its objective. If failed test is greater than the objective:

Excursion =
$$\left(\frac{\text{Failed Test value}}{\text{Objective}}\right) - 1$$
 (iii)

If failed test is less than the objective:

Excursion =
$$\left(\frac{Objective}{Failed Test value}\right) - 1$$
 (iv)

Normalized Sum of Excursions (NSE) =
$$\left(\frac{\sum \text{Excursion}}{\text{Total Number of Test}}\right)$$
 (v)

Amplitude,
$$F_3 = \left(\frac{NSE}{0.01NSE + 0.01}\right)$$
 (vi)

CCME WQI calculation:

CCME WQI =
$$100 - (\frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732})$$
 (vii)

2.5 Water Quality Index (WQI)

This study used the CCME (Canadian Council of

Ministers of the Environment) Water Quality Index (WQI) to assess the water quality status in the study area. A total

of 22 The WQI score was determined by taking into account the following water quality parameters: temperature, pH, DO, EC, TSS, TDS, BOD₅, COD, Phenol, Cl⁻, SO₄²⁻, NO₃⁻-N, PO₄³⁻, HCO₃⁻, Na, K, Ca, Cu, Mn, Zn, Cr, Pb, Cd and Fe (Eq. vii). The three (3) elements that make up the CCME WQI are scope (F1), frequency (F2), and amplitude (F3). F₁ denotes the percentage of parameters which don't settle their objectives at least once (failed parameters) by the period (Eq. i). F₂ denotes the percentage of isolate tests which don't settle their objectives (failed tests) (Eq. ii), and F₃ denotes the degree by which failed tests don't settle their objectives (Eq. vi) [30-32, 35]. The equations are mentioned above.

3. Results and Discussion

3.1. Public perception survey

The social survey report showed that most respondents had a negative attitude regarding the discharge of paper mill effluent into surface water. Before, the paper mill started the respondents perception towards functional water usage was 68, 62, 88, 70, and 12 % for washing, bathing, fishing, irrigation, and no use, respectively, and after the paper mill started, the perception was 0, 0, 16, 12 and 82 % for washing, bathing, fishing, irrigation, and no use, respectively (Figure 2).

Figure 3 illustrates that according to the public perception, crop production, and fishery decreased, livestock diseases, and skin diseases problems were very severe in the study area, whereas soil fertility decreased and other human health effects were marginal.

3.2 Physicochemical characterization of effluent

Table 2 lists the physicochemical parameters of the effluents from paper mills. It shows that the range of electrical conductivity (EC), total suspended solids (TSS), biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), Phenolic compounds, nitrate-nitrogen (NO₃⁻-N), and potassium ion (K⁺) were 2053 to 2070 μ S/cm, 592 to 600 mg/L, 280 to 288 mg/L, 843 to 850 mg/L, 2.95 to 3.0 mg/L, 28.40 to 29.00 mg/L, and 78.9 to

81.4 mg/L, respectively, in the paper mill effluents which exceeded the standard limit, whereas the DO (dissolved oxygen) level ranged 1.0 to 1.2 mg/L was below the prescribed value. In Bangladesh, there is no permissible value of turbidity, TOC, TH, phosphate (PO_4^{3-}), bicarbonate (HCO_3^-), and magnesium ion (Mg^{2+}). However, the turbidity ranged from 270 to 276 mg/L, and TOC ranged from 106 to 110 mg/L in the effluent was very high. The temperature, pH, TDS, Cl⁻, SO₄²⁻, Na, Ca, Cu, Fe, Mn, Zn, Pb, Cd, and Cr values were within the permissible limit.

3.3 Physicochemical characterization of surface water

Tables 3 and 4 list the physicochemical parameters of the surface water near the places where paper mill effluents are discharged. The research showed that the average temperatures at sites S-1, S-2, and S-3 were 33.8, 29.5, and 27.0 °C, respectively, within the standard level of surface water of Bangladesh (BD-SW standard). The average values of pH at the sites S-1, S-2, and S-3 were 8.15, 7.53, and 7.30, respectively, within the prescribed level. The DO level varied from 1.3 to 4.5 mg/L, which was less than required level. Several reports illustrated that the surface water near the paper mill discharge point was highly polluted and dangerous for aquatic life [36, 37].

The lowest electrical conductivity (EC) value was 665 μ S/cm at S-3 in the monsoon of 2019, whereas the highest value was 2050 μ S/cm at S-1 in the pre-monsoon of (2020). It exceeded the permissible limit at most sites and seasons. According to Devi et al. [14], who made a similar observation, the presence of inorganic ions is indicated by a high EC value [13]. The range of turbidity was 44.0 to 270.0 NTU.

Though there is no surface water standard for turbidity in Bangladesh, the turbidity values in the three sampling sites showed much higher values, and the values decreased with the distance from the effluent discharge point. The results indicated that the paper mills discharge untreated effluent that might influence the turbidity of the surface water bodies in the areas (Table 3).



Figure 2 Functional water usage of canal and river around paper mill effluents discharge areas.



Figure 3 Impacts of paper mill effluents around the discharge areas.

The TSS (total suspended solids) ranged from 157.0 to 592.0 mg/L, above the acceptable level, as shown in Table 4. The values decreased with distance from the effluent discharge point indicating that the paper mill effluent might influence the TSS value of the surface water body in the area. Mishra et al. [36] reported a comparable outcome. High TSS value imports high COD and BOD₅. The TSS (Total suspended solids) may shift

the soil texture, porosity, soil fertility and water-holding capacity [37]. The TDS (total dissolved solids) varied from 394.0 to 1499.0 mg/L, which was within the permissible limit. The BOD₅ and COD varied from 134.0 to 278.0 mg/L and 177.0 to 843.0 mg/L respectively, and were higher than the permissible limits. Similar observations were reported by Giri et al. [17] and Devi et al. [14]. High BOD₅ and COD values indicate the presence of organic

and inorganic pollutants in high volumes [38].

The TOC and TH ranged from 50.6 to 105 mg/L, and 140 to 604 mg/L, respectively (Table 4). There is no surface water standard for TOC and TH in Bangladesh. However, the TOC and TH values decreased with the distance from the effluent discharge point indicating that the paper mill effluent might influence the TOC and TH levels of the surface water bodies in the area. Ahmed et al. [39] showed a maximum TOC of 46 mg/L in the surface water bodies in the Dhaka export processing zone (DEPZ) area [39]. Compared to that, the TOC level of the surface water bodies is very high in the effluent discharge area. The drinking water standard for TH is 200-500 mg/L [40], and the TH was found within the tolerance level. The phenolic compound varied from 0.925 to 2.946 mg/L, exceeded the permissible limit. Toczyłowska-Mamińska, (2017) reported a similar observation [41].

The chloride ion (Cl⁻) and sulfate ion (SO₄²⁻) ranged from 57.90 to 238.0 mg/L and 32.0 to 123.0 mg/L respectively (Table 4), were found within the standard level. At most of the sampling sites, The concentration of nitratenitrogen (NO₃⁻-N) varied from 8.80 to 28.90 mg/L, which higher than the prescribed limit. Chandra et al. [42] observed a similar observation. Due to the discharging of effluents in the surface water bodies the concentration of nitrate-nitrogen was at higher level [42]. The bicarbonate (HCO3⁻) and phosphate (PO4³⁻) varied from 20.89 to 99.52 mg/L, and 1.11 to 7.93 mg/L respectively. Due to the discharging of effluents in the surface water bodies, the PO43- concentration was found to be higher in the study area. The sodium ion (Na⁺) and potassium ion (K⁺) varied from 12.56 to 45.98 mg/L, and 13.67 to 78.94 mg/L respectively. The potassium ion concentration exceeded the limit whereas, the concentration of the sodium ion was within the prescribed limit. Kumar et al. [18] reported a similar result, that the concentration of magnesium ion (Mg²⁺) and calcium ion (Ca²⁺) ranged from 2.08 to 7.31, and 6.08 to 26.30, respectively. The concentration of calcium ion was within the prescribed

level. The utmost concentrations of heavy metals Fe, Cu, Zn, Mn, Pb, Cr, and Cd ions were 1.67, 0.853, 0.0593, 0.987, 0.0867, 0.0120, and 0.0189, respectively. Hence, heavy metal contamination was not found in the study.

3.4 Organic pollutants

Several organic functional groups were identified by the FTIR analysis of the effluent (Figure 4). Peak 3435 cm-1 in the range 3500-3200 cm-1 denoted H-bonded OH groups of alcohols and phenols. Peak 1640 cm-1 in the range 1650-1640 correspondents to C=C and C=O bonds. Peak 1542 indicated lignin compounds. Peak 1431 at the range 1460-1380 represented the O-H bond of phenolic compounds. Peak 619 at the range 850-550 denoted chloro-organic compounds presented in the paper mill effluent. Several reports showed a similar observation [19, 43-45]. These detected pollutants may have hepatotoxic, carcinogenic, and endocrine-disrupting effects.

Due to a high concentration of toxic organic pollutants in the paper mill effluent, it inhibits the germination of seeds and plant growth. Moreover, cytotoxic and genotoxic effects were reported by Yadav & Chandra [43].

Several reports showed the presence of organic pollutants i.e., chlorophenols, ethers, amines, lignins, carboxylic acids, dioxin derivatives, furan derivatives, etc. in paper mill effluents [43, 46-49]. Lignin compounds presented in paper mill wastewater can break down into phenolic compounds. Whereas, chlorine is used as a bleaching agent, continuously mixing with the wastewater. As a result, phenolic compounds and chlorine may yield chlorophenols in wastewater, which were reported as estrogenic and mutagenic compounds [12, 50-51]. Other reports showed that chlorophenols produce dioxins and furans, which are well-known toxic compounds and persistent (Figure 5) [48-49].

Organic pollutants presented in the paper mill effluent may induce pathogenic bacteria. The organic pollutants in the paper mill effluent, including recalcitrant chloro-organic compounds and the toxic heavy metals, are getting into the ecosystem and accumulating in the fatty tissues of the

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Table 2: Physicochemical 1	parameters of	paper mill	effluents.
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Parameters	Minimum	Maximum	Mean±SD	Permissible limit (ECR 1997)
Temperature	37	39	38.3±0.8	40
pH	8.4	8.6	8.5±0.07	6.0-9.0
DO	1	1.2	1.12±0.07	4.5-8.0
EC	2053	2070	2060±6	1200
Turbidity	270	276	273.5±2	-
TSS	592	600	595.5±3	150
TDS	1502	1513	1507±4	2100
BOD ₅	280	288	284.8±3.2	50
COD	843	850	846.2±2.6	200
TOC	106	110	108.3±1.6	-
TH	605	609	607±1.4	-
Phenols	2.95	3	2.97±0.02	1
Cl	240	245	242.8±2.1	600
SO4 ²⁻	125	127	126±0.89	400
NO ₃ - N	28.4	29	28.7±0.2	10
PO4 ³⁻	7.94	8	7.96±0.02	-
HCO ₃ -	99.55	105	100.9±2	-
Na ⁺	45.99	48.8	46.78±1.2	200
\mathbf{K}^+	78.95	81.4	79.75±0.98	12
Ca ²⁺	26.24	28.21	27.1±0.94	75
Mg^{2+}	7.33	7.89	7.49±0.21	-
Fe	1.67	1.77	1.72 ± 0.04	2
Cu	0.76	0.82	0.78±0.02	0.5
Zn	0.0594	0.065	0.06 ± 0.00	5
Mn	0.786	0.805	0.80 ± 0.00	5
Pb	0.0869	0.0885	0.087 ± 0.00	0.1
Cr	0.012	0.015	0.014 ± 0.00	0.5
Cd	0.019	0.0198	0.019 ± 0.00	0.05

(The temperature, EC and Turbidity are in ⁰C, µS/cm and NTU respectively and the others are in mg/L except the pH)

Table 3 Physical parameters of surface water body in paper mill effluents discharge areas.

	Period								
Parameter	Sample spot	Pre- mon. 2019	Mon. 2019	Post- mon. 2019	Pre- mon. 2020	Mon. 2020	Post- mon. 2020	Mean±SD	BD SW Standard (ECR 1997)
	S-1	35	37	30	35	36	30	33.8±3.06	
Tempe-	S-2	34	33	22	33	34	21	29.5±6.22	40
Tature	S-3	31	32	18	32	32	17	27±7.38	
	S-1	8.2	8	8.1	8.3	8.1	8.2	8.15±0.1	
pН	S-2	7.6	7.4	7.5	7.7	7.5	7.5	7.53±0.1	6.0-9.0
	S-3	7.4	7.2	7.3	7.4	7.2	7.3	7.3±0.09	
	S-1	1.4	1.7	1.6	1.3	1.6	1.5	1.52±0.15	
DO	S-2	1.3	2.1	1.9	1.3	2	1.7	1.72±0.35	4.5-8.0
	S-3	2	4.5	3.2	1.9	4.3	3	3.15±1.1	
	S-1	2043	1890	1944	2050	1898	1955	1963±69	
EC	S-2	1566	1267	1298	1570	1265	1303	1378±147	1200
	S-3	1208	665	1045	1208	789	1067	997±223	
	S-1	267	253	269	266	256	270	263±7	
Turbidity	S-2	170	172	198	177	173	209	183±16	-
	S-3	99	45	66	102	44	87	74±26	



Figure 4: FTIR spectra of pulp and paper mill effluents.

Journal of Chemistry and Environment **Table 4:** Physicochemical parameters, anions, cations and heavy metals of surface water body around paper mill effluents discharge areas.

				Mean±SD				
Parameter	Minimum	Maximum	S-1 S-2 S-3		S-3	standard (ECR 1997)		
TSS	157	592	579±14	310±51	180±16	150		
TDS	394	1499	1406±100	1071±258	589±154	2100		
BOD ₅	134	278	250±30	192±18	158±33	50		
COD	177	843	726±95	528±147	313±110	200		
TOC	50.6	105	100±2.8	77.6±8.3	57.3±7.6	-		
TH	140	604	536±61	290±71	162±19	-		
Phenols	0.925	2.946	2.2 ± 0.8	1.6±0.38	1.1±0.25	1		
Cl	57.9	238	207±26	135±58	90±23	600		
SO4 ²⁻	32	123	110±7.6	71±18	45±7	400		
NO ₃ - N	8.8	28.9	25.7±2.7	17±6	10.6±2.7	10		
PO4 ³⁻	1.11	7.93	7.2±0.77	2.95±0.57	2.38±0.89	-		
HCO ₃ -	20.89	99.52	95.7±3.8	53.1±18.8	36.4±7.9	-		
Na ⁺	12.56	45.98	37.7±5.5	24.7±4.2	17.9±3.8	200		
K^+	13.67	78.94	69.1±12.9	42.6±11.7	30.4±12.4	12		
Ca^{2+}	6.08	26.3	24.3±2.2	20.0±5.2	13.8±4	75		
Mg^{2+}	2.08	7.31	7±0.16	5.5±1.07	3.6±1.2	-		
Fe	0.425	1.67	1.5±0.11	0.94±0.15	0.62±0.18	2		
Cu	0.02	0.853	0.197 ± 0.28	0.199±0.32	0.039±0.01	0.5		
Zn	0.0126	0.0593	0.057 ± 0.00	0.039 ± 0.00	0.029 ± 0.01	5		
Mn	0.189	0.987	0.65 ± 0.09	0.42 ± 0.14	0.46±0.28	5		
Pb	0.0229	0.0867	0.074 ± 0.00	0.052 ± 0.00	0.032 ± 0.00	0.1		
Cr	0.0020	0.0120	0.009 ± 0.00	0.006 ± 0.00	0.004 ± 0.00	0.5		
Cd	0.0021	0.0189	0.014±0.00	0.006 ± 0.00	0.004 ± 0.00	0.05		

Table 6 The calculated terms of the CCME WQI for the surface water body in paper mill effluents discharge areas.

Sample	Scope, F ₁	Frequency,F ₂	\sum Excursion	NSE	Amplitude, F ₃	WQI	Ranking
location						score	
S-1	36.36	36.36	117.97	0.89	47.19	59.70	Marginal
S-2	36.36	36.36	68.07	0.52	34.02	64.39	Marginal
S-3	36.36	25.76	32.01	0.24	19.52	71.91	Fair

human body through the food chain.

3.5. Water Quality Index

At three sampling locations (i.e., S-1, S-2, S-3), the surface water quality was evaluated using the CCME (Canadian Council of Ministers of the Environment) water quality index (WQI). Some parameters (TOC, Turbidity, TH, Mg^{2+} , PO_4^{3-} and HCO_3^{-}) have no permissible limit for surface water quality. Hence, a total of 22 parameters (i.e., pH, temperature, EC, DO, TDS, TSS, COD, BOD₅, phenol, Cl⁻, NO₃⁻-N, SO₄²⁻, K, Na, Ca, Fe, Zn, Cu, Pb, Mn, Cd and Cr) were considered to evaluate the WQI score. The calculated terms of the index are mentioned in Table 5. In the present study, the CCME WQI scored 59.70, 64.39, and 71.91 at the three different locations S-1, S-2, and S-3, respectively (Table 5). The WQI ratings of 59.70 and 64.39 show that the surface water quality at sites S-1 and S-2 was only marginal, indicating that the area's water quality was in danger and frequently deviated from the natural or desirable levels found at both sites. Whereas the score of 71.91 represents that the ranking was fair at site S-3, which means the water quality was often preserved but occasionally threatened and deviated from ideal or expected values. [32].



Figure 5: Possible reactions to produce dioxins and furans in paper mill effluents.

From site S-1 to site S-2 to site S-3, the WQI ratings revealed a tendency in favor of improvement. This pattern shows that the surface water quality at the discharge site (S-1) was worsened by the discharge of paper mill effluent, and that the water quality gradually improved as discharge distance increased. Similar observations were made by Dinu et al. [52] and Al-Janabi et al. [53].

4. Conclusions

The survey results regarding the public perception of the crop, fish, livestock, and skin diseases showed negative impacts in the study area because of the discharging untreated paper mill effluent. It revealed that 82 percent of the respondents did not use the canal or the river water for domestic purposes due to the paper mill effluent discharge. The analytical results for both the effluents and the surface water samples showed the concentrations of TSS, EC, COD,

BOD₅, phenolic compounds, K⁺ and NO₃⁻-N higher than the permissible limits. Moreover, the DO levels were below the standard level. However, there was no evidence that the heavy metal concentrations exceeded the permissible standard limits. The FTIR analysis results showed the presence of several toxic pollutants, including lignin, phenol, and halo- compounds, in the effluent samples. The CCME water quality index revealed that the water quality of the nearby surface water bodies in the paper mill effluent discharge area was marginal from the discharge point to the middle of the canal (about 350 meters downstream) and fair at 700 meters downstream before falling into the river. Concerning the analysis results of the study, the surface water quality of the area was deteriorating and causing harm to the aquatic environment. Therefore, immediate measures should be taken to stop the discharge of untreated effluent from the paper mills to the surface water bodies, and thus help the restoration of the ecosystem.

The study carefully analyzed the findings extracted from the social survey and

experimental results and finally, made some recommendations that would be helpful

to reduce environmental degradation regarding paper mill effluents discharge.

The recommendations are as follows:

a) Advanced manufacturing technologies with less water used in the production processes should be installed in the paper manufacturing industry.

b) Modern and effective ETP comprises of combined treatment (i.e., coagulation, flocculation, adsorption, membrane filtration, advanced oxidation, and biological) facilities should be accommodated in paper mills.

c) Wastewater recycling systems or reusing effluent water from processing should be introduced to ensure sustainable water resource management.

d) Paper mills should not be set up on agricultural land. It should be established in industrial zones with advanced effluent treatment technology.

e) Proper monitoring should be ensured to maintain the surface water quality standards for effluent discharge.

Authors Contribution

M.S.Z.S., and M.G.M., have the main idea of the manuscript. MSZS wrote the the manuscript. M.G.M revised the manuscript and provide suggestions.

Conflicts of Interest

The authors declare that they have no conflict of interest.

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Data Availability statement

The data presented in this study are available on request from the corresponding author.

REFERENCES:

 Shakil, M.S.Z. and Mostafa, M.G., Paper Industries Concern Water Pollution: A Review. International Journal of Innovative Research and Review, 2021a. 9: p.19-31.

- Tareque, M.H., Islam, M.A. and Mostafa, M.G., Photocatalytic decomposition of textile dyeing effluents using TiO2, ZnO, and Fe2O3catalysts, Nep J Environ Sci, 2023. 10(2): p. 49-58.
- Rahim, M.A. and Mostafa, M.G., Impact of sugar mills effluent on environment around mills area. AIMS Environmental Science, 2021. 8(1): p. 86-99. http://dx.doi.org/10.3934/environsci.2021006
- Rafiqul, I. and Mostafa, M.G., Characterization of textile dyeing effluent and its treatment using polyaluminum chloride. Applied Water Science, 2020. 10: p. 119. https://doi.org/10.1007/s13201-020- 01204-4
- Vincent-Hubert, F., Heas-Moisan, K., 5. Munschy, С., Tronczynski, J., Mutagenicity and genotoxicity of suspended particulate matter in the Seine river estuary. Mutat Res, 2012. 741: 7-12. p. https://doi.org/10.1016/j.mrgentox.2011.09.019
- Baruah, B., Baruah, K.D., Das, M., Study on the effect of paper mill effluent on the water quality of receiving wet lands. Pollution Research, 1996. 15(4): p. 389–393.
- A., Gupta, B. S., Pollution 7. Dev. abatement in Indian the pulp and paper industry. Environmentalist, 1992. 12(2): 123-129. p. https://doi.org/10.1007/BF01266551
- Shakil, M.S.Z., Hasan, M.R. and Mostafa, M.G., Groundwater Exploitation and Its Environmental Consequences in Bangladesh: A Review. BAUET Journal, 2020. 2: p. 11-16.
- Ramana, K. Effluent Water for Agricultural Use. Proc. of 4th National Symposium on hydrology of minor water resources scheme, Madras, 1991. p. 298 - 302.
- Waghmare, S.M., Bhole, A.G., Dhabadgaonkar, S.M., Evaluation of wastewater treatment plant of pulp and paper mill. IAWPC. The. Annul, 1986. 13: p. 51-54.
- Subrahmanyam, P.V.R., Waste management in pulp and paper industry. Journal of Indian Association for Environmental Management, 1990. 17: p. 79–94.

- Singh, A.K., Chandra, R., Pollutants released from the pulp paper industry: Aquatic toxicity and their health hazards. Aquatic toxicology, 2019. 211: p. 202-216. https://doi.org/10.1016/j.aquatox.2019.04.007
- Shakil, M.S.Z. and Mostafa, M.G., Water Quality Assessment of Paper Mills Effluent Discharge Areas. Al-Nahrain Journal of Science, 2021b. 24(3): p. 63-72. https://doi.org/10.22401/ANJS.24.3.10
- Devi, N.L., Yadav, I.C., Shihua, Q.I., Singh, S., and Belagali, S.L. Physicochemical characteristics of paper industry effluents—a case study of South India Paper Mill (SIPM). Environmental monitoring and assessment, 2011. 177(1): p. 23-33. https://doi.org/10.1007/s10661-010-1614-1
- Kesalkar, V.P., Khedikar, I.P. and Sudame, A.M., Physico-chemical characteristics of wastewater from paper industry. Int. J. Eng. Res. Appl, 2012. 2(4): p. 137-143.
- [16] Ali, M. and Sreekrishnan, T.R., Aquatic toxicity from pulp and paper mill effluents: a review. Advances in environmental research, 2001. 5(2): p. 175-196. https://doi.org/10.1016/S1093-0191(00)00055-1
- Giri, J., Srivastava, A., Pachauri, S.P. and Srivastava, P.C., Effluents from paper and pulp industries and their impact on soil properties and chemical composition of plants in Uttarakhand, India. J Environ Waste Manag, 2014 1: p. 26-32. https://www.thedailystar.net/business/news/exportsprove-boon-paper-mills-1686010
- Kumar, A., Singhal, V., Joshi, B.D., and Rai, J.P.N., Impact of pulp and paper mill effluent on lysimetric soil and vegetation used for land treatment. Journal of Science and Industrial Research, 2003. 62: p. 883-891.
- Lacorte, S., Latorre, A., Barcelo, D., Rigol, A., Malmqvist, A., & Welander, T., Organic compounds in paper-mill process waters and effluents. TrAC Trends in Analytical Chemistry, 2003. 22(10): p. 725-737. https://doi.org/10.1016/S0165-9936(03)01009-4

- Izadi, A., Hosseini, M., Darzi, G.N., Bidhendi, G.N. and Shariati, F.P., Treatment of paper-recycling wastewater by electrocoagulation using aluminum and iron electrodes. Journal of Environmental Health Science and Engineering, 2018. 16(2): p. 257-264. https://doi.org/10.1007/s40201-018-0314-6
- Lindholm-Lehto, P.C., Knuutinen, J.S., Ahkola, H.S. and Herve, S.H., Refractory organic pollutants and toxicity in pulp and paper mill wastewaters. Environmental Science and Pollution Research, 2015. 22(9): p. 6473-6499. https://doi.org/10.1007/s11356-015-4163-x
- Kumar, V., Sharma, S. and Maheshwari, R.C., Removal of COD from paper mill effluent using low cost adsorbents. Indian Journal of Environmental Protection, 2000. 20: p. 91–95.
- Chowdhury, M., Mostafa, M.G., Tapan Kumar Biswas, and Ananda Kumar Saha, Treatment of leather industrial effluents by filtration and coagulation processes. Journal of Water Resource and Industry, 2013. 3: p. 11-22 (Elsevier Science). https://doi.org/10.1016/j.wri.2013.05.002
- Islam, M.S. and Mostafa, M.G., Development of an integrated irrigation water quality index (IIWQIndex) model. J of water supply, 2021a. 22(2): p. 2322- 2337; https://doi.org/10.2166/ws.2021.378
- Ball, R.O. and Church, R.L., "Water Quality Indexing and Scoring". J. of Environmental Engineering, ASCE, 1980. 106(4): p. 757–771. https://doi.org/10.1061/JEEGAV.0001067
- Khan, H., Khan, A.A., Hall, S., "The Canadian water quality index: a tool for water resources management". In Proceedings: MTERM International Conference, 2005. p. 6–10 June 2005, AIT, Thailand.
- Couillard, D. and Lefebvre, Y., "Analysis of water quality indices". J. of Environmental Management, 1985. 21: p. 161–179.
- 28. Islam, M.S. and Mostafa, M.G., Comparison of classical and developed indexing methods for assessing the

groundwater suitability for irrigation, J of Sustainable Agriculture and Environment, 2022a. 1(2). DOI: 10.1002/sae2.12027

- Islam, M.S. and Mostafa, M.G., Comparison of classical and developed indexing methods for assessing the groundwater suitability for irrigation, J of Sustainable Agriculture and Environment, 2022b. 1(2) (Wiley). DOI: 10.1002/sae2.12027
- Terrado, M., Borrell, E., Compos, S., Surface-waterquality indices for the analysis of data generated by automated sampling networks. Trends Anal. Chem, 2010. 29 (1): p. 40-52. https://doi.org/10.1016/j.trac.2009.10.001
- Selvam, S., Manimaran, G., Sivasubramanian, P., GISbased evaluation of water quality index of groundwater resources around Tuticorin Coastal City. South India. Environ. Earth Sci, 2014. 71 (6): p. ... 2847 -2867. https://doi.org/10.1007/s12665-013-2662y
- CCME, 2001 Canadian water quality guidelines for the protection of aquatic life: Canadian Water Quality Index 1.0 Technical Report. In Canadian environmental quality guidelines. 1999. Winnipeg.
- APHA, Standard methods for the examination of the water and waste water, 21st edn. APHA (American Public Health Association), AWWA, WPCF, Washington, DC, 2005. 1134.
- Rafique, I. and Mostafa, M.G., Adsorption kinetics, isotherms and thermodynamic studies of methyl blue in textile dye effluent on natural clay adsorbent. Sustainable Water Resources Management, 2022. 8:52 (Springer). https://doi.org/10.1007/s40899-022-00640-1
- Islam, M.S., and M. G. Mostafa, Influence of chemical fertilizers on arsenic mobilization in the alluvial Bengal delta plain: a critical review. Journal of Water Supply: Research and Technology-Aqua, 2021b. 70(7), p. 948 (IWA Pub.).

https://doi.org/10.2166/aqua.2021.043

- Mishra, S., Mohanty, M., Pradhan, C., Patra, H.K., Das, R. and Sahoo, S., Physico-chemical assessment of paper mill effluent and its heavy metal remediation using aquatic macrophytes—a case study at JK Paper mill, Rayagada, India. Environmental monitoring and assessment, 2013. 185(5): p. 4347- 4359. https://doi.org/10.1007/s10661-012-2873-9
- Chowdhury, M., Mostafa, M.G., Biswas, T.K., Mandal, A. and Saha, A.K., Characterization of the effluents from leather processing industries. Environmental Processes, 2015. 2(1): p. 173-187. https://doi.org/10.1007/s40710-015-0065-7
- Pandey, S., Parvez, S., Sayeed, I., Haque, R., Hafeez, B.B., Raisuddin, S., Biomarkers of oxidative stress: A comparative study of river Yamuna fish Wallago Attu (Bl. & Schn.). Science of the Total Environment, 2003. 309: 105–115. https://doi.org/10.1016/S0048-9697(03)00006-8
- 39. Ahmed, G., Miah, M.A., Anawar, H.M., Chowdhury, D.A. and Ahmad, J.U., Influence of multi-industrial activities on trace metal contamination: an approach towards surface water body in the vicinity of Dhaka Export Processing Zone (DEPZ). Environmental monitoring and assessment, 2012. 184(7): p. ..4181-4190. https://doi.org/10.1007/s10661-011-2254-9
- ECR, Environmental Conservation Rules. Department of Environment. Ministry of Environment and Forest. People's Republic of Bangladesh, 1997.
- Toczyłowska-Mamińska, R., Limits and perspectives of pulp and paper industry wastewater treatment–A review. Renewable and Sustainable Energy Reviews, 2017. 78: p. 764-772. https://doi.org/10.1016/j.rser.2017.05.021
- Chandra, R., Sharma, P., Yadav, S. and Tripathi, S., Biodegradation of Endocrine-Disrupting Chemicals and Residual Organic Pollutants of Pulp and Paper Mill Effluent by Biostimulation. Front. Microbiol, 2018. 9: p. 960. https://doi.org/10.3389/fmicb.2018.00960

- Yadav, S., Chandra, R., Detection and assessment of the phytotoxicity of residual organic pollutants in sediment contaminated with pulp and paper mill effluent. Environmental monitoring and assessment, 2018. 190(10), p. 1-15. https://doi.org/10.1007/s10661-018-6947-1
- Mathiyarasi, K., Maheswar, M., Balasubramaniam, P., Sebastian, S.P., Characterization of organic compounds in soil irrigated with treated paper board mill effluent using FTIR. The Pharma Innovation Journal. 2020. 9(10): p. 14-17
- Jackson, M.J., and Line, M.A. Organic composition of a pulp and paper mill sludge determined by FTIR, 13C CP MAS NMR, and chemical extraction techniques. Journal of Agricultural and Food Chemistry, 1997. 45(6), p. 2354-2358. https://doi.org/10.1021/jf9609461
- Rigol, A., Latorre, A., Lacorte, S., & Barceló, D., Determination of toxic

compounds in paper-recycling process waters by gas chromatography-mass

spectrometry and liquid chromatography-mass spectrometry. Journal of

Chromatography A, 2002. 963(1-2): p. 265-275.

- 47. Terasaki, M., Fukazawa, H., Tani, Y., & Makino, M., Organic pollutants in paper-recycling process water discharge areas: First detection and emission in aquatic environment. Environmental Pollution, 2008. 151(1): p. 53-59.
- Criado, M.R., Da Torre, S.P., Pereiro, I.R., Torrijos, R.C., Optimization of a microwave-assisted derivatization–extraction procedure for the determination of chlorophenols in ash samples. Journal of Chromatography A 2004. 1024(1-2), p. 155-163. https://doi.org/10.1016/j.chroma.2003.10.068
- Vallejo, M., San Román, M.F., Ortiz, I., Irabien, A., Overview of the PCDD/Fs degradation potential and formation risk in the application of advanced oxidation processes (AOPs) to wastewater treatment.

Chemosphere, 2015. 118, p. 44-56. https://doi.org/10.1016/j.chemosphere.2014.05.077

- 50. Knuutinen, J., Synthesis, Structure Verification and Gas Chromatographic Determination of Chlorinated Catechols and Guaiacols Occurring in Spent Bleach Liquors of Kraft Pulp Mills. Dissertation. University of Jyväskylä, 1984.
- Michalowicz, J., Duda, W., Phenols-sources and toxicity. Pol. J. Environ. Stud, 2007. 16: p. 347–362.
- 52. Dinu, C., Scutariu, R.E., Vasile, G., Tenea, A.G., Petre, J., Cruceru, L., Evaluation of wastewater quality using water quality index. Romanian Journal of Ecology & Environmental Chemistry. 2020. 2 (2): p. 99-108.
- 53. Al-Janabi, Z.Z., Al-Obaidy, A.H.M.J., Al-Kubaisi, A.R., Applied of CCME Water Quality Index for Protection of Aquatic Life in the Tigris River within Baghdad city. Al-Nahrain Journal of Science, 2015. 18(2): p. 99-107. http://5.10.230.12/index.php/anjs/article/view/335/278

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