



**SURFACE MODIFICATION OF BIOWASTE-
DERIVED ACTIVATED CARBON FOR REMOVAL OF
WATER POLLUTANTS.**

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

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DEDICATIONS

I humbly dedicate this Ph.D thesis to my beloved family, whose enduring love and steadfast support have been the cornerstone of my academic journey.

To my late parents, **Apo and Azu**, who longed to see the completion of my Ph.D. but left this world before its fulfillment. Their hopes and dreams for my future continue to guide me, and their sacrifices, values, and unwavering faith remain a constant source of strength and inspiration. Though their absence is deeply felt, their presence endures in my heart and in every step I take.

To my three beloved brothers — **Ato, Ajoy and Aneyi** — and my four cherished sisters — **Ane Khosa, Ane Sasülü, Aba and Atalü** — whose selfless encouragement, boundless patience, and unwavering help have been my pillar of strength. Through every trial and moment of doubt, your love and support have lifted me, guiding me toward the fulfillment of this dream. I am eternally grateful for your unshakable belief in me and for standing beside me every step of the way.

This work stands as a testament to your collective love, sacrifices and encouragement. I dedicate this accomplishment to you all with the deepest respect and gratitude.



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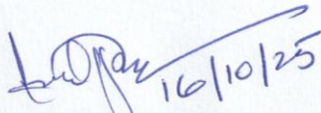
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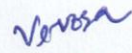
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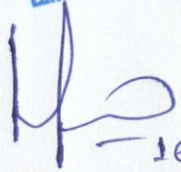
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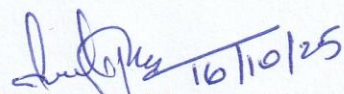
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I am highly impressed by his dedication and sincere efforts in completing the thesis and wish him great success in all his future endeavours.


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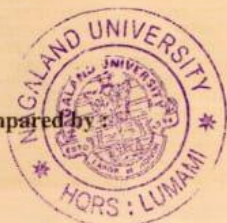
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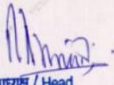
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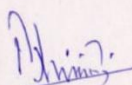
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CONTENTS

<i>List of figures</i>	i-iii
<i>List of tables</i>	iv-v
CHAPTER 1: Introduction	Page No.
1.1. Introduction	1
1.2. History of using activated carbon	1-3
1.3. Types of activated carbon	3
1.4. Functional groups present in activated carbon	4-5
1.5. Synthesis of activated carbon	5-6
1.6. Preparation of charcoal	6
1.7. Activation of carbon	6
1.7.1. Physical Activation	6
1.7.2. Chemical Activation	6
1.8. Post activation modification	7
1.8.1. Chemical functionalization	7
1.8.2. Biological Modification	7-8
1.8.3. Magnetization of AC	8
1.8.4. Doping with nanomaterials	8
1.9. Classification of activated carbon	8
1.9.1. Powdered AC (PAC):	8
1.9.2. Granulated AC (GAC):	8-9
1.9.3. Extruded AC:	9
1.10. Application of activated carbon	9-10
1.11. Adsorption phenomena	10
1.12. Classification of adsorption phenomena	10
1.12.1. Based on the nature of interaction	10-11
1.12.2. Based on the phases involved	11
1.12.3. Based on adsorption kinetics	11
1.12.4. Based on adsorption mechanism	11
1.13. Adsorption studies	12-13
1.14. Adsorption isotherms	13
1.14.1. Langmuir	13-14
1.14.2. Freundlich	14-15

	1.14.3. Temkin	15-16
1.15	Adsorption kinetics modelling	16
	1.15.1. Pseudo-first order kinetic model	16-17
	1.15.2. Pseudo-second order kinetic model	17-18
	1.15.3. Weber and Morris intraparticle diffusion model	18
	1.15.4. Elovich model	19
1.16	Fitness of the kinetic models	19
	1.16.1. Chi-square analysis	20
	1.16.2. Coefficient of determination (R^2)	20
	1.16.3 Sum of squared errors (SSE)	20-21
1.17	Thermodynamic studies:	21
1.18	Density Functional Theory (DFT)	21-22
1.19	Importance of the study:	23
	Aim and objectives of the work:	24
	Overall view of research thesis structure	25
	References	26-50

CHAPTER 2: Review of Literature

2.1	Introduction	51-52
2.2	Animal biomass and target pollutants	53
2.3	Biosorbent preparation methodology	53
2.4	Morphology of AC derived from Animal biomass.	54-58
2.5	Appraisal of recent literature	58-61
2.6	Adsorption Mechanisms	61-62
2.7	Factors affecting adsorption capacity	62-63
	2.7.1. Chemical properties of pollutants	63
	2.7.2. Ionic strength	63-64
	2.7.3. Adsorbent size	64
	2.7.4. Adsorbent dosage	64-65
	2.7.5. Initial concentration	65
	2.7.6. Contact time	65-66
	2.7.7. pH level	66
	2.7.8. Co-existing ions	66-67

	2.7.9. Temperature	67
2.8	Adsorption as a process	67-68
2.9	Equilibrium isotherm and kinetics modeling	69-70
2.10	Thermodynamic studies	71-72
2.11	Future prospect	72-73
	Conclusion	74
	References	75-91

CHAPTER 3: Synthesis and Characterization of Activated Carbon

3.1	Introduction	92-93
3.2	Assortment of raw materials for the synthesis of activated carbon	93
3.3	Preparation of activated carbons	93-94
3.4	Physico-chemical characterization of activated carbon	94-95
	3.4.1. Proximate analysis	95
	3.4.1.1. Moisture content	95
	3.4.1.2. Ash content	95
	3.4.1.3. Volatile matter	96
	3.4.1.4. Fixed carbon	96
	3.4.1.5. Acid soluble matter	96
	3.4.1.6. Water soluble matter	97
3.4.2	Apparent density, bulk density and porosity	97-98
3.4.3	Iodine number	98
3.4.4	pH and Conductivity	98-99
3.4.5	Zero-point charge (pH _{zpc})	99
3.5	Analytical instrument employed for characterization	99
	3.5.1. Scanning electron microscopy (SEM)	99
	3.5.2. Energy-Dispersive X-Ray (EDX) study	99-100
	3.5.3. Fourier Transform Infrared Spectroscopy (FT-IR) study	100
	3.5.4. Powder X-ray Diffraction (PXRD) study	100
	3.5.5. Pore volume and surface area (BET method)	100-101
	3.5.6. Thermo Gravimetric analysis (TGA) study	101
3.6	Result and Discussion	102
	3.6.1. Optimization of Pyrolysis Temperature	102

3.6.2. Moisture content	102
3.6.3. Volatile matter	102-103
3.6.4. Acid soluble	103
3.6.5. Water soluble	103
3.6.6. Ash content	104
3.6.7. Fixed carbon	104
3.6.8. Apparent density	104-105
3.6.9. Iodine number	105
3.6.10. pH and conductivity	106
3.6.11. Comparison of physiochemical properties with other AC.	106-107
3.6.12. Zero-point charge	107-108
3.6.13. Scanning electron microscopy (SEM)	109-110
3.6.14. Energy-Dispersive X-ray Spectroscopy (EDX)	110-111
3.6.15. Fourier Transform Infrared Spectroscopy (FT-IR)	111-112
3.6.16. X-ray diffraction (XRD)	112-113
3.6.17. Thermogravimetric analysis (TGA).	113
Conclusion	114
References	115-119

CHAPTER 4: Removal of Congo Red dye from aqueous solution

4.1	Introduction	120-121
4.2	Materials and Methods	121
	4.2.1. Adsorbent preparation	122
	4.2.2. Adsorbate preparation	122
	4.2.3. Adsorption Experiments	122-123
4.3	Results and discussion	123
	4.3.1. Scanning electron microscopy	123
	4.3.2. Batch Adsorption Studies	124-125
	4.3.3. Effect of Initial Concentration and Contact Time	125
	4.3.4. Effect of adsorbent dosage	125
	4.3.5. Effect of pH	126
4.4	Adsorption isotherms studies	126-127
4.5	Adsorption Kinetic studies	128-129

4.5.1.	The pseudo-first-order kinetic model	129
4.5.2.	The pseudo-second order kinetic model	129
4.5.3.	Elovich model	129
4.5.4.	Weber and Morris intraparticle diffusion model	130
4.6	Thermodynamic studies	131-132
4.7	Comparative studies	132-133
4.8	Regeneration of adsorbent	133
	Conclusion	134
	References	135-144

CHAPTER 5: Removal of 17 β - Estradiol from aqueous solution

5.1	Introduction	145-146
5.2	Experiments	146
5.2.1.	Materials and methods	146
5.2.2.	Mixed fish scale (MFS) activated carbon production	147
5.2.3.	Adsorption studies	147
5.2.4.	Isotherm studies	147
5.2.5.	Kinetic studies	148
5.2.6.	Analytical statistics	148
5.2.7.	Thermodynamic studies	148
5.3	Computational studies	148-149
5.4	Results and discussion	149
5.4.1.	Batch adsorption studies	149
5.4.2.	Effect of adsorbent dose	150
5.4.3.	Effect of concentration and reaction time	150
5.4.4.	Effect of pH	150
5.4.5.	Effect of temperature	151
5.4.6.	Adsorption isotherm studies	152-153
5.4.7.	Adsorption kinetics studies	154-155
5.4.8.	Thermodynamic studies	155
5.4.9.	Theoretical calculations	155-156
5.4.10.	Adsorption on pristine and functionalized AC	157-158
5.5	Regeneration studies	158-159

5.6	Comparative studies	159-160
	Conclusion	161
	References	162-168

CHAPTER 6: Surface modification of activated carbon through bacterial adsorption and its effect on Cadmium removal from aqueous solution.

6.1	Introduction	169-171
6.2	Materials and methods	171
	6.2.1. Preparation of carbon	171
	6.2.2. Culturing of bacteria	171
	6.2.3. Column construction and removal efficacy of bacteria	172
	6.2.4. Formation of Cd-dithizone colour complex	173
	6.2.5. Effect of pH on formation of Cd-dithizone colour complex	173-174
	6.2.6. Batch adsorption study	174
	6.2.7. Adsorption isotherm models	174
	6.2.8. Adsorption kinetic models	175
	6.2.9. Statistical analysis	175
	6.2.10. Thermodynamic studies	175
6.3	Results and discussion	175
	6.3.1. Adsorption of bacteria through column method	175-176
	6.3.2. Batch adsorption study	176-177
	6.3.3. Fourier transform infrared spectra	177-178
	6.3.4. Adsorption isotherm studies	178-180
	6.3.5. Adsorption kinetic studies	180-182
	6.3.6. Thermodynamic studies	182
	6.3.7. Comparison of Cadmium adsorption using FSAC-M and FSAC	183
	6.3.8. Comparison of adsorption performance using microbes-supported adsorbents	183-184
	6.3.9. Performance Comparison of mFS-AC/M with other activated carbon for Cadmium removal.	184-185
6.4	Future scope	185-186

Conclusion	186
References	187-197
CHAPTER 7: Summary and Conclusion	198-202

Abstract

This research focuses on the synthesis, characterization, and application of activated carbon (AC) derived from waste fish scales for the adsorption of diverse water pollutants. Fish scales were pyrolyzed at controlled temperatures and chemically activated with potassium hydroxide to produce high-surface-area AC. The prepared AC was extensively characterized using physicochemical and surface analytical techniques to assess its structural, morphological, and functional properties. Its adsorption performance was evaluated for multiple classes of contaminants, including Congo red dye, the endocrine-disrupting hormone 17 β -estradiol, and heavy metals such as cadmium. A novel bio-modification strategy was employed by pre-adsorbing *Staphylococcus aureus* onto AC, yielding a bio-modified adsorbent with enhanced heavy metal removal efficiency due to synergistic interactions between microbial surface functionalities and the porous AC structure. Adsorption kinetics, isotherm, and thermodynamic studies were performed to elucidate the underlying mechanisms. Furthermore, Density Functional Theory (DFT) calculations were carried out to investigate the molecular-level interactions between 17 β -estradiol and the AC surface, providing theoretical support for the experimental observations. The findings highlight the potential of waste fish scale-derived AC, both in its raw and bio-modified forms, as a sustainable and versatile adsorbent for the remediation of a wide range of water pollutants.

As a result, the following chapters present the work completed as a part of this study.

Chapter 1	Introduction. This chapter introduces activated carbon, detailing its history, classification, structural features, and functional groups that influence adsorption. Sustainable production from renewable resources, particularly waste fish scales, is highlighted as an eco-friendly alternative to conventional sources. Adsorption mechanisms, key influencing factors, and the application of isotherm, kinetic, and thermodynamic models are discussed to explain pollutant removal processes. The role of Density Functional Theory (DFT) in supporting experimental studies is also outlined. The chapter concludes by presenting the research objectives, focused on preparing fish scale–based activated carbon for the adsorption of dyes, hormones, bacteria, and heavy metals.
Chapter 2	Review of Literature. This chapter reviews activated carbon (AC) derived from animal biowastes for wastewater treatment. It covers raw materials, preparation methods, structural properties, and adsorption mechanisms. Heavy metals are the most studied pollutants, with Langmuir/Freundlich isotherms and pseudo-second-order kinetics widely reported. Few thermodynamic studies exist, indicating research gaps. Overall, animal biowaste-based AC is highlighted as a sustainable, low-cost, and effective alternative to conventional adsorbents with strong potential for large-scale applications.
Chapter 3	Synthesis and Characterization of Activated Carbons. This chapter outlines the synthesis of activated carbon from mixed fish scales using carbonization and KOH activation. Characterization through physicochemical tests, BET, FTIR, SEM-EDX, XRD, and TGA confirmed high porosity, functional groups, residual minerals, and strong thermal stability. The 1:2 carbon–KOH ratio produced the most favorable surface area and adsorption properties. The results demonstrate the successful preparation of sustainable, fish scale–derived activated carbon with strong potential for pollutant removal.
Chapter 4	Efficient Removal of Congo Red Dye Using Activated Carbon Derived from Mixed Fish Scales Waste: Isotherm, Kinetics and Thermodynamics Studies.

	This chapter investigates the adsorption of Congo red dye onto fish scale-derived activated carbon synthesized by KOH activation. Characterization confirmed a surface area of 150.049 m²/g and pore volume of 0.119 cm³/g. Adsorption followed the Freundlich isotherm with 99.04% removal and 19.58 mg/g capacity. Kinetics fit the pseudo-second-order model, while thermodynamics indicated spontaneous and exothermic behavior. The adsorbent demonstrated good reusability over six cycles, confirming its potential for dye removal.
Chapter 5	Adsorption of 17 β-Estradiol from aqueous solution using waste fish scales activated carbon: Experimental and computational analysis. This chapter evaluates the adsorption of 17β-estradiol (E2) from wastewater using mixed fish scales activated carbon (mFSAC). Under optimized conditions, 98.35% removal was achieved. Adsorption followed the Langmuir isotherm and pseudo-second-order kinetics, indicating monolayer chemisorption. Thermodynamics revealed a spontaneous, endothermic process. Density functional theory (DFT) confirmed strong affinity, with carboxyl groups playing a key role. The adsorbent exhibited good reusability over five cycles, highlighting its potential for sustainable hormone removal.
Chapter 6	Surface modification of activated carbon through bacterial adsorption and its effect on Cadmium removal from aqueous solution. This chapter examines the adsorption of <i>Staphylococcus aureus</i>, <i>Klebsiella pneumoniae</i> and cadmium using microbial-modified activated carbon (FSAC-M) compared to unmodified FSAC. FSAC-M showed superior adsorption of both microbes and cadmium due to additional binding sites introduced by microbial modification. Adsorption followed the Langmuir isotherm and pseudo-second-order kinetics, while thermodynamic analysis indicated an endothermic process governed primarily by physisorption. Maximum cadmium adsorption capacities were 6.51 mg/g for FSAC-M and 5.43 mg/g for FSAC. Overall, microbial modification enhanced activated carbon performance, offering an effective strategy for removing microbial and heavy metal contaminants from water.

Chapter 7	Conclusion This chapter summarizes the previous chapters and outlines the future scope of the research. The study highlights mFSAC's versatility in removing dyes, hormones, microbes and heavy metals, with regeneration studies confirming its reusability, making fish scale-derived activated carbon an eco-friendly and efficient adsorbent for sustainable wastewater treatment.
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CHAPTER 1

INTRODUCTION

This chapter introduces activated carbon, covering its history, classification, structure, and properties. It also describes the raw materials, activation methods, and modification techniques used in its preparation. In addition, the adsorption process is explained through different isotherm and kinetic models, along with the applications of activated carbon.

1.1 Introduction

Activated carbon (AC) is used as an adsorbent material because of its remarkable porosity, large surface area, and excellent ability to capture a wide range of substances. These unique features make it indispensable in applications such as water and wastewater purification, gas separation, air filtration, food processing, pharmaceuticals, and environmental cleanup [1]. Its efficiency comes mainly from the intricate network of pores that provides numerous adsorption sites, as well as from the surface functional groups that allow strong interactions with different types of pollutants [2].

Composition-wise, AC is made up largely of carbon (about 87–97%), with smaller amounts of oxygen, hydrogen, nitrogen, and minerals [3]. However, its exact chemical makeup and surface properties can vary depending on the raw material chosen and the activation process whether physical or chemical [4].

What makes AC especially valuable is its versatility [5]. It has been successfully employed to remove dyes, heavy metals, pesticides, pharmaceuticals, endocrine-disrupting compounds, volatile organic compounds, and even harmful microbes. Because it can effectively target both organic and inorganic contaminants, AC has become an important tool for tackling pollution challenges, particularly those linked to industrial discharges and urban wastewater [6].

In recent years, researchers have increasingly focused on producing AC from inexpensive, renewable, and eco-friendly sources [7]. Agricultural residues, forestry by-products, and even animal-derived biowaste have shown great potential as sustainable precursors. Using such materials not only lowers production costs but also turns waste into something useful [8].

1.2 History of using AC

The earliest recorded use of carbon for purification dates back to ancient Egypt around 1500 BCE, where charcoal was utilized for medicinal purposes and as a preservative in embalming processes [9,10]. Egyptian manuscripts mention the use of charcoal to treat wounds and purify water, highlighting its early recognition as a decontaminant. Around the same period, the Phoenicians stored drinking water in charred barrels to maintain its quality during long sea voyages [1]. During the Roman Empire, around 200 BCE, the Romans used crude carbon filtration techniques to improve the taste and safety of their drinking water, demonstrating an understanding of its absorptive properties. Similarly, in

ancient India and China, texts from the Ayurveda and traditional Chinese medicine also reference the use of burnt plant materials and charcoal for detoxification and medicinal treatments [11].

With the rise of chemical industries, researchers began exploring carbon's ability to remove impurities from liquids and gases, properties of charcoal was conducted by Carl Wilhelm Scheele in the late 18th century [12]. His experiments demonstrated that charcoal could absorb various gases, laying the foundation for future research [13].

In the early 19th century, scientists such as Michel Bertrand and Henry Stenhouse made critical contributions to the field. Bertrand (1815) discovered that charcoal could remove toxins from the digestive system, leading to its use as an antidote for poisoning. In 1854, Stenhouse developed the first practical application of activated carbon in gas masks, which played a crucial role in removing harmful vapors [1]. Additionally, the sugar refining industry began incorporating AC for decolorization, setting the stage for its widespread use in food processing.

The 20th century witnessed significant advancements in AC production. In 1901, Ostrejko, a German chemist, patented a process for producing highly porous activated carbon through steam activation, revolutionizing its commercial production [9]. This method enabled the large-scale manufacture of AC with superior adsorption capacity.

During World War I, AC played a vital role in military applications, particularly in gas masks used to protect soldiers from chemical warfare agents such as chlorine and phosgene. This period also saw the expansion of AC in sugar refining, water treatment, and pharmaceutical applications. Following World War II, further improvements in activation techniques led to the development of highly efficient carbon adsorbents.

The chemical activation method, which involves treating carbonaceous materials with phosphoric acid or zinc chloride, was introduced, allowing greater control over pore structure and surface area [13]. This innovation contributed to the rapid growth of industrial applications, including solvent recovery, gas purification, and precious metal recovery. Researchers have focused on optimizing pore structure, surface chemistry, and functionalization to enhance adsorption performance. Innovations in nanotechnology have led to the development of carbon-based nanomaterials with superior adsorption

properties, including carbon nanotubes and graphene oxide composites [14–17]. In the medical field, it is utilized for treating poisoning and drug overdoses [18,19]. It also plays a significant role in energy storage, particularly in supercapacitors and fuel cells [20,21]. In environmental remediation, AC is employed to adsorb contaminants from wastewater and industrial effluents [22–24]. The food and beverage industry benefits from its use in decolorization and purification processes for edible oils, sugar, and alcoholic beverages [25–27]. Additionally, in catalysis and chemical processing, it serves as a catalyst support in chemical synthesis and gas separation [28,29].

1.3 Different types of AC

AC has a well-developed porous structure, classified as:

- i. **Micropores**- comprise the bulk of activated carbon's surface area and are principally in charge of adsorbing tiny molecules including organic contaminants and gases [9,30].
- ii. **Mesopores**- offer transitional areas that promote the migration of bigger molecules. They are crucial for liquid-phase adsorption processes [1,31].
- iii. **Macropores**- act as transport channels, enabling molecules to enter the mesopores and inner micropores. They are essential for promoting molecular diffusion and improving the adsorption process kinetics, especially for big molecules [13,32].

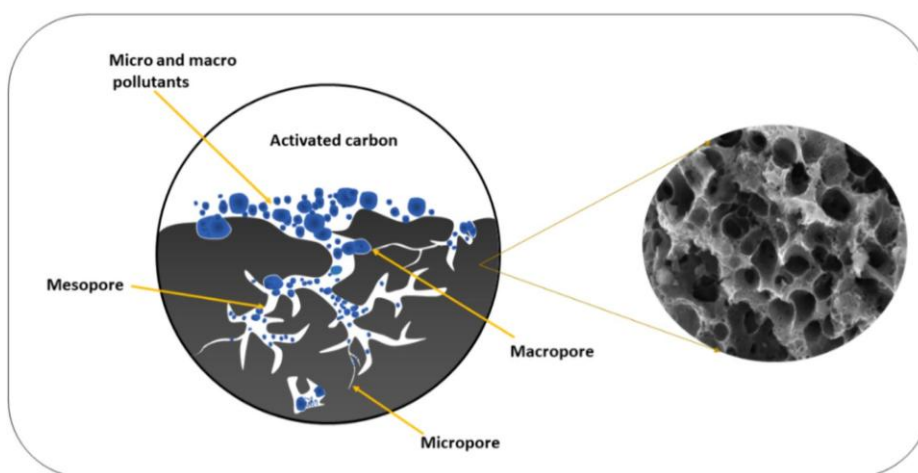


Fig.1.1 AC displaying well-developed pores

1.4 Functional groups present in activated carbon

AC contains a variety of surface functional groups like oxygen, nitrogen, sulfur, and hydrogen-based species, which are introduced during activation, oxidation, or chemical modification processes. Among these, carboxyl (-COOH), lactone (-COO-), phenol (-OH), carbonyl (-C=O), and quinone structures plays pivotal role in adsorption. These groups aid surface polarity, acidity, and reactivity, enhancing the adsorption of metal ions and organic pollutants [13,33].

In addition to oxygen functionalities, nitrogen-containing groups such as amine (-NH₂), pyridine-like (-N-), and pyrrole (-NH-) can be introduced through nitrogen doping or carbonization of nitrogen-rich precursors. These groups modify the basicity and catalytic behavior of activated carbon, making it effective for specific adsorption and electron transfer reactions [34]. Similarly, sulfur-containing functional groups, including sulfonic (-SO₃H) and thiol (-SH), enhance the material's selectivity for heavy metal adsorption and catalytic applications. These groups are particularly useful in environmental remediation and industrial catalysis due to their strong affinity for toxic metals like mercury and cadmium [35].

Additionally, AC surfaces may contain ether (-C-O-C-) and hydroxyl (-OH) groups, which influence wettability and adsorption selectivity [9,36]. Understanding the nature and distribution of these surface functional groups is essential for optimizing AC for specific industrial and environmental applications.

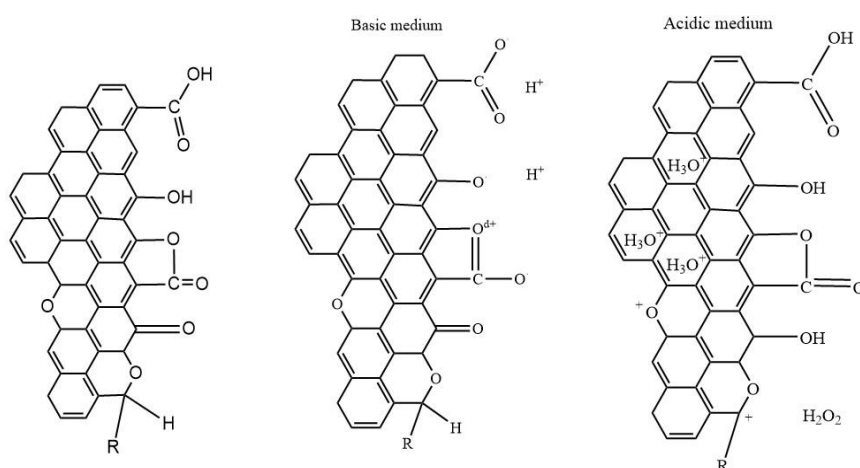


Fig.1.2 Schematic representation of the acidic and basic behaviour of the oxygen containing surface groups and delocalized π -electrons of the basal plane [37].

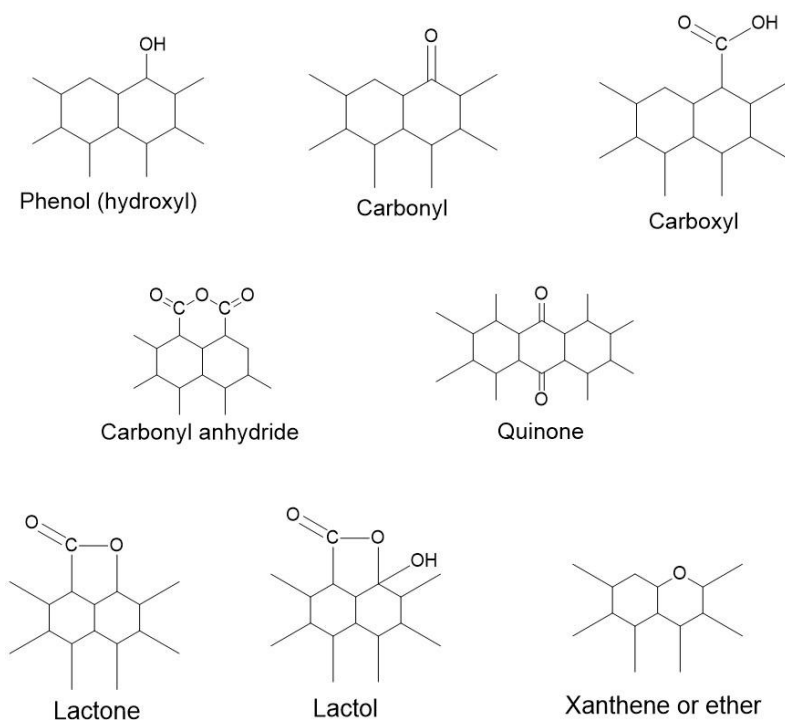


Fig.1.3 Common oxygen surface functional groups present on the surface of carbon 3-electrons of the basal plane materials [38].

1.5 Synthesis of AC

Most of the commercial AC are derived from either coal [39] or petroleum pitch [40], both of which are finite resources susceptible to depletion. Therefore, as natural renewable resources, biomaterials present a promising alternative for carbon material production instead of relying on fossil fuels.

AC plant sources like rice husk [41,42], rice straw[43], coconut shell [44], bamboo, agricultural residues and natural biomaterial [45], Oil-palm stone [46], bagasse [47], olive stone [48], *Manihot esculenta* [49], Marine macro-algal biomass [50], palm shell [51], gelam wood bark (Abdullah et. al., 2001), sugarcane and vetiver roots [53], *Eucalyptus camaldulensis* Dehn bark [54], Corn Cob [55], Neem husk [56], waste litchi shell [57], *Delonix regia* Fruit Pod and Banana Bunch [58], Biomass of *Jacaranda mimosifolia* and *Prunus domestica* [59], pine wood [60], casuarina [61,62], corn cob [63], corn stalks [64], guava seeds[65], kenaf core fiber[66], jatropha seed coat[67], mango leaves[68], oat hulls[69], orange peel[70], pea nut hulls[71], pine cone [72], saw dust[73], walnut shell[74] have also utilized these for the production of AC materials.

Animal biomass has been shown to be widely available for water treatment applications at no cost or at a minimal cost [75]. Few reports have been made on activated carbon derived from animal biomass such as eggshell [40–72], feathers [109–114], animal bones [75,115–155] animal hooves and horns [156–164] dung/manure, waste snail shells [165], hair [166–176].

1.6 Preparation of charcoal

Carbonization occurs at 400–800 °C, where volatile components are removed, strengthening the material and forming an initial porous structure. Higher carbonization temperatures enhance material strength but reduce pore volume due to increased condensation. To achieve optimal properties, balancing temperature, time, and atmospheric conditions is crucial for producing activated carbon with desired porosity and adsorption capacity.

1.7 Activation of carbon

Activation of carbon is a crucial process that enhances the porosity and surface area of carbon materials, making them highly effective for adsorption applications. The activation process increases the number of micropores and mesopores, which provide more binding sites for adsorbates. The activation of carbon can be carried out through physical activation and chemical activation.

1.7.1 Physical Activation

Physical activation is a process in which carbonized material is exposed to high temperatures (800 and 1100 °C) under controlled conditions in the presence of oxidizing gases [177]. It is known for its simplicity, affordability, and eco-friendly approach, as it eliminates the need for chemical agents.

1.7.2 Chemical Activation

Unlike physical activation, which depends on high temperatures and oxidizing gases [177], this method utilizes chemical agents as activators to develop pore structures and improve the adsorption characteristics of the raw material [178–180]. Alkaline substances are frequently utilized for their effectiveness in facilitating char formation [181–183] and enhancing pore structure development [184,185]. Acidic substances aid in pore formation by chemically interacting with the precursor material [177,186].

1.8 Post activation modification

Post-activation modification refers to the enhancement of activated carbon after the initial activation process to improve its adsorption efficiency, selectivity, and functionality [187]. While activation (physical or chemical) creates the porous structure and increases the surface area, post-activation modifications introduce additional chemical, biological, or physical properties that optimize activated carbon for specific applications. These modifications help tailor activated carbon for targeted pollutant removal, regeneration, and enhanced stability. Some commonly used post activation modifications are chemical functionalization [188], biological modification [189], magnetization [190] and doping with nanomaterials [191].

1.8.1 Chemical functionalization: Acidic or basic treatments can modify the surface chemistry, increasing selectivity for certain contaminants.

- **Acid Treatment** (e.g., HNO_3 , H_2SO_4) introduces oxygen-containing functional groups enhancing affinity for heavy metals [181].
- **Base Treatment** (e.g., NaOH , KOH) increases surface basicity, improving adsorption of organic acids and anionic pollutants [192].
- **Oxidation with H_2O_2 or Ozone** enhances adsorption by introducing oxygen functionalities that improve hydrophilicity [193].
- **Impregnation with Metal Ions** (e.g., Fe , Mn , Zn) enhances catalytic properties and selectivity for specific contaminants [194,195].

1.8.2 Biological Modification

Biological modification enhances the adsorption capacity of AC by utilizing microorganisms. Through their metabolic activities, microbes promote pollutant oxidation and allow microorganisms to attach to AC surfaces, where they form biofilms that further aid in pollutant removal [196–198]. Biofilm formation enhances the pollutant removal efficiency of AC by providing a protective environment for microbial growth [199,200]. Microorganisms immobilized on AC contribute to pollutant removal through enzymatic activities such as oxidoreductases, hydrolases, and dehalogenases, which degrade complex organics and drive oxidation reactions.

Their metabolism also promotes biomineralization, enabling the precipitation and sequestration of heavy metals, thereby improving overall removal efficiency [198,201]. Biological modification of activated carbon creates synergy between microbes and the

adsorbent, enhancing metal ion binding through additional active sites. Microbial metabolism also aids in regenerating spent carbon by promoting pollutant desorption and biodegradation of organics [197].

1.8.3 Magnetization of AC

This enhances its separation and recovery efficiency by incorporating magnetic nanoparticles like iron oxides (Fe_3O_4 or Fe_2O_3) [202]. This modification retains the high adsorption capacity of activated carbon while enabling easy retrieval using an external magnetic field. Various methods, including co-precipitation, impregnation with thermal treatment, sol-gel synthesis, and mechanical mixing, are used for magnetization. Magnetic activated carbon (MAC) offers advantages such as improved pollutant removal, easy regeneration, and reduced secondary pollution. It is widely applied in water treatment for heavy metal and organic pollutant adsorption, as well as in catalytic and environmental remediation processes.

1.8.4 Doping with nanomaterials

Incorporating nanomaterials like graphene, carbon nanotubes (CNTs), or metal oxides into AC improves its electrical, catalytic, and adsorption properties. This modification is particularly useful in energy storage, catalysis, and advanced water treatment [191].

1.9 Classification of activated carbon

AC are highly complex materials, making it difficult to classify them based on their behavior, surface properties, and manufacturing processes. However, for general applications, they are broadly categorized based on their physical characteristics.

- i. **Powdered AC (PAC):** PAC is a fine, highly porous adsorbent with particle sizes smaller than 100 micrometers. It is widely used in water treatment, pharmaceuticals, and chemical industries, particularly for batch treatment processes. However, due to its fine particle size, it requires efficient separation after use and is generally not reusable. While highly effective for short-term applications, proper handling and disposal are essential to optimize its benefits and minimize environmental impact [9].
- ii. **Granulated AC (GAC):** GAC is a porous adsorbent with particle sizes ranging from 0.2 to 5 mm, making it suitable for continuous treatment systems like fixed-bed adsorption columns. Unlike Powdered Activated Carbon (PAC), GAC has

slower adsorption kinetics but provides efficient long-term performance with lower pressure drop [9].

- iii. **Extruded AC:** EAC is a cylindrical, pelletized form of AC, offering high mechanical strength, low dust formation, and efficient flow characteristics. It is commonly used in gas-phase applications like air purification, gas treatment, and solvent recovery. Compared to Granular Activated Carbon (GAC), EAC is more durable, resistant to breakage, and suitable for high-pressure systems. Its uniform shape ensures minimal pressure drop and efficient mass transfer, making it a cost-effective choice for industrial-scale adsorption processes [9].

1.10 Application of AC

AC is a highly versatile adsorbent material extensively used across various. Its ability to adsorb volatile organic compounds (VOCs) also makes it essential in air purification systems, including indoor air filters, industrial gas treatment, and air pollution control during processes like painting, dry cleaning, and fuel dispensing. Furthermore, activated carbon is frequently used in spill response operations, particularly for the adsorption of oil and hazardous chemicals in both field and industrial settings. These environmental applications underline its critical role in reducing environmental and health hazards posed by chemical contaminants [203–205]. In the field of medicine, AC is used as treatment for poisonings and drug overdoses [19,206]. When administered orally, it binds to toxins in the gastrointestinal tract and prevents their absorption into the bloodstream.

This makes it a standard protocol in emergency rooms and by first responders in cases of suspected toxic ingestion. Additionally, AC is incorporated into some over-the-counter medications to alleviate bloating and gastrointestinal discomfort, highlighting its use beyond emergency interventions [207]. Industrially, AC plays an essential role in the metal finishing and electroplating industries, where it is used to purify electroplating solutions by removing organic impurities that interfere with metal deposition. Its use extends to gas purification as well, particularly in the removal of impurities such as chlorine, hydrogen sulfide, and various hydrocarbons from industrial gas streams [208]. In more recent developments, AC is used in filter tips to effectively trap tar and reduce the inhalation of combustion by-products [209]. It is also commonly used in household products such as water purification units, refrigerator air filters, aquarium filtration systems, and personal air purifiers, reflecting its broad utility in daily life.

Its efficient adsorption mechanisms, which arise from both physical interactions facilitated by its porous structure and chemical interactions involving its surface functional groups. These mechanisms allow activated carbon to function effectively in diverse scenarios, from environmental protection and industrial processes to healthcare and consumer applications, underscoring its indispensable role in modern science and technology.

1.11 Adsorption phenomena

Smaller particles like powdered AC (PAC) offer a higher surface area and faster adsorption kinetics, making them ideal for batch processes, whereas larger particles are more suitable for continuous systems due to their durability and lower pressure drop. Several factors influence adsorption efficiency. The pore structure and surface area of activated carbon play a crucial role, with micropores being more effective for gas adsorption and mesopores or macropores being better suited for liquid-phase adsorption. Adsorbate properties, including molecular size, polarity, and solubility, also affect how well a substance is adsorbed. Certain factors can enhance the adsorption efficiency of activated carbon. The activation process, whether thermal or chemical, increases porosity and improves adsorption capacity. Impregnation with chemicals or functional groups can enhance selectivity for specific pollutants. Pre-treatment of the adsorbate, such as adjusting pH or removing interfering substances, can improve adsorption outcomes. Optimizing operational conditions, including flow rate, pressure, and temperature in gas-phase applications, ensures that the adsorption process remains efficient and effective [210]. These forces contribute to the effectiveness of AC in adsorbing non-polar molecules and organic contaminants from air and water.

1. 12 Classification of adsorption phenomena

1.12.1 Based on the nature of interaction

- i. **Physical adsorption (Physisorption):** It is a reversible process that does not significantly alter the electronic structure of the adsorbate. Physisorption is typically more favorable at lower temperatures and is effective for non-polar gases, vapors, and organic compounds.
- ii. **Chemical adsorption (Chemisorption):** Chemisorption is generally irreversible and highly selective for certain molecules, such as heavy metals and reactive

gases. Unlike physisorption, it requires activation energy and occurs at higher temperatures.

1.12.2 Based on the phases involved

- i. **Gas-solid adsorption:** This occurs when gases or vapors adhere to the surface of a solid adsorbent. It is commonly applied in air purification, gas storage, and catalytic processes.
- ii. **Liquid-solid adsorption:** It is widely utilized in wastewater treatment, as well as in chemical separation techniques.
- iii. **Gas-liquid adsorption:** This involves the adsorption of gases into a liquid medium. It plays a key role in processes like gas absorption, including carbon dioxide capture in water.

1.12.3 Based on adsorption kinetics

- i. **Monolayer adsorption:** In this type of adsorption, molecules form a single layer on the surface and follows the Langmuir isotherm model, which assumes a limited number of adsorption sites and uniform adsorption energy across the surface.
- ii. **Multilayer adsorption:** Here, adsorption occurs in multiple layers as adsorbate molecules continue to accumulate beyond the first layer. This process is described by the Freundlich and BET (Brunauer-Emmett-Teller) isotherm models and is commonly observed in porous materials.

1.12.4 Based on adsorption mechanism

- i. **Ion exchange adsorption:** It is widely used for heavy metal removal, particularly when activated carbon is modified with functional groups to enhance ion exchange capacity.
- ii. **Electrostatic adsorption:** In this mechanism, charged adsorbates are attracted to oppositely charged adsorbent surfaces. It is commonly observed in aqueous-phase adsorption processes.
- iii. **Pore-filling adsorption:** Adsorption occurs when molecules diffuse into the micropores and mesopores of the adsorbent. This mechanism is typical in materials like AC and zeolites, where high porosity enhances adsorption efficiency.

1.13 Adsorption Studies

The AC prepared in this study were applied for the removal of various water pollutants, including dyes, hormones, heavy metals, and biological contaminants. The specific pollutants selected for investigation were Congo red dye, 17 β -estradiol, and cadmium. Batch adsorption experiments were performed to assess the removal efficiency of these contaminants. In each experiment, a predetermined amount of adsorbent was added to a conical flask containing a fixed volume of pollutant solution at the desired concentration. The solution pH was adjusted using NaOH or HCl, and the mixtures were agitated on a rotary shaker at 180 rpm under controlled temperature for a specified contact time. Following the adsorption period, the suspensions were filtered, and the residual concentrations of pollutants were determined using a UV-Visible spectrophotometer (Model: Lambda 35, Perkin Elmer). The percentage removal of the pollutants and the adsorption capacity of the AC were subsequently calculated using Equations (1) and (2), respectively.

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{M} \times V \quad (2)$$

Where C_0 is the initial pollutant concentration (mg/L), C_e is the concentration at equilibrium (mg/L), q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), M is the mass of adsorbent (g) and V is the volume of the solution (L).

Detailed batch adsorption experiments for the removal of selected pollutants are presented in Chapters 4, 5 and 6.

The bacterial strains used in this study were *Staphylococcus aureus* and *Klebsiella pneumoniae*. Their removal from water was carried out using a fixed-bed column method. Activated carbon was tightly packed into glass columns with a diameter of 2 cm and a length of 30 cm. Bacterial solutions were passed through the column at a flow rate of 1 mL/min. The bacterial concentrations at the column outlet were measured at regular intervals using the standard plate count method, and the log reduction of bacteria by the filter column was calculated using Equation (3).

$$\log_{10}\text{reduction} = -\log_{10}\left(\frac{N}{N_0}\right) \quad (3)$$

where N and N_0 are the final and initial bacterial concentration in CFU/ml respectively. The detailed experimental setup for bacterial removal is presented in Chapter 6.

1.14 Adsorption isotherms

Adsorption isotherms play a crucial role in describing how pollutants interact with the surface of an adsorbent, and they are instrumental in optimizing the design of adsorption systems for pollutant removal from aqueous solutions [218].

An adsorption isotherm illustrates the equilibrium amount of adsorbate retained on the adsorbent surface (q_e) in relation to the adsorbate concentration remaining in the solution (C_e) at a constant temperature. The correlation between q_e and C_e is typically fitted to one or more established equilibrium isotherm models.

The various isotherm models, kinetic models, and thermodynamic equations employed in this study are described in the following sections.

1.14.1 Langmuir adsorption isotherm

The Langmuir isotherm model, proposed by Irving Langmuir in 1918, is widely utilized to interpret adsorption behavior in both gas-solid and liquid-solid systems, particularly in chemisorption. The model can be expressed in linear and non-linear forms. The linear and non-linear form Langmuir equation is given in equation (4) and (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_e is the equilibrium adsorption capacity (mg/g), q_m is the maximum monolayer adsorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and K_L is the Langmuir constant related to adsorption affinity (L/mg) [219].

The suitability of the Langmuir model is evaluated through the dimensionless separation factor (R_L), which determines the favorability of adsorption:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where C_0 is the initial concentration of the adsorbate (mg/L). The adsorption process is considered favorable when $0 < R_L < 1$, unfavorable when $R_L > 1$, linear when $R_L = 1$ and irreversible when $R_L = 0$ [220].

1.14.1.1 Assumptions of the Langmuir isotherm

The Langmuir isotherm model is based on several fundamental [219,221,222] such as:

1. All adsorption sites have identical energy and capacity.
2. There are no interactions between adsorbed molecules, so the presence of one molecule does not influence the adsorption of others.
3. Adsorption and desorption proceed at a constant rate, maintaining equilibrium between adsorbed and free molecules.
4. The enthalpy change during adsorption remains uniform across all sites and is independent of surface coverage.

These assumptions make the Langmuir model highly applicable to systems dominated by chemisorption, as it effectively describes adsorption on microporous materials such as activated carbon, zeolites, and metal oxides [223]. However, when multilayer adsorption occurs or the surface is heterogeneous, alternative models like the Freundlich or BET isotherms may offer a more accurate representation [220,224].

1.14.2 Freundlich adsorption isotherm

The Freundlich isotherm model, developed by Herbert Freundlich in 1906, is particularly useful for characterizing adsorption in materials such as activated carbon, clays, and other porous adsorbents used in environmental remediation [225]. The linear and non-linear form of Freundlich adsorption equation is expressed in equation (7) and (8):

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (7)$$

$$q_e = K_F C_e^{1/n} \quad (8)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_F is the Freundlich constant and $1/n$ is the heterogeneity factor, which indicates adsorption intensity and surface heterogeneity.

The applicability of the Freundlich model is assessed through the heterogeneity factor ($\frac{1}{n}$), which provides insights into the favorability of adsorption:

$$0 < \frac{1}{n} < 1 \quad (9)$$

A value of $\frac{1}{n}$ between 0 and 1 indicates favorable adsorption, while values greater than 1 suggest cooperative adsorption where adsorption becomes more favorable as coverage increases [220].

1.14.2.1 Assumptions of the Freundlich isotherm

The Freundlich isotherm is based on the following fundamental assumptions [220,221,223,225] The adsorbent surface contains sites with varying adsorption energies, resulting in a range of binding affinities.

- i. There is no defined maximum adsorption capacity, allowing adsorption to continue as the adsorbate concentration increases.
- ii. Adsorption initially occurs at high-energy sites, leading to greater efficiency at lower adsorbate concentrations.
- iii. The Freundlich equation is empirically derived from experimental data rather than based on a theoretical adsorption mechanism, making it ideal for practical modeling.

The Freundlich model is well-suited for adsorption studies involving materials like activated carbon, biochar, and zeolites, commonly used in wastewater treatment, heavy metal removal, and gas adsorption. However, its lack of an adsorption saturation point makes it less effective for systems needing precise monolayer adsorption predictions [220,224].

1.14.3 Temkin adsorption isotherm

The Temkin isotherm is suitable to heterogeneous surfaces with low coverage and is especially helpful in adsorption processes when the overall adsorption behavior is influenced by strong interactions between adsorbed molecules [226].

The Temkin adsorption equation is given as:

$$q_e = \frac{RT}{B_T} \ln(A_T C_e) \quad (10)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of adsorbate in solution (mg/L), A is the Temkin isotherm constant (L/g), related to the binding energy, R is the universal gas constant (8.314 J/mol·K), T is the absolute temperature (K) and B is the Temkin heat of adsorption constant (J/mol).

1.14.3.1 Assumptions of the Temkin isotherm

The Temkin isotherm is based on the following key assumptions [31,220,221,226].

- i. The adsorbent surface is heterogeneous, with adsorption energy distribution following a logarithmic function rather than a simple power law.
- ii. The model describes a monolayer adsorption process but considers variations in adsorption energy.
- iii. It accounts for adsorbate-adsorbent interactions, distinguishing it from purely empirical models like the Freundlich isotherm.
- iv. The Temkin isotherm is most suitable for moderate adsorbate concentrations, where the linear decline in adsorption energy is relevant, but it does not fully capture behavior at extremely low or high concentrations.

1.15 Adsorption kinetics modelling

This studies help evaluate the adsorption mechanisms by determining the reaction order and rate constants, offering valuable insights into potential rate-limiting steps [227].

1.15.1 Pseudo first order (PFO) kinetic models

The adsorption of solutes from a liquid phase onto a solid adsorbent was initially described by Lagergren (1898) using the PFO kinetic model, commonly referred to as the Lagergren equation. Based on the idea that diffusion and physisorption processes are the main factors controlling adsorption, this model is frequently used in adsorption studies to predict the rate of adsorption [228,229]. The linear and non-linear equation of PFO is expressed in equation (11) and (12).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (11)$$

$$q_t = q_e (1 - e^{-k_1 t}) \quad (12)$$

Where q_e is adsorption capacity at equilibrium(mg/g), q_t is adsorption capacity at time t (min) and k_1 is the rate constant PFO adsorption.

1.15.1.1 Assumptions of the PFO model

The PFO kinetic model is based on the following [228–230].

- i. Each adsorbate molecule adheres to an adsorption site independently, without affecting other molecules.
- ii. The model assumes that adsorption is predominantly controlled by diffusion, especially during the initial phase.
- iii. As this model is mainly suited for physisorption, it considers weak van der Waals forces rather than strong chemical interactions.
- iv. The PFO model is most effective at lower concentrations, where adsorption sites on the surface are more readily available.

1.15.2 Pseudo second order (PSO)

One of the models most frequently used to describe adsorption kinetics is the PSO kinetic model. It was initially presented by Ho and McKay (1999) to describe adsorption systems in which the rate-limiting phase is chemisorption. According to the PSO model, adsorption is regulated by the availability of adsorption sites and surface chemical interactions, as compared to the PFO model, which suggests that adsorption is controlled by diffusion [229,230]. Equation (13) and (14) expressed the linear and non-linear form of PSO.

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (14)$$

where q_e is adsorption capacity at equilibrium (mg/g), q_t is adsorption capacity at time t (min) and k_2 is the rate constant PSO adsorption.

1.15.2.1 Assumptions of the PSO model

The PSO kinetic model is based on the following assumptions [220,229,230].

- i. Adsorption primarily occurs through chemical interactions, such as ion exchange, covalent bonding, or electron sharing, rather than simple diffusion.
- ii. The overall adsorption rate is influenced by the number of available adsorption sites, highlighting the importance of adsorbate-adsorbent interactions.

- iii. Unlike the Langmuir model, which assumes uniform adsorption sites, this model accounts for surface heterogeneity.
- iv. While the PFO model is most suitable for low concentrations, the pseudo-second-order model provides accurate predictions even at higher adsorbate concentrations.

1.15.3 Weber and Morris intraparticle diffusion

This model is useful for examining the function of intraparticle diffusion in mass transfer processes in adsorption [229,231]. According to this approach, adsorption is not just controlled by surface adsorption or external film diffusion, but also by diffusion occurring within the adsorbent's pores. The Weber and Morris equation is given as:

$$q_t = k_{id}t^{1/2} + A \quad (15)$$

where k_b is the rate constant of intra-particle diffusion ($\text{mg/g/min}^{1/2}$), q_t is the amount of adsorbate adsorbed at time t (mg/g), k_{id} is intraparticle diffusion rate constant ($\text{mg/g/min}^{1/2}$) and A is the thickness of the boundary layer.

1.15.3.1 Assumptions of the Weber and Morris Model

- i. Adsorption Occurs in Three Consecutive Stages:
 - a) **Stage 1:** External mass transfer (film diffusion) – Adsorbate molecules move from the bulk solution to the adsorbent surface.
 - b) **Stage 2:** Intraparticle diffusion – Adsorbate diffuses into the pores of the adsorbent.
 - c) **Stage 3:** Equilibrium is established as adsorption reaches saturation.
- ii. Intraparticle diffusion may not be the only rate-limiting step:
 - a) If the plot of q_t vs. $t^{1/2}$ does not pass through the origin ($C \neq 0$), then other processes also influence the adsorption process.
 - b) If the plot is linear and passes through the origin ($C=0$), intraparticle diffusion is the sole rate-controlling mechanism.
- iii. The Rate Constant k_{id} Reflects the Speed of Intraparticle Diffusion:
 - a) A higher k_{id} value indicates faster diffusion into the adsorbent pores.
 - b) A lower k_{id} value suggests stronger resistance to intraparticle diffusion.

1.15.4 Elovich adsorption kinetic

Zeldovich (1934) developed the Elovich model first for use in the study of catalysis and heterogeneous chemical processes. However, it was later modified and used extensively in investigations of adsorption kinetics, especially for the adsorption of gases on solid surfaces by Elovich and Larinov (1962). Low (1960) further developed the model to explain chemisorption kinetics, and it has subsequently been applied in a number of adsorption investigations, particularly for systems with heterogeneous surfaces and adsorption energy that varies with time [232]. The model assumes that adsorption occurs through a chemisorption process and that the rate of adsorption decreases over time due to the gradual saturation of available adsorption sites [229]. The Elovich equation can be expressed in linear and non-linear form and it is expressed in equation (16) and (17).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta t) + \frac{1}{\beta} \ln(t) \quad (16)$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) \quad (17)$$

where q_t amount of adsorbate adsorbed at time t (mg/g), α is initial adsorption rate constant (mg/g/min), β represents desorption constant related to surface coverage (g/mg) at time t .

1.15.4.1 Assumptions of the Elovich model

- i. The model assumes that adsorption occurs through chemical interactions, such as covalent bonding, electron exchange, or ion exchange [232].
- ii. As the adsorbent surface becomes occupied, repulsive forces increase, reducing the probability of additional adsorption [229].
- iii. The model assumes variable activation energies across different adsorption sites, making it suitable for porous and heterogeneous adsorbents [220].
- iv. The Elovich model is especially useful for low concentration adsorption systems, where surface interactions dominate the adsorption process [233].

1.16 Fitness of the kinetic models

In adsorption studies, evaluating the fitness of kinetic models is crucial for understanding the adsorption mechanism and rate. Statistical tools like the chi-square test are used to compare predicted and experimental data, with lower values indicating a better fit. Additional metrics such as coefficient of determination (R^2) and the sum of squared errors (SSE) further enhance the accuracy of the model assessment.

1.16.1 Chi-square analysis

In adsorption studies, chi-square (χ^2) analysis is a valuable statistical tool used to evaluate how well an isotherm or kinetic model fits the experimental data. It quantifies the discrepancy between the experimental adsorption values and the values predicted by theoretical models, such as Langmuir, Freundlich, Temkin, or various kinetic models. The chi-square statistic is calculated using the given formula:

$$\chi^2 = \sum \frac{(q_{\text{exp}} - q_{\text{cal}})^2}{q_{\text{cal}}} \quad (18)$$

where q_{exp} is the experimentally measured adsorption capacity at equilibrium, and q_{cal} is the adsorption capacity calculated using a theoretical model. A low chi-square value indicates good agreement between experimental and predicted data, showing the model accurately describes adsorption behavior, while a high value suggests poor model fit due to greater discrepancies.

1.16.2 Coefficient of determination (R^2)

The coefficient of determination (R^2) is a statistical measure that evaluates how well a model explains the variability of a dependent variable based on independent variables. It is widely used in regression analysis, including adsorption studies, to assess the goodness of fit of isotherm and kinetic models. Some of the features of R^2 are:

- a) The coefficient of determination is a number between 0 and 1 inclusive (i.e. $0 \leq R^2 \leq 1$)
- b) If $R^2 = 1$, The model perfectly explains the variance in the data (ideal case)
- c) $R^2 = 0$, The model does not explain any of the variance.

1.16.3 Sum of squared errors (SSE)

The best fit among the kinetic models was assessed by sum of squared errors (SSE), also known as the residual sum of squares (RSS), is a key statistical measure used to quantify the discrepancy between observed values and predicted values in a regression model. It represents the total squared difference between actual data points and their estimated values, providing insight into the accuracy of a model [234]. In adsorption studies, it is widely used to compare isotherm and kinetic models, with lower SSE values indicating a better fit. The SSE is calculated using the given equation:

$$\text{SSE} = \sum \frac{(q_{\text{e}(\text{exp})} - q_{\text{e}(\text{cal})})^2}{q_{\text{e}(\text{exp})}^2} \quad (19)$$

where, $q_{e(exp)}$ and $q_{e(cal)}$ are the experimental sorption capacity of pollutants (mg g⁻¹) at equilibrium time and the corresponding value that is obtained from the kinetic models. Some features of SSE are:

- a) If SSE = 0, the model perfectly predicts all observed values.
- b) The lower the SSE, the better the model's predictive accuracy.
- c) The higher the SSE, the worse the model fits the data, leaving a large amount of unexplained variance.

1.17 Thermodynamic studies:

Thermodynamic studies in adsorption provide insights into the nature, feasibility, spontaneity, and energy changes involved in the adsorption process. By analyzing thermodynamic parameters, it determines whether the adsorption is physical or chemical, endothermic or exothermic, and how temperature influences adsorption capacity. The thermodynamic parameters were obtained by using the equation [235].

$$\Delta G^\circ = -RT \ln K_d \quad (21)$$

$$K_d = \frac{q_e}{c_e} \quad (22)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (23)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (24)$$

where K_d represents the distribution coefficient for adsorption, while q_e denotes the amount of adsorbate retained by the adsorbent per liter of solution at equilibrium. C_e is the equilibrium concentration of the adsorbate in solution, and T is the absolute temperature, R is the universal gas constant (8.31445 J K⁻¹ mol⁻¹). The thermodynamic parameters ΔG° (Gibbs free energy change), ΔH° (enthalpy change), and ΔS° (entropy change) characterize the adsorption process. The values of ΔH° and ΔS° are determined from the slope and intercept of the Van't Hoff plot of $\ln K_d$ versus $1/T$, which are obtained using a curve-fitting method.

1.18 Density Functional Theory (DFT)

DFT is a quantum mechanical approach extensively applied to explore the electronic structures of atoms, molecules, and condensed matter systems [236,237]. The central idea of DFT is that the ground-state properties of a multi-electron system can be entirely described by its electron density, [238] removing the need to solve the more complex many-body wavefunction [239]. The computational practicality of DFT is achieved

through the Kohn–Sham formalism, which replaces the interacting electron system with an equivalent non-interacting system that yields the same density, thus enabling efficient calculations [240].

In adsorption studies, DFT serves as a powerful tool for elucidating the interaction mechanisms between adsorbates (e.g., pollutants) and adsorbents such as activated carbon or biochar at the atomic scale [241]. It enables the prediction of favorable adsorption sites, computation of adsorption energies, assessment of charge transfer phenomena, and examination of modifications in molecular orbitals following adsorption [242]. Furthermore, DFT facilitates the identification of surface functional groups actively involved in binding processes, including hydroxyl (–OH), carboxyl (–COOH), and amine (–NH₂) functionalities [238]. The adsorption energy (E_{ads}) is generally determined using the following equation:

$$E_{\text{ads}} = E_{\text{adsorbent+adsorbate}} - (E_{\text{adsorbent}} + E_{\text{adsorbate}}) \quad (25)$$

where $E_{\text{adsorbent/adsorbate}}$ is the total energy of the optimized adsorbent–adsorbate complex, $E_{\text{adsorbent}}$ is the energy of the isolated adsorbent, and $E_{\text{adsorbate}}$ is the energy of the isolated adsorbate.

For accurate adsorption modeling, [243] hybrid functionals such as B3LYP combine DFT with Hartree–Fock exchange to improve accuracy [244], and dispersion corrections like Grimme’s DFT-D2 or D3 are often incorporated to capture van der Waals interactions in physisorption [245]. DFT simulations are commonly performed using computational packages such as Gaussian, VASP, CASTEP, Quantum ESPRESSO, or ORCA [246–249]. The workflow typically involves constructing an adsorbent model (e.g., graphene sheet, activated carbon cluster), placing the adsorbate, optimizing the geometry to locate the most stable configuration, and then carrying out single-point energy calculations, charge distribution analysis (Mulliken or Natural Bond Orbital), density of states (DOS) analysis, and electron density difference plotting. Key computational outputs—such as adsorption energies, HOMO–LUMO gap shifts, vibrational frequency changes, and DOS modifications—complement experimental data obtained from techniques like FTIR, XPS, and BET surface analysis [250]. These combined insights not only explain adsorption mechanisms but also assist in predicting the performance of modified adsorbents prior to synthesis.

1.19 Importance of the study:

The research on activated carbon derived from waste animal waste (fish scales) holds significant importance in both waste management and environmental sustainability. By utilizing fish scales, a common animal waste byproduct, this study contributes to the waste-to-wealth approach, transforming discarded materials into valuable resources. Instead of allowing animal biowaste (fish scales) to accumulate as waste and contribute to pollution, their conversion into AC provides an eco-friendly and cost-effective alternative for water treatment.

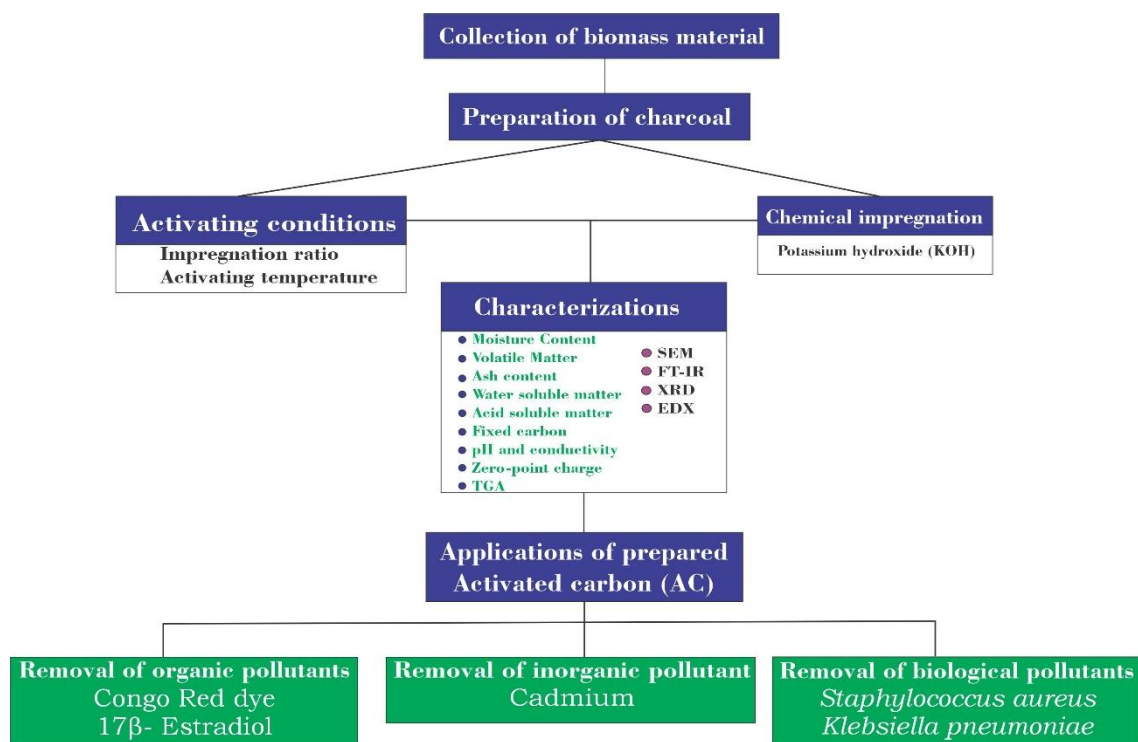
AC production from fish scales presents an environmentally sustainable solution compared to conventional activated carbon sources like coal and wood, which rely on non-renewable resources. This method not only reduces waste disposal concerns but also offers a low-cost adsorbent with high efficiency for pollutant removal.

Beyond its application in water purification, this research aligns with the principles of the circular economy by promoting resource recovery and sustainable waste utilization. It contributes to reducing environmental pollution while enhancing water treatment technologies in a cost-effective manner. By adopting this approach, industries and communities can benefit from an affordable and efficient solution for wastewater treatment, supporting cleaner water systems and better environmental management.

Overall, this work highlights the potential of turning waste into valuable materials while addressing pressing environmental issues. The development of activated carbon from waste fish scales reinforces the importance of green technologies in adsorption science, offering a practical and sustainable method for pollution control.

Aims and objectives of the work

1. To prepare activated carbon from waste fish scales using KOH as an activating agent.
2. To evaluate the adsorption capacity of the prepared AC for the removal of Congo red dye from aqueous solutions.
3. To investigate the adsorption efficiency of the AC for β -estradiol removal.
4. To study the adsorption of bacteria (*Staphylococcus aureus* and *Bacillus subtilis*) onto the AC surface.
5. To utilize *S. aureus*-pre-adsorbed carbon for the adsorption of cadmium, assessing its potential for heavy metal removal.



Scheme 1. An overview of the Ph.D. research framework outlined in this thesis.

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CHAPTER 2

LITERATURE REVIEW

In this chapter, a review of previous studies on activated carbon derived from animal-based precursors has been presented. The discussion highlighted different raw materials, preparation methods, activation techniques, and modifications applied to enhance adsorption performance. Key findings from earlier works on adsorption mechanisms, isotherm and kinetic models, as well as applications in pollutant removal, were also summarized to provide a foundation for the present study.

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2.1 Introduction

Freshwater scarcity is one of the most pressing challenges the world has been trying to tackle over the last few years. The already existing severe freshwater crisis is aggravated by population growth, unplanned rapid urbanization, technological advancements, and agricultural operations, etc. Nowadays, wastewater pollution from diverse industrial activities has escalated into a global concern. Unchecked discharge of pollutants poses substantial dangers to aquatic habitats, contributing to acute and chronic toxicity for aquatic animals, ecosystem pollution biodiversity damage, habitat destruction, and human health problems [1]. Toxic metal ions containing discharge from various sources such as industrial and sanitary wastes, domestic effluents, agricultural runoff has added to the prevailing strain on usable freshwater supply [2]. Long-term negative consequences in aquatic and human health have been seen to be directly related to consumption of polluted waters containing persistent metal ions or recalcitrant organic compounds. In addition, aesthetic value of surface waters are lost due to the presence of such pollutants and renders them unfit for both drinking and recreational purposes [3]. The issues on establishing techniques for cleanup of such contaminated waterways have been examined by a vast number of researchers [4–9].

Owing to their easy availability and efficiency [10,11], adsorption using conventional methods for water treatment, like chemical coagulation, flocculation, sedimentation, and filtration methods are typically used in water treatment plants to eliminate suspended solids and some dissolved contaminants. However, these approaches may be ineffective for eliminating specific contaminants including heavy metals, dyes, and organic chemicals, which require more advanced treatment methods such adsorption utilizing activated carbon (AC) [12,13]. Usually, biomass residues are disposed of which can have adverse effects on the environment. Burning biomass can produce by-products that contribute to significant air pollution, impacting the surrounding ecosystem. As a result, converting solid waste into high-quality, porous AC material is an excellent alternative. The conversion process provides a sustainable approach for managing biomass waste while providing a valuable resource that may be used in a variety of ways, including as an excellent adsorbent for eliminating organic and inorganic water contaminants other applications.

AC is a typical form of adsorbent widely used in wastewater treatment technologies. Its high surface area, well-distributed pores, and robust mechanical and thermal durability

make it a suitable adsorbent [14]. However, the majority of the AC on the market is sourced from non-renewable resources such as coal, lignite, and coke, causing high costs and environmental issues [15]. To overcome the limitations of AC manufacturing, current efforts have concentrated on preparing it with renewable, sustainable, and easily available precursors. These properties are highlighted by the utilization of lignocellulosic biomass as a precursor for manufacturing AC, which offers renewability, plentiful availability, cost-effectiveness, and eco-friendliness [16].

Adsorption methods are widely used to remove heavy metals, dyes, organic solvents, phenol and its replacements, pharmaceutical effluents, herbicides, pesticides, surfactants, hydrocarbons, esters, phthalates, alcohols, chlorinated organic contaminants, etc [9,17,18]. Adsorbents that have found significance for water pollutant removal are clays, carbon nanotubes, nanocellulose, hydrogels, nano- fibers and AC amongst which, versatility of AC as adsorbents are noteworthy [19,20]. The use of charcoal as adsorbents, the forerunner of the present day's AC, has been known for water filtration as early as 2000 BC [21,22]. The specific surface area of most economically applicable carbons have been found to range from 215 to 3532 m²/g (BET surface area) [23,24].

Over the years, AC has been widely derived from plant sources like rice husk [25,26], coconut shell [27], bamboo [28,29], agricultural residues and natural biomaterial [12], oil-palm stone [30], oak fruit hull [31], olive stone [32,33], *Manihot esculenta* [34,35], marine macro-algal biomass [36], palm shell [30], sugarcane [37], *Eucalyptus camaldulensis* Dehn bark [38], corn stalk [39], neem husk [40], cactus fruit peel [41], tea residue [42], corn cob [43,44], groundnut shell [45], rawfava bean peels [17] etc.

However, despite its projected advantage over plant equivalents, especially in terms of removal efficiency, AC generated from animal biowaste has not received similar attention. Animal biomass has been shown to be widely available for water treatment applications at no cost or at a minimal cost [46]. Few reports have been made on AC derived from animal biomass such as eggshell [47–49], hen feathers [50–52], animal bones [53–57], hooves and horns [58,59], dung/manure [13,60,61], snail shells [62], animal hair [58] etc. In line with this, the present mini review is aimed to investigate the recent advances made in the use of animal biomass or waste animal parts derived AC in wastewater treatment and the purpose is to highlight current research trends, knowledge gaps, and future research directions in the use of animal biomass.

2.2 Animal biomass and target pollutants

Although there is a gradual spike in interest in the application of animal wastes or biomass as a biosorbent for eliminating contaminants from aqueous solutions, it's also worth noting that animal bones have piqued researchers' curiosity the most and its applications have been published more frequently in open literature [46,53,63]. Other parts that have attracted similar attention are eggshell [48,64], horn and hoof [59,65], turkey manure [66], cow manure [67,68], animal hair [58], and chicken feathers [52]. A compilation of reports AC derived animal biowastes and the targeted corresponding pollutant is presented in Table 2.1.

2.3 Biosorbent preparation methodology

The preparation of biosorbents from animal waste typically begins with cleaning and drying of the raw material, followed by grinding and sieving. Subsequently, the material undergoes carbonization and other modifications to enhance its properties for adsorption applications. Typically, the biowaste material is washed with distilled water [41,69,70], ultrapure water, ethanol, chloroform, hot water [71], boiled in distilled water [72,73], shampoo [21], detergent [74], or direct pyrolyzation of manures or litters [75], etc. to remove impurities. The charcoal or washed-dried samples are activated through reheating or soaking with H_3PO_4 [27,34], KOH [76,77], NaOH [48,78], HNO_3 [79], ZnCl_2 [80–82], K_2CO_3 [71,83] and HCl [78]. The detailed methodology ensures that the biosorbent is prepared in a standardized and effective manner, suitable for use in research studies involving adsorption processes as shown in Fig. 2.1

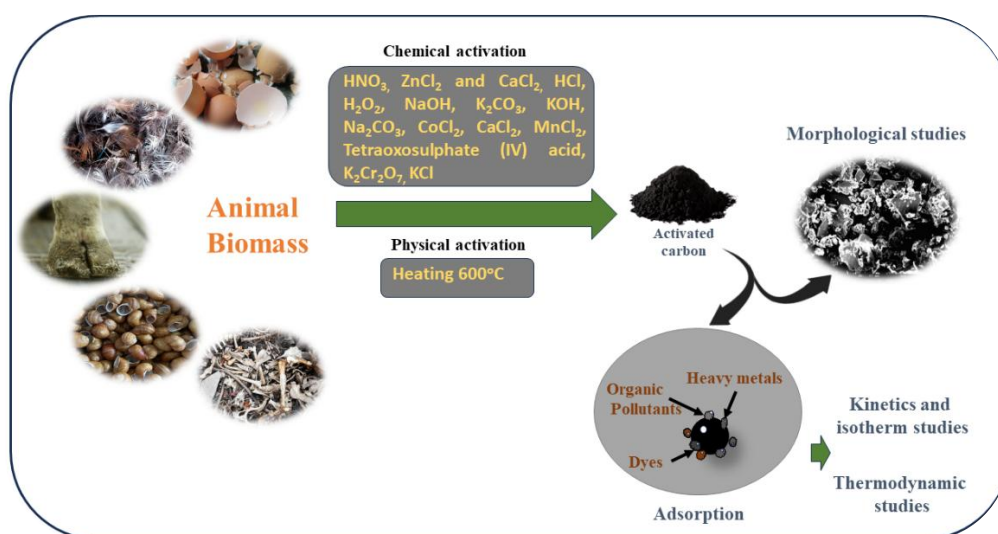


Fig. 2.1 AC production from animal biomass using diverse chemical activation

Table 2.1 Synthesis of AC from animal biowastes for adsorption applications

Target pollutants	Raw Materials	Activating Agents	References
Tetracycline	Chicken feather	KOH	[51]
Pb ²⁺	Goat teeth	HCl	[84]
H ₂ S	Kernel shell	KOH	[85]
Perchlorate	Cow dung	NaOH	[86]
Chitin from Shrimp shell	Cow bones	H ₃ PO ₄ , ZnCl ₂	[73]
Cd ²⁺	Hoof- horn powder	KOH	[65]
Methylene blue	Cow manure	KOH	[68]
Bisphenol A	Human hair	KOH	[87]
Basic red 9	Bovine bones and fish scales	-	[53]
Pb ²⁺	Cow dung	Na ₂ CO ₃	[88]
Pb ²⁺ and Cu ²⁺	Pig bone char	NH ₂	[89]
Methylene blue	Cashmere guard hair	K ₂ CO ₃	[71]
Cd ²⁺	Cow dung	KOH	[39]
Methylene blue	Eggshell	NaOH and H ₃ PO ₄	[48]
Cd ²⁺	Cow dung	NaOH	[13]
Methylene blue	Cow dung	H ₃ PO ₄	[90]
Blue dye	Cow hair	KOH	[91]
Carbofuran	Cow dung	KOH	[92]
Bisphenol A	Bovine horn	NaOH	[93]
Brilliant blue G 250	Goat dropping	H ₃ PO ₄	[94]
Rhodamine B	Cow dung	KOH, NaOH	[95]
Methylene blue	Cow manure	KOH	[96]
Phenol	Cow dung	KOH	[97]
Cr ⁶⁺	Lamb bone	H ₃ PO ₄	[70]
Pb ²⁺	Chicken eggshell	NaOH	[98]
Methylene blue	Sheep and goat dung	ZnCl ₂ , KOH	[61]
Cr ⁶⁺	Chicken feather	NaOH, CS ₂	[99]
As ³⁺	Chicken manure	KOH	[100]
Thiamethoxam	Cow manure	ZnCl ₂	[101]

2.4 Morphology of AC derived from Animal biomass

The morphology of AC derived from animal biomass is a crucial aspect that directly impacts its adsorption properties. Several research groups have done morphological investigations utilizing analytical techniques such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Fourier-transform infrared

spectroscopy (FT-IR) and X-ray diffraction (XRD). For example, Djilani's et al. [55] presented SEM images revealing the irregular morphology of chicken bone AC (CAB) (Fig. 2.2).

The surface of CAB was heterogeneous, demonstrating structural heterogeneity with mesopores and macropores of varying sizes and shapes. The group discovered that the presence of mesopores promoted the adsorption of bigger molecules and resulted to faster adsorption rates [55]. Also, Zou et al. [71] has demonstrated, using SEM images of cashmere guard hair AC, that the charred form retains the fiber-shaped structure of hair, but this structure is not preserved in the AC form, likely due to the more intensive processing involved (Fig. 2.3). Subjecting the cuticle or cortex structure derived from wool fibers to high activation temperatures resulted in AC with well-developed pores and this could be achieved through the continuous de-volatilization of the chars, leading to enhanced porosity [71].

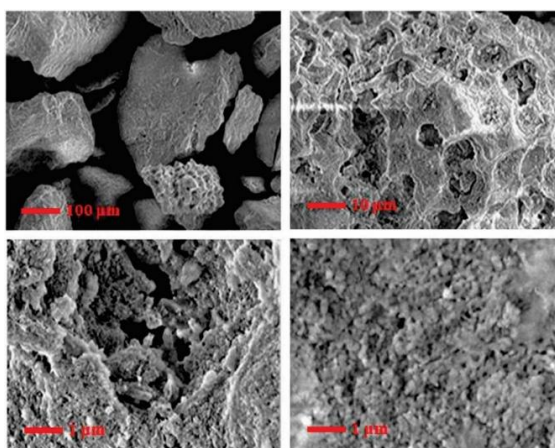


Fig. 2.2 SEM Images of chicken bones at different magnifications [55]

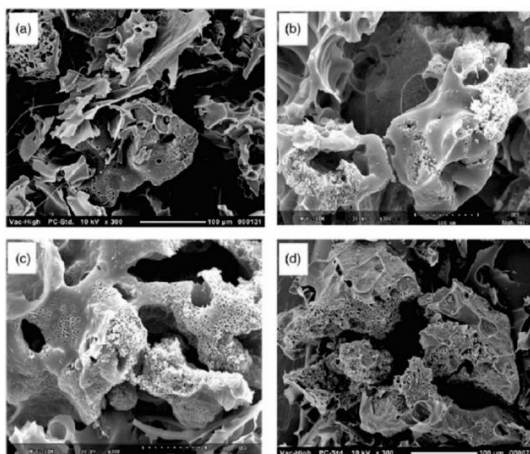


Fig. 2.3 SEM images of AC powder obtained under various activation temperatures [71]

Ahmed et al. [48], explored the morphology of AC derived from eggshell, revealing an irregular and non-uniform carbon structure with micropores (Fig. 2.4b). The average crystalline size, crystal structure, micro strain, density dislocation, and micro strain were determined from the XRD spectrum wherein it was also shown that the hexagonal crystal structure of carbon and the reflection plane fit the rhombohedral structure of CaCO_3 .

A comparison between NaOH and H_3PO_4 as activating agents showed that while H_3PO_4 yielded more crystalline peaks and improved the porous structure of the carbon, NaOH was more effective in removal of silica and ash content [48]. Irregularities in porosity nature of eggshell produced AC has also been observed by Balasubramanian et al. [64]. The synthesised particles were found to be strongly agglomerated, porous, and unevenly dispersed throughout the AC's surface. The use of H_3PO_4 as activating agent facilitates electrolyte penetration, allowing for ion diffusion, charge transfer, and capacitance enhancement thus enhancing the porosity of the prepared AC. Further, Country hen eggshell AC were seen to be flake-like with partial geometrical form, while the surface morphology of broiler hen eggshell AC were found to be more dense. XRD and FT-IR analysis have confirmed the variations in the types of eggs shells [64].

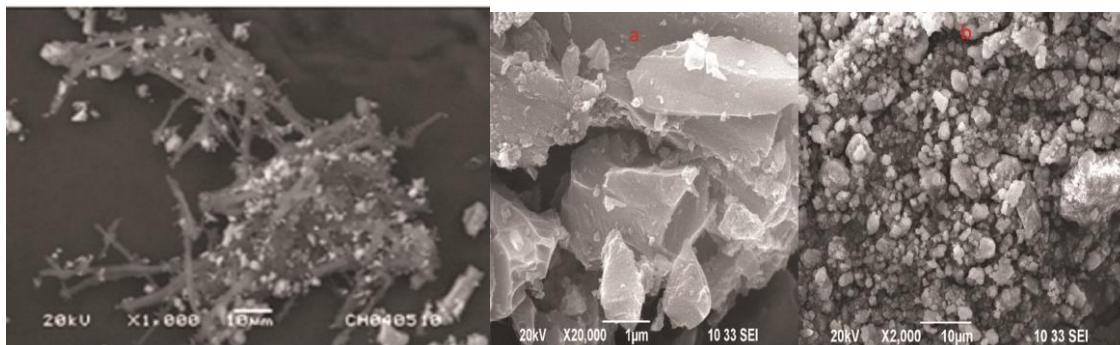


Fig. 2.4a Egg shell SEM [102] **Fig. 2.4b** FESEM images egg shell based AC (a) NaOH
(b) H_3PO_4 [48]

Powdered horn-hoof that have been produced by heat treatment revealed morphology of monodisperse distribution ($\text{PI} = 3.14$) with a volume weighted mean diameter of 161.19 μm and a specific surface area of $0.245 \text{ m}^2/\text{g}$ [59] (Fig. 2.5). Morphological investigation of human hair-derived AC showed flake-like cuticle features and a diameter around $63 \mu\text{m}$. However, images from NSC-700 and NSC-800 (Fig 2.6a and Fig 2.6b) shows how pyrolysis changes the fibrous form to carbon skeletons that are irregularly interconnected. With further degradation of organic precursors, the structure was seen to disintegrate as

the temperature climbed to 900 °C (Fig 2.6b). Numerous micropores were detected on the margins of carbon aggregates in NSC-800 (Fig 2.6d), coupled with hollow carbon bubbles and a mesoporous structure (Fig 2.6e).

The atypical XRD patterns seen in NSC-X are further corroborated by the abundance of pores [87]. SEM photos of human hair before and after adsorption of hexavalent chromium has been shared by Mondal & Basu [21]. The human hair exhibited a layered structure with minimal deformation (Fig. 2.7a), transitioning to a coarse surface after Cr(VI) adsorption (Fig. 2.7b). This change is believed to facilitate the efficient interaction of Cr(VI) with the keratin present in hair [21]. According to SEM images of animal bone AC reported by Nwanko et al. [103], chemical activation involving evaporation of chemical reagent (H_3PO_4) during drying, produces an extensive external surface with irregular cavities and pores for adsorption of material unto them. Additionally, the study noted a significant reduction in carbon content in human hair when heated between 250 °C to 300 °C, compared to controlled heating up to a maximum of 250 °C [74]. The XRD spectrum of ZnCl_2 activated samples at different temperatures indicated an amorphous structure. Additionally, an increase in pore intensity was observed with a rise in temperature, leading to reduced reflection and spectrum expansion [74].

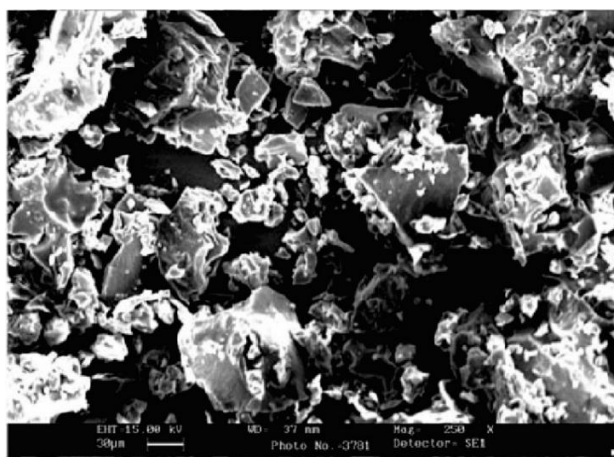


Fig. 2.5 Thermally processed horn-hoof powder SEM micrograph (250x magnification) [59]

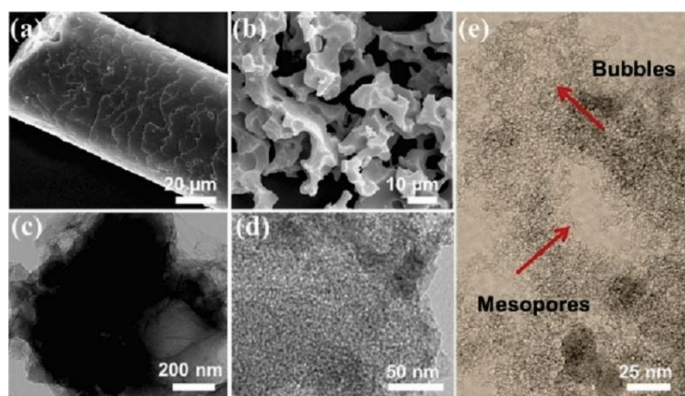


Fig. 2.6 Human hair SEM picture (a), NSC-800 SEM and TEM images (b and c), and the matching HRTEM images (d and e) [87]

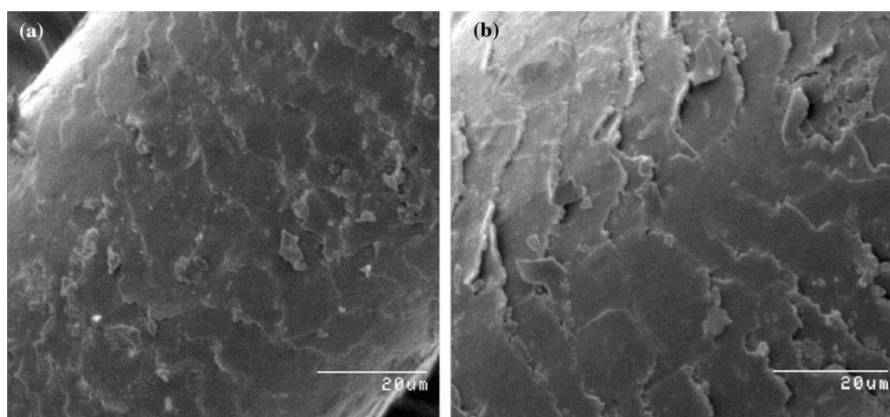


Fig. 2.7(a) Human hair pre-adsorption of Cr(VI) ($\times 1500$) and **2.7(b)** post-adsorption of Cr(VI) ($\times 1500$) [21]

2.5 Appraisal of recent literature

Appraising recent literature on AC derived from animal biowaste reveals a growing interest in utilizing unconventional sources for sustainable and efficient adsorbents. Studies have focused on various aspects, including preparation methods, morphological characterization, and adsorption capabilities. One notable trend is the use of different animal biowastes, such as bones, hair, and feathers, to produce AC with specific properties tailored for various applications. Morphological investigations utilizing methods like SEM and XRD have offered insights into the porous architectures, showing the relevance of pore size and distribution in adsorption effectiveness. Moreover, research have studied the impact of activation temperature and impregnation procedures on the final qualities of AC, showing a quest for improving manufacturing processes. The adsorption capacities and efficiencies reported in recent studies indicate the potential of

animal biowaste-derived AC as effective and sustainable adsorbents for various contaminants [53,57,70,82,84]. However, additional study is needed to examine its scalability, cost-effectiveness [104,105], and environmental effect versus traditional AC sources. It is noteworthy that there is limited documentation on AC derived from animal biowaste before the year 2000, with few records from the last two decades.

However, there has been significant interest in materials such as fish scales [45] wherein, other animal parts haven't received as much attention. As a recent review is available on use of fish scales as source of AC [45], we have not included the same in this report. Out of the 53 papers reviewed, bones received the most attention with 13 studies, followed by hair and feathers with 12 studies, horns with 6 studies, hooves with 4 studies, and snail shells and teeth with 1 study each. Among the target pollutants for removal using AC derived from animal biowaste, heavy metals were the most frequently addressed at 23 reports, followed by dyes at 10 reports, and clinical waste at 1 report. This highlights the concern regarding removal of heavy metal pollutants and the effectiveness of AC.

Maria et al. [106] conducted a study where they produced AC from cow bones and used it for lead (Pb^{2+}) adsorption. Both Langmuir and Freundlich models were employed, revealing correlations; however, the Langmuir model offered a better description of the equilibrium with a higher R^2 value. The initial lead concentrations tested followed the pseudo-second-order (PSO) kinetic model, displaying stronger linear correlation coefficients. The maximum desorption efficiency was obtained with HCl, achieving a recovery rate of approximately 50%, and desorption equilibrium was reached in as little as 3 hours. The presence of acid functional groups on the AC surface was ascribed to efficient cationic exchange [106].

The impact of heat and acid on AC preparation was studied on bones of cow, chicken, donkey, and horse by Nworu Jerome Sunday et al. [82], wherein the superiority of chicken bone AC as an adsorbent was shown over AC from bones of Chicken, cow, horse and donkey. Bone AC yield by acid activation was (48.92%) > horse (48.64%) > donkey (46.34%) > chicken (44.80%) while heat activation gave yield in the order: horse (37.03%) > cow (36.21%) > donkey (34.96%) > chicken (30.18%). Percentage of hardness was seen to be higher on heat activation than on acid activation or for non-activated carbons. The Bulk densities was in the order: cow (0.80g/m^3) > donkey (0.78g/m^3) > horse (0.78g/m^3) > chicken (0.49g/m^3). Ash content was seen to be lowest in chicken bones in the order: non-activated (15.84%) > acid (12.84%) > heat (11.05%).

In another study, chicken bones (CAB) were used to remove organic micropollutants such as o-nitrophenol (o-NP) and p-nitrotoluene (p-NT) from aqueous solutions [55]. When the initial concentration was kept at 5 mg/L, the percentage of organic micropollutant removal by CAB was found to be 77% and 78% respectively for o-NP and p-NT. At a concentration of 20 mg/L, removal rate was reported to be 68% and 80% respectively for o-NP and p-NT. The adsorption efficacy of CAB was shown by kinetics data analyzed using five adsorption kinetic models: an intraparticle diffusion equation, Elovich and Avrami equations, pseudo-first- and second-order equations. Amongst these, the best fit was shown by the intraparticle diffusion equation [55].

Tonetti et al. [59] utilized biosorbent derived from thermally-treated “horn–hoof” powder in wastewater treatment for the removal of copper (II) ions. The adsorption isotherm was calculated via Langmuir model while a PSO model involving an endothermic process was suggested by thermodynamic and kinetic data. The effect of the temperature, pH, initial metal ion concentration, contact time and biosorbent dosage were also studied in relation to the biosorption characteristics of Cu(II) ion on the AC. While the optimum pH value for adsorption of Cu(II) ions was found to be 5.5, total time taken to reach the adsorption equilibrium was 48 hours [59].

In yet another report by Mondal et al. [21], the removal of Cr(VI) using human hair derived AC revealed a highly pH sensitive Cr(VI) adsorption maximum at pH 1.0. While adsorption equilibrium was analyzed with Freundlich, Langmuir and Dubinin–Radushkevich isotherm models, kinetic study revealed PSO model and thermodynamic properties showed dominant physisorption. Superiority of the human hair AC was comparatively validated with Langmuir adsorption capacity of 9.852 mg g^{-1} [21].

Ahmad et al. [48] used H_3PO_4 and NaOH activated egg shell derived carbon for photocatalytic decay of dye. H_3PO_4 demonstrated higher degradation efficiency, while free radicals and superoxides played a pivotal role in the decolorization of methylene blue. The adsorption efficiency of the AC increased with an increase in time. XRD patterns and SEM images revealed the hexagonal structure and irregular shapes of the carbon.

Altuntas et al. [74] and Liu et al. [58] independently investigated the synthesis and characterization of AC derived from waste human hair and animal hair. Waste human hair was impregnated and then carbonized at temperatures ranging from 250–300 °C.

Morphological studies of the hair-derived AC were conducted using FT-IR, SEM, XRD, and Raman spectroscopy.

A different research effort investigated AC derived from human hair for its ability to selectively remove Fe(III). The results showed that ACH600 could adsorb up to 15.54 mg/g of Fe(III), with a selectivity coefficient of 8.3 and a removal rate of 98.6%. Nitric acid was employed as an eluent for regenerating the AC, emphasizing its potential for reuse [107].

Adsorption of heavy metal ions such as Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} and Ni^{2+} was done using AC derived from eggshell and feather. To enable easy separation from water media, magnetization of the prepared AC was done resulting in an iron oxide magnetized ESCFC (IOM-ESCFC) whose efficacy was validated in terms of its high sorption speed, maximum mono-layer sorption capacities and thermodynamic studies [52].

Mashrafi et al. [108] reported on the adsorption performance of hydroxyapatite (HAp) for eliminating Congo Red (CR) dye using chicken eggshells. (XRD) analysis verified the presence of biphasic hydroxyapatite (HAp) with approximately 15.5% beta-tricalcium phosphate (b-TCP). Elemental composition was assessed using XPS and EDX analysis. Field emission scanning electron microscopy (FESEM) revealed that the particles exhibited both plate and spherical shapes, a characteristic further supported by transmission electron microscopy (TEM) images. Maximum adsorption capacity (q_{max}) was determined to be 9.64 mg g⁻¹, fitting best to the Langmuir isotherm model with a non-linear fit ($R^2 = 0.98$).

2.6 Adsorption Mechanisms

Heavy metals adsorption by AC may be divided into five major processes, as depicted in Fig. 2.8. Physical adsorption is a method wherein ions of heavy metals attract to and concentrate within the pores of an adsorbent material without creating chemical interactions and is largely controlled by the size of the pore variation and surface area of the AC.

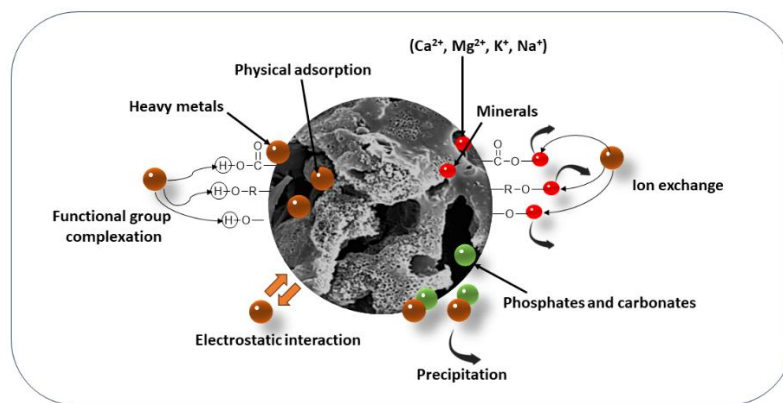


Fig. 2.8 Heavy metal ion adsorption mechanism by AC

Higher abundance of mesopores and larger surface area enable the dispersal of contaminants, hence increasing the total physical adsorption and its related kinetics. Ion exchange is a mechanism where ions swap via protonated oxygen-containing functional groups (like $-OH$, $-COOH$) and divalent metal cations (M^{2+}) [109]. Electrostatic interaction happens when an adsorbent surface with a negative or positive charge causes an electrostatic attraction force, drawing oppositely charged metal ions to it. Previous work on heavy metals removal using AC have shown electrostatic interaction as a possible adsorption mechanism [110]. Notably, various AC can have surfaces with diverse forms of charges. Furthermore, pH and pH_{zpc} have an influence on the electrostatic interaction.

Studies have noticed the electrostatic interaction via distinct protonated or deprotonated functional groups occurring on the surface of the AC adsorbent and the oppositely charged metal ions. For example, Interactions via negatively charged metal ions $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-} and the positively charged NH_4^+ [111]. As a result, these interactions allow the surface complexation process to produce multi-atom structures [112]. Numerous studies have indicated that one of the following metal cations and oxygenated functional groups may undergo a complexation process [113,114]. The majority of coprecipitation takes place in aqueous solutions containing significant levels of ions from heavy metals. Moreover, on the surface of AC adsorbents, the phenomenon might recur. For example, the production of Cd^{2+} to some extent. In some cases, the reduction procedure has a significant impact on heavy metal extraction [112].

2.7 Factors affecting adsorption capacity

Although industrial wastes are the major causes of heavy metal pollution, several studies have proven the equally large threats caused by the presence of such contaminants in

diverse water sources. Because of the different characteristics and conditions of the water, the usage of adsorbents in removing heavy metals from these unique contaminated water sources can vary in terms of effectiveness and efficacy. In addition, the wastewater may contain acids, compounds with carboxyl groups, nitrogen, halogens, or high-sensitivity bacteria (such as anammox) that can act as inhibitors. These compounds, which have negative charges, have a tendency to retain heavy metals (which have positive charges) in the wastewater environment. In order to accurately assess the adsorption capacity of a certain treatment, it is essential to take into account the characteristics of heavy metals and the adsorbent properties in different physiochemical conditions found in the water source being examined. The quality of water is primarily determined by characteristics such as pH, temperature, and ionic strength.

2.7.1 Chemical properties of pollutants

Unregulated discharge of wastewater from industrial activities is a major cause of heavy metal pollution in the environment. Due to their inherent characteristics, heavy metals have the ability to resist natural decomposition and build up over time, which presents a serious environmental problem. Poisoning from heavy metals arises as a result of the inadvertent ingestion of contaminated food and water by people and animals. Accumulation of excessive amounts of heavy metals in the human body can cause damage to internal organs and result in severe illnesses. Living organisms require trace amounts of metallic elements, such as zinc (Zn), copper (Cu), and chromium (Cr), to facilitate proper metabolism. However, exceeding the prescribed safety thresholds for these metals can have severe detrimental effects on human life.

2.7.2 Ionic strength: The ionic strength of the water supply can considerably alter the behaviour of heavy metals and their possible interaction with the adsorbent materials throughout the treatment process. Higher chloride concentrations in water can expedite the development of neutrally or negatively charged heavy metal-chloride complexes that are water-soluble and more difficult to remove [115]. As reported by Thuan et al. [116], Cu^{2+} and Ni^{2+} adsorption effectiveness decreased as ionic strength increased due to more active production of heavy metal-chloride complexes. This results in a reduced affinity of the adsorbents for the metal ions. In another study, Wang et al. [117], investigated trace metals present in river estuaries and discovered a substantial positive link between salinity and dissolved metal concentrations such as copper, cadmium, and zinc.

Furthermore, enhanced electrostatic interactions between heavy metals and adsorbent surfaces can cause changes in heavy metal behavior and potential adsorption capacity due to elevated levels of ionic strength in aqueous solutions. Based on surface chemistry basics, one may observe the reduction in electric double layer generated by changes in electrostatic interactions from rising ionic strength [118]. This condition eventually leads to a reduction in the adsorbents' ability to absorb heavy metals. Yang et al. [119] observed that increasing the ionic strength of the solution from 0.01 to 1.0 M enhanced As^{3+} and Ni^{2+} elimination by up to 25%.

2.7.3 Adsorbent size: The porous structure of biomass-derived AC enhances its effectiveness as an adsorbent, with the arrangement and size distribution of its pores being key factors in determining its capacity to adsorb heavy metals [120]. It exhibits a range of pore sizes, which are visible under an optical microscope, and down to those comparable to the size of the adsorbed molecules. Micropores serve as the primary adsorption sites, while mesopores aid in intraparticle diffusion, accelerating the adsorption process. The size of these pores plays a significant role in the AC's ability to adsorb heavy metals. Macropores, often referred to as transport pores, act as channels for adsorbate molecules during adsorption. The molecules first enter through the macropores, then travel through the mesopores, ultimately reaching the micropores, where they are adsorbed within the AC particles. Mesopores, also referred to as transition pores, are smaller than macropores yet substantially larger than the adsorbate molecules. The adsorption process typically starts with the formation of a single molecular layer, which gradually builds into a multi-layered structure. This process continues until the adsorbate molecules reach the smallest pores in the carbon, known as micropores, which have an exceptionally small effective radius, providing the primary sites for adsorption [79,121].

2.7.4 Adsorbent dosage: One crucial factor that significantly influences adsorption performance is the adsorbent dosage, or the quantity of adsorbent material used in the system. A thorough understanding of the relationship between adsorbent dosage and adsorption capacity is essential for optimizing adsorption-based processes [122]. Adsorption capacity, defined as the maximum amount of adsorbate retained per unit mass of the adsorbent, is commonly evaluated using isotherm models such as the Langmuir and Freundlich models. Numerous studies have shown that adsorption capacity is affected by multiple variables, including the adsorbent's physical and chemical characteristics, the properties of the adsorbate, and the specific conditions under which

adsorption occurs [123]. Thus, the dosage of the adsorbent plays a pivotal role in determining the available surface area and the number of active sites available for adsorption. As the adsorbent dosage increases, so too does the surface area and the availability of active sites, resulting in a greater adsorption capacity up to a certain threshold. However, beyond this optimal dosage, the adsorption capacity may begin to level off or even decline. This reduction can be attributed to phenomena such as particle aggregation, which reduces the effective surface area and limits the overall efficiency of the adsorption process.

2.7.5 Initial concentration: Considering that the adsorbents have not reached their maximum capacity for absorption, the initial concentration of heavy metal may positively affect their ability to remove the metal. Typically, an elevated starting concentration results in a more powerful attraction force that pulls metal ions from the liquid solution onto the carbon-based adsorbent material's surface [113]. Subsequently crossing a particular threshold, a larger initial concentration hinders further adsorption due to the smaller number of accessible and vacant binding sites on the adsorbent surface. Elevated initial heavy metal concentrations will limit the adsorbent's removal efficacy later in the operation. Furthermore, the beginning heavy metal concentration effects the general model fitness of the selected adsorption isotherm. The best-performing model in terms of fitness might alter when the initial concentration rises, prompting the move from single to multimolecular layer adsorption.

2.7.6 Contact time: The adsorption process plays a critical role in various industries such as water treatment, air purification, and catalysis, where the interaction between a solid surface and a fluid phase (liquid or gas) is employed to remove or concentrate specific components. The adsorption capacity of an adsorbent is heavily influenced by factors related to contact time. Initially, adsorption occurs rapidly due to the large number of active sites available on the adsorbent surface, resulting in a swift rise in capacity [121]. However, as contact time increases, more of these sites become occupied, causing the rate of adsorption to gradually slow down. Eventually, the system reaches equilibrium, where further adsorption is minimal regardless of additional time [124]. The diffusion rate of adsorbate molecules into the adsorbent's internal pores is another crucial factor.

Over time, the slower diffusion into micropores can limit the overall adsorption efficiency. Prolonged contact may also lead the adsorbent to reach its saturation point,

where all active sites are fully occupied, and no further adsorption is possible. According to the Langmuir adsorption model, the adsorption rate is directly related to the number of unoccupied sites on the adsorbent's surface. As contact time increases, adsorbate molecules have more opportunity to interact with these available sites, which in turn enhances adsorption capacity. Optimizing contact time is therefore essential for maximizing adsorption efficiency in industrial applications [61].

2.7.7 pH level: The pH which controls the degree of H^+ concentration in the aqueous solution, has a major influence on ion exchange and electrostatic interaction during the adsorption process. The pH_{zpc} values, which capture the pH value when the zeta potential of adsorbents equals zero, could vary substantially depending on the nature of AC. In the event that the pH is lower than the pH_{zpc} the higher H^+ concentration permits more robust ion exchange with heavy metal ions and promotes the protonation of functional groups ($-NH_2$, $-OH$) on the adsorbent surface, thereby yielding a more positively charged surface. As a result, anions (e.g. $HCrO_4^-$) adsorb better, but heavy metal cations are repelled due to electrostatics [125]. In contrast to lower pH values, pH levels over pH_{zpc} allow the return of negative charges to functional groups, which has an inverse effect on cations and anions [126]. Generally, depending on whether cations or anions are removed from aqueous solutions, pH_{zpc} should be more acidic or alkaline.

In addition, ions of heavy metals can interact with H^+ , resulting in distinct ionic forms with varied degrees of attraction for surface functional groups, influencing total adsorption effectiveness. Previous research on higher pH solutions has demonstrated that carboxyl groups influence the adsorption of heavy metal ions onto the surface of AC [112,126,127]. A presence of carboxylic acid on the surface of AC facilitates acidic dissociation and the generation of chelating agents in complexes produced by the interaction of heavy metal ions with surface functional groups.

2.7.8 Coexisting ions: Presence of co-existing anions and cations with different ionic strengths could impact the removal of heavy metal ions by AC materials in three ways [128]. The affinity of the binding sites on the surface of the adsorbent onto heavy metal ions in binary or multi-system is directly influenced by the competing behaviors of the cations [129] and is controlled by the nature of a charge and the hydrated radius. For instance, it is clear that coexisting heavy metal ions in an identical location fight for the restricted number of adsorption sites. As a result, the same adsorbent may be expected to

have a reduced degree of adsorption effectiveness in a system with more than two kinds of ions (cations or anions), as compared to a single heavy metal ion system.

Park et al. [130] suggested a lower ability for adsorption of heavy metals in a mixed solution having both Pb^{2+} and Cd^{2+} than a system comprising a single of the aforementioned components. Next, increasing quantities of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} in the aqueous solution compete directly with heavy metal ions, resulting in a decrease in overall adsorption effectiveness. For example, the presence of SO_4^{2-} promotes Cr^{6+} precipitation and reduction processes, while HCO_3^- reduces Cr^{6+} removal efficiency and Fe valence transition [131] whereas SO_4^{2-} reduces Cr^{6+} adsorption by AC due to greater competition and lower attraction compared to Cl^- and NO_3^- [132].

2.7.9 Temperature: Temperature is a critical component that has to be taken into consideration while studying the overall process of adsorption. At higher temperatures, the lower solution viscosity allows for greater dispersion of the adsorbate molecules throughout the surface of the adsorbents, resulting in improved adsorption capacity which can be decreased by elevated temperatures in an exothermic process, while in an endothermic reaction, the opposite is true. As a result, metal ions at binding sites on the adsorbent surface may become more unstable. Therefore, the amount of metal ions that may be stably connected to AC decreases as the solution temperature rises. Moreover, in an exothermic adsorption process, a lower attraction in the electrostatic connection between the adsorbent and ions was seen at high temperatures [133]. Additionally, a higher frequency of interaction between the metal ions and the binding sites on the adsorbent surface is anticipated as a result of the more active ionic mobility [112].

2.8 Adsorption as a process

Adsorption techniques based on solid sorbents are often applied to remove various types of chemical pollutants from water, particularly those that are essentially unaffected by biological wastewater treatment methods. However, of all the sorbent materials investigated, AC is the most recommended for the removal of pollutants from effluent [9].

Table 2.2 provides a non-exhaustive list of AC applications in wastewater treatment. AC is created by the thermochemical conversion of organic molecules at high temperatures in the absence of oxygen. The raw material, production technique, and conditions all have a considerable impact on the adsorption efficacy [9]. Their shape and size dictate whether

they are categorized as granules, powders, or pellets. AC exhibit well-developed micro, meso, and macropores with a range of surface functional groups, as illustrated in Fig. 2.9.

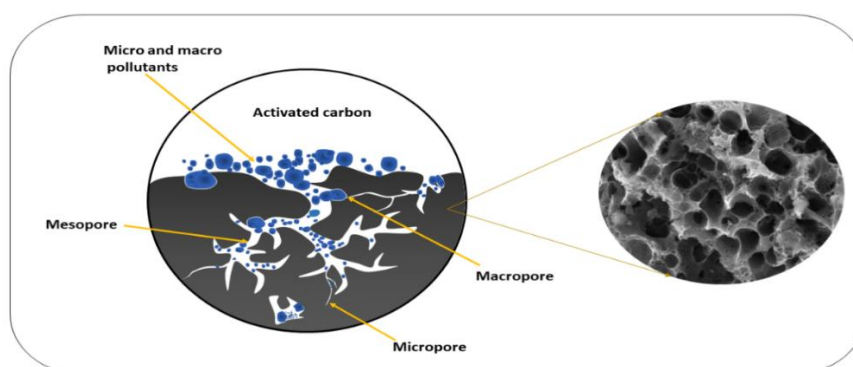


Fig. 2.9 AC displaying well-developed pores

Table 2.2 Overview adsorption capabilities of animal biosorbents to various pollutants

Animal biowaste	Pollutants	Adsorption capacity (mg/g)	Best adsorption isotherm	pH	References
Cow hooves	Methylene blue	5.71	Freundlich	2	[134]
Egg shells	Phenol	192	Prausnitz–Radke	5.7	[135]
Goat teeth	Pb ²⁺	62.32	Langmuir	5	[84]
Chicken feather	Tetracycline	388.33	Langmuir and Elovich	4	[51]
Chicken egg shells	Hydrogen sulfide	289.3	Freundlich	4.5-5.5	[136]
Cow manure	Methylene blue	501	-	-	[67]
Animal bone	Potassium permanganate	1.25	Freundlich	5.0	[44]
Cow dung	Perchlorate	1.787	Langmuir	-	[86]
Chicken bone part	Pb	263.2	Langmuir	5	[137]
Chicken feather and egg shells	Cd ²⁺	76.3	Langmuir	5.5	[52]
	Cu ²⁺	56.5			
	Pb ²⁺	113.3			
	Ni ²⁺	32.6			
	Zn ²⁺	45.5			
Pig bone	Pb ²⁺	120	Langmuir	6	[89]
	Cu ²⁺	30			

Cow dung	Congo red	12.46	Langmiur	7	[138]
Chicken manure	Phenol	106.2	Langmuir	7.0	[75]
	2,4-dinitophenol	148.1			
Cow dung	Fluoride	15	Freundlich	7-8	[60]
Bovine bone	Cu ²⁺	83.71	Elovich	5.5	[139]
Cow dung	Cd ²⁺	5.8800	-	-	[140]
Goat dropping	Brilliant blue G 250	270.3	Langmuir	3.98	[94]
Cow dung	Phenol	518.89	Freundlich	6	[97]
Cow dung	Rhodamine B	951	Freundlich		[95]
Chicken eggshell	Pb ²⁺	25.189	Langmuir	5	[98]
Chicken bone	Curcumin	4.582	Jovanovic	-	[141]
Chicken eggshell	Congo red	9.64	Langmuir	5	[108]
Sheep and goat dung	Methylene blue	24.81	Langmuir	6	[61]
Cow manure	Cu ²⁺	78.63	Langmuir	6	[142]
Bovine bone	Boron	0.24	Freundlich	7.72	[143]
Chicken feather	Cr ⁶⁺	90.90	Langmuir	2	[99]
Cow bone	Methyl red	7.2	Freundlich	6	[144]
Bovine bone	Cd ²⁺	78.969	Langmuir	-	[145]
	F ⁻	38.724			

2.9 Equilibrium isotherm and kinetics modeling

Different isotherm modeling has been proposed for most of the pollutant sorption studies onto animal biowastes AC. A summary of best fit isotherm and kinetic model is presented in Table 2.3. Majority of the studies stated the Langmuir, Freundlich isotherm and pseudo second order (PSO) as the best fit. Freundlich isotherm was reported as the best fit for Methylene blue dye with $R^2 = 0.9961$ [61], Cu²⁺ with $R^2 = 0.93$ [146], Cr⁶⁺ with $R^2 = 0.9886$ using H₃PO₄ [70], methylene blue using CaCl₂ with $R^2 = 0.969$ [147], Cr⁶⁺ with $R^2 = 0.992$ [21], and H₂S with $R^2 = 0.9874$ [136]. Several studies have also shown Langmuir isotherms as the best fit in respect of Cu(II) with R^2 of 0.992 [59]; Cd²⁺ with R^2 of 0.9982 [52]; Cu²⁺ with R^2 of 0.999 [89]; phenol with R^2 of 0.989 [135]; Acid blue

193 with R^2 of 0.998 [148]; Pb^{2+} with R^2 of 0.993 [106]; Cr^{6+} with R^2 of 0.912 [21]; removal of Pb^{2+} using goat hair, human hair and sheep wool with R^2 of 0.09, 0.87, and 0.58 respectively, norfloxacin and acetaminophen with R^2 of 0.9934 and 0.409 respectively [89]; methylene blue with R^2 of 0.996 using $CaCl_2$ as activating agent and 0.957 using $ZnCl_2$ as activating agent [147]. Various kinetic models were used for studying the equilibrium isotherm and kinetic modelling of Cu^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} adsorptions. Among the many models used, PSO and Ritchie second-order kinetic models revealed better fits of the experimental results based on the statistical indices (χ^2 and HYBRID values) as well as the R^2 values [52]. Ortho and para nitrotoluene (o-NT and p-NT) were studied using intra-particle diffusion with R^2 of 0.9807 and 0.9816 respectively, Elovich modelling with R^2 of 0.9674 and 0.9532, Avrami models with R^2 of 0.9878 [55]. N_2 adsorption-desorption isotherm was fitted best for Methylene blue with R^2 of 0.96675 [71], and Cd^{2+} with R^2 of 0.9983 [52].

Table 2.3 Summary of best fit isotherm model and kinetic model

Pollutants	Best fit isotherm model	Best fit kinetic model	Reference
H_2S	Freundlich isotherm	PSO	[136]
Pb^{2+}	Langmuir isotherm	PSO	[84]
Tetracycline	Langmuir isotherm	Elovich	[51]
Chromium (VI)	Langmuir isotherm	PSO	[21]
Phenol	Langmuir isotherm	PSO	[75]
Cu^{2+}	Freundlich isotherm	Elovich	[139]
Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Ni^{2+}	Langmuir isotherm	PSO	[52]
Pb^{2+} , Cu^{2+}	Langmuir isotherm	PSO	[89]
Brilliant blue G 250	Langmuir isotherm	PSO	[94]
Phenol	Freundlich isotherm	PSO	[97]
Rhodamine B	Freundlich isotherm	PSO	[95]
Methylene blue	Langmuir isotherm	PSO	[61]
Curcumin	Jovanovic isotherm	-	[141]
Cr(VI)	Langmuir isotherm	PSO	[99]
Congo red	Langmuir isotherm	PSO	[108]
Pb^{2+}	Langmuir isotherm	PSO	[98]
Methyl red	Freundlich isotherm	PSO	[144]
Cu^{2+}	Langmuir isotherm	-	[142]

Boron	Freundlich isotherm	PSO	[143]
Cd ²⁺	Langmuir isotherm	PSO	[145]
F ⁻			

2.10 Thermodynamic studies

A cursory examination of the literature reports indicates that very few groups have undertaken the thermodynamic investigation of their adsorption experiments on animal generated AC thus indicating the amount that needs to be investigated in this field. Thermodynamic studies are utilized to analyse several components of the adsorption process, including change in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). The enthalpy change (ΔH°) indicates thermal behaviour, whether exothermic or endothermic, whereas the Gibbs free energy change (ΔG°) indicates the spontaneity of the adsorption process.

In addition, the system's disorderliness or its reversibility is indicated by the entropy change (ΔS°) [45]. A negative ΔG° value implies an elimination process via adsorption at higher temperatures is spontaneous, practical, and consequently more desirable [52]. Few reports of thermodynamic studies are being discussed as follows. C. Tonetti et al. [59] has explored the uptake of Cu(II) using horn-hoof powder while J.O. Tijani et al. [149] has reported a feasible but non-spontaneous (+ve ΔG°) elimination of Ni (II), Mn (II) and Cd (II) using cow horn AC. Asep et al. [141] has also studied the removal of curcumin dye using chicken bone. Spontaneity of a system means that a process occurs without any external input to the system, which herein means that even in the absence of a catalytic incentive, an extra chemical, physical or thermal intervention, sorption of the pollutant happens on introduction of the biosorbent into the pollutant solution. Spontaneity was observed for uptake of Cu(II) [89], phenol [135], and for heavy metal ions like Cd²⁺, Pb²⁺, Zn²⁺, Cu²⁺ and Ni²⁺ uptake [52]. When the adsorption process is favored by a lower temperature, the process is said to be exothermic while the opposite is true for endothermic sorption. Uptake of Phenol [135], methyl red dye [144], Mn [150], and Cr(VI) [21] was shown to be an exothermic sorption process. Endothermic sorption was also observed for uptake of Ni (II), Mn (II), Cd (II) [149], Cr(VI) [99], metal ions like Cd²⁺, Cu²⁺, Pb²⁺, Zn²⁺ and Ni²⁺ [52], cucumin dye [141], copper ions [59]. Similarly, for entropy change, increased randomness at the solid/solution interphase is shown by a positive value (+ve ΔS°) which also indicate a better adsorbate-biosorbent affinity.

Alternatively, a negative entropy value (-ve ΔS°) specifies that the sorption process is enthalpy driven [45].

2.11 Future prospect

Animal biowaste based AC offers several prospects for future study and application. One of the key areas of focus could be the development of tailored adsorbents for specific pollutants, leveraging the unique properties of different animal biowastes. Several possible uses for ACs have been researched and verified in laboratory tests.

However, further research into the potential industrial-scale production and commercial applications of AC is desperately needed. One potential drawback of using ACs as adsorbents is that some pollutants, including as salt, nitrate, fluoride, and viral and bacterial infections, are not attracted to the carbon atoms. Thus, future studies might look into potential process enhancements or modifications to strengthen AC's efficiency against these unique contaminants. Once at capacity, the contaminated air conditioners have outlived their useful lives and should be replaced or reactivated. Therefore, a thorough assessment of AC's possibility of long-term applications is necessary to ascertain its pertinency as a wastewater treatment strategy.

When assessing AC, cost production is a pivotal factor to take into account. As long as the manufacturing cost is reasonable, AC with a high density of mesopores and a wide surface area is generally much more suited as an adsorbent. Additionally, further exploration into the synthesis of composite materials could lead to enhanced adsorption capabilities, making these materials even more effective in water treatment applications. Another option for future study is the discovery of innovative activation techniques that might increase the efficiency and sustainability of the production process.

This could involve the use of alternative activation agents or techniques that reduce energy consumption and waste generation. The development of regeneration methods that allow for multiple uses of the AC could significantly enhance its cost-effectiveness and environmental sustainability. Moreover, the integration of animal biowaste-based AC into existing water treatment systems and processes could be explored which involve the design of hybrid systems that combine adsorption with other treatment methods, such as filtration or oxidation, to achieve higher levels of pollutant removal. Overall, the future of animal biowaste-based AC holds great promise for addressing water pollution challenges. Prolonged investigation and creativity in this domain possess the capability

to transform methods of treating water, providing long-term and efficient remedies for safeguarding our water reserves.

The majority of heavy metal removal research has mainly focused on batch adsorption until recently. Scholars have grounds to assume that the developing potential of AC as a highly effective adsorbent will motivate future research on column studies and industrial bed type adsorption. The existing circumstances are particularly suitable for implementing large-scale manufacture and usage of air conditioners built from diverse forms of waste biomass. Lastly, it is worth mentioning that the majority of AC research in water pollution treatment have not widened their emphasis beyond heavy metals to embrace additional non-traditional pollutants including non-metallic organic compounds and pesticides.

The proposals given above offer possible study areas on the present issue that might potentially generate useful findings in contributing to the ongoing advancement in the development of AC. Future study attempts may comprise a pilot-scale inquiry to investigate the efficacy of the specified AC in treating industrial wastewater. Despite the existing deficiencies and challenges in the research, development, and implementation of AC, further advancements are strongly justified due to the recent significant breakthrough in the sector. In addition, it is vital to extensively examine the application of biomass waste-derived AC as a cost-efficient adsorbent compared to other costlier options for the treatment of water contamination. Furthermore, using biomass waste as the primary fuel for the production of AC is considered a part of the larger waste reduction plan and it's critical to develop a variety of modified AC-based adsorbents that remove heavy metal species from aqueous solutions with remarkable effectiveness.

Conclusion

From an environmental standpoint, biomass wastes are a readily available and environmentally desirable form of feedstock for the manufacturing of AC. Producing AC from biomass waste is less expensive and has the potential to replace expensive coal-based AC. This rationale informs the current work, which focuses on the possible utilization of biomass waste-derived AC as adsorbents in the remediation of environmental contaminants. It may be created from several types of biomass waste in a number of processes, while chemical activation is the favoured approach as it shortens the preparation process as well as lower activation temperature. The use of animal biowaste-based AC as biosorbents for water pollutants holds promise as a long-term solution to water pollution concerns, proving the efficiency of these materials in removing various toxins from water. Promising findings for the manufacture of AC with a large surface area, high microporosity, and selectivity were obtained. For many applications, animal waste might be utilized instead of commercially generated AC since it is very affordable, locally accessible, and effective. This mini-review focuses on recent improvements in biosorption utilizing animal biowaste-based AC, ignoring the frequently reported fish scale-derived AC. Bones have been the most intensively explored animal component for the synthesis of AC, followed by hair and feathers. Heavy metal removal has been the most extensively researched target water contaminant. The preparation of AC typically involves washing, drying, grinding, and sieving, followed by carbonization and/or modification. In kinetic research, the Freundlich isotherm and PSO model are frequently used as best fits. This review also focuses on limited thermodynamic studies on Gibbs free energy change (ΔG°), entropy change (ΔS°), and enthalpy change (ΔH°). The future of this research field is promising, with potential for further exploration and innovation. Developing nanostructured and composite materials, investigating regeneration and reusability, developing a better knowledge of adsorption processes might lead to substantial advances. Despite the wide interest in plant-based AC, animal-based counterparts have not received similar attention, although it has high sorption efficiency. Overall, it is a less expensive, more ecologically friendly, and longer-lasting alternative to standard water treatment adsorbents. Continued research and development are crucial for fully realizing the potential of these materials in addressing water pollution and ensuring access to clean water for all.

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CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF ACTIVATED CARBON DERIVED FROM MIXED FISH SCALES.

This chapter presented the synthesis of activated carbon from mixed fish scales through carbonization followed by chemical activation (KOH) with different ratios to enhance its surface area and porosity. The prepared activated carbon was systematically characterized using BET surface area analysis, FTIR spectroscopy, XRD, and SEM to evaluate its textural, structural, and morphological properties. The results confirmed the successful development of a highly porous material with functional groups favorable for adsorption, establishing its potential as an efficient adsorbent for subsequent adsorption studies.

3.1 Introduction

Activated carbon (AC) is a widely used adsorbent known for its effectiveness in removing diverse contaminants from both air and water environments. With the growing environmental challenges brought about by rapid industrialization, the demand for efficient and sustainable treatment technologies has increased significantly. It has demonstrated strong adsorption capacity for pollutants such as harmful bacteria, dyes, heavy metals, and pharmaceuticals [1]. The synthesis of AC typically involves two major stages: carbonization and activation. Carbonization refers to the thermal decomposition of carbon-rich precursors under an inert atmosphere, resulting in a char that retains the basic structure of the original material but with limited surface area [2,3].

Traditionally, the majority of AC production has relied on plant-based biomass such as coconut shells, wood, sawdust, rice husks, and agricultural residues [4]. These materials are abundant, renewable, and cost-effective. However, with increasing concerns over sustainability and circular economy, attention has turned toward underutilized waste streams, especially those derived from animal-based biowastes, for the development of functional carbon materials. While plant-based materials have long been used for AC production due to their availability and carbon content, animal-derived biowastes are emerging as promising alternative precursors.

Using animal biomass also supports the concept of zero-waste and circular economy, by converting non-edible, discarded animal byproducts into high-value materials. In contrast to agricultural residues, which are already widely used or repurposed as fertilizers, fuels, or livestock feed, animal biowastes are often underutilized and pose environmental disposal challenges. Therefore, the choice of animal waste (fish scales) not only leverages their inherent material advantages but also addresses waste management issues, offering a sustainable and value-added solution for AC production. Choosing fish scale waste as a precursor aligns with the goals of waste valorization, resource recovery, and sustainable material development. Utilizing such animal biowastes not only reduces environmental burdens associated with organic waste disposal but also provides a cost-effective route for producing high-performance activated carbon. Moreover, fish scale-derived activated carbon has been reported to exhibit promising adsorption capacities for heavy metals, dyes, and other aquatic pollutants due to its unique physicochemical properties.

This study focuses mixed fish scales AC, employing chemical activation using potassium hydroxide (KOH). The activation parameters, including temperature and chemical ratio,

were optimized to achieve high surface area and desirable porosity. This chapter provides a detailed account of the synthesis methodology, rationale behind precursor selection, and subsequent characterization of AC. The prepared material was further utilized in adsorption studies involving various pollutants, as discussed in later chapters.

3.2 Assortment of raw materials for the synthesis of AC

Mixed fish scales (MFS), comprising scales from various commonly consumed freshwater and marine fish species, were collected as biowaste from the local fish market situated in Mokokchung town, Nagaland, India. The geographical coordinates of the collection site are approximately 26°19'38" North latitude and 94°31'26" East longitude. These scales, typically discarded during routine fish cleaning processes, were chosen as a low-cost and sustainable precursor for AC synthesis due to their abundance and underutilization.

Upon collection, the raw MFS were initially subjected to a thorough pre-treatment process to remove residual flesh, fats, blood, and any adhering impurities. The scales were first rinsed under running tap water to eliminate loose dirt and debris. Following this, they were soaked in a mild detergent solution for 3 to 4 h to help dissolve organic matter and oily substances. After soaking, the scales were again washed thoroughly with tap water to remove the detergent and remaining impurities. A final rinse using distilled water was performed to ensure the complete removal of any residual salts or chemicals, thereby preparing the sample for subsequent processing. After the cleaning procedure, the washed fish scales were spread evenly on clean trays and left to dry under direct sunlight for a period of 2 to 3 days. Sun drying was carried out under ambient conditions to reduce the moisture content and prevent microbial degradation, facilitating easier handling and storage before further treatment and pyrolysis.

3.3 Preparation of AC

The adsorbent in the current study was carried out in two main stages: carbonization of the raw material and chemical activation of the resulting char. These steps were systematically designed to enhance surface area and porosity of the final AC product for efficient adsorption performance. In the initial step, the pre-cleaned and sun-dried mixed fish scales (MFS) were subjected to carbonization at temperatures ranging from 500 to 900 °C. The carbonized product obtained after this step was then allowed to cool down at 25 °C. Once cooled, the carbonized fish scales were crushed using a mixer grinder to break them into fine powder. This powder was then sieved through a 212 µm mesh sieve

tray to ensure uniform particle size suitable for further processing. The resulting sieved sample was designated as mixed fish scale unactivated carbon (mFSUC) and stored in airtight containers for subsequent activation. The carbonization temperature was systematically optimized based on proximate analysis (moisture, volatile matter, ash content and fixed carbon) to identify the optimum condition, considering both yield and the physicochemical properties of the prepared carbon.

In the second step, the charcoal prepared at the optimized pyrolysis temperature was subjected to chemical activation. The activation of mFSUC was carried out using KOH as the activating agent with varying mass ratios of carbon to KOH (1:1, 1:2, and 1:3) to investigate the influence of KOH concentration on the physicochemical properties of the resulting activated carbon. A fixed amount of mFSUC was impregnated with the corresponding KOH solutions under continuous stirring at ambient temperature for 2 hours to ensure uniform chemical impregnation. The impregnated samples were then dried at 105 °C for 24 h in a hot air oven to eliminate moisture and enhance activation efficiency during pyrolysis.

The dried, KOH-impregnated sample was then transferred into a muffle furnace and pyrolyzed at 500 °C. The heating rate was carefully controlled at 10 °C per minute, starting from ambient temperature to the target temperature of 500 °C. The sample was maintained at this temperature for 60 minutes to complete the activation process. This step facilitates the development of micro- and mesopores as the KOH reacts with carbon, enhancing the specific surface area and pore volume of the adsorbent.

After activation, the sample was cooled to room temperature and subjected to a rigorous washing process to remove residual activating agents and inorganic salts. The AC was washed several times with 0.1 M hydrochloric acid (HCl) followed by repeated rinsing with distilled water until the filtrate attained a neutral pH, indicating the removal of all acidic and basic residues. The clean, activated carbon sample was then dried overnight at 105 °C in a hot air oven. The final product was labeled as mixed fish scales AC (mFSAC) and stored in clean, airtight glass containers to prevent contamination and moisture absorption prior to further physicochemical characterization and adsorption studies.

3.4 Physico-chemical characterization of AC

In this study, both the physical and chemical properties of the prepared AC were evaluated using a range of techniques and analytical instruments. Proximate analysis was carried out in accordance with ASTM guidelines [5]. Ultimate analysis was performed to

assess the elemental composition, while the point of zero charge was determined using the batch equilibrium method. In addition, various analytical instruments were employed to comprehensively characterize the activated carbon.

3.4.1. Proximate analysis

This analysis was carried out by heating the AC at different temperatures to evaluate its moisture content, volatile matter, fixed carbon, and ash content. The detailed experimental procedures for these tests are described below:

3.4.1.1 Moisture content

Moisture content is a crucial factor in characterizing activated carbon, as it impacts adsorption efficiency and experimental accuracy. It represents the percentage of water, either physically adsorbed or loosely bound, within the carbon's structure. Excess moisture can block active sites and distort measurement accuracy, making its control and quantification vital for reliable adsorption results. To determine the moisture content, a clean silica crucible was first preheated at 110 °C for 1 hour to eliminate any residual moisture. After cooling to room temperature in a desiccator, one gram of AC sample was accurately weighed and placed into the pre-weighed crucible. The crucible containing the sample was then placed in a hot air oven and dried continuously. The sample was reweighed at 10-minute intervals until a constant weight was achieved, indicating complete moisture removal. The moisture content was then calculated as the percentage reduction in the sample's original weight, based on the weight change observed during drying, in accordance with ASTM standards (2004) [6].

$$\text{Moiture content (\%)} = \frac{(A-B)}{A} \times 100 \quad (26)$$

Where, A = Mass of sample before drying (g) and B = Mass of sample after drying (g)

3.4.1.2 Ash content

Ash content represents the non-combustible inorganic residue left behind after the complete burning of AC at elevated temperatures. It primarily includes mineral impurities and metal oxides that remain stable and do not evaporate during the pyrolysis process. For ash content determination, about 1 gram of AC was placed in a pre-weighed silica crucible and heated at 1000°C for 1 hour to ensure complete combustion. After cooling in a desiccator, the residue was weighed to calculate the ash content [7].

$$\text{Ash content (\%)} = \frac{(A-B)}{C} \times 100 \quad (27)$$

Where, A= Weight of crucible and ash after combustion (g), B= weight of empty crucible (g) and C= Weight of sample taken (g).

3.4.1.3 Volatile matter

Volatile matter is the fraction of substances, excluding moisture, that is released as gases or vapors from activated carbon when heated in the absence of oxygen, consisting of components that are not fully carbonized during pyrolysis. Volatile matter was determined by placing 1 gram of the carbon sample into a preheated crucible, partially covered with a lid, and heating it at approximately 900 °C for 7 minutes. After heating, the crucible and its contents were cooled in a desiccator to prevent moisture absorption. The reduction in weight corresponds to the volatile matter content, as per ASTM standards (2003)[5].

$$\text{Volatile matter (\%)} = \frac{(A-B)}{C} \times 100 \quad (28)$$

Where, A= Weight of crucible with sample before heating (g), B= Weight of crucible with sample after heating (g) and C= Weight of sample taken (g)

3.4.1.4 Fixed carbon

It refers to the solid combustible residue that remains in activated carbon after the removal of moisture, volatile matter, and ash. The percentage of fixed carbon is calculated by deducting the combined percentages of volatile matter, moisture content, acid-soluble matter, water-soluble matter, and ash content from 100%. The fixed carbon content of the sample was determined using the following formula:

$$\text{Fixed carbon (\%)} = 100 - (\text{Moisture content} + \text{Volatile matter} + \text{Acid soluble} + \text{Water soluble} + \text{Ash content}) \quad (29)$$

3.4.1.5 Acid soluble matter

It refers to the fraction of the material that dissolves upon treatment with strong acids like HCl and HNO₃. This portion typically includes impurities like metal compounds and inorganic salts that are not structurally integrated into the carbon framework. To assess the acid soluble fraction, 1 g of the adsorbent was mixed with distilled water to form a slurry in an evaporating dish. Concentrated hydrochloric acid (5–10 mL) was added, and the mixture was gently heated. This digestion step was repeated three times using 5 mL of acid each time. The digested sample was then diluted with 100 mL of distilled water and filtered through a pre-weighed sintered crucible. The residue was dried at 110°C to

a constant weight, and the amount of acid-insoluble matter was calculated by the weight difference.

$$\text{Acid insoluble matter (\%)} = \frac{(A-B)}{C} \times 100 \quad (30)$$

Where, A= Weight of crucible and dried residue after digestion (g), B= Weight of empty crucible (g), C= Weight of sample taken.

3.4.1.6 Water soluble matter

It refers to the fraction of the AC that dissolves in water. It primarily consists of soluble inorganic salts and trace elements that may be present as residual impurities. The mixture was then filtered, and the remaining residue was dried, cooled, and weighed. The weight loss after drying indicated the percentage of water-soluble matter, following ASTM standards (2009) [8].

$$\text{Water soluble matter (\%)} = \frac{(A-B)}{A} \times 100 \quad (31)$$

Where, A= Initial sample weight and B= Final weight after water treatment.

3.4.2 Apparent density, bulk density and porosity

These are important physical properties of activated carbon that influence its adsorption performance and handling. Apparent density considers the mass per volume of particles excluding voids, while bulk density includes both particles and void spaces. Porosity represents the proportion of the total volume occupied by pores. These parameters help assess the material's structure, packing behavior, and efficiency in adsorption processes. To assess these parameters, a known weight of activated carbon was placed in a pre-weighed silica crucible and dried in an oven at 105°C until a constant weight was obtained. The final weight of the dried carbon was then recorded. A clean, pre-weighed density bottle with a secure cork was partially filled with a measured volume of water, sealed, and reweighed. Dried carbon was then gradually added to the bottle in small amounts, and the bottle was reweighed after each addition until it was filled up to the calibration mark. The bulk density, dry density, and porosity of the sample were subsequently calculated using standard formulas, as outlined by [2,9].

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{Mass of wet sample}}{\text{Mass of volume}} \quad (32)$$

$$\text{Apparent density (g/cm}^3\text{)} = \frac{\text{Mass of dry sample}}{\text{Volume of solid particles (excluding voids)}} \quad (33)$$

$$\text{Posity } (\eta) = \frac{V_v}{V_t} \quad (34)$$

Where, V_v = Volume of void, V_t = total volume

The void volume (V_v) was calculated by first measuring the total volume of the cylinder used in the experiment, followed by determining the volume occupied by the solid material, i.e., the activated carbon.

$$V_t = \pi r^2 h \quad (35)$$

$$V_s = \frac{M_s}{G_s \rho_w} \quad (36)$$

r = radius of cylinder, h = height of cylinder, M_s = mass of solid, G_s = specific gravity, ρ_w = density of water. Subsequently, the volume of voids (V_v) was determined as follows:

$$V_v = V_t - V_s \quad (37)$$

3.4.3 Iodine number

To determine the iodine number, which indicates the adsorption capacity of activated carbon, the amount of iodine (in milligrams) that can be adsorbed by 1 g of the carbon is measured. A 0.1N iodine solution was prepared by dissolving 2.7 grams of iodine crystals and 4.1g of KI in 1L of distilled water. This iodine solution was then standardized using 0.1N sodium thiosulfate. In the analysis, 0.5 g of activated carbon was placed in a 100 ml volumetric flask along with 10 mL of 5% HCl. The mixture was gently stirred to ensure the carbon was thoroughly wetted. Afterward, 100 ml of the prepared iodine solution was added, and the flask was shaken for one hour using a rotary shaker. The contents were then filtered through a sintered glass crucible, and 20 mL of the filtrate was titrated with 0.1N sodium thiosulfate, using starch as an indicator. The iodine number was determined by calculating the amount of iodine adsorbed per gram of AC at room temperature [2].

$$\text{Iodine number (mg/g)} = \frac{(B-S) \times N \times 253.81}{W} \quad (38)$$

Where, N = normality of sodium thiosulfate, 253.81 = molecular weight of I_2 in mg/mmol and W = weight of activated carbon in g.

3.4.4 pH and Conductivity

In this study, 1.0 g of AC was mixed with 100 ml of distilled water in a beaker and stirred continuously for one hour, following ASTM standards (2011) [10]. After allowing the

mixture to stabilize, its pH and conductivity were measured using a Thermo Scientific Orion 4 Star ISE instrument.

3.4.5 Zero-point charge (pH_{zpc})

It plays a key role in determining how the adsorbent interacts with ions in a solution. The pH_{zpc} of the AC samples was determined by adding 0.1 g of each sample into separate 200 ml solutions of 0.1 M NaCl in conical flasks. The pH of each solution was adjusted to varying levels (acidic or basic) using 0.1 N HCl or 0.1 N NaOH as needed. The flasks were then sealed and shaken for 24 hours. After this period, the final pH of each mixture was measured. The pH_{zpc} was identified as the point where there was no change between the initial and final pH values, which corresponds to the intersection point of the pH_{final} vs. $\text{pH}_{\text{initial}}$ plot on a graph [2].

3.5 Analytical instrument employed for characterization

A range of analytical techniques, including Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis (SEM/EDX), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), BET surface area analysis, Thermogravimetric Analysis (TGA), and X-ray Photoelectron Spectroscopy (XPS), were employed to characterize the prepared activated carbon samples. A brief description of each instrument utilized in this study is provided below.

3.5.1 Scanning Electron Microscopy (SEM) Study

Scanning Electron Microscopy (SEM) was used to analyze the surface morphology of the activated carbon. The images showed a rough, porous structure with visible surface irregularities, confirming the development of pores during activation. These features support the material's potential for effective adsorption. Therefore, to examine the surface morphology, SEM analysis was performed at different magnifications using a JEOL JMS 6390 LV scanning electron microscope.

3.5.2 Energy-Dispersive X-Ray (EDX) study

It is a technique commonly used in conjunction with SEM to examine the elemental composition of a material's surface. In this study, EDX was utilized to detect and measure the elements present on the surface of AC. When the sample is exposed to an electron beam during SEM imaging, it emits characteristic X-rays that correspond to specific elements. These X-rays are captured by the EDX detector, enabling both qualitative and semi-quantitative analysis. The resulting data provides valuable insights into the surface

chemistry, confirming the existence of functional groups and identifying any inorganic impurities within the AC.

3.5.3 Fourier Transform Infrared Spectroscopy (FT-IR) study

FTIR analysis was carried out to examine the functional groups present on the surface of the activated carbon. This method helps identify the chemical bonds and surface functionalities by measuring the absorption of infrared light over a specific range of wavelengths. For the analysis, FTIR spectra were obtained for the AC samples. The sample preparation involved blending 1 mg of the powdered carbon with 199 mg of potassium bromide (KBr, Merck, spectroscopy grade). This mixture was then compressed into a pellet under vacuum conditions. The spectra were recorded within the wavenumber range of 400 to 4000 cm^{-1} . Each peak in the FTIR spectrum corresponds to the vibration of a particular functional group.

3.5.4 Powder X-ray Diffraction (PXRD) study

PXRD analysis was conducted to investigate the structural characteristics and graphitic nature of the activated carbon samples. The diffraction patterns were obtained using an XRD instrument (Rigaku-Ultima IV, Japan) equipped with $\text{CuK}\alpha$ radiation, operated at a scanning rate of 0.2° per minute. This analytical method helps in identifying crystallographic structure, estimating crystallite size, and detecting preferred orientation in powdered or polycrystalline materials. Due to the low crystallinity of carbon materials, the diffraction peaks typically appear broad. In this study, the structural order of the AC was assessed with reference to graphite by examining the X-ray diffractograms. The Scherrer equation is given as:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (39)$$

Where, τ = mean crystallite size, K = shape factor (typically ~ 0.9), λ = X-ray wavelength (e.g., 1.5406 Å for Cu $\text{K}\alpha$), β = full width at half maximum (FWHM) of the diffraction peak (in radians) and θ = Bragg angle.

3.5.5 Pore volume and surface area (BET method)

The pore volume and specific surface area of AC are critical parameters that significantly affect its adsorption capacity. These characteristics are commonly determined using the Brunauer–Emmett–Teller (BET) method, which involves the physical adsorption of nitrogen gas at liquid nitrogen temperature (77 K). This method evaluates both the

external and internal (pore) surface areas to calculate the total specific surface area (in m^2/g), offering valuable insights into the effects of porosity and particle size—key factors in a wide range of applications. The BET surface area was calculated using the Brunauer–Emmett–Teller (BET) equation as described by Bansal and Goyal (2005) [11].

$$\frac{P}{V(P-P_0)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P}{P_0} \quad (40)$$

$$S_{\text{BET}} = \frac{N_A A_M V_m 10^{-20}}{m_s V_M} \quad (41)$$

where, S_{BET} = BET surface area (m^2/g), N_A = Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), A_M = Cross-sectional area of the adsorbate molecule (0.162 nm^2 for Nitrogen), V_m = Monolayer volume of adsorbed gas ($\text{cm}^3 \text{ STP}$), m_s = Mass of the sample (g), V_M = Molar volume of gas at STP ($22400 \text{ cm}^3/\text{mol}$) and 10^{-20} = Conversion factor to convert nm^2 to m^2 .

When nitrogen is used as the adsorbate gas, Equation (42) is modified as follows:

$$S_{\text{BET}} = \frac{4.35 M}{m_s} \quad (42)$$

where, V_M = monolayer volume in $\text{cm}^3 \text{ (STP)}$, m_s = mass of the sample in grams (g) and 4.35 is the constant in BET surface area equation (when nitrogen gas is used). The constant 4.35 includes values such as Avogadro's number, cross-sectional area of nitrogen, and the molar volume at STP, assuming nitrogen gas at 77 K as the adsorbate.

3.5.6 Thermo Gravimetric analysis (TGA) study

Thermogravimetric analysis (TGA) was performed to evaluate the thermal behavior of activated carbon and to gain insights into its decomposition characteristics at varying temperatures. The study utilized a TA Instrument (SDT Q600, USA), with alumina used as the reference material. The analysis was carried out under an argon atmosphere at a constant heating rate of 20°C per minute. The findings revealed that less stable surface functional groups, responsible for CO_2 release, begin to break down around 350°C , while more stable groups that emit CO degrade only at temperatures exceeding 500°C . This technique offers valuable information about the structural integrity and thermal stability of the activated carbon.

3.6 Result and discussion

The results of pyrolysis temperature optimization and the detailed characterization of the synthesized mFSAC are presented and discussed in the following sections.

3.6.1 Optimization of Pyrolysis Temperature

The effect of pyrolysis temperature on the physicochemical properties of the prepared carbon was investigated in the range of 500–900 °C and the results are presented in Table 3.1. As the temperature increased, the yield decreased from 35% at 500 °C to 25% at 900 °C which can be attributed to the progressive decomposition of organic components and release of volatile matter.

A gradual decrease in moisture content (15.0% to 9.0%) and volatile matter (38.5% to 25.0%) was observed with increasing temperature, indicating enhanced carbonization. In contrast, the ash content increased from 10.0% to 21.0%, likely due to the accumulation of inorganic residues at higher temperatures [12]. The fixed carbon content increased from 36.5% at 500 °C to a maximum of 45.5% at 800 °C followed by a slight decrease at 900 °C, suggesting possible structural degradation at excessive temperatures [13]. Similarly, the iodine number, which is an indicator of microporosity and adsorption capacity, increased significantly from 343.4 mg g⁻¹ at 500 °C to 423.6 mg g⁻¹ at 700 °C, with only marginal improvement at higher temperatures (425.7 mg g⁻¹ at 800 °C and 427.04 mg g⁻¹ at 900 °C) [14]. Based on these observations, 700 °C was selected as the optimum pyrolysis temperature, as it provides a balance between high adsorption capacity (iodine number), relatively higher fixed carbon content, and acceptable yield. Although slightly higher iodine values were observed at 800 and 900 °C, the marginal improvement does not justify the increased energy consumption and reduced yield at elevated temperatures. Therefore, 700 °C was considered the most efficient and economical condition. Accordingly, the charcoal obtained at this temperature was selected for subsequent chemical activation and was used in further studies with different KOH impregnation ratios.

Table 3.1 Effect of Pyrolysis Temperature on MFS Charcoal Properties.

Temperature (°C)	Yield (%)	Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)	Iodine number (m ² g ⁻¹)
500	35	15.0	10.0	38.5	36.5	343.4

600	32	13.5	12.0	34.5	40.0	398.76
700	30	12.25	14.8	29.8	42.9	423.6
800	27	10.0	18.0	26.5	45.5	425.7
900	25	9.0	21.0	25.0	45.0	427.04

3.6.2 Moisture Content

The moisture content of KOH-treated AC derived from waste fish scales is summarized in Table 3.2. Lower moisture content generally indicates enhanced adsorption capacity, as supported by Adebayo, G. B., et al (2015) [15]. Excessive moisture can hinder the adsorption efficiency of activated carbon. Among the samples, the moisture content followed the order: 1:3 > 1:1 > 1:1.

Table 3.2 Moisture content of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	Moisture Contents (%)
mFSAC	1:1	14.22
	1:2	12.25
	1:3	16.04

3.6.3 Volatile matter

The Table 3.3 presents the volatile matter content (%) of mFSAC activated at different carbon to KOH ratios (1:1, 1:2, and 1:3). The volatile matter values for the various ratios are as follows: 31.7% for the 1:1 ratio, 29.8% for the 1:2 ratio, and 32.02% for the 1:3 ratio. These values reflect the proportion of the sample that can be vaporized at high temperatures, providing insight into the thermal stability and composition of the activated carbon produced at each ratio.

Table 3.3 Volatile matter content of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	Volatile matter (%)
mFSAC	1:1	31.7
	1:2	29.8
	1:3	32.02

3.6.4 Acid soluble

The acid soluble matter content of the synthesized activated carbon samples is summarized in Table 3.4. The observed low values indicate good acid resistance, suggesting that the activated carbons prepared from waste fish scales via KOH activation are suitable for use in acidic water treatment applications [16].

Table 3.4 Acid soluble content of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	Acid soluble matter (%)
mFSAC	1:1	1.6
	1:2	0.9
	1:3	0.94

3.6.5 Water soluble

The water-soluble matter content is provided in Table 3.5. The low values for all adsorbents indicate their near-insolubility in water, making them suitable for water treatment without altering the physical properties of the water. Low solubility is a key property for adsorbents in water treatment, as it minimizes leaching.

Table 3.5 Water soluble content of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	Water soluble matter (%)
mFSAC	1:1	0.23
	1:2	0.18
	1:3	0.42

3.6.6 Ash content

Low ash content is crucial for activated carbon to be considered an effective adsorbent. Lower ash content indicates well-preserved pores with sufficient active sites for efficient adsorption. Impurities such as ash occupy available surface area, reducing the adsorption capacity (Table 3.6).

Table 3.6 Ash content of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	Ash content (%)
mFSAC	1:1	14.9

1:2	14.8
1:3	15.3

3.6.7 Fixed carbon

Fixed carbon represents the carbon content remaining in the sample after exposure to physical tests. The results, shown in Table 3.7, indicate a high percentage of carbon in all three samples, confirming that the raw bio-waste materials used are excellent carbon sources. Higher fixed carbon content is associated with increased surface area, active sites, and porosity, which enhances adsorption capacity.

Table 3.7 Fixed carbon of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	Fixed carbon content (%)
mFSAC	1:1	42.3
	1:2	42.9
	1:3	42.6

3.6.8 Apparent density

Apparent density is crucial for estimating packing volume or determining the appropriate carbon grade for a system. The low density of activated carbons results from the random arrangement of micro-crystallites with strong cross-linking, leading to a porous structure. Bulk density is another important property, especially when evaluating the filterability of activated carbon. Porosity, which indicates the number of pores in a sample, enhances the adsorption capacity. The results are provided in Table 3.8.

Table 3.8 Apparent density of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	Apparent density (g/mL)	Bulk density (g/cm ³)	Porosity (%)
mFSAC	1:1	1.02	0.45	62.4
	1:2	0.98	0.42	66.7
	1:3	0.95	0.4	67.3

3.6.9 Iodine number

This provides an estimate of the surface area (m² g⁻¹) of AC [17,18]. Iodine adsorption is a rapid test used to estimate the surface area of activated carbons with pores larger than approximately 1 nm. Micropores formed during activation contribute significantly to the

high surface area and serve as primary sites for adsorption. The iodine number specifically indicates the porosity associated with pores ≥ 1.0 nm. The values for the various carbon samples are shown in Table 3.9.

Table 3.9 Iodine number of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	Iodine number (m^2g^{-1})
mFSAC	1:1	210.67
	1:2	423.6
	1:3	507.6

3.6.10 pH and conductivity

The pH and electrical conductivity values for the different activated carbon samples are provided in Table 3.10. The pH of the carbon samples ranged from 6.77 to 7.65, which is within the acceptable range of 6-8 for most applications [19,20]. Electrical conductivity reflects the mineral content in water, which is proportional to the total dissolved solids (TDS).

Table 3.10 pH and conductivity of synthesized mFSAC

Adsorbent	Ratio (Carbon: KOH)	pH	Conductivity ($\mu\text{S}/\text{cm}$)
mFSAC	1:1	6.77	72
	1:2	7.2	168
	1:3	7.65	214

3.6.11 Comparison of physiochemical properties of mFSAC with other AC.

The physicochemical properties of activated carbons made from different precursors are compared in the Table 3.11. The findings show that the type of raw material and the preparation technique have a major impact on the moisture content, volatile matter and ash content [12,21]. The animal-derived precursor (fish scales), which are rich in inorganic minerals like calcium and phosphorus and contribute to increased ash following carbonization, is responsible for the comparatively higher moisture and ash content of the mFSAC produced in this work [22]. In addition, the presence of surface functional groups enhances the hydrophilic nature of the material, leading to higher moisture retention [23]. The volatile matter remains within a comparable range to other reported adsorbents. The iodine number suggests the presence of a reasonably developed microporous structure

[22]. Overall, despite variations in certain parameters, the prepared adsorbent demonstrates acceptable physicochemical properties and holds significant potential for adsorption applications.

Table 3.11 Physiochemical properties of mFSAC with other AC

S/No.	Activated carbon (AC)	Parameters				References
		Moisture content (%)	Volatile matter (%)	Ash content (%)	Iodine number (m^2g^{-1})	
1.	mFSAC	12.25	29.8	14.8	423.6	This study
2.	Waste tea	4.82	31.18	5.63	593.41	[24]
3.	Doum palm shell	5.3	—	11.2	—	[25]
4.	Sludge	1.00	51.0	20.5	531.8	[26]
5.	Animal bone	10.65	—	3.50	576.84	[27]
6.	Saw dust	5.04	10.80	3.85	—	[28]
7.	Rice husk	5.87	14.35	5.34	—	[29]
8.	Rice straw	28.5	40	—	—	[30]
9.	Apricot stone	0.59	2.64	4.23	359.40	[31]
10.	Tyre char	1.8	18.8	16.6	343	[32]
11.	Groundnut shell	9.0	8.2	11.4	765	[33]

3.6.12 Zero-point charge

The pH_{ZPC} values were measured to determine the surface charge density of the synthesized activated carbon. The pH_{ZPC} values for activation ratios of 1:1, 1:2, and 1:3 (carbon:KOH) were 7.08, 7.64, and 7.86, respectively, while the corresponding equilibrium pH values of the carbons in water were 6.77, 7.20, and 7.65. Since surface charge depends on the relationship between solution pH and pH_{ZPC} , and all measured pH values were lower than their respective pH_{ZPC} values, the surfaces of all three samples were positively charged under the measured conditions. When the pH exceeds the pH_{ZPC} , the surface becomes negatively charged due to the dissociation of acidic functional groups, releasing protons into the medium. Conversely, when the pH is lower than the pH_{ZPC} , basic surface sites bind protons from the medium, resulting in a positively charged

surface [34]. The pH_{ZPC} values for the different carbon samples are shown in Tables 3.12a-3.12c, with corresponding plots in Fig.3.1a, 3.1b and 3.1c.

Table 3.12a Determination of initial and final pH of mFSAC at 1:1 Carbon:KOH ratio

Adsorbent	Ratio (Carbon: KOH)	pH_i	pH_f	ΔpH
mFSAC	1:1	2	4.36	-2.36
		4	5.12	-1.12
		6	6.7	-0.7
		8	7.4	0.6
		10	8.2	1.8
		12	9.2	2.8

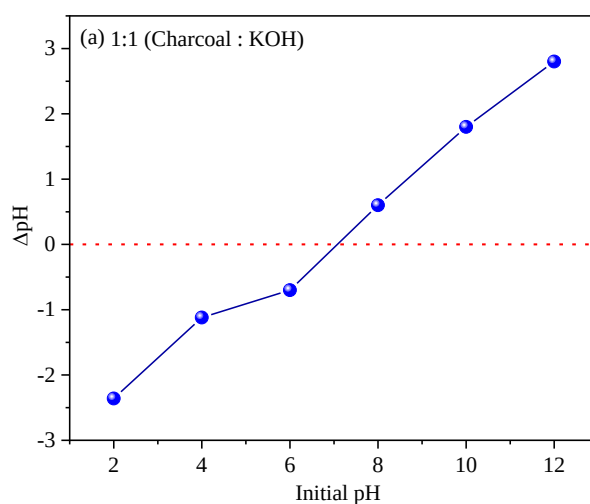


Fig.3.1a Plot of initial pH (pH_i) vs. ΔpH for 1:1 ratio (charcoal:KOH)

Table 3.12b Determination of initial and final pH of mFSAC at 1:1 Carbon:KOH ratio

Adsorbent	Ratio (Carbon: KOH)	pH_i	pH_f	ΔpH
mFSAC	1:2	2	4.46	-2.46
		4	5.22	-1.22
		6	6.8	-0.8
		8	7.8	0.2
		10	8.8	1.2
		12	9.4	2.6

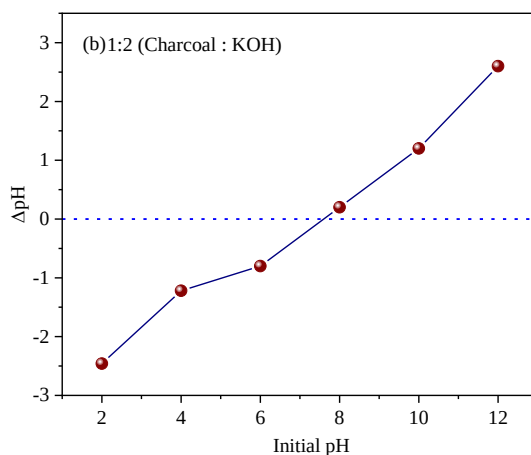


Fig.3.1b Plot of initial pH (pH_i) vs. ΔpH for 1:2 ratio (charcoal:KOH)

Table 3.12c Determination of initial and final pH of mFSAC at 1:1 Carbon:KOH ratio

Adsorbent	Ratio (Carbon: KOH)	pH_i	pH_f	ΔpH
mFSAC	1:3	2	4.52	-2.52
		4	5.36	-1.36
		6	7.3	-1.3
		8	7.9	0.1
		10	8.6	1.4
		12	9.8	2.2

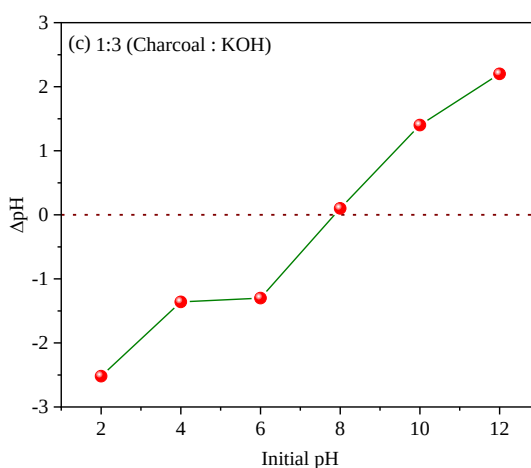


Fig.3.1c Plot of initial pH (pH_i) vs. ΔpH for 1:3 ratio (charcoal:KOH)

3.6.13 Scanning electron microscopy (SEM)

The images reveal a complex and disordered surface structure characterized by pores of diverse sizes, shapes, and dimensions, reflecting the heterogeneous nature of the adsorbent. From Fig.3.2a and 3.2b, the images display the bulk morphology characterized

by flake-like fragments, prominent macropores, and roughened surfaces. At higher resolution, the carbon surface exhibits irregular textures, microcavities, lamellar sheet-like structures, grooves, and cracks, reflecting the layered collagenous origin of fish scales. Tubular and hollow porous structures with interconnected channels are also observed, enhancing surface accessibility. The slanted flakes, surface corrugation, and oval pore openings indicate that KOH activation promoted significant surface etching, resulting in a hierarchical porous network comprising micro-, meso-, and macropores.

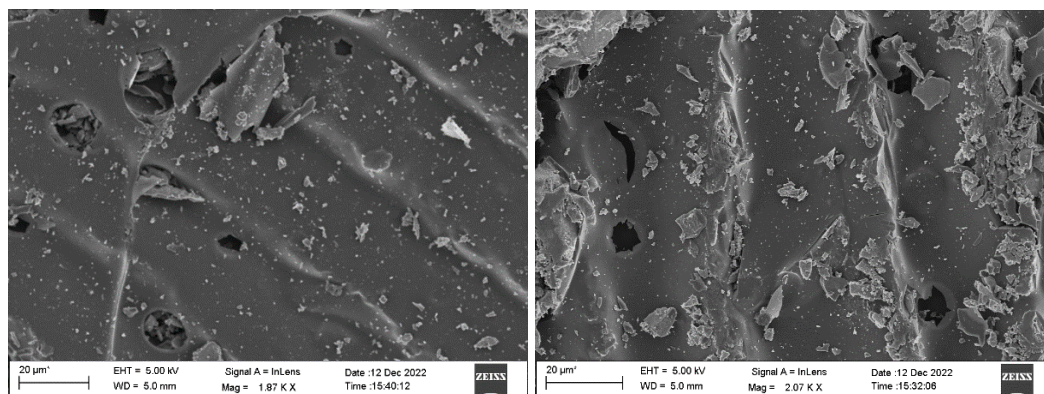


Fig. 3.2a SEM micrograph of mFSAC at x1900 and x2070, scale bar= 20µm (Formation of macropores in a non-uniform pattern were observed)

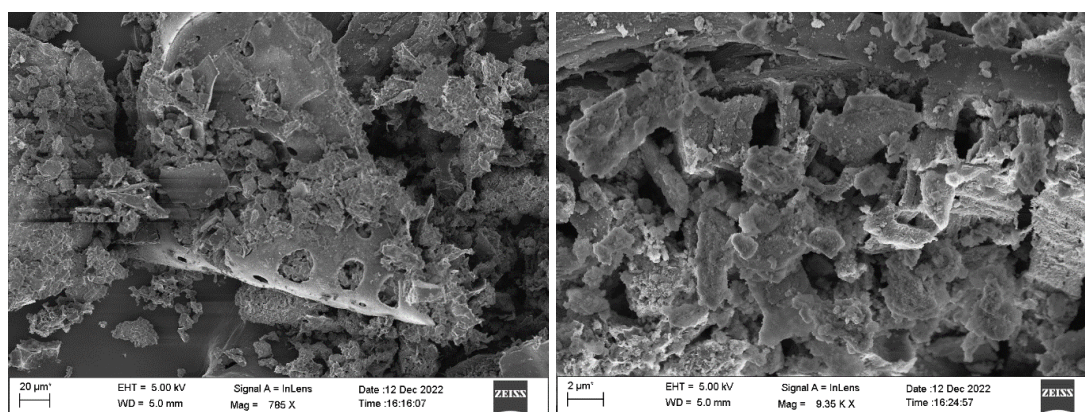


Fig.3.2b SEM micrograph of mFSAC at x9.35K and x785 (Disorganised surface structure with different pores dimensions were observed)

3.6.14 Energy-Dispersive X-ray Spectroscopy (EDX)

(Fig.3.3) displayed prominent signals of C and O, verifying the carbonaceous framework with oxygenated surface groups, while the presence of Ca and P peaks reflected residual hydroxyapatite from fish scales [35,36]. A weak S peak was also observed, possibly linked to sulfur-bearing compounds in the precursor. The corresponding quantitative data

are summarized in Table 3.11 confirming the representative elemental composition of the prepared activated carbon.

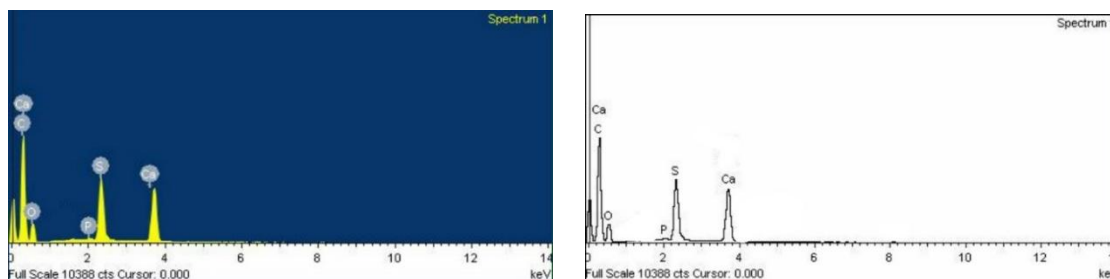


Fig.3.3 EDX spectra of mFSAC.

Table 3.13. Elemental composition of mFSAC

Elements	Weight %	Atomic %
C K	60.7	73.56
O K	22.17	19.54
P K	0.57	0.19
S K	7.01	3.32
Ca K	9.11	3.40
Total	100	100

3.6.15 Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectra show clear changes after KOH activation as shown in Fig. 3.4. The broad O–H band ($\sim 3200\text{--}3500\text{ cm}^{-1}$) decreases, indicating removal of moisture and hydroxyl groups [11]. The aliphatic C–H peaks ($\sim 2850\text{--}2950\text{ cm}^{-1}$) are reduced, confirming decomposition of organic components [37]. The band around $\sim 1600\text{ cm}^{-1}$ decreases, suggesting reduction in certain oxygenated or aromatic functional groups [38]. In contrast, the C–O stretching peak ($\sim 1000\text{--}1100\text{ cm}^{-1}$) increases, indicating the development or exposure of oxygen-containing functional groups [39]. The carbonate peak at $\sim 873\text{ cm}^{-1}$ becomes more prominent after activation, suggesting the presence or enrichment of carbonate species [40]. Overall, these changes confirm that KOH activation modifies both surface chemistry and mineral components, enhancing the adsorption potential of the activated carbon.[41].

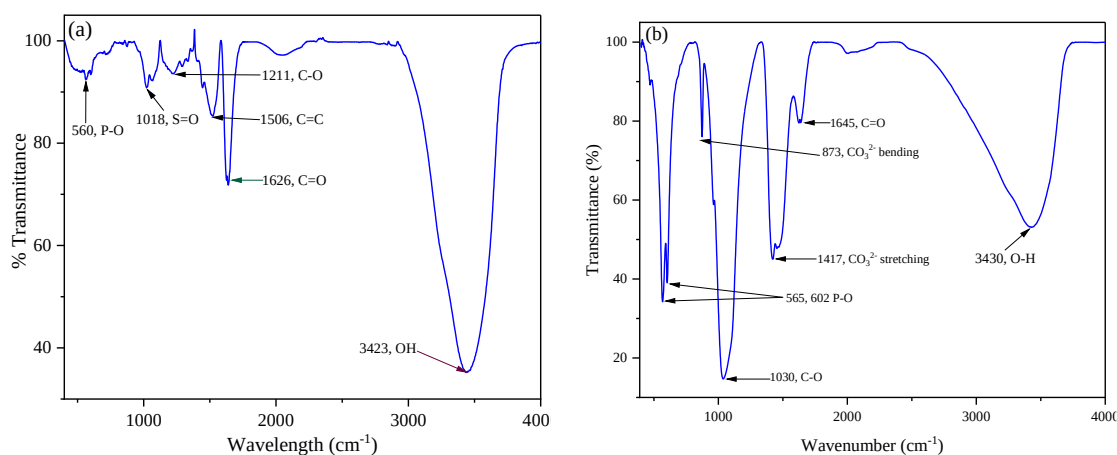


Fig.3.4 FT -IR spectra of activated carbon before (a) and after (b) KOH activation.

3.6.16 X-ray diffraction (XRD)

XRD analysis of the prepared mFS-AC was performed in the 2θ range of 10° – 90° to investigate its crystalline structure. The diffractogram (Fig. 3.5) exhibited distinct diffraction peaks at $2\theta = 26.24^\circ$, 32.15° , 39.8° , 49.0° , 58.86° , 64.33° , 76.0° , and 88.10° , corresponding to d-spacings of 0.34, 0.278, 0.225, 0.185, 0.145, 0.156, 0.125, and 0.12 nm, respectively. These peaks were indexed to the (002) plane of graphitic carbon and the (112), (104), (024), (116), (122), (214) and (300) planes of residual calcite (CaCO_3), indicating the coexistence of amorphous carbon with graphitic domains and mineral residues in the prepared activated carbon [32,42]. The prominent diffraction peaks at 26.24° and 32.15° are characteristic of hydroxyapatite (HAp), which originates from the inorganic mineral fraction of fish scales [43,44]. In addition, the peak at $2\theta = 49.0^\circ$ can be assigned to calcium carbonate (CaCO_3), a residual mineral phase commonly reported in fish-scale-derived carbon materials [45]. This consistency further validates the presence of crystalline mineral residues embedded within the activated carbon framework. The average crystallite size of mFSAC was found to be 4.2 nm, while the degree of crystallinity was estimated at 15.01%, indicating that the material predominantly exhibits an amorphous carbon structure with embedded crystalline mineral phases [46].

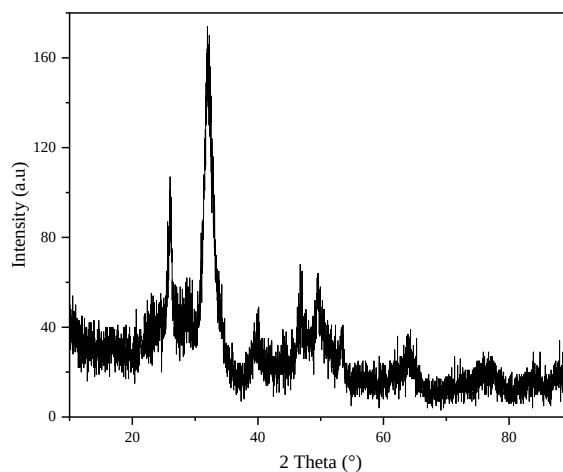


Fig. 3.5 XRD spectra of mFSAC

3.6.17 Thermogravimetric analysis (TGA).

The thermal stability and decomposition behavior of the activated biocarbon were evaluated using TGA. As shown in Fig. 3.6, the TGA curve exhibits three distinct stages of weight loss between room temperature and 800 °C. The first stage, with a weight loss of approximately 5.35% below 200 °C, is attributed to the evaporation of physically adsorbed water and moisture from the carbon surface [47]. The second stage, showing a further weight reduction of about 2.24% between 200–550 °C, corresponds to the decomposition of oxygen-containing surface functional groups and the release of light gaseous species such as CO and CO₂ [48]. The third stage comprising approximately 6.64% weight loss beyond 550 °C is due to the degradation of more thermally stable oxygen functionalities and partial decomposition of the carbonaceous framework [49]. Despite these reductions, over 85% of the initial mass remains at 800 °C, indicating significant resistance to thermal decomposition and underscoring the excellent thermal stability of the AC [50].

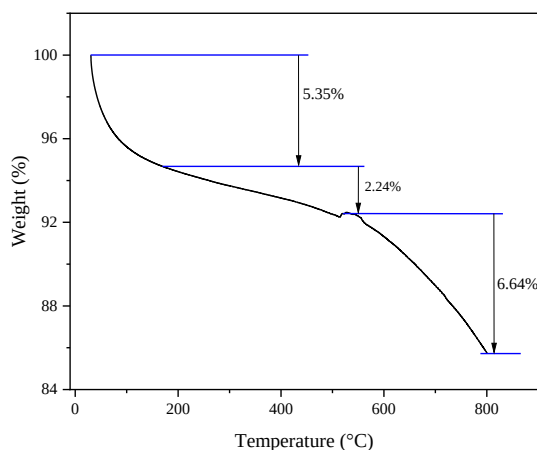


Fig. 3.6 TGA profile of mFSAC.

Conclusion

A comprehensive study was conducted on the preparation and characterization of AC derived from mixed fish scales. The synthesis involved a two-step process, starting with carbonization of the fish scales at high temperatures, followed by chemical activation using KOH at varying carbon-to-activating agent ratios. The physicochemical properties of the prepared activated carbons were systematically evaluated. These measurements indicated that the activation process effectively increased the carbon content and porosity while reducing impurities, thereby creating a material with desirable characteristics for pollutant removal. Further detailed characterization was carried out using advanced analytical techniques. The BET analysis revealed a surface area of 150.049 m²/g and a total pore volume of 0.119 cm³/g, confirming the highly porous structure essential for adsorption processes. FTIR identified the presence of oxygen-containing functional groups, which played a significant role in the interaction between the adsorbent and various pollutants. SEM-EDX provided insights into the surface morphology and elemental composition, showing a rough, porous surface with residual hydroxyapatite originating from the fish scales. XRD analysis further corroborated the presence of crystalline phases, and TGA demonstrated high thermal stability, indicating that the activated carbons could withstand elevated temperatures during practical applications. Among the different carbon-to-KOH ratios investigated, the sample prepared with a 1:2 ratio exhibited the highest surface area and optimal porosity, suggesting that this proportion was most effective for activating the carbon while preserving its structural integrity. This sample was therefore expected to perform most efficiently in adsorption applications. Overall, the results confirmed that mixed fish scale derived AC could be successfully synthesized through carbonization and KOH activation, producing a material with enhanced structural and chemical properties suitable.

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CHAPTER 4

EFFICIENT REMOVAL OF CONGO RED DYE USING ACTIVATED CARBON DERIVED FROM MIXED FISH SCALES WASTE: ISOTHERM, KINETICS AND THERMODYNAMICS STUDIES

This chapter explores the use of activated carbons for the removal of Congo red dye from aqueous solutions. Adsorption experiments were carried out in batch mode to determine the optimal conditions, including adsorbent dosage, contact time, initial Congo red dye concentration, and solution pH. Various fluoride adsorption isotherm models—such as Langmuir, Freundlich, and Temkin—were analyzed to assess their applicability. Additionally, four simplified kinetic models—namely pseudo first-order, pseudo second-order, intraparticle diffusion, and Elovich—were evaluated to understand the adsorption rate and kinetics of fluoride on different activated carbons. The chapter also presents the thermodynamic parameters associated with the fluoride adsorption process.

The contents of this chapter have been patented and published as:

- Activated carbon from mixed fish scales for adsorption of Congo Red Dye.
Vevosa Nakro, Tsenbeni Nonghobemo Lotha, Ketiyala Ao, Lemzila Rudithongru, Imkongyanger Ao, Vimha Ritse, Latonglila Jamir (Indian Patent: 202431045241 A, Date of Grant: 12/06/2024)
- **Nakro, V.**, Ao, K., Lotha, T. N., Ao, I., Rudithongru, L., Pongener, C., ... & Jamir, L. (2025). Efficient Removal of Congo Red Dye Using Activated Carbon Derived from Mixed Fish Scales Waste: Isotherm, Kinetics and Thermodynamics Studies. *Nature Environment & Pollution Technology*, 24(S1):339-353. DOI: [10.46488/NEPT.2024.v24iS1.026](https://doi.org/10.46488/NEPT.2024.v24iS1.026)

4.1 Introduction

Dyes, possessing significant level of toxicity in aqueous solutions even at low concentrations, causes serious risks to the environment and people's health. Coloring material are mainly sourced from industries of nourishments, printing, textile, leather, pulp/paper mills, plastics, cosmetics, restoratives, and dye synthesis [1] and has the potential to create a hypoxic environment in water which attributes to its severe toxicity [2]. On an average, it is estimated that over 10,000 distinct dyes and pigments at a massive 700,000 tonnes are employed in industrial settings annually out of which, about 10-15% are released into water bodies [3,4]. Based on their properties and structural makeup, dyes can be cationic, anionic, or non-ionic [5].

In line with this, the six aromatic rings in Congo red (represented as CR henceforth), an anionic diazo dye, contribute to its increased toxicity. A water-soluble diazo dye, CR has a solubility of 1g/30 mL being the first synthetic azo dye manufactured that can directly colour cotton [6]. It is stable in the atmosphere and exists as a brownish-red crystal [7,8] which also serves as an indication by turning reddish-brown in an alkaline medium and blue in an acidic one. Since its colour fades with radiation strength, it is also utilized in gamma-ray dosimeter. [9]. The dye is extremely hazardous to both humans and animals, such that both brief and extended dye contact with the skin or eyes can produce significant irritability [10]. When consumed, it causes nausea, vomiting, and diarrhea as a result of gastrointestinal irritation [11]. The dye also shows various forms of toxicity such as acute, algal, bacterial, protozoan, skin-related, environmental, microbial, and yeast toxicity. Additionally, it displays cytotoxic effects, genotoxic effects, adverse effects on blood, impacts on the nervous system, and the potential to cause cancer and genetic mutations [12–14]. Considering the grave health and environmental concerns related to CR dye, it is now pertinent to develop newer cost-effective and practical tools and removal techniques for this dye from wastewater systems.

Generally, the removal of dyes from wastewater has been made possible by many different methods over the years, including biological treatment [15–18], photocatalysis [19–22] ultrafiltration [23–26], electrochemical processes [27–30], adsorption [31–34], etc. Adsorption is a widely used technique for the removal of dyes from wastewater due to its high efficiency and low operational cost.

In recent years, activated carbon has gained significant attention as an efficient adsorbent for the removal of various pollutants from wastewater, including dyes. Activated carbon

is a porous and high surface area material with excellent adsorption properties due to its high adsorption capacity, low cost, and easy availability [35]. The production of activated carbon from various waste materials has also received attention due to environmental and economic benefits.

Over time, activated carbon has been prepared from a variety of plant sources, including rice husk [36], coconut shell [37], bamboo [38], agricultural residues [39], bagasse [40], olive stone [41], *Manihot esculenta* [42], palm shell [37], sugarcane [43], *Eucalyptus camaldulensis* Dehn bark [44], Neem husk [45], waste litchi shell [46], banana bunch [47], pine cone [48], *Tithonia diversifolia* [49], etc.

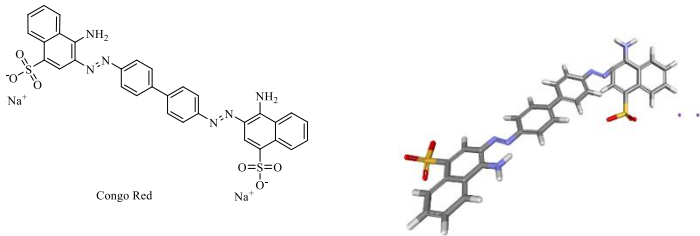
On the other hand, a limited number of reports is available on activated carbon derived from animal biomass, such as eggshells [50], hen feathers [8], animal bones [51], animal hooves [52] and horns, dung/manure, waste snail shells [53], and hair [54], etc. Despite the expected advantages of activated carbon derived from animal biowaste, particularly regarding removal efficiency, it has not received comparable attention.

Fish scales, a by-product of the fish processing industry, are considered to be a potential source for the production of activated carbon due to their high carbon content and low ash content [55]. Several studies have reported the use of activated carbon derived from various waste materials for the removal of CR from wastewater. For instance, [56] prepared activated carbon from shrimp shell and reported a maximum adsorption capacity of 288.2 mg/g for CR removal. Similarly, [57] prepared activated carbon from bael shells and reported a maximum adsorption capacity of 98.03 mg/g for CR removal. However, literature documents no record of the removal of CR from wastewater using activated carbon derived from fish scales. Therefore, in this study, we investigated the potential of fish scales-derived activated carbon for the adsorption of CR dye from aqueous solutions. Further, the efficiency of fish scales-derived activated carbon as an adsorbent for the removal of CR from aqueous solutions was evaluated. The study also aimed to investigate the adsorption mechanism.

4.2 Materials and method

Mixed fish scales (MFS) were collected from the local fish market in Mokokchung town, Nagaland, India, located at 26°19'38" N latitude and 94°31' 26" E longitude. CR dye used in the current work was procured from Thermo Scientific™. The properties and chemical structure of CR are shown in Table 4.1.

Table 4.1 Properties and chemical structure of Congo red.

Chemical name (IUPAC)	disodium 4-amino-3-[4-[4- (1-amino-4-sulfonato-naphthalen-2yl) diazenylphenyl] phenyl]diazanyl-naphthalene-1-sulfonate	
Molecular weight (g/mol)	696.665	
Molecular formula	C ₃₂ H ₂₂ N ₆ Na ₂ O ₆ S ₂	
Chemical structure	2D	3D
	 The image displays two representations of the Congo Red molecule. On the left is a 2D chemical structure showing a central biphenyl core with two 4-amino-1-sulfonatophenyl groups attached via azo (-N=N-) linkages. The sulfonate groups are shown as -SO₃⁻Na⁺. On the right is a 3D ball-and-stick model of the same molecule, showing the spatial arrangement of atoms and the overall shape of the dye.	
Maximum wavelength (λ_{max})	497nm	
C.I. name	Direct red 28	
Density	0.995mL at 25 °C	

4.2.1 Adsorbent preparation

The activated carbon used in this study was derived from waste fish scales (mFSAC) as described in Chapter 3. Prior to adsorption experiments, the prepared carbon was fully characterized for its physicochemical properties. For the current experiments, the activated carbon was used directly without any additional modification.

4.2.2 Adsorbate preparation

0.5 g of CR dye was dissolved in 500 mL of distilled water to make a stock solution of 1000 mg/L of CR dye. The stock solution having 1000 mg/L dye concentration was further diluted to the desired concentrations (10 to 100 mg/L). All chemicals were used directly in the current study without any further purification. All experiments were done using distilled water.

4.2.3 Adsorption Experiments

The removal of CR dye from aqueous solution was investigated in a batch system. All the adsorption studies were carried out in a 250 mL conical flask with a rotary shaker operating at a constant speed of 150 rpm. A needed dose of activated carbon was added to 25ml of CR dye at different initial concentrations, and the mixture was maintained for

a specific amount of time. 0.1N HCl and 0.1 N NaOH solutions were used to adjust the pH. The effect of different process parameters such as solution pH (3–10), adsorbent dosage (0.1–0.5 grams), initial dye concentration (10–100 mg/L), and temperature (25–55 °C) on the CR dye removal was investigated. After the experiments, the dye solutions were filtered through a Whatman filter paper, and the clear solution was analyzed for CR dye concentration. The remaining CR dye concentration in the filtrate was determined by measuring absorbance at 497 nm using UV–Visible Spectrophotometer (lambda 35, PerkinElmer). All the adsorption experiments were run in triplicate.

Adsorption isotherms and kinetic experiments were investigated with different initial concentrations of CR at a fixed adsorbent dosage and were agitated in a rotary shaker for the specific time duration and filtered to collect the residual solution.

4.3 Results and discussion

4.3.1 Scanning electron microscopy

In reference to the surface structure of the prepared activated carbon, SEM analysis provided valuable insights. The micrograph of the mixed fish scales activated carbon (mFSAC) (Fig. 4.1) revealed an uneven surface with pores of varying sizes and shapes distributed throughout. This porosity likely results from the interaction with KOH during activation, which drives off volatile substances and leaves behind a porous structure [58]. Before adsorption, the activated carbon exhibited a highly porous surface with well-developed cavities, indicating a large surface area available for dye uptake. After Congo red adsorption, many pores appeared partially filled, and the surface became smoother, confirming the successful adsorption of dye molecules. These morphological changes support the effectiveness of the prepared activated carbon in removing Congo red from solution.

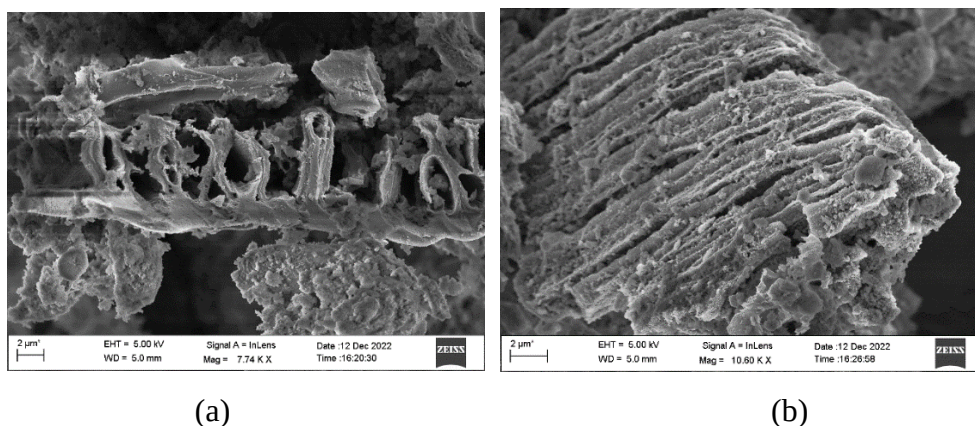
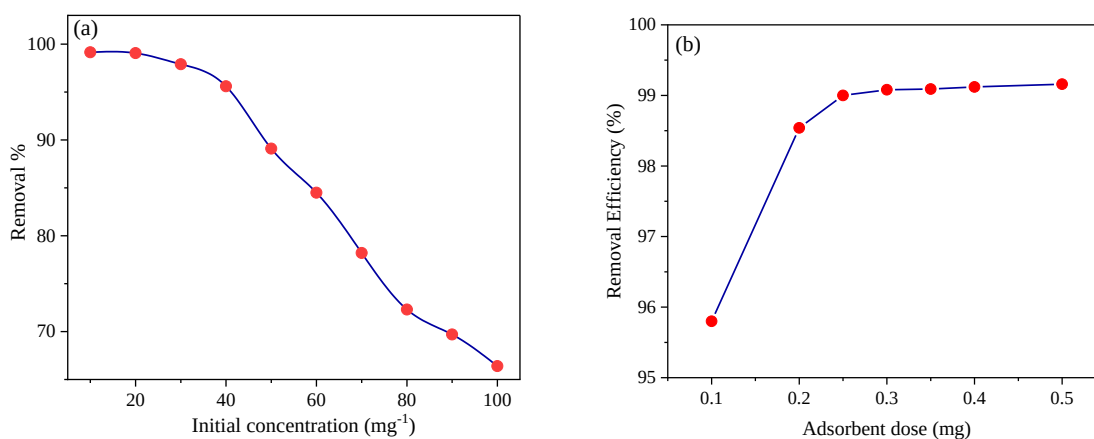


Fig. 4.1 SEM Micrograph of mFSAC before (a) and after (b) adsorption.

4.3.2 Batch Adsorption Studies

Batch adsorption studies were carried out to examine the effects of several experimental factors, including initial CR concentration, pH, adsorbent dosage, contact time, and temperature. The ideal equilibrium adsorption conditions were determined by placing 25 ml of various initial CR concentrations (10 mg/L to 100 mg/L) in a conical flask with varying quantity of activated carbon (0.1 to 0.5 g) at various pH (3-10) and at 25°C. The mixture was shaken in a rotary shaker at a constant speed of 150 rpm for a defined time. The optimum initial concentration of CR and adsorbent dosage was found to be 20mg/L and 0.25 g respectively. To determine the optimum pH, the initial concentration, adsorbent dose, temperature and contact time were kept constant at 20mg/L, 0.25 g, 25°C, and 60mins. The research explored the adsorption of CR across a pH range of 3 to 10, finding a decline in both the removal efficiency and adsorption capacity of CR with increasing pH. Nevertheless, the CR adsorption displayed high removal efficiency, achieving 98.6% at pH 6, and 97% at neutral pH 7. The study suggests that pH values of 6 and 7 could be optimal for CR removal via adsorption. The effect of different experimental parameters on the removal of Congo red is shown in Fig 4.2. Because more OH ions were present in the solution and were competing with the anionic dye for adsorption sites, the adsorption considerably decreased at high pH values [67].



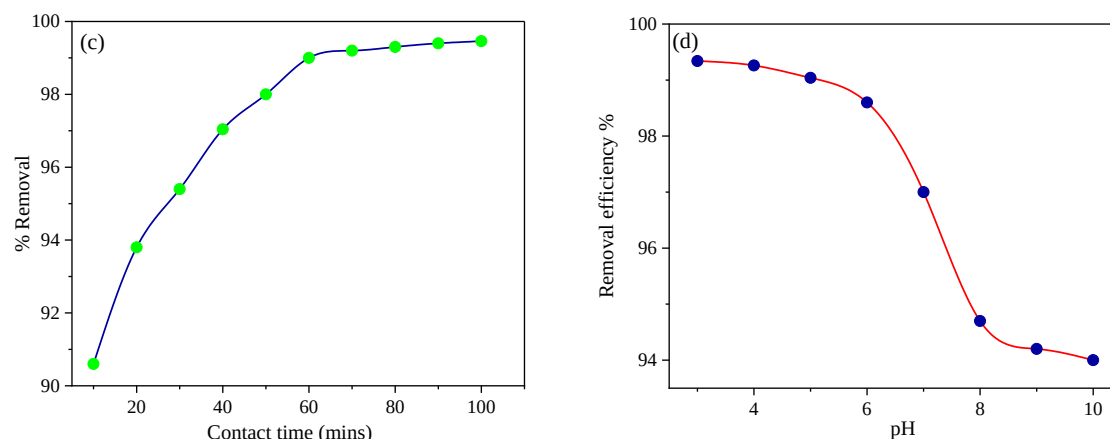


Fig. 4.2 Effect of different parameters onto CR removal (a) Initial concentration (b) adsorbent dose (c) contact time (d) pH

4.3.3 Effect of Initial Concentration and Contact Time

A key aspect of assessing the effectiveness of an adsorbent is to examine the impact of contact time and dye concentration. To this end, we have investigated the influence of contact time and initial dye concentration on adsorption using varying dye concentrations (10 mg/L to 100 mg/L) throughout 0 to 100 minutes, with the findings presented in Fig. 4.2(a) and (c). The results indicated that adsorption uptake increased with rising dye concentration, with equilibrium reached after approximately 60 minutes. Beyond this point, adsorption slowed down, possibly due to saturation of active sites on the adsorbent's surface. This trend was consistent across all the dye concentrations studied.

4.3.4 Effect of adsorbent dosage

Figure 4.2(b) illustrates the impact of the activated biocarbon dose on different concentrations of CR. The percentage of CR removal increased with the rise in adsorbent dose for all concentrations of CR until a dosage of 0.25 g of carbon was reached. This increase till 0.5 g of adsorbent dose can be attributed to the augmented surface area of mFSAC and the availability of more adsorption sites. However, it was observed that when the dosage exceeded 0.25g, there were no significant changes in the removal percentage. This phenomenon can be attributed to the saturation of adsorptive sites with dye molecules on the adsorbent's surface. A study on Ponceau 4R adsorption by activated Tilapia fish scales treated with sodium hydroxide revealed a similar result [68]. Consequently, the optimal adsorbent dosage for subsequent studies was determined to be 0.25 g.

4.3.5 Effect of pH

The study investigated the adsorption of CR dye using activated carbon at varying pH levels from 3 to 10 (Fig. 4.2d). The results showed that the removal efficiency and adsorption capacity of CR decreased as pH increased from 3 to 10. At pH values below the zero point charge (pH_{ZPC}) of the activated carbon, the surface had a net positive charge, attracting negatively charged CR molecules through electrostatic interactions. However, at pH values above the ZPC, the surface had a net negative charge, repelling negatively charged CR molecules and reducing adsorption. Despite this, a high removal percentage (94%) was still observed at pH 10. The pH_{ZPC} of the activated carbon was close to neutral pH (7.64), suggesting that the adsorption of CR dye was likely governed by both electrostatic and non-electrostatic interactions. A similar result was shown by [45] using neem leaf powder on Congo red adsorption and KOH-modified Black cardamom waste [69] on adsorption of Congo red using Machine Learning techniques. At pH values higher than the pH_{ZPC} , an increase in negatively charged -OH groups may compete with adsorption sites for negatively charged CR molecules, leading to a reduction in dye removal percentage. Similar studies have been conducted to investigate the effect of pH on the removal of Congo red using different types of activated carbon. For instance, previous research has examined the adsorption of Alizarin Red S using pine cone activated carbon, the adsorption of CR dye using coconut residual fiber activated carbon, and the adsorption of Ponceau 4R using Tilapia fish scales activated carbon. [48,68,70].

4.4 Adsorption isotherms studies

The heterogeneity factor, nF , is employed in Freundlich isotherm analysis to determine if the adsorption is a chemical process ($nF < 1$), linear process ($nF = 1$), or physical process ($nF > 1$). The results for $nF = 0.278$ and $1/nF = 3.602$ show that physical processes and cooperative adsorption are advantageous. Fitting experimental data to the Freundlich isotherm yields an R^2 value of 0.99 depicts the best fit for this study.

The Langmuir isotherm assumes that adsorption takes place on a homogenous surface with equally energetic adsorption sites. It also assumed that the equilibrium between an adsorbate and an adsorbent system occurs when the adsorbate adsorption is restricted to one molecular layer at or before a relative pressure of unity is attained [71]. The Langmuir isotherms for the current studies had maximum adsorption capacity (q_m) values of 19.58 mg/g and R^2 values of 0.96, indicating a satisfactory fit of this isotherm to the

experimental data. The separation factor (R_L) of the Langmuir isotherm is found to be 0.035 indicating a favorable adsorption.

Temkin isotherm evaluated the adsorbent-adsorbate interactions explicitly [72]. When compared to the Langmuir and Freundlich isotherms, the Temkin isotherm model is less effective for explaining the adsorption of Congo red onto mFSAC, with an R^2 value of 0.92. The experimental data suggest an exothermic process using the constant B_T , which is related to the heat of adsorption and has a positive value ($B_T = 8.56$).

Chi-square analysis was carried out for each isotherm to validate the adsorption isotherms model that was utilized. According to the χ^2 analysis, when comparing the various adsorption isotherm models, the Freundlich model has the lowest χ^2 values, followed by the Langmuir and Temkin models. This suggests that the Freundlich model of adsorption fits Congo red dye adsorption better than the Langmuir and Temkin isotherm models. The values for each parameter for adsorption isotherms are all shown in Table 4.3.

Table 4.2 Isothermal models and equations

Isothermal models	Parameters	Values
Freundlich	$1/nF$	3.602
	K_L	0.166
	R_L	0.231
	K_F	46.697
	χ^2	0.00031
	R^2	0.99
Langmuir	q_{max}	19.58
	$1/nF$	0.787
	K_L	0.961
	R_L	0.035
	χ^2	0.0034
	R^2	0.96
Temkin	B_T	8.56
	A	3.16
	χ^2	0.1801
	R^2	0.92

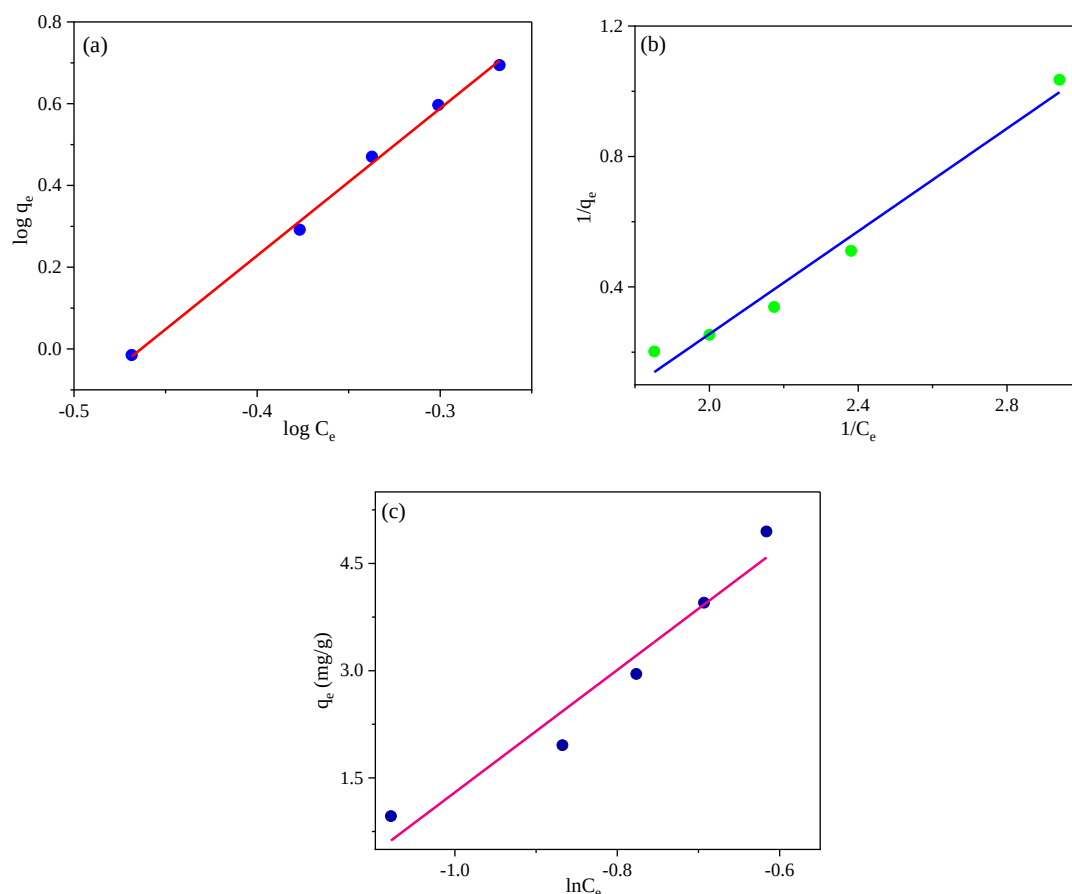


Fig. 4.3 (a) Freundlich isotherm (b) Langmuir isotherm and (c) Temkin isotherm plot of Congo Red adsorption unto mFSAC.

4.5 Adsorption kinetics and mechanism

To design and model the adsorption process as well as for comprehending the dynamics of the adsorption reactions in terms of the order of the rate constant, kinetics parameters are crucial information. To analyze the experimental data for Congo red adsorption onto the prepared activated carbon, various kinetic models—including pseudo-first-order, pseudo-second-order, Weber–Morris intraparticle diffusion, and the Elovich model—were applied. The corresponding results are presented in Fig. 4.3 and Table 4.3. The pseudo-first-order model [73] is the earliest known equation that describes the adsorption rate based on the adsorption capacity, while the pseudo-second-order model [74] state that the adsorption process is controlled by chemisorption, which involves valency forces through electron sharing or exchange between the solvent and the sorbate. The fractional uptake of solute on particles in a liquid-solid system is explained by the Weber and Morris intraparticle diffusion model to determine a sorption rate that regulates the rate-limiting

step [75,76] The extent of surface covering and activation energy for chemisorption are described by the Elovich model [77,78].

4.5.1 The pseudo-first-order kinetic model

The linear plot of $\ln(q_e - q_t)$ vs time can be used to derive the pseudo-first-order equilibrium rate constant K_1 . The Congo red sorption on prepared activated carbon is shown in Fig. 6(a) as a plot of pseudo-first-order kinetics, and the related findings are presented in Table 4. Congo red sorption on the mFSAC system was found to have a K_1 of 0.00126/min and an R^2 value of 0.850 mFSAC was discovered to have an equilibrium sorption capacity (q_e) value of 1.958mg/g. Pseudo-first order is less advantageous than pseudo-second order due to its lower correlation coefficient and higher Sum of Squares Error (SSE) value [79].

4.5.2 The pseudo-second order kinetic model

The values are listed in Table 4.3 and the linear graphs of t/q_t vs time (t) in Fig 3(b) demonstrate good agreement between experimental and estimated $q_{e(\text{exp})}$. The second-order kinetics model's correlation coefficient $R^2 = 0.999$ value proves that it is applicable to the adsorption of Congo red on mFSAC. The R^2 values in this instance are higher than those of the pseudo first-order model, indicating that the kinetics data matches the pseudo second-order model more closely. The results of SSE study further show that the pseudo second-order model can more accurately and satisfactorily describe the adsorption kinetics of Congo red onto mFSAC. Additionally, the similar values of $q_{e(\text{cal})}$ and $q_{e(\text{exp})}$ further imply that the adsorption mechanism most likely follows the pseudo-second-order kinetics model that has previously been described by several publications. Similar outcomes were attained by [70] HCl-modified activated carbon from coconut fiber, [80] activated carbon from Coir pith, [8] with hydrogen peroxide-modified activated carbon using hen feathers.

4.5.3 Elovich model

The model implies that the rate of adsorption reduces with time as a result of a reduction in the number of available adsorption sites on the surface. Diffusion is taken into account in the Elovich kinetics pattern, which could be interpreted as proof that the rate-determining phase is diffusion in nature [72,81]. This is shown by a plot of q_t vs $\ln(t)$ in the Elovich model, which yields a correlation coefficients R^2 value of 0.926.

4.5.4 Weber and Morris intraparticle diffusion model

In Fig. 3(c), intraparticle diffusion plots of qt vs $t^{1/2}$ are displayed, and Table 4.3 lists the corresponding values that were determined from the plot. The thickness of the boundary layer is determined by the value of the intercept; so, the larger the value, the thicker the boundary layer [82,83]. The figure make it clear that the adsorption process involved only one stage. It implies that intraparticle diffusion is the sole variable influencing the adsorption process. It was found that the correlation coefficient value is high i.e 0.958 which indicate homogeneous pore structures with a strong linear relationship between solute uptake and square root of time throughout the adsorption process. [84,85]

Table 4.3 Kinetic parameters with equations of Congo red adsorption on prepared AC.

Kinetics	Parameters	Values
Pseudo-first order	$q_{e(exp)}$	1.958
	$k_1 \times 10^{-1}$	0.00126
	R^2	0.85
	SSE	5.16
	MSE	0.73
Pseudo-Second order	$q_{e(exp)}$	1.958
	$q_{e(cal)}$	1.97
	$k_2 \times 10^{-1}$	1.08
	R^2	0.999
	SSE	0.043
	MSE	0.007
Weber and Morris intraparticle diffusion model	$q_{e(exp)}(mg\ g^{-1})$	1.958
	k_b	0.010
	$\times 10^{-1}mg\ g^{-1}m$	1.864
	$A(mg\ g^{-1})$	0.958
	R^2	
Elovich model	$q_{e(exp)}(mg\ g^{-1})$	1.958
	B	3.278
	R^2	0.926
	A	2.765
	SSE	0.54
	MSE	0.18

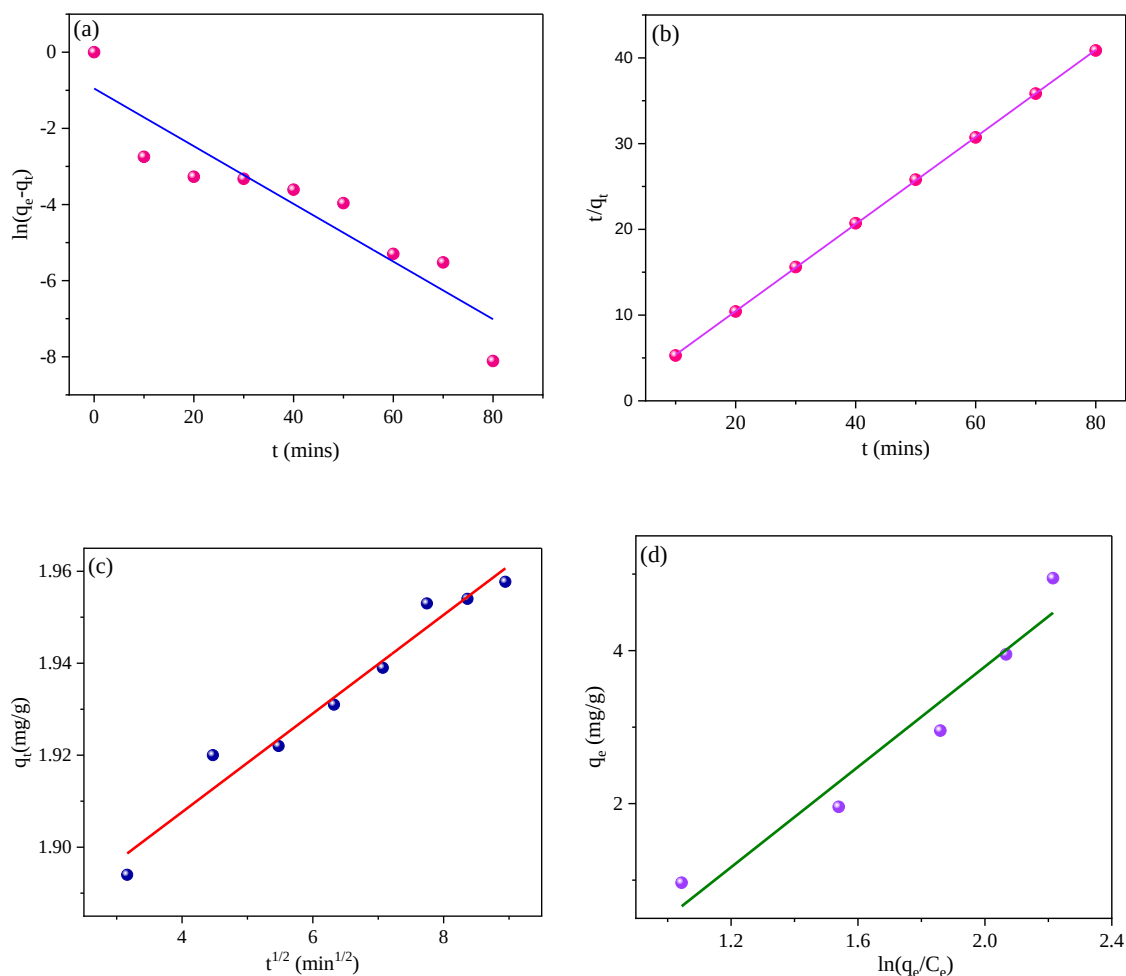


Fig. 4.4 (a) Pseudo first-order model (b) Pseudo second order model (c) Weber and Morris intraparticle diffusion model (d) Elovich model plot of Congo Red adsorption unto mFSAC.

4.6 Thermodynamic studies

The thermodynamic study of the adsorption of Congo red was studied over the temperature range 298 K to 328 K as shown in Table 4.4. The thermodynamic parameters, enthalpy change (ΔH), and entropy change (ΔS) were graphically determined.

Table 4.4 Thermodynamic parameters for Congo red adsorption onto activated carbon

ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)			
		298K	308K	318K	328K
-96.62	-287.9	-11.40	-8.57	-3.19	-3.76

The values of ΔH for Congo red adsorption were found to be -96.62 kJ/mol. It was implied from the negative ΔH values that the adsorption process was exothermic. However, negative entropy (-ve ΔS) shows that the sorption is enthalpy-driven during the adsorption phase, and the negative ΔG values showed the viability and spontaneity of the adsorption process. The favorability of the adsorption process at lower temperatures was revealed by the rise in ΔG value with temperature up to 318K.

4.7 Comparatively Study.

The current study on Congo Red removal was compared to previously conducted research, which is listed in a table. After analyzing all the results, it was concluded that the activated fish scale proved to be effective in eliminating Congo Red from aqueous solutions. Unlike other studies which removed the dye at highly acidic pH levels (pH 2 to pH 4), this research was conducted at a neutral pH of 7.0. The treatment time was 60 minutes, which is significantly shorter than the experimental time in other studies that exceeded 120 minutes. Moreover, the efficiency rate of 99.04% was relatively higher than most of the findings considered in the literature for the present study.

Table 4.5 Different activated used for removal of Congo Red

S/No.	Activated carbon	Optimum parameters	Removal efficiency	References
1.	Fish bone	IC=150mg/L, CT=60min, AD=5g/L, pH=2, T=328K	96.3%	[86]
2.	Cuttlefish bone	pH= 2, CT=60 min, AD=50mg	94%	[87]
3.	Bael shell	IC=50 mg/l, pH=3, CT=180min T=303K	92%	[57]
4.	<i>Trichoderma</i> (T. <i>virens</i> and T. <i>viride</i>)	IC=50 mgL ⁻¹ , CT= 24 h, pH= 6 T=298K	88%	[88]
5.	Coffee waste	CT=180 min, IC=50 mg/L, pH = 3, T=298K, AD=4g	96.8%	[89]
6.	<i>Azolla filiculoides</i>	pH=6.2, T=303K, AD=2g	95%	[90]
7.	Saw dust	pH=2, T=303K, CT=2.5h AD = 1.0g	96.76%	[91]
8.	<i>Raphanus sativus</i> peels and <i>Grewiaasiatica</i> leave	AD=2.0g and 0.5g, CT=20m and 30min pH=3.0 and 7.0 T= 293K and 303K	87.26% and 96.35% respectively	[92]

9.	Mixed fish scales	AD= 0.25g CT=60min	99.04%	This Study
		IC=20mg/L, pH=7.0 T=298K		

AD=Adsorption dosage, CT= Contact time, IC=Initial concentration, T=Temperature (K)

4.8 Regeneration of adsorbent

Regeneration of the adsorbent in any adsorption process is crucial since it influences the adsorbent's economic viability. Desorption tests on the used activated carbon (mFSAC) were carried out to comprehend the biocarbon's capacity for regeneration. To determine how well the regenerated carbon was removed, regeneration cycles up to the sixth cycle were conducted. To achieve saturation of the adsorbent, 0.25 g of adsorbent was stirred for 60 minutes with 50 ml of a 20 mg/L dye solution. 0.1 M NaOH solution was used to desorb the saturated carbon for 2 hours while stirring. It was then filtered, cleaned with distilled water, dried in an oven at 105 °C, and used again for the next adsorption.

The process of adsorption and desorption was investigated up to sixth cycle to comprehend the regeneration cycle. The results are shown in Fig. 4.7, and the reusability of current adsorbent is confirmed by the fact that the adsorption effectiveness of activated carbon decreases to 72.68 percent after the sixth cycle from 99.34 percent in the first cycle.

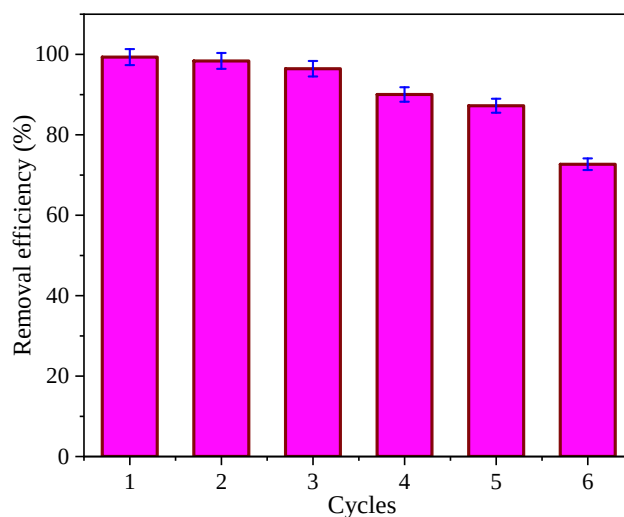


Fig 4.5 Regeneration of activated carbon over six cycles

Conclusion

The present study investigated the potential of waste fish scales (mFSAC) for the preparation of activated carbon aimed at dye adsorption. Batch experiments were conducted to examine the adsorption kinetics of Congo red dye on mFSAC under varying conditions, including initial dye concentration, pH, adsorbent dosage, and temperature. The results revealed that higher initial dye concentrations enhanced dye adsorption, with pH 6 identified as optimal. Increasing the adsorbent dose improved Congo red removal across all concentrations, reaching maximum efficiency at 0.25 g of carbon. Kinetic analysis indicated that the adsorption followed a pseudo-second-order model ($R^2 > 0.99$), suggesting chemisorption as the rate-limiting step. Among the isotherm models evaluated, the Freundlich isotherm best described the adsorption behavior. Thermodynamic studies further indicated that the process was exothermic. Overall, the findings demonstrate that activated carbon derived from waste fish scales is an effective adsorbent for Congo red dye, offering a sustainable approach to repurpose waste materials, reduce environmental impact, and contribute to a circular economy.

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CHAPTER 5

ADSORPTION OF 17 β -ESTRADIOL FROM AQUEOUS SOLUTION USING WASTE FISH SCALES ACTIVATED CARBON: EXPERIMENTAL AND COMPUTATIONAL ANALYSIS.

This chapter focuses on the application of activated carbon prepared from waste fish scales for the removal of 17 β -estradiol (E2). The adsorption process was optimized by adjusting parameters such as pH, adsorbent dosage, initial concentration, contact time, and temperature. The underlying adsorption mechanism was examined through isotherm and kinetic modeling, while thermodynamic analysis was conducted to assess the feasibility and nature of the process. Furthermore, density functional theory (DFT) calculations were employed to gain deeper insight into the adsorption interactions. The developed adsorbent exhibited excellent efficiency, stability, and reusability across several adsorption–desorption cycles.

5.1 Introduction

One of the most pressing global challenges of recent times has been the contamination of water resources and the complexities involved in their remediation [1]. Among the numerous pollutants present in water, pharmaceutical compounds like hormones have been identified as particularly harmful to both human health and aquatic ecosystems [2]. Persistent endocrine-disrupting chemicals (EDCs) have emerged as a major concern because of their toxic effects and potential to cause mutations and cancer [3–5]. It is estimated that around 750 kg of synthetic steroid hormones from contraceptive pills, along with approximately 30,000 kg of common steroid hormones, particularly estrogens, are released into sewage systems annually [6]. 17 β -Estradiol (E2), a naturally occurring hormone in humans and animals, as well as its synthetic counterpart, has become a significant concern in water pollution due to its endocrine-disrupting effects, even at trace levels [7]. This is attributed to its high reactivity and strong affinity for estrogen receptors. E2 has also been shown to cause serious effects such as inhibiting fish egg production and inducing sex reversal in male fish, which can ultimately lead to the failure of local fish populations [8,9]. Major sources of synthetic E2 in water bodies include the discharge of treated and untreated wastewater from sewage treatment plants [10] and animal waste [11]. Synthetic E2 commonly used in hormone replacement therapy and oral contraceptives, also makes its way into aquatic environments when released [12]. As such, there is a crucial need for practical and effective strategies to control E2 pollution. Numerous approaches have been employed for E2 removal, including advanced oxidation processes such as Fenton's reagent, ultraviolet treatment, photocatalysis, filtration, biodegradation, and ozonation [13]. Among these techniques, adsorption has been recognized to be the most effective, offering an economically practicable and accessible solution [14]. Researchers have used adsorption technique for E2 removal from aqueous solution via graphene oxide [15,16], carbon nanotubes [12,17], zeolites [18], montmorillonite/hydrochar [19], rice straw [20] and dewatered sludge biochar [21]. However, many sorbents face limitations such as low adsorption capacity or high costs, creating a strong need for a high-performance, cost-effective, and reusable adsorbent. Hence, activated carbon (AC) has shown promise in removing E2 from wastewater, as it exhibits a strong affinity for binding organic substances,

even at low concentrations [22,23]. In such applications, the key factor is the adsorptive performance of the AC at solid–liquid interface [24].

Accordingly, this study is the first to investigate the effectiveness of mixed fish scales in removing E2 from aqueous solutions through a sequence of comprehensive adsorption and kinetic experiments. Factors such as contact time, E2 concentration, pH, temperature and ionic strength were systematically analyzed. Its reusability and cost efficiency of the AC were evaluated through five cycles of desorption and regeneration. The distinctive feature of employing fish scales is their high carbon content, affordability, and widespread availability, which makes them an effective and sustainable raw material for the synthesis of activated carbon. Although earlier studies have examined the usage of AC produced by different biomass sources for the removal of E2, discarded mixed fish scales have not been reported for the same. Additionally, while it is true that AC production by pyrolysis technique is inevitably associated with emissions, pyrolysis-produced activated carbon can be regarded as sustainable because it frequently uses waste biomass as its feedstock, efficiently turning a waste product into a valuable resource while lowering the demand for virgin materials. Proper management of large-scale production, such as using the heat produced to warm new feedstock or generate heat for other uses, may help create a more circular economy at the same time. Theoretical calculations using DFT provide valuable insights into the interactions between E2 and activated carbon. This analysis highlights the influence of surface functional groups and their roles in enhancing the adsorption process.

5.2. Experiment

5.2.1 Materials and methods

β -Estradiol ($C_{18}H_{24}O_2$; $\geq 98\%$ purity) was used as the adsorbate and obtained from Sigma-Aldrich, while HPLC-grade acetonitrile used in this study was acquired from Thermo Scientific. Fig. 5.1 illustrates the molecular structure of E2. A freshly prepared stock solution of E2 (50 mg/L) was created by dissolving it in a 1:1 mixture of Milli-Q water and acetonitrile. Only analytical grade reagents and deionized water were utilized throughout this study.

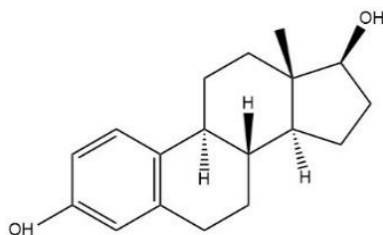


Fig. 5.1 Molecular structure of β -Estradiol (E2).

5.2.2 Mixed fish scale (MFS) activated carbon production

Biomass from mixed fish scales (MFS) was obtained from a local fish market in Mokokchung, Nagaland, India (26°19'38"N, 94°31'26"E) and converted into activated carbon, referred to as mixed fish scale activated carbon (mFSAC). The methods for its preparation and characterization have been detailed in our previous study [25] with the complete procedure presented in Chapter 3.

5.2.3 Adsorption studies

Experiments for the batch adsorption of E2 from aqueous solutions were conducted in 250 mL Erlenmeyer flasks, with solutions agitated at 180 rpm on a rotary shaker [26,27]. Key parameters examined included adsorbent dose (0.05–0.25 g/L), pH (3–10), initial concentration (4–20 mg/L), contact time (5–180 mins), and temperature (298–328 K). E2 concentrations in the filtrate were determined at 280 nm using a UV-Vis Spectrophotometer (Lambda 35, PerkinElmer).

5.2.4 Isotherm studies

Isotherm models play a crucial role in adsorption studies by revealing the interaction between adsorbates and the adsorbent surface, estimating adsorption capacity, and identifying its adsorption process. They also allow for the prediction of adsorption performance under different conditions and assist in optimizing and designing effective adsorption systems for practical use. In the present study, we employed non-linear models to analyze E2 adsorption onto the prepared activated carbon.

5.2.5 Kinetic studies

It helps to reveal how quickly an adsorbate is removed from solution and identify the controlling factors, such as surface interactions or diffusion through the boundary layer. Models like pseudo-first-order, pseudo-second-order, and Elovich provide insights into different aspects of adsorption behavior. In the present study, these kinetic models were applied to assess the adsorption rate of E2 onto the prepared AC and to determine whether chemisorption or physical adsorption dominated the process.

5.2.6 Analytical statistics

In this study, the adsorption isotherm and kinetic models that best fit the experimental data were identified using Chi-squared (χ^2) [33]. This statistical test evaluates the agreement between experimental adsorption results and theoretical model predictions. Lower χ^2 values indicate a closer fit, aiding in the selection of the most appropriate isotherm or kinetic model and ensuring accurate interpretation of the adsorption process.

5.2.7 Thermodynamic studies

Thermodynamic evaluation is vital in sorption research to distinguish between chemical and physical adsorption mechanisms. For E2 adsorption, thermodynamic parameters were analyzed across 298–328 K.

5.3 Computational studies

The interaction between pharmaceutical pollutants and carbonaceous materials was investigated by using a 6-membered carbon ring. An investigation by Perry et al. 2000 [35], revealed that the surfaces of carbonaceous materials comprised 3 to 7 fused benzene rings. Several theoretical studies have employed cluster models of fused benzene rings to simulate the carbon surface, proving useful in understanding the adsorptive interactions between various species and its carbon surface.

All molecular structures were modeled using the GaussView 05 graphical interface and calculated with the Gaussian 09 W software package [36]. The DFT method, with B3LYP hybrid functional and 6-31G basis set, optimized geometrical structures at the ground state. The IEFPCM model [37] simulated water solvent effects during optimization [38–40]. An

armchair model (mFSAC) represented the AC surface, with top carbon atoms unsaturated for interactions and terminal carbons hydrogen-saturated. Oxygen-containing functional groups: carboxyl (COOH), hydroxyl (OH), and aldehyde (CHO) were added to active sites, forming variants: pristine (p-mFSAC), COOH-mFSAC, CHO-mFSAC, and OH-mFSAC. Optimized structures of mFSAC and E2 adsorbate are shown in Fig. 5.2. The favorability of the interaction was evaluated by calculating the adsorption energy (E_{ad}). The larger the negative of E_{ad} values, the stronger the adsorption, resulting in a more stable system and robust adsorption process.

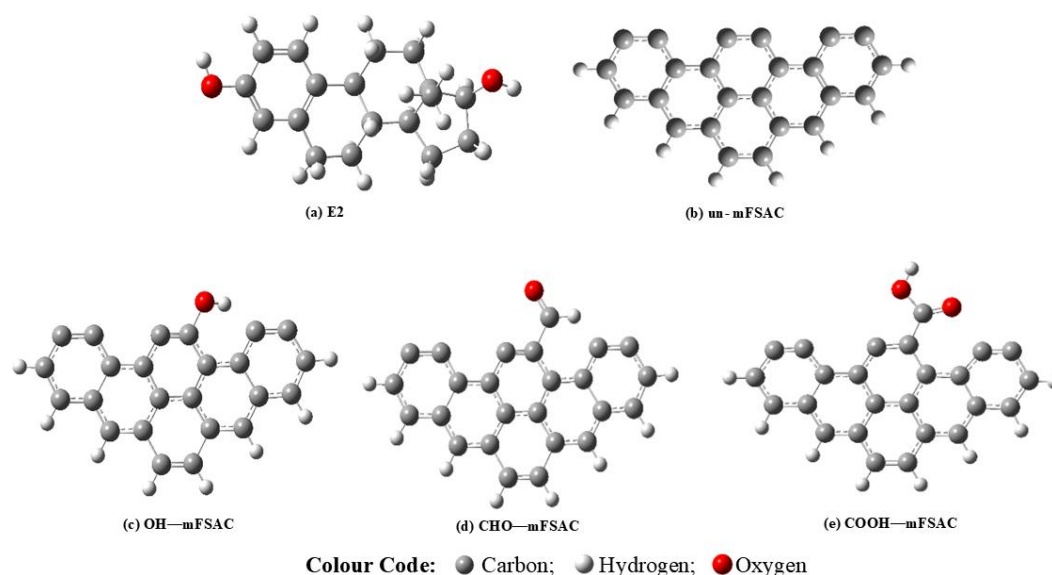


Fig. 5.2 E2 adsorbate with optimized structures, along with pristine and functionalized AC (mFSAC).

5.4 Results and discussion

5.4.1 Batch adsorption studies

Batch adsorption studies evaluated the effects of initial E2 concentration, pH, adsorbent dosage, contact time, and temperature. E2 solutions (4–20 mg/L) were mixed with AC (0.05–0.25 g/L) at pH 2–10 and 25 °C, agitated at 180 rpm. Optimal conditions for maximum adsorption efficiency were determined. These optimized parameters ensured enhanced interaction between the adsorbent and E2 molecules, promoting effective removal. The findings suggest that maintaining these conditions is crucial for achieving consistent and reliable adsorption performance in subsequent experiments.

5.4.2 Effect of adsorbent dose

Fig. 5.3(a) shows that removal efficiency improves with increased adsorbent dosage due to more active sites. At 0.05 g/L, limited surface area results in 87% efficiency, while 0.15 g/L achieves 98.35% as most sites are occupied. Beyond this, improvements are minimal, indicating surface saturation. Thus, 0.15 g/L was selected as the optimal dosage, consistent with the Langmuir isotherm model describing monolayer adsorption [28].

5.4.3 Effect of concentration and reaction time

The effect of E2 concentration on mFSAC removal efficiency was studied for 4–20 mg/L, showing a decline in removal percentage with increasing E2 concentration (Fig. 5.3(b) and 3(c)). This decrease is due to limited active adsorption sites on the AC surface. At lower concentrations, more adsorption sites are available relative to E2 molecules, resulting in higher removal efficiency. Equilibrium was reached at 120 min, achieving 97.96% removal at 8 mg/L.

5.4.4 Effect of pH

The adsorption efficiency of E2 on AC depends on pH, influencing the adsorbent's surface charge and the adsorbate's ionization. Using 8 mg/L E2 concentration, 0.15 g/L adsorbent, and 120 min reaction time, the pH was varied from 2 to 10 (Fig. 5.3(d)). With a pHzpc of 7.64, the AC surface is positively charged below this pH and negatively charged above it, while E2 (pKa 10.23) is neutral below pH 10.23 and negatively charged above [41]. Maximum removal efficiency (97.96%) occurred at pH 4, where the carbon surface is positively charged, and E2 remains neutral, suggesting non-electrostatic interactions dominate. Instead, the improved removal efficiency is attributed to hydrogen bonding between carboxylic groups on the activated carbon and hydroxyl groups in E2. Additionally, the presence of hydronium ions (H_3O^+) at low pH further enhances adsorption by stabilizing hydrogen bonds and promoting interactions between E2 molecules and the carbon surface [42]. As the pH increased, the adsorption efficiency declined. This reduction is likely due to hydroxyl ion (OH^-) competition for active sites, the formation of aqua complexes, and increased E2 solubility, all of which hinder adsorption [43]. Consequently, acidic conditions are more favorable for E2 removal, while alkaline conditions reduce adsorption efficiency.

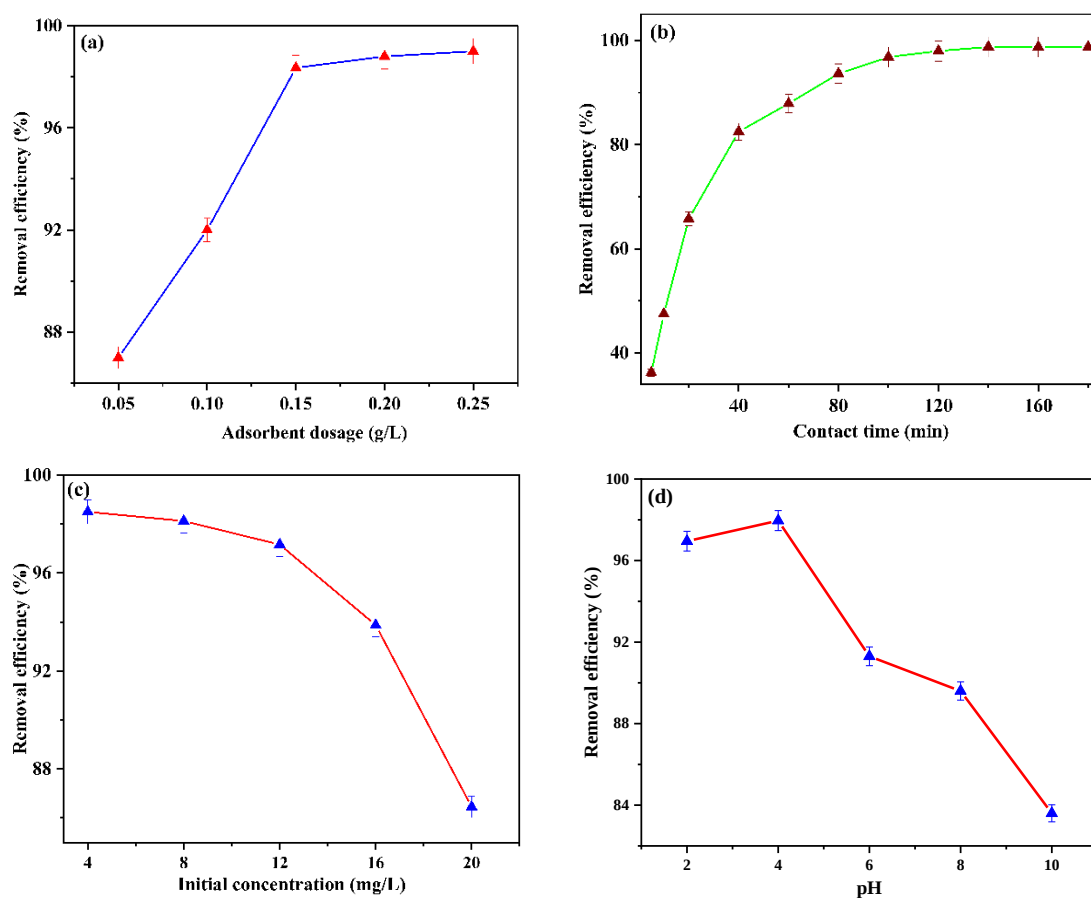


Fig. 5.3 Effect of (a) adsorbent dose (b) contact time (c) initial concentration and (d) pH for E2 adsorption.

5.4.5 Effect of temperature

The effect of temperature on E2 adsorption by mFSAC was studied from 298 K to 328 K, keeping constant parameters: 0.15 g/L adsorbent, pH 4, 120 min contact time, and 8 mg/L initial concentration. As shown in Fig. 5.4, removal efficiency declines from approximately 97% at lower temperatures to 74 % at higher temperatures, indicating an exothermic adsorption process. The observed trend aligns with previous studies on adsorption of E2, which emphasize that lower temperatures are crucial for improving adsorption efficiency [29,44].

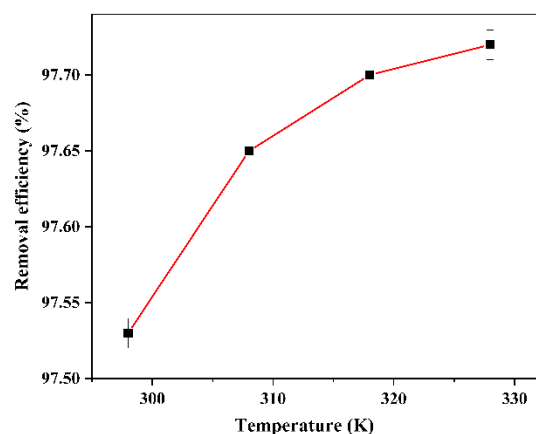


Fig. 5.4 Effect of temperature for E2 adsorption by mFSAC (mFSAC dose= 0.15 g/L; initial concentration= 8 mg/L; contact time= 120 min; pH= 4).

5.4.6 Adsorption isotherm studies

This study utilized three non-linear isotherm models [45]: Langmuir, Freundlich, and Temkin to analyze E2 adsorption onto AC, as depicted in Fig. 5.5. Model parameters and corresponding χ^2 values are summarized in Table 5.1. The Langmuir model best described the data, with a maximum adsorption capacity (q_m) of 6.16 mg/g and (K_L) of 4.14 mg/L. A high correlation coefficient ($R^2 = 0.998$) and a low chi-square value ($\chi^2 = 0.005$) indicate strong agreement, suggesting monolayer adsorption on a uniform surface [46]. The Freundlich isotherm analysis yielded an 'n' value greater than 1 ($n = 3.44$), indicating that E2 adsorption onto AC is favourable. The corresponding correlation coefficient ($R^2 = 0.883$) and a relatively low chi-square value ($\chi^2 = 0.357$) further support this observation. The Temkin model analysis yielded a Temkin constant (B_t) of 2.09 kJ/mol, indicating weak adsorbate-adsorbent interactions typical of physisorption. The model showed a strong correlation ($R^2 = 0.974$) and a low chi-square value ($\chi^2 = 0.081$), demonstrating a good fit to the data. Similar observation was stated by [12] using carbon nanotubes and Zhong and co-workers [18] using modified zeolites, where E2 adsorption adhered to the Langmuir model.

Table 5.1 Isotherm parameters for E2 adsorption

Isotherm	Parameters	Values
Langmuir	q_m (mg/g)	6.16
	K_L (L/mg)	4.18
	R^2	0.998
	χ^2	0.005
Freundlich	K_F (mg/g (L/mg) ^{1/2})	4.59
	n	3.44
	R^2	0.883
	χ^2	0.357
Temkin	K_T (L/mg)	60.84
	b_T (kJ/mol)	2.09
	R^2	0.974
	χ^2	0.081

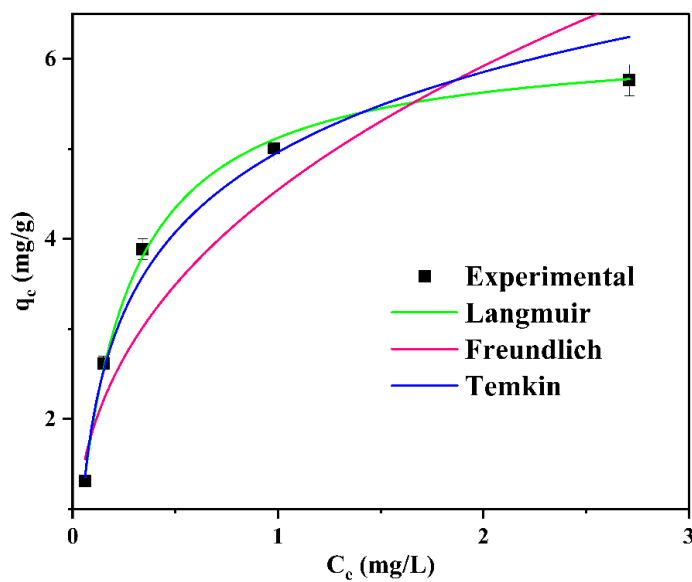


Fig. 5.5 Non-linear fitting of Langmuir, Freundlich and Temkin isotherm models for E2 adsorption (mFSAC dose= 0.15 g/L; initial concentration= 8 mg/L; contact time= 120 min; pH= 4).

5.4.7 Adsorption kinetics studies

Kinetic parameters are essential for modelling and understanding adsorption dynamics and rate constants [47]. This study analyzed adsorption kinetics using the PFO, PSO, and Elovich models, as shown in Fig. 5.6, with detailed results in Table 5.2. Conversely, the PSO model demonstrated a higher correlation coefficient ($R^2 = 0.99$) and a lower χ^2 value, indicating a superior fit. The PSO model's $q_{e(\text{cal})}$ closely matched $q_{e(\text{exp})}$, confirming its reliability and suggesting that chemisorption dominates the process.

The Elovich model, which accounts for the chemical nature of adsorption and considers diffusion as the rate-determining step, showed that the adsorption rate decreases over time. Its q_t versus time plot yielded a strong correlation ($R^2 = 0.983$) and a χ^2 value of 6.489, supporting its applicability.

Table 5.2 Kinetic parameters of E2 adsorption onto prepared mFSAC.

Kinetics	Parameters	Values
PFO	k_1 (min^{-1})	0.077
	$q_{e(\text{cal})}$ (mg/g)	2.502
	$q_{e(\text{exp})}$ (mg/g)	2.713
	R^2	0.955
	χ^2	19.164
PSO	k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	0.030
	$q_{e(\text{cal})}$ (mg g^{-1})	2.799
	$q_{e(\text{exp})}$ (mg g^{-1})	2.713
	R^2	0.991
	χ^2	3.72
Elovich	A	0.567
	B	1.854
	R^2	0.983
	χ^2	6.498

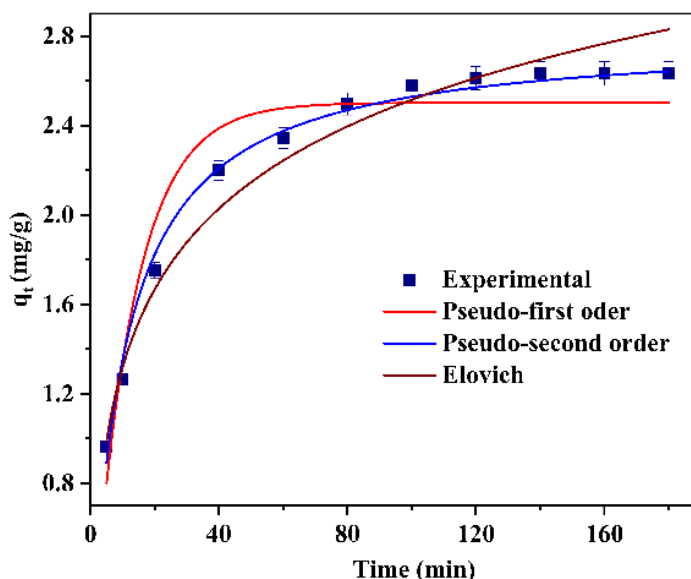


Fig. 5.6 Non-linear fitting of PFO, PSO and Elovich kinetic models for E2 adsorption (mFSAC dose= 0.15 g/L; initial concentration= 8 mg/L; contact time= 120 min; pH= 4).

5.4.8 Thermodynamic studies

The increasing negativity of ΔG° with rising temperature suggests enhanced favorability at higher temperatures (Table 5.3) [48]. A positive ΔH° value (71.43 kJ/mol) indicates the endothermic process, with greater efficiency at elevated temperatures, and supports chemisorption as the dominant mechanism. Additionally, the positive ΔS° value (0.246 kJ mol⁻¹K⁻¹) reflects increased randomness at the solid-liquid interface, likely due to the displacement of solvated water molecules, leading to higher system disorder [49].

Table 5.3 Thermodynamic characteristics of E2 adsorption onto mFSAC.

Adsorbent	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)			
			298K	308K	318K	328K
mFSAC	71.43	0.25	-1.62	-4.19	-7.94	-8.49

5.4.9 Theoretical calculations

Various interactions, including π - π interactions, hydrogen bonding, and electrostatic forces, contribute to the adsorption of E2 onto carbon surfaces [50]. Of these, hydrogen bonding plays a vital role amid the adsorbate and adsorbent [51–53]. Through DFT modeling, this study intends to offer perceptions into the potential formation of hydrogen bonds between E2

and the AC adsorbent, further clarifying the mechanisms underlying the adsorption process. The adsorption behaviour was explored using an armchair model [54]. Fig. 5.7 illustrates the optimal configurations of interactions between E2 and AC whereas, Table 5.4 summarizes the calculated adsorption energies (E_{ad}) and bond lengths for the various interaction modes, shedding light on the strength and nature of these interactions.

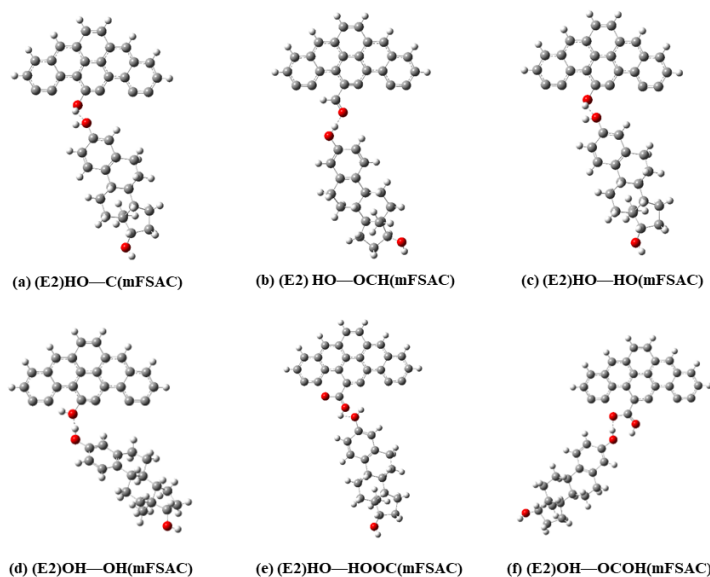


Fig. 5.7. Optimized molecular structures of E2 molecule interaction with mFSAC.

Table 5.4 E_{ad} and bond distance between E2 and mFSAC.

System	Mode of Interaction	Bond length (nm)	E_{ad} (kJ/mol)
E2 + mFSAC	(H _{E2} -C _{mFSAC})	0.214	-14.135
E2 + (mFSAC)CHO	(H _{E2} -O _{mFSAC})	0.172	-34.843
E2 + (mFSAC)OH	(H _{E2} -O _{mFSAC})	0.173	-31.865
	(O _{E2} -H _{mFSAC})	0.163	-39.448
E2 + (mFSAC)COOH	(H _{E2} -O _{mFSAC})	0.207	-46.521
	(O _{E2} -H _{mFSAC})	0.148	-69.869

5.4.10 Adsorption on pristine and functionalized AC

The optimized structure of (E2)HO—C(mFSAC), shown in Fig. 5.7a, revealed a slight elongation of the C-C bond length from 0.140 nm to 0.142 nm upon adsorption, facilitating electron migration towards the adsorption site. The adsorption energy for this configuration was calculated as -14.135 kJ/mol.

To explore E2 adsorption on functionalized AC, a hydrogen bond was identified amid the hydrogen atom of the (E2)OH group and oxygen atom of the CHO group on CHO-functionalized mFSAC, as illustrated in Fig. 5.7b. This interaction exhibited an adsorption energy of -34.843 kJ/mol. For hydroxyl-functionalized mFSAC, two interaction modes were analyzed: (E2)OH—OH(mFSAC) and (E2)HO—HO(mFSAC), as depicted in Fig. 5.7c. Among these, the (E2)HO—HO(mFSAC) mode showed higher adsorption energy and shorter bond lengths, indicating its higher favourability. The adsorption of E2 onto carboxyl-functionalized mFSAC was also investigated via two modes: (E2)HO—HOOC(mFSAC) and (E2)OH—OCOH(mFSAC). The (E2)HO—HOOC(mFSAC) mode demonstrated higher adsorption energy and reduced bond lengths compared to the latter, making it the more energetically favorable interaction. Table 5.4 further confirms this preference. The energy profile diagram in Fig. 5.8 highlights that the HOOC(mFSAC) mode exhibited the most negative adsorption energy values, underscoring its strong interaction with E2. These findings suggest that incorporating -COOH groups into mFSAC significantly enhances E2 adsorption, surpassing the performance of both OH(mFSAC) and CHO(mFSAC) functional groups.

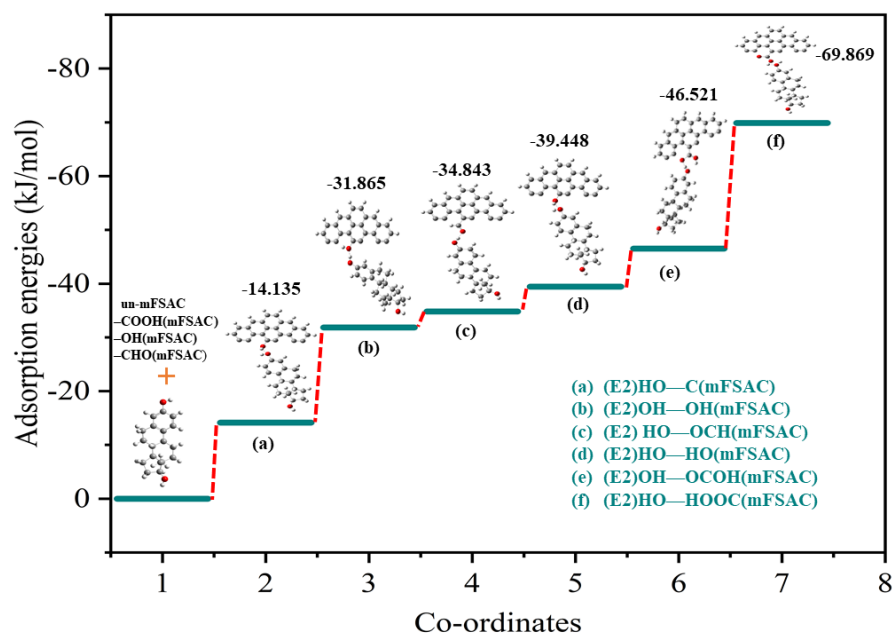


Fig. 5.8 Calculated energy diagram for the adsorption of E2 onto mFSAC

5.5 Regeneration studies

The regeneration study evaluated the reusability of modified fish scale activated carbon (mFSAC) through multiple adsorption-desorption cycles. For this, 1 g/L of mFSAC was added to 50 mL of E2 solution with an initial concentration of 50 mg/L and stirred for 24 hours to achieve saturation. Desorption was then conducted using 0.1 M NaOH for 2 hours, followed by filtration, rinsing with Milli-Q water, and drying at 105°C before reuse. This process was repeated for five cycles to assess the regenerated carbon's adsorption performance. As illustrated in Fig. 5.9, the removal efficiency was initially 96.06% in the first cycle but gradually declined to 72.6% by the fifth cycle, indicating that while some efficiency is lost over time, the regenerated mFSAC remains viable for reuse across multiple cycles.

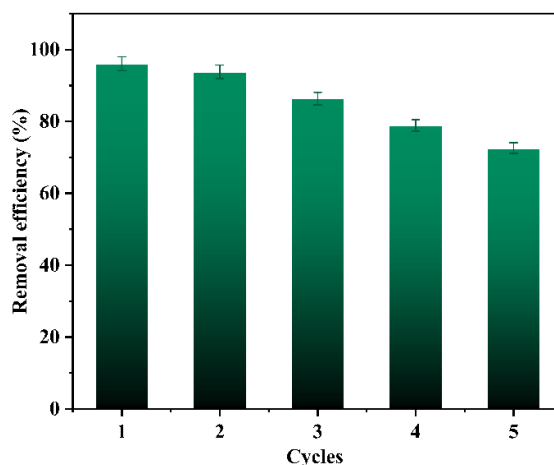


Fig. 5.9 Regeneration studies of mFSAC adsorbent E2 removal

5.6 Comparative studies of mFSAC with other adsorbents.

The performance of AC synthesized from mixed fish scales (mFSAC) was assessed by comparing its effectiveness in E2 removal with other adsorbents, as presented in Table 5.5. The findings reveal that mFSAC exhibits an adsorptive capacity comparable to other materials, underscoring its potential as a highly effective adsorbent for E2 removal.

Table 5.5 Comparison studies of prepared mFSAC with some other adsorbents.

Adsorbent	S _{BET} (m ² g ⁻¹)	Dosage	Time (min)	pH	C ₀ (mg L ⁻¹)	Isotherm model	R ²	Ref.
Graphene oxide	15.4	0.04	240	7	0.5-2.5	Freundlich	0.92	[55]
	132	0.08	330	6.5	0.2-8	Langmuir	0.98	[56]
Fe ₂ O ₃ /Carbon nanotubes	146	0.05	2400	3	0.4-2.4	Langmuir	0.99	[12]
Humic-mineral complexes	45.2	2.5	240	3	0.1-0.8	Langmuir	0.98	[7]
Granular activated carbon	-	0.08	480	7-8	1-6.5	Langmuir	0.98	[57]
Montmorillonite -carbon hybrids	98.14	0.05	360	3	0.2-6	Freundlich	0.99	[58]

Few-layered graphene oxide nanosheets	149.4	0.1	480	7	0.05-4	Langmuir	0.94	[59]
Carbon nanotubes/CoFe ₂ O ₄ composites	134.4	0.1	120	3.1	0.4-2.4	Freundlich	0.90	[17]
Rice straw- Derived Biochar	7.658	0.2	-	3	0.2-6	Freundlich	0.96	[20]
Dewatered sludge biochar	185.3	0.1	480	3	0.5-4	Langmuir	0.97	[21]
Montmorillonite /hydrochar nanocomposite	49	0.05	360	3	1-7	Freundlich	0.99	[15]
Modified zeolites	38.11	0.5	-	7	2-20	Langmuir	0.99	[18]
mFSAC	150.049	0.15	120	4	2-10	Langmuir	0.99	This study

Conclusion

This study introduces an activated carbon derived from mixed fish scales (mFSAC), demonstrating exceptional efficacy in removing β -Estradiol (E2) from aqueous solutions. We systematically optimized several operational factors including adsorbent dosage, initial E2 concentration, contact time, pH, and temperature to achieve maximum removal. The highest efficiency, 98.35%, was recorded under optimal conditions: pH 4, 0.15 g of mFSAC, 8 mg/L initial E2, and a 120-minute contact time. Mechanistically, the adsorption followed the Langmuir isotherm ($R^2=0.99$), pointing to a monolayer process on a uniform surface. Kinetic analysis confirmed the PSO model as the best fit, highlighting that chemisorption is the dominant rate-controlling step. Finally, thermodynamic studies confirmed the process is spontaneous, endothermic, and favored by increased temperature. DFT simulations revealed that the carboxyl (-COOH) group exhibited the strongest interaction with E2 compared to other functional groups, significantly enhancing adsorption performance. The presence of diverse functional groups on the activated carbon surface further boosted its adsorption capacity. Overall, these findings underscore the potential of mFSAC as a sustainable and efficient adsorbent for β -Estradiol removal, contributing to water treatment advancements.

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CHAPTER 6

SURFACE MODIFICATION OF ACTIVATED CARBON THROUGH BACTERIAL ADSORPTION AND ITS EFFECT ON CADMIUM REMOVAL FROM AQUEOUS SOLUTION

This chapter focused on the adsorption of Staphylococcus aureus, Klebsiella pneumoniae, and cadmium using microbial-modified activated carbon (FSAC-M) and its unmodified counterpart (FSAC). The experimental work included microbial adsorption studies, equilibrium modelling, kinetic analysis, and thermodynamic evaluation to understand the adsorption behaviour and mechanisms involved.

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6.1 Introduction

Water forms the foundation of all life on Earth, as the entirety of numerous biological functions in living organisms are dependent on it. However, limited access to safe and potable water has become a pressing global issue [1,2]. Furthermore, extensive environmental pollution has resulted in the contamination of water sources with inorganic, organic and biological pollutants. The World Health Organization (WHO) reports that almost 80% of wastewater is released into natural water bodies without proper treatment. The presence of pathogenic microorganisms in both treated and freshwater supplies poses a serious threat to human health worldwide.

Pathogenic microorganisms present in both treated and untreated drinking water represent a major global threat to human health. It is estimated that approximately 485,000 deaths occur annually worldwide due to diseases caused by the consumption of microbially contaminated water. Such waterborne illnesses include cholera, dysentery, typhoid, typhoid fever, and polio [3]. *Staphylococcus aureus*, a gram-positive bacterium and a leading cause of food poisoning, can contaminate drinking water and is associated with various infections including skin infections, endocarditis and sepsis [4,5]. The detection of *S. aureus* in water sources is particularly concerning owing to its pathogenic potential and its well-documented resistance to multiple antibiotics [6]. Likewise, *Klebsiella pneumoniae*, a gram-negative bacterium is linked to severe clinical conditions such as pneumonia, bacteremia, meningitis and infections of the liver, urinary tract and gastrointestinal tract, and is a significant cause of nosocomial infections [7–10]. The World Health Organization has classified *K. pneumoniae* as a priority pathogen due to its alarming resistance to several antibiotics including carbapenems, which are considered the ultimate treatment option for multidrug-resistant gram-negative bacterial infections [11–13].

Various techniques have been employed to remove bacteria from drinking water [14], including boiling, distillation, reverse osmosis, filtration, ozonation, electrolysis, UV irradiation, water softeners, activated alumina and sediment filters [15–21]. However, these methods do not guarantee complete removal of pathogen and often produce secondary byproducts, require continuous power supply and involve intensive maintenance, thereby increasing operational costs and limiting applicability under certain conditions. Therefore, developing an alternative and more sustainable approach for bacterial removal from water is essential. In this regard, adsorption using

activated carbon could be considered a suitable technique due to its high porosity and large surface [22,23].

In addition to microbial contamination, rapid industrial development has resulted in heavy metal ion pollution emerging as a major global environmental concern. Among these pollutants, cadmium (Cd^{2+}) is particularly significant and is commonly discharged from industries such as electroplating, pigment and paint manufacturing, electronics and textile printing [24,25]. Cd(II) can enter the human body via the food chain and accumulate in organs like the liver, kidneys and bones posing a serious threat to human health and life even at low concentrations [26,27]. The guideline for drinking water quality recommended the permissible limit of Cadmium is 0.003 mg L^{-1} [28]. Several approaches are employed to remove cadmium from wastewater including, ion exchange, membrane separation, chemical precipitation and adsorption [29–32]. Among these techniques, adsorption is regarded as the most efficient and practical due to its low cost, simplicity of operation, mild conditions, rapid adsorption rate, high removal efficiency and excellent reusability [33–35].

Several studies have highlighted the potential benefits of using bacterial pre-adsorbed activated carbon for heavy metal removal. For instance, Rivera-Utrilla et al. (2003) reported that the presence of bacteria on the activated carbon surface significantly enhanced the adsorption of cationic metals such as Pb(II) and Cd(II) while slightly reducing the uptake of anionic Cr(VI) [36]. Similarly, Quintelas and Tavares (2001) demonstrated that bacterial biofilms provide additional active sites including carboxyl, hydroxyl and phosphate groups which enhance heavy metal binding. In their study, Cr(VI) and Cd(II) removal was investigated employing a granular activated carbon-supported *Arthrobacter viscosus* biofilm [37]. The synergistic effect of bacterial bioadsorption and carbon adsorption was also reported by López-Ramón et al. (2019) who examined the removal of endocrine-disrupting compounds, bisphenols A and S using activated carbon cloths in the presence and absence of *Escherichia coli* [38]. A similar enhancement phenomenon was observed in the removal of Cr(VI) using *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Enterobacter cloacae* further supporting the potential of bacterial-assisted adsorption in water treatment [39]. As per available literature, pre-adsorption of *S. aureus* and *K. pneumoniae* on activated carbon for subsequent adsorption of Cd has not been studied. Therefore, this study aims to adsorb microorganism (*S. aureus* and *K. pneumoniae*) on the prepared activated carbon through column method. Furthermore, the pre-

adsorbed bacteria (*S. aureus*) and its unmodified activated carbon is used to adsorb cadmium for comparison. Microorganisms attached to activated carbon surfaces have enzymatic functions that aid in breaking down organic pollutants and transforming heavy metal ions. Enzymes like oxidoreductases, hydrolases and dehalogenases play key roles in catalyzing the oxidation of pollutants and biodegrading complex organic substances [40,41]. When microorganisms are immobilized, they settle on the activated carbon surface and form biofilms which are organized clusters of microorganisms enclosed in an extracellular matrix [42,43]. Biological modification of activated carbon creates a synergistic relationship between microorganisms and the adsorbent. Microorganisms on the surface of activated carbon improve its adsorption capacity by offering more binding sites for heavy metal ions [42]. Additionally, microbial activity helps regenerate used activated carbon by releasing adsorbed pollutants and aiding in the biodegradation of organic contaminants [44].

6.2 Materials and methods

Diphenylthiocarbazone (Dithizone), dimethyl sulfoxide (DMSO), Luria-Bertani agar (LBA) used in the present work was obtained from HiMedia. CdCl_2 and KOH was obtained from Thermo Scientific™. All compounds used in this study were taken directly from their packages without any additional purification and deionized water was utilized for all experiments. This study used activated carbon from discarded mixed fish scales for adsorption. First, *S. aureus* and *K. pneumoniae* were adsorbed onto the prepared activated carbon via column experiment. Furthermore, *S. aureus* adsorbed carbon was utilized for cadmium removal through batch adsorption.

6.2.1 Preparation of carbon

The detailed procedure for preparing the AC and its characterization is presented in Chapter 3. The waste fish scale-derived carbon (mFSAC) was used directly in the adsorption experiments without further modification.

6.2.2 Culturing of bacteria

Luria Bertani Broth (LBB) media was prepared by adding 25g of LBB media in 1000ml of distilled water and autoclaving at 121°C for 15 minutes. One gram-positive bacteria, *S. aureus* and one gram-negative bacteria, *K. pneumoniae* were grown in LBB media for 24 hours at 30°C±2 in an incubator.

6.2.3 Column construction and removal efficacy

Initially, the column was filled with sterilized cotton to prevent the activated carbon from falling through, and then the adsorbent was loaded to a height of 5 cm. Subsequently, another layer of sterilized cotton was placed on top of the activated carbon to prevent it from floating (Fig. 6.1). LBB media containing the bacteria were serially diluted up to two times (1:99 v/v) using sterile distilled water and was allowed to pass through column at 2.26 mL min⁻¹ flow rate. Eluents were collected in sterile test tubes at an interval of every 10 minutes till 80 minutes and were inoculated in petri dishes containing Luria Bertani Agar (LBA) media using spread plate method [45]. After about 24 hours of incubation at 30°C±2, the Colony-forming unit (CFU) of each batch of eluents were calculated to determine the removal efficacy of the column [46]. The formation of bacteria colony was determined. After the column experiment, the carbon with adsorbed bacteria (*S. aureus*) was oven dried at 105°C for 24 h. It was then labeled as discarded mixed fish scale activated carbon with microbes (FSAC-M) for subsequent use in the adsorption of heavy metal cadmium.

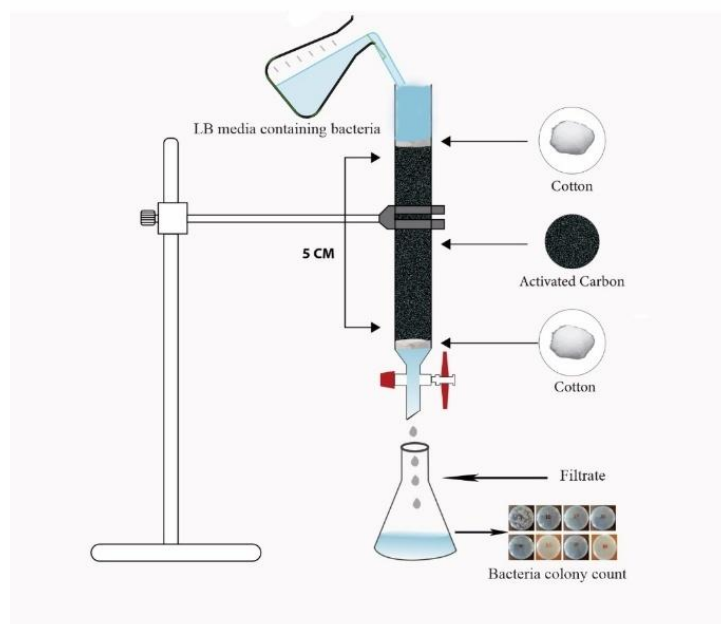
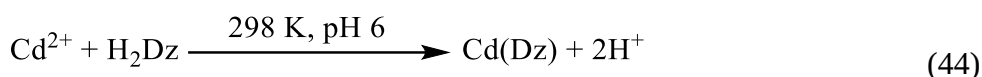
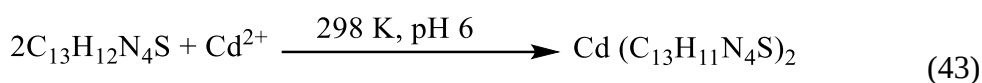


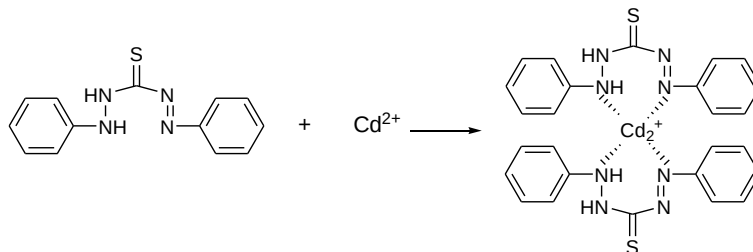
Fig. 6.1. Schematic representation of AC supported-column set up.

6.2.4 Formation of Cd-dithizone colour complex

In heavy metal removal studies, cadmium was removed from an aqueous solution using activated carbon with pre-adsorbed bacteria (FSAC-M), and the results were compared to the removal efficiency of activated carbon without bacteria (FSAC). This was achieved using the colorimetric method by adding dithizone, wherein, 500 mg L⁻¹ of dithizone solution was set by dissolving 50 mg of dithizone in 100 mL of dimethyl sulfoxide (DMSO). Further, 45.6 mL of dithizone solution was added to 100 mL of Cadmium chloride solution to form a yellow-orange Cd-dithizone color complex (Cd(Dz)). The formation of Cd(Dz) color complex is crucial in the spectrophotometric determination of Cadmium (Cd) [47]. This complex formation allows for the quantification of Cd due to its distinct color, as shown in Eqs. (43) and (44) and can be measured using a UV–Visible spectrophotometer, as illustrated in Scheme (1).



where, Cd(Dz) represents Cd-dithizone colour complex



Scheme 6.1: Formation of Cadmium-dithizone colour complex

6.2.5 Effect of pH on formation of Cadmium-dithizone colour complex

The dithizone-cadmium colour complex formation was studied throughout a pH range of 3 to 10. Significant reduction in color intensity was observed at pH 4. Dithizone protonation is thought to be the cause of this colour loss as it reduces its capacity to efficiently chelate cadmium ions, destabilizing the complex. At below pH 3, cadmium hydroxide (Cd(OH)₂) precipitates, reducing the quantity of free cadmium ions accessible for complexation suggested that Cd²⁺ were interacting with OH⁻ rather than staying complexed with dithizone. Within the pH range of 5-7, cadmium ions (Cd²⁺) stay dissolved and readily form a stable complex with dithizone. Within this pH range,

dithizone is in its most effective form, enabling efficient binding with cadmium ions and producing a yellow-orange color.

Additionally, as the pH increases from 8-10, the solubility of cadmium ions decreases. The rising concentration of hydroxide ions (OH^-) encourages the formation of cadmium hydroxide ($\text{Cd}(\text{OH})_2$), which is insoluble in water and precipitates out, thereby reducing the concentration of free Cd^{2+} ions available in solution [48–50]. Therefore, our batch studies focused on the pH range of 5-7, where the dithizone-cadmium complex exhibited optimal stability and vibrant coloration. In this pH range, the deprotonated form of dithizone enhances chelation, minimizing interference from competing reactions and ensuring accurate and reliable measurements of cadmium concentration.

6.2.6 Batch Adsorption Study

The adsorption process was investigated in a batch system by varying several experimental parameters such as adsorbent dosage, initial concentration of the Cd(Dz) color complex, solution pH, contact time and temperature. To determine the optimal equilibrium adsorption conditions, 50 mL samples with different initial Cd(Dz) concentrations (ranging from 10 mg L^{-1} to 100 mg L^{-1}) were placed in conical flasks containing varying amounts of activated carbon (0.1 to 1.0 g) at different pH levels (5-7) and maintained at 25°C . The mixtures were shaken in a rotary shaker at a constant speed of 150 rpm for a specified duration. The Cd(Dz) solutions were then filtered through Whatman filter paper and the clear solutions were analyzed for Cd(Dz) colour complex concentration. The remaining Cd(Dz) colour complex concentration in the filtrate was determined by measuring absorbance at 517 nm using a UV-Visible Spectrophotometer (Lambda 35, PerkinElmer). All adsorption experiments were performed in triplicate and the percentage removal of Cd(Dz) was calculated.

6.2.7 Adsorption isotherm models

The experimental data were analyzed using isotherm models to understand the adsorption behavior and mechanism of Cd(Dz) on the prepared activated carbon [51,52].

6.2.8 Adsorption kinetic models

The adsorption kinetics was investigated by analyzing the adsorbate uptake by the activated carbon at different time intervals. To understand the adsorption process, the non-linear forms of the PFO, PSO, and Elovich models were employed [52,53].

6.2.9 Statistical analysis

The Chi-square (χ^2) test assess the goodness of fit between experimental data and theoretical models. Chi square (χ^2) test is developed by Karl Pearson [54]. A lower χ^2 value indicates a better fit between experimental and predicted data and higher χ^2 value suggests a poor fit, indicating that the model does not accurately represent the data [55].

6.2.10 Thermodynamic studies

A thermodynamic study was carried out to assess the energy changes, spontaneity, and feasibility of the adsorption process. This analysis offers insights into the stability of interactions amid the adsorbent and adsorbate, as well as the influence of temperature on adsorption behavior. The distribution adsorption coefficient (K_d) and Gibbs free energy change (ΔG) were also determined.

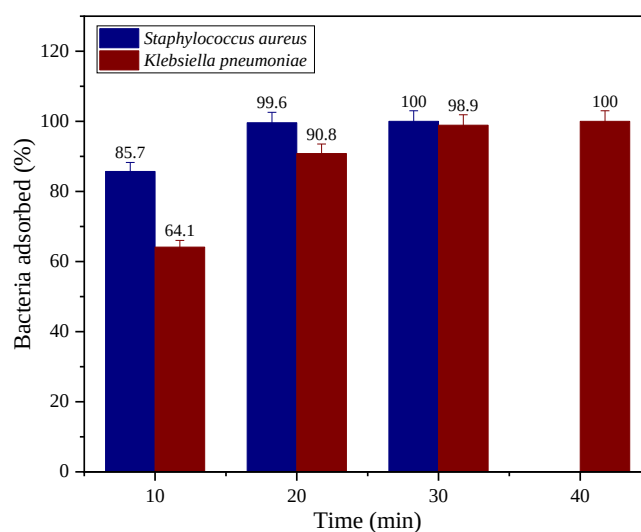
6.3 Results and discussion

6.3.1 Adsorption of bacteria through column method

The efficiency of bacterial adsorption by the activated carbon column was evaluated by measuring the CFU/mL at 10-minute intervals (Table 6.1). Within the first 10 minutes, the column adsorbed 85.7% of *Staphylococcus aureus* and 64.1% of *Klebsiella pneumoniae*. After 20 minutes, 99.6% of *S. aureus* was removed, reaching complete adsorption at 30 minutes. In contrast, 90.8% and 98.9% of *K. pneumoniae* were adsorbed at 20 and 30 minutes respectively with complete removal achieved after 40 minutes. These results demonstrate that the column efficiently adsorbed all colonies of both *S. aureus* and *K. pneumoniae* within 30 and 40 minutes respectively, highlighting its high adsorption potential for both gram-positive and gram-negative bacteria (Fig. 6.2).

Table 6.1. CFU/ml after an interval of every 10 minutes of filtration

Bacterial Strain	Time (Minutes)	No. of Colonies appeared	CFU/ml	Bacteria Adsorbed (%)
<i>S. aureus</i>	0 (Initial)	448 ±10	224000000	0
	10	64 ±9	32000000	85.7
	20	2 ±1	1000000	99.6
	30	0	0	100
<i>K. pneumoniae</i>	0 (Initial)	714 ±7.9	357000000	0
	10	256 ±6.5	128000000	64.1
	20	66 ±4	33000000	90.8
	30	3 ±1	1500000	98.9
	40	0	0	100

**Fig. 6.2. Adsorption efficacy of activated carbon.**

6.3.2 Batch adsorption study.

In the batch adsorption experiments, the optimal initial concentration of Cd(Dz) and adsorbent dosage for both FSAC-M and FSAC were determined to be 40 mg L⁻¹ and 0.5 g, respectively. To evaluate the effect of pH on adsorption, all other parameters including initial concentration, adsorbent dose, temperature and contact time were maintained constant at 40 mg L⁻¹, 0.5 g, 25 °C and 80 min. Under these conditions, the adsorption efficiency of Cd(Dz) reached a maximum at pH 6 with removal percentages of 97.04% and 91.7% for FSAC-M and FSAC respectively indicating that bacterial pre-adsorption significantly enhances adsorption performance. The optimal pH can be attributed to the

balance between protonation and deprotonation of functional groups on the adsorbent surface. At lower pH values, competition between H^+ ions and $Cd(Dz)$ for active adsorption sites reduces metal uptake whereas at higher pH values, the formation of metal hydroxide species can decrease free $Cd(Dz)$ availability for adsorption [56,57]. The higher removal efficiency of FSAC-M compared to FSAC may also be related to the presence of bacterial surface functional groups which provide additional binding sites and facilitate stronger interactions with $Cd(Dz)$ thereby enhancing the overall adsorption capacity.

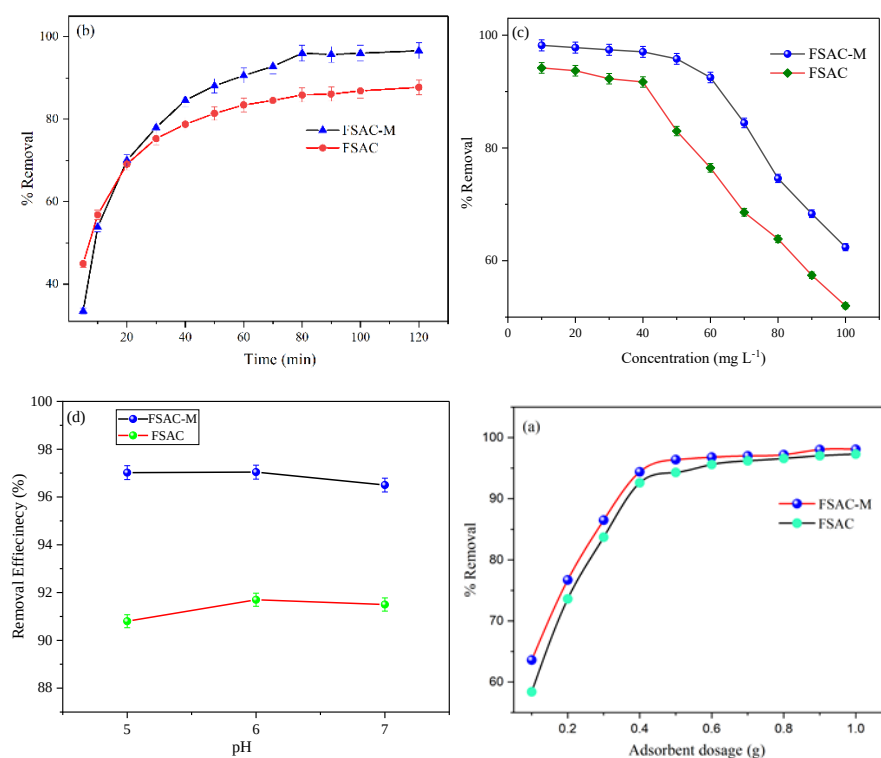


Fig. 6.3. Effect of (a) adsorbent dosage (b) contact time (c) initial concentration and (d) pH for the removal of Cd (Dz)

6.3.3 Fourier Transform Infrared Spectra

The presented FTIR spectra (Fig. 6.4) provide information on the interaction between cadmium ions and surface functional groups by comparing the functional groups on FSAC-M and FSAC before and after $Cd(Dz)$ adsorption. The wide band seen in the 3200–3600 cm^{-1} range corresponds to O–H stretching vibrations commonly attributed to hydroxyl groups or water molecules adsorbed on the surface [58–60]. Changes in intensity of this peak after adsorption, especially in the spectra of FSAC-M indicate that hydroxyl groups or surface moisture participate in cadmium binding [61–63]. The

changes are more noticeable for FSAC-M, indicating that bacteria improve the adsorption capacity by providing extra active sites as reported in research on biosorbent materials [64–68]. Shifts or changes in intensity observed in the 1600–1700 cm^{-1} region, which is associated with C=O stretching vibrations indicate that carbonyl or carboxylic acid groups are crucial in the coordination of cadmium [69–71]. The spectra differences between FSAC and FSAC-M further emphasize the contribution of bacterial cell components such as proteins or polysaccharides to cadmium binding [72,73]. Changes in the peaks within the 1000–1300 cm^{-1} range related to C–O stretching vibrations of alcohols, ethers or esters after adsorption indicate the involvement of oxygen-containing groups in the adsorption process [60,71,74]. Moreover, the new M–O (Cd–O) peak at 500–600 cm^{-1} confirms cadmium adsorption, indicating Cd^{2+} binding with oxygen-containing functional groups like hydroxyl and carboxyl on the adsorbent surface [75,76]. Overall, the comparison underscores the significant role that hydroxyl, carbonyl and other oxygen-rich functional groups play in cadmium adsorption. Moreover, the more noticeable changes observed in the FSAC-M spectra imply that bacteria pre-adsorbed onto activated carbon provide additional functional groups such as amines or protein residues that enhance cadmium binding efficiency [73,77]. Biological modification of activated carbon creates a synergistic relationship, increasing its adsorption capacity by providing more binding sites for heavy metals [78–82].

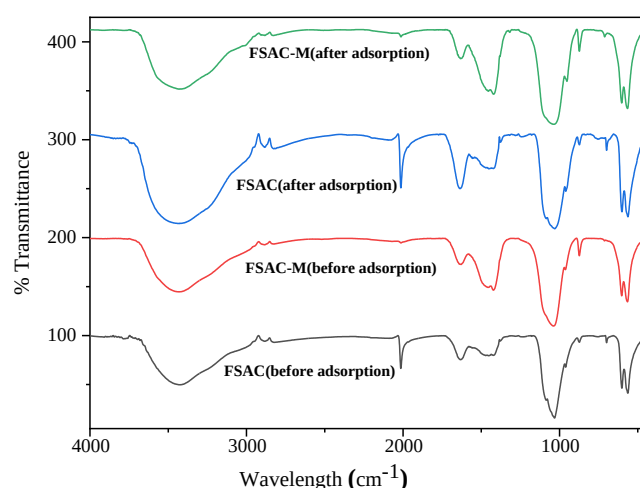


Fig. 6.4. FT-IR spectra of FSAC and FSAC-M before and after Cd(Dz) adsorption.

6.3.4. Adsorption isotherm studies

This study utilized three commonly used non-linear isotherms: Langmuir, Freundlich and Temkin to analyze the adsorption behavior of Cd (Dz) colour complex on the activated

carbon with and without bacteria pre-adsorbed (Fig. 6.5). The parameters obtained from these isotherm models, along with the chi-squared value (χ^2), are presented in Table 6.2. The maximum adsorption capacity (q_m) was observed to be 6.51 mg g^{-1} for FSAC-M and 5.43 mg g^{-1} for FSAC. This indicates that FSAC-M possesses a higher adsorption capacity compared to FSAC.

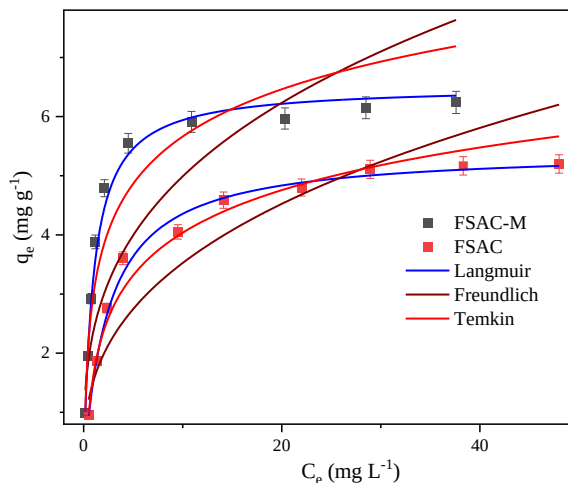


Fig. 6.5. Isotherm studies of FSAC-M and FSAC (adsorbent dose= 0.5 g L^{-1} ; initial concentration= 40 mg L^{-1} ; contact time= 80 min; pH= 6).

The Langmuir constant (K_L) values were recorded as 1.02 L mg^{-1} for FSAC-M and 0.40 L mg^{-1} for FSAC suggesting that the modified adsorbent has a stronger binding affinity for the Cd(Dz) complex. The correlation coefficient (R^2) for both adsorbents was 0.994 demonstrating an excellent fit to the Langmuir model. Furthermore, the χ^2 values were notably low with 2.84 for FSAC-M and 1.91 for FSAC reinforcing the strong agreement between the experimental and predicted data. In the case of the Freundlich model, the adsorption intensity constant (η) was found to be 3.11 for FSAC-M and 2.7 for FSAC. Both values fall within the favorable adsorption range ($1 < \eta < 10$). The Freundlich constant (K_F) was found to be 2.38 mg g^{-1} for FSAC-M and 1.53 mg g^{-1} for FSAC indicating improved adsorption capacity in the microbe-modified adsorbent. However, the Freundlich model exhibited poor data alignment for FSAC-M which is reflected in the lower R^2 value (0.81) and a substantially higher χ^2 value (92.39) indicating a weaker model fit. In contrast, FSAC showed better conformity with the Freundlich model as indicated by an R^2 value of 0.897 and a lower χ^2 value of 0.90 [83]. The Temkin isotherm model showed that the heat of adsorption constant (b_T) was found to be 1.15 kJ mol^{-1} for

FSAC-M and 1.03 kJ mol^{-1} for FSAC respectively. These values are well below 8 kJ/mol , confirming that the adsorption process follows a physisorption mechanism [84]. The Temkin constant (K_T) was notably higher for FSAC-M (13.61 L mg^{-1}) compared to FSAC (4.85 L mg^{-1}) suggesting that the modified adsorbent exhibits a stronger adsorption potential [85,86].

Table 6.2. Isothermal models and parameters

Adsorbents		FSAC-M	FSAC
Isotherms	Parameters	Values	Values
Langmuir	$q_m \text{ (mg g}^{-1}\text{)}$	6.51	5.43
	K_L	1.02	0.40
	R^2	0.995	0.994
	χ^2	2.84	1.91
Freundlich	η	3.11	2.7
	$K_F \text{ (mg g}^{-1}\text{) (L mg}^{-1}\text{)}^{1/2}$	2.38	1.53
	R^2	0.811	0.897
	χ^2	92.39	0.90
Temkin	$b_T \text{ (kJ mol}^{-1}\text{)}$	2.15	2.40
	$K_T \text{ (L mg}^{-1}\text{)}$	13.61	4.85
	R^2	0.958	0.958
	χ^2	20.02	6.26

6.3.5. Adsorption Kinetics Studies

Adsorption kinetics govern the rate of uptake influencing how long the adsorbate remains at the solid-liquid interface [87]. The non-linear kinetic models of pseudo-first-order, pseudo-second-order and Elovich were used to analyze the adsorption kinetics. The non-linear kinetic curves are shown in Fig. 6.6 and the corresponding fitting parameters are presented in Table 6.3.

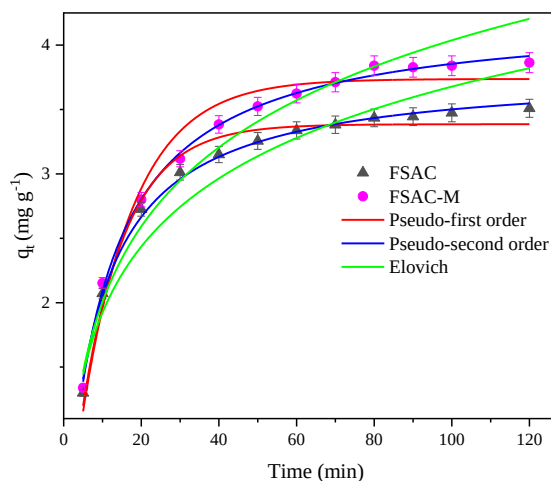


Fig. 6.6. Kinetic studies of FSAC and FSAC-M (adsorbent dose= 0.5 g L⁻¹; initial concentration= 40 mg L⁻¹; contact time= 80 min; pH= 6).

The pseudo-first-order model demonstrated relatively high correlation coefficients ($R^2 = 0.965$ for FSAC-M and 0.978 for FSAC). However, the calculated adsorption capacities ($q_{e(cal)}$) differed from the experimental values ($q_{e(exp)}$) and the χ^2 values were comparatively higher (0.021 for FSAC-M and 0.009 for FSAC). These inconsistencies suggest that the pseudo-first-order model does not sufficiently describe the adsorption process. In contrast, the pseudo-second-order model exhibited the highest R^2 values (0.997 for FSAC-M and 0.995 for FSAC) indicating a superior fit to the experimental data. The calculated adsorption capacities (4.25 mg g^{-1} for FSAC-M and 3.798 mg g^{-1} for FSAC) closely matched the experimental values (3.89 mg g^{-1} for FSAC-M and 3.584 mg g^{-1} for FSAC). Additionally, this model had the lowest chi-square values (0.0016 for FSAC-M and 0.002 for FSAC) signifying minimal deviation between the theoretical and experimental data. These results confirm that the adsorption process follows the pseudo-second-order model implying that chemisorption is the dominant mechanism.

The Elovich model exhibited relatively high R^2 values (0.975 for FSAC-M and 0.962 for FSAC), however its chi-square values were considerably higher (9.273 for FSAC-M and 13.784 for FSAC) suggesting a weaker fit compared to the pseudo-second-order model. While the Elovich model can offer valuable insights into the adsorption mechanism, it does not accurately capture the overall kinetic behavior. Based on these findings, the pseudo-second-order model best describes the adsorption behavior of both FSAC-M and FSAC. Furthermore, FSAC-M exhibited a slightly higher adsorption capacity than FSAC, as indicated by its greater q_e values, suggesting superior adsorption performance.

Table 6.3. Kinetic parameters for adsorption of Cd(Dz) colour complex.

Adsorbents		FSAC-M	FSAC
Models	Parameters	Values	Values
Pseudo first order	k_1 (min^{-1})	0.974	0.087
	$q_{e(\text{cal})}$ (mg g^{-1})	3.73	3.35
	$q_{e(\text{exp})}$ (mg g^{-1})	3.89	3.584
	R^2	0.965	0.978
	χ^2	0.021	0.009
Pseudo second order	K_2 (min^{-1})	0.022	0.030
	$q_{e(\text{cal})}$ (mg g^{-1})	4.25	3.798
	$q_{e(\text{exp})}$ (mg g^{-1})	3.89	3.584
	R^2	0.997	0.995
	χ^2	0.0016	0.002
Elovich	A	0.713	0.821
	B	1.07	1.265
	R^2	0.975	0.962
	χ^2	9.273	13.784

6.3.6. Thermodynamic studies.

The thermodynamic analysis (Table 6.4) showed positive ΔH values (16.33 and 16.99 kJ mol^{-1} for FSAC-M and FSAC respectively) indicating that cadmium adsorption is endothermic and favored at higher temperatures. Positive ΔS values (0.055 and 0.054 $\text{kJ mol}^{-1} \text{K}^{-1}$) suggest increased randomness at the solid–solution interface while the progressively more negative ΔG values with rising temperature confirm the spontaneous nature of the process. FSAC-M consistently exhibited lower ΔG values than FSAC demonstrating that bacterial pre-adsorption enhances thermodynamic favorability and adsorptive affinity. Although the adsorption kinetics followed a pseudo-second-order model typically associated with chemisorption, the low ΔH values and positive ΔS trends indicate that physisorption predominates with the rate likely controlled by surface site availability and ion surface interactions as observed in previous studies [88–91].

Table 6.4. Thermodynamic parameters

Adsorbent	ΔH (kJ mol^{-1})	ΔS ($\text{kJ mol}^{-1} \text{K}^{-1}$)	ΔG (kJ mol^{-1})			
			298K	308K	318K	328K
FSAC-M	16.33	0.055	-0.15	-0.50	-1.53	-1.63
FSAC	16.99	0.054	0.47	0.26	-0.47	-1.12

6.3.7. Comparison of Cadmium Adsorption Using FSAC-M and FSAC

The adsorption of cadmium was studied using two different types of activated carbon, one with pre-adsorbed bacteria (FSAC-M) and another without bacterial pre-adsorption (FSAC). The removal efficiencies of both adsorbents were evaluated under the same conditions in order to ascertain the effect of microbial presence on cadmium adsorption. The experimental parameters including an initial cadmium concentration of 40 mg L⁻¹, a pH of 6 and an adsorbent dose of 0.5 g were maintained consistently for both materials. The results revealed that FSAC-M exhibited a slightly higher removal efficiency of 6.51 mg g⁻¹ compared to 5.43 mg g⁻¹ for FSAC as shown in Table 6.5. The slight increase of adsorption capacity indicates that the cadmium adsorption was improved by the presence of pre-adsorbed microorganisms. The increased binding sites offered by bacterial cells and their extracellular polymeric substances (EPS) which are known to interact with metal ions may be responsible for the increase in removal effectiveness [41]. Moreover, the biological activity of the bacteria might have influenced the adsorption mechanism, potentially facilitating metal uptake through bioaccumulation or biosorption processes. Since all experimental conditions including pH, Cd(Dz) concentration and adsorbent dosage remained constant, the observed differences in adsorption performance can be directly linked to the presence of bacteria on the activated carbon surface. The study highlights the potential advantages of incorporating microbial biomass into adsorbent materials for heavy metal removal.

Table 6.5. Removal efficiency of FSAC-M and FSAC

S/No.	Adsorbent	Pollutant	Concentration (mg L ⁻¹)	Removal efficiency (mg g ⁻¹)	pH	Adsorbent dosage
1.	FSAC-M	Cd(Dz)	40	6.51	6	0.5g
2.	FSAC	Cd(Dz)	40	5.43	6	0.5g

6.3.8 Comparison of adsorption performance using microbes-supported adsorbents.

The adsorption performance of various microorganism-supported adsorbents for different pollutants was analyzed based on removal efficiency, pH and temperature conditions. The study highlights the effectiveness of biofilm, zeolite-supported and activated carbon (AC)-supported microbial systems in pollutant removal (Table 6.6). The present study on AC-supported *S. aureus* demonstrated a high removal efficiency of 96.0% for the

cadmium-dithizone complex at pH 6 and 25°C. The significant adsorption efficiency suggests that bacterial surface interactions enhance the binding of cadmium making it an effective approach for heavy metal removal.

Table 6.6. Comparison of mFS-AC/M with other microorganism-supported adsorbents.

S/No.	Adsorbent	Pollutants	Removal Efficiency	pH	Temperature	References
1	Biofilm-developed polystyrene microplastics	Cu ²⁺	28.3 $\mu\text{mol g}^{-1}$	6	25°C	[65]
		Pb ²⁺	25.2 $\mu\text{mol g}^{-1}$			
2	Zeolite-supported sulfatereducing bacteria	Cu ²⁺	98.2%,	—	37°C	[92]
		Ni ²⁺	90.1%,			
		Cr ⁶⁺	99.8%			
3	AC-supported five gram-negative bacteria.	Phenanthrene	90%	—	21 $\pm$ 2°C	[93]
4	AC-supported <i>Thiomonas sp</i>	H ₂ S	98%	3.36	—	[94]
5	AC-supported diesel-oil degrading bacteria	Diesel-oil contaminated water	86.35%	7	30°C	[95]
6	AC-supported <i>S. aureus</i>	Cadmium-dithizone complex	97.04%	6	25°C	This study

6.3.9 Performance Comparison of mFS-AC/M with other activated carbon for Cadmium removal.

Table 6.7 provides a comparative evaluation of cadmium adsorption capacities of activated carbons derived from different precursors under varying experimental conditions. The results show that adsorption performance is largely influenced by the type of raw material, activation method and solution pH. A considerable variation in

adsorption capacity is observed, with some adsorbents exhibiting low performance, while others display relatively higher efficiency. Among the reported materials, orange peel–derived activated carbon exhibits the highest adsorption capacity, whereas several other biowaste-derived adsorbents show moderate to low uptake. The activated carbon supported with *S.aureus* developed in this study shows an adsorption capacity of 6.51 mg g⁻¹ at pH 6, which is comparable to many previously reported adsorbents. Overall, these results suggest that the prepared adsorbent is effective and has good potential for application in cadmium removal from aqueous system.

Table 6.7 Performance Comparison of mFS-AC/M with other activated carbon for Cadmium removal.

S/No.	Activated carbon	Activating agent	pH	Adsorption capacity (mg g ⁻¹)	References
1.	Nut shell	SO ₂	8-12	7.964	[96]
2.	Cow dung	—	5.5	5.6	[97]
3.	Chicken feather and eggshell	HNO ₃	5.5		[98]
4.	Horn hoof powder	KOH	—	0.0985	[99]
5.	Waste tea	H ₂ SO ₄	6	0.0462	[100]
6.	Granulated AC	H ₂ SO ₄	6	8.36	[101]
	Activated clay	H ₂ SO ₄	6	7.43	
7.	Orange peel	—	7	51.6	[102]
8.	Bovine bone	—	7	17.54	[103]
9.	AC-supported <i>S. aureus</i>	KOH	6	6.51	This study

6.4. Future scope.

In the present dual-purpose method of bacterial adsorption onto activated carbon, studies suggest that bacteria may significantly enhance surface interactions and give carbon materials functional groups to boost their adsorption capacity. These groups use complexation, ion exchange, and electrostatic attraction to improve contact with pollutants. Additionally, by pre-treating organic contaminants, the fixed bacteria increase the carbon's capacity to adsorb heavy metals. Future research might concentrate on using various microbial strains with particular biosorptive qualities and refining bacterial immobilization methods. Bacteria with improved functional groups for adsorption might potentially be produced through genetic engineering.

Furthermore, the results of this study may be incorporated into bio-filtration systems for the treatment of municipal and industrial wastewater. Extensive research on the environmental effect and reusability of bacteria-adsorbed carbon is essential for the expansion of this technology. A complete approach to dealing with complicated pollutant mixes in polluted water sources may be developed by combining this technique with other cutting-edge treatment technologies.

Conclusion

This study demonstrates that bacterial pre-adsorbed activated carbon (FSAC-M) significantly enhances adsorption performance compared to unmodified FSAC for the removal of *S. aureus*, *K. pneumoniae* and the Cd(Dz) complex. FSAC-M efficiently removed all *S. aureus* and *K. pneumoniae* colonies within 30 and 40 minutes respectively, indicating strong affinity toward both gram-positive and gram-negative bacteria. The bacterial pre-adsorption introduces additional functional groups (carboxyl, hydroxyl and amine) and extracellular polymeric substances, increasing available binding sites and improving adsorption capacity. Cd(Dz) adsorption followed the Langmuir isotherm, suggesting monolayer adsorption on homogeneous surfaces with maximum capacities of 6.51 mg g⁻¹ for FSAC-M and 5.43 mg g⁻¹ for FSAC. Kinetics were best explained by a pseudo-second-order model reflecting that adsorption rates are governed by site availability and ion-surface interactions rather than chemical bonding. Thermodynamic results revealed that the adsorption process was endothermic and spontaneous, with positive ΔH and ΔS values, negative ΔG trends and greater thermodynamic favorability for FSAC-M. The relatively low enthalpy values confirm that the process is predominantly physisorption. Overall, microbial modification of activated carbon enhances surface functionality and binding site availability, improving simultaneous removal of bacterial cells and cadmium complexes, and demonstrating a sustainable and practical “waste-to-wealth” approach for water treatment applications.

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CHAPTER 7

SUMMARY AND CONCLUSION

This chapter provides an overview of the major findings of the thesis, emphasizing the synthesis, characterization, and application of activated carbon derived from mixed fish scales. It highlights the adsorption performance of the developed material, discusses key limitations related to energy consumption and cost, and underscores the advantages of waste-derived adsorbents. The chapter further presents future research directions to enhance performance and enable large-scale environmental applications.

Animal biowaste, such as discarded fish scales, served as a promising precursor for the synthesis of activated carbon. The surface properties of the prepared activated carbon were effectively modified to improve its adsorption performance for a wide range of pollutants, including dyes, hormones, heavy metals, and bacterial pathogens. A summary of the overall work conducted in this thesis is presented below:

1. Porous activated carbon was successfully synthesized from discarded mixed fish scales using potassium hydroxide (KOH) activation. The material was characterized by elemental analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET) surface area analysis, X-ray photoelectron spectroscopy (XPS), carbon-hydrogen-nitrogen (CHN) analysis, and zero-point charge determination. The synthesized carbon exhibited a BET surface area of 150.049 m²/g and a total pore volume of 0.119 cm³/g. This work underscores the potential of biomass waste, particularly animal biowaste such as fish scales, as a sustainable feedstock for activated carbon production. Compared with conventional coal-based AC, biowaste-derived AC is cost-effective, locally available, and environmentally friendly, offering a promising alternative for wastewater treatment.
2. Literature on animal biowaste-derived activated carbon (AC) highlights bones, hair, and feathers as the most widely investigated precursors, with heavy metal removal being the predominant focus. Most studies report that adsorption follows the Freundlich isotherm and pseudo-second-order kinetics, while limited thermodynamic analyses confirm the process to be spontaneous and feasible. Despite promising findings on surface area, porosity, and reusability, animal-based AC remains less explored than plant-based alternatives. Overall, evidence suggests that animal biowaste-derived AC is a cost-effective, sustainable, and efficient adsorbent with significant potential for future water purification applications.

3. Congo red dye was successfully removed using waste fish scale–derived activated carbon. The study confirmed that activated carbon prepared via KOH activation is an efficient adsorbent for Congo red dye removal. Batch adsorption experiments showed that contact time, initial dye concentration, and temperature significantly influenced the process, achieving a maximum removal efficiency of 99.04% with an adsorption capacity of 19.58 mg/g. The adsorption followed the Freundlich isotherm and pseudo-second-order kinetics, indicating multilayer chemisorption as the predominant mechanism. Thermodynamic analysis revealed that the process was both spontaneous and exothermic, while regeneration studies demonstrated good reusability over six cycles. Overall, the findings highlight the potential of waste fish scales as a sustainable, low-cost precursor for activated carbon production and an effective adsorbent for dye removal from wastewater.
4. Porous carbon prepared from waste mixed fish scales was used to adsorb the endocrine-disrupting hormone 17 β -estradiol (E2). The study demonstrated that mixed fish scale–derived activated carbon (mFSAC) is a highly effective adsorbent for E2 removal from wastewater. Under optimized conditions, a maximum removal efficiency of 98.35% was achieved, with adsorption best described by the Langmuir isotherm and pseudo-second-order kinetics, confirming monolayer chemisorption on a homogeneous surface. Thermodynamic analysis indicated that the process was spontaneous and endothermic, while DFT calculations revealed strong interactions between E2 and oxygen-containing functional groups, particularly carboxyl groups. The adsorbent also exhibited excellent reusability, maintaining high performance through five adsorption–desorption cycles.
5. A simple and efficient activated carbon biofilter column was developed for the treatment of bacteria-contaminated water using fish scale–derived activated carbon. The biofilter achieved high removal efficiencies of up to 99.99% for *Staphylococcus aureus* and *Klebsiella pneumoniae* within 30 and 40 minutes, respectively. Furthermore, bacterial pre-adsorbed activated carbon (FSAC-M) was employed for the adsorption of the cadmium–dithizone (Cd–Dz) complex

and compared with unmodified FSAC. FSAC-M exhibited a higher adsorption capacity ($6.51 \text{ mg}\cdot\text{g}^{-1}$) than FSAC ($5.43 \text{ mg}\cdot\text{g}^{-1}$), attributed to the increased availability of binding sites provided by microbial modification. Both bacterial and cadmium adsorption followed the Langmuir isotherm, indicating monolayer adsorption, while kinetics were best described by a pseudo-second-order model, reflecting that adsorption rates are governed by site availability and ion–surface interactions. Thermodynamic analysis revealed that cadmium adsorption is endothermic and spontaneous, with positive ΔH and ΔS values and negative ΔG at higher temperatures, confirming that the process is predominantly physisorption. Overall, microbial modification enhances surface functionality and binding site availability, improving the efficiency of simultaneous removal of bacterial cells and cadmium complexes from aqueous solutions.

Overall, the results demonstrate that animal biowaste–derived activated carbon is a promising, low-cost, and eco-friendly adsorbent with high sorption efficiency across multiple classes of pollutants, including bacteria, metals, and organic compounds. The adsorption processes predominantly followed pseudo-second-order kinetics, while isotherm analyses indicated both monolayer and multilayer adsorption depending on the pollutant type. Thermodynamic and kinetic analyses suggest that adsorption mechanisms involve both physisorption and chemisorption, depending on the nature of the pollutant. This work highlights the potential of fish scale–derived activated carbon as an effective, sustainable, and versatile adsorbent for environmental pollution control, supporting a “waste-to-wealth” approach and promoting circular economy–based clean water solutions.

Limitation for large scale application

- The prepared activated carbon shows promising adsorption performance; however, certain limitations exist for its large-scale application in water treatment.
- The synthesis process involves high-temperature carbonization (700°C) followed by thermal activation (500°C), both of which require significant energy input.
- The high energy requirement may increase the overall production cost, especially at an industrial scale.

- The use of chemical activating agents such as KOH further adds to the processing cost.
- Additionally, the use of KOH necessitates careful handling and proper post-treatment procedures.

Advantages

- The use of waste fish scales as a precursor provides a cost advantage due to their low cost and wide availability.
- This helps to partially offset the overall production cost of the activated carbon.
- The valorization of fish scale waste contributes to effective waste management and reduces environmental burden.
- The prepared activated carbon exhibits good adsorption performance, indicating its potential as an efficient adsorbent for pollutant removal.
- The material demonstrates versatility in removing different types of contaminants, including heavy metals and organic pollutants.
- The preparation method is relatively simple and can be adapted with further optimization.
- This work highlights the potential of fish scale-derived activated carbon as an effective, sustainable, and versatile adsorbent for environmental pollution control.
- It supports a “waste-to-wealth” approach, converting low-value biological waste into a value-added functional material.
- The study promotes circular economy-based clean water solutions, contributing to sustainable resource utilization and environmental protection.

Future Scope

- Surface modification can be explored to enhance adsorption efficiency and selectivity toward specific pollutants, including the use of green antibacterial reagents to impart antimicrobial properties.
- The applicability of the prepared carbons can be extended to the removal of heavy and trace metals, pharmaceuticals, pesticides, and other emerging contaminants.

- Development of nanostructured and composite materials by doping activated carbon with functional additives may broaden its applications in catalysis, energy storage, and environmental remediation.
- Advanced spectroscopic and computational studies, along with extended kinetic and thermodynamic modeling, can provide deeper insights into adsorption mechanisms.
- Regeneration and reuse of spent carbons should be investigated using biological, chemical, and physical methods to establish cost-effective and sustainable strategies.
- Pilot-scale studies and testing with real wastewater samples are essential for validating practical performance and facilitating industrial-scale application.



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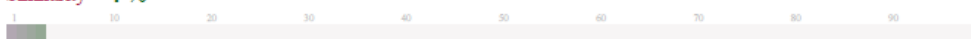
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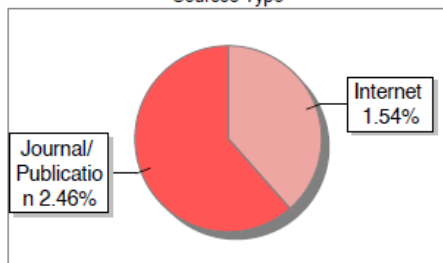
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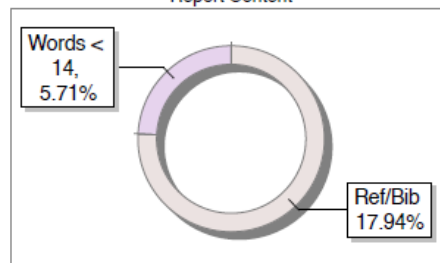
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13	springeropen.com	<1	Internet Data
18	The physical and surface chemical characteristics of activated carbons by Shaobi-2005	<1	Publication
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27	Influence of step sites in the molecular mechanism of the water gas shift reacti by Jos-2009	<1	Publication

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Academic qualifications

Exam Passed	Board/ University	Year of Passing	Subjects
Matriculation (10 th)	Nagaland Board of School Education	2009	Mathematics, Science, Social Science, English, Tenyidie.
Higher Secondary (12 th)	Nagaland Board of School Education	2012	Mathematics, Chemistry, Physics, Biology, English, Tenyidie.
B.Sc.	Kohima Science College, Jotsoma (Autonomous)	2015	Chemistry, Botany, Zoology, English, Env.Sc., Computer Skills.
M.Sc.	Nagaland University, Lumami	2018	Environmental Science.
Ph.D. Thesis Submitted			

Additional Education Qualifications

- Qualified UGC -NET (Lectureship) in Environmental Science, Date of award:10/12/2020.
- Diploma in Computer Application under All India Computer Saksharta Mission.
- Completed Three-months course on Research Exposure cum Training Programme in Artificial Intelligence and Machine Learning.

Areas of Research Interest

- Sustainable adsorbent development from waste resources.
- Adsorption mechanisms for diverse pollutants.
- Bio-modification of adsorbents for enhanced performance.
- Eco-friendly water treatment solutions.
- Adsorption modelling and molecular-level interaction studies.
- Waste valorisation for environmental applications.

Research Publications

Journal publications:

- Recent advances in applications of animal biowaste-based activated carbon as biosorbents of water pollutants: a mini-review. *Environmental Monitoring and Assessment*, 196(10), 974, (2024).

Vevosa Nakro, Tsenbeni N Lotha, Ketiyala Ao, Vimha Ritse, Lemzila Rudithongru and Latonglila Jamir.

- Efficient Removal of Congo Red Dye Using Activated Carbon Derived from Mixed Fish Scales Waste: Isotherm, Kinetics and Thermodynamics Studies. *Nature Environment & Pollution Technology*, 24(1), 339-353, (2025).

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- Surface Modification of Activated Carbon through Bacterial Adsorption and its Effect on Cadmium Removal from Aqueous Solution.

Current Science, Engineering & Technology, (2026)

Vevosa Nakro, Alemtoshi and Latonglila Jamir

- An environmentally benign synthesis of Tetrabutylphosphonium tribromide (TBPTB)—a versatile and efficient phase transfer reagent for organic transformations. *Green Chemistry Letters and Reviews*, 14(2), 425-434, (2021).

Visekhono Kuotsu, **Vevosa Nakro**, Imkongyanger Ao, Tsenbeni N Lotha, Ketiyala, Upasana Sinha and Latonglila Jamir.

- Valorizing pig hooves for activated carbon production with efficient Methyl green adsorption, DFT insights and bacterial removal via bio-adsorbent column. *Green Chemistry Letters and Reviews*, 17(1), 2431261, (2024).

Tsenbeni N Lotha, Ritu Karmaker, Ketiyala, **Vevosa Nakro**, Lemzila Rudithongru, Imkongyanger and Loatonglila Jamir.

- Sustainable Synthesis of Guanidine Derivatives and Computational Assessment of their Antidiabetic Efficacy. *Endocrine, Metabolic & Immune Disorders-Drug Targets*, 25(4), 326-339, (2025).

Imkongyanger Ao, Kikoleho Richa, Tsenbeni N Lotha, Lemzila Rudithongru, **Vevosa Nakro** and Latonglila Jamir.

- Climate Change Impact and Traditional Adaptation Practices in Northeast India: A Review. *Current World Environment*, 19(2), 558, (2024).

Tsenbeni N Lotha, Vimha Ritse, **Vevosa Nakro**, Lemzila Rudithongru, Nabajit Hazarika and Latonglila Jamir.

- Environmentally benign synthesis of unsymmetrical ureas and their evaluation as potential HIV-1 protease inhibitors via a computational approach. *Molecular Diversity*, 28(2), 749-763, (2023).

Tsenbeni N Lotha, Viphrizolie Sorhie, Ketiyala, **Vevosa Nakro**, Imkongyanger and Latonglila Jamir.

- Experimental and theoretical insights on biomass-derived activated carbon for the removal of aniline blue and malachite green dyes. *Biomass Conversion and Biorefinery*, 15(1-19), 25591–25609, (2025).

Tsenbeni N Lotha, Lemzila Rudithongru, **Vevosa Nakro**, Ketiyala and Latonglila Jamir.

- A microwave assisted environmentally benign protocol for preparation of ester compounds and computational evaluation of their antimicrobial efficacy. *Biochemical & Cellular Archives*, 24(1), 219-227, (2024).

Imkongyanger, Tsenbeni N. Lotha, **Vevosa Nakro**, Ketiyala, Lemzila Rudithongru, Pranay Punj Pankaj and Latonglila Jamir.

Book Chapters

- Climate Impact in North East India." In Environmental Intimacies from India's North East, 18(17-34), Routledge India, (2024).

Tsenbeni N Lotha, Ketiyala, **Vevosa Nakro** and Latonglila Jamir.

Patents

1. Title of Invention: An activated carbon production system using animal waste.
Inventor's name: Tsenbeni Nonghobemo Lotha, Imkongyanger Ao, Ketiyala Ao, **Vevosa Nakro**, Lemzila Rudithongru, Vimha Ritse, Upasana Bora Sinha, Latonglila Jamir.
German Patent: 202024101249
Date of Grant: 09/04/2024
2. Title of Invention: A system for the synthesis of activated carbon from animal biowaste for the removal of cationic dye.
Inventor's name: Ketiyala Ao, Tsenbeni Nonghobemo Lotha, **Vevosa Nakro**, Imkongyanger Ao, Lemzila Rudithongru, Vimha Ritse, Nima Dontu Namsa, Latonglila Jamir.
German Patent 202024102131
Date of Grant: 03/05/2024
3. Title of Invention: A system for environment friendly synthesis of Tetrabutylphosphonium tribromide (TBPTB) and organic compounds mediated by the reagent.

Inventor's name: Imkongyanger Ao, Ketiyaia Ao, Tsenbeni Nonghobemo Lotha, **Vevosa Nakro**, Lemzila Rudithongru, Viha Ritse, Upasana Bora Sinha, Latonglila Jamir.

German Patent: 202024101576

Date of grant: 08/05/2024

4. Title of Invention: Activated Carbon from mixed fish scales for adsorption of Congo Red Dye.

Inventor's name: **Vevosa Nakro**, Tsenbeni Nonghobemo Lotha, Ketiyaia Ao, Lemzila Rudithongru, Imkongyanger Ao, Vimha Ritse, Latonglila Jamir.

Indian Patent: 202431045241 A

Date of grant: 21/06/2024

Appendix 2

List of Conferences/Seminars/Webinars/Workshops Attended

- **Oral presentation** on the topic “*Waste to wealth: Sustainable conversion of animal biowaste to bio-sorbents*” at the International Conference on “Environmental Humanities in the Anthropocene Era: Ecojustice and Sustainability”, organized by Fazl Ali College, Mokokchung, on 4th–5th October 2023.
- **Oral presentation** on the topic “*Adsorption of Congo red dye from aqueous solution onto fish scales derived activated carbon: kinetics, isotherms and thermodynamic studies*” in the SJU 1st International Conference on Multidisciplinary Research & Innovation (ICMRI-2023) organized by Internal Quality Assurance Cell (IQAC), St. Joseph University, Chumoukedima, Nagaland on 09th & 10th November, 2023.
- Attended three months training on the “*DST Sponsored Research Exposure cum Training Program in AI and Machine Learning Domain Areas for Students from North East States and UT's of Jammu and Kashmir and Ladakh region*” organised by CSIR-NEIST, Jorhat from February to April, 2023.
- Attended two-days workshop on “*Research Ethics, Paper Writing and IPR*” on 14th-15th November, 2019, organised and sponsored by UGC-SAP (DRS-III), Department of Botany and Department of Biotechnology, Govt. of India sponsored Advance Level Institutional Biotech Hub, Nagaland University, Lumami.
- Attended One-day workshop on “*Python and Machine Learning in Bioinformatics*” organized by Advanced Computational and Data Sciences Division, CSIR-NEIST, Jorhat, Assam on 4th April, 2023.

- Participated National Webinar on “*Development and Planning: Relevance of Geography and the Applicability of GIS and Remote Sensing*”, on 8th of November 2021, organised by the Department of Geography, Kohima Science College, Jotsoma, Nagaland.
- Attended one day-workshop on “*Quality Improvement Parameters in Research Publications*” on 19th April, 2023 organised by Department of Chemistry and IQAC, Nagaland University.
- Attended two-days workshop on “*Quality Enhancement in Research*” on 22nd to 23rd March, 2021.
- Participated National Webinar on “*Multifaceted Research in the Field of Chemistry*” organised by the Department of Chemistry, Model Christian College on 17th April, 2021.
- Participated National Level Online Faculty Development Programme on “*Effective Teaching Techniques and Skills for Career Advancement* ” held from 23rd to 28th June 2021, organized by Faculties of Science Stream, Sao Chang College, Tuensang; Nagaland.
- Attended one day Seminar on “*Advance in Bioscience and Technology*” on 6th May, 2022 organized by the Department of Biotechnology, St. Joseph University, Chumoukedima, Nagaland.
- Attended two days online workshop on “*Official Language Hindi: History and Introduction*” held on 7th -8th June, 2021 organized by Hindi Cell, Nagaland University, Lumami.
- Participated in the Webinar on “*Impact of Covid-19 on the Environment*” organized by Department of Botany, Sao Change College, Tuensang, Nagaland held on 28th August 2020.

- Participated in the International Webinar on “*Self-care in the Time of COVID-19*” organized by IQAC, Kohima Science College, Jotsoma, Nagaland on 30th July, 2020.



Recent advances in applications of animal biowaste-based activated carbon as biosorbents of water pollutants: a mini-review

Vevosa Nakro · Tsenbeni N. Lotha · Ketiyala Ao · Imkongyanger Ao · Vimha Ritse · Lemzila Rudithongru · Chubaakum Pongener · Merangmenla Aier · Dipak Sinha · Latonglila Jamir

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Abstract Advances in green engineering and technology have revealed a number of environmentally acceptable alternatives for water purification. In line with this, recent advances in biosorption of pollutants from aqueous solutions using animal biowaste-based activated carbon (AC) are reported herein. Apart from the fish scale-derived AC which is extensively documented, animal bones, among the rest others, have been studied most widely, followed by hair and feathers. Out of the various target water pollutants, removal of heavy metals has been mostly studied. Majority of the reports showed the Freundlich isotherm and pseudo second order as the best fit. Few investigations on the thermodynamics of the adsorption studies and reports on the Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) have also been discussed in this report. It has been concluded that while plant-based AC has gained wide interest, the same is not true for the

animal-based counterpart albeit the latter's potential for high sorption efficiency as seen in the present report.

Keywords Activated carbon · Water pollutants · Animal biowaste · Biosorption · Heavy metals · Dyes

Introduction

Freshwater scarcity is one of the most pressing challenges the world has been trying to tackle over the last few years. The already existing severe freshwater crisis is aggravated by population growth, unplanned rapid urbanization, technological advancements, and agricultural operations. Nowadays, wastewater pollution from diverse industrial activities has escalated into a global concern. Unchecked discharge of pollutants poses substantial dangers to aquatic habitats, contributing to acute and chronic toxicity for aquatic animals, ecosystem pollution biodiversity damage, habitat destruction, and human health problems (Palani et al., 2021). Toxic metal ions containing discharge from various sources such as industrial and sanitary wastes, domestic effluents, and agricultural runoff has added to the prevailing strain on usable freshwater supply (Mustafa et al., 2021). Long-term negative consequences in aquatic and human health have been seen to be directly related to consumption of polluted waters containing persistent metal ions or recalcitrant organic compounds. In addition, aesthetic

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Efficient Removal of Congo Red Dye Using Activated Carbon Derived from Mixed Fish Scales Waste: Isotherm, Kinetics and Thermodynamics Studies

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Mixed fish scales

ABSTRACT

The discharge of large quantities of organic dyes into the environment causes significant harm to humans and the environment. Thus, there is an urgent need to develop cost-effective adsorbents for removing these dyes. In the present study, the synthesis of activated carbon (AC) derived from mixed fish scale waste using KOH activation was investigated for Congo red (CR) dye removal. The finding shows that the obtained biocarbon has a fixed carbon of 42.9% with a crystallinity index of 15.01%. N₂ adsorption-desorption isotherm was found to be type IV, signifying mesoporous structure with a surface area and total pore volume of 150.049 m² g⁻¹ and 0.119 cm³ g⁻¹. Batch adsorption was carried out by various adsorbent doses, initial concentration, contact time, and pH to comprehend the effect of operating parameters on its removal efficacy. The isotherm studies fitted well for Freundlich with an R² of 0.99%. Adsorption kinetics was best fitted by the pseudo-second-order model and thermodynamic studies revealed the adsorption process to be exothermic and spontaneous. The efficiency of AC was also studied by an amount of sorption and desorption cycles which showed its potential for reusability up to the sixth cycle. Thus, the findings suggest that activated carbon derived from mixed fish scale waste is a promising adsorbent for removing Congo red dye from aqueous solutions.

INTRODUCTION

Dyes present in aqueous solutions are highly visible even at low concentrations and pose significant health and environmental risks due to their harmful effects on humans and ecosystems. It can be classed as cationic, anionic, or non-ionic depending on its properties and structure (Agarwal et al. 2023). The sources include industries like food, printing, textiles, leather, pulp/paper mills, plastics, cosmetics, and pharmaceuticals (Jasińska et al. 2019), which can lead to the creation of a hypoxic environment in water. Approximately 10,000 diverse dyes and pigments, totaling 700,000 tons, are used in industries each year out of which 10-15% end up in water bodies (Bhatia et al. 2017). Among them, congo red (CR) is a widely used anionic azo dye in textile and paper dyeing (Fig. 1) (Lade et al. 2015). Known for its six aromatic rings, this anionic diazo dye is highly toxic and mutagenic, also resistant to natural degradation. It can irritate the skin and gastrointestinal tract, and it decomposes into carcinogens, posing significant risks to both human health and environmental safety (Li et al. 2023). Additionally,

it is often illicitly added to meat and meat products as a coloring agent due to its low cost, high stability, and excellent dyeing properties (Wang et al. 2023). According to Jain and co-workers (Jain & Sikarwar 2014), it is stable in the atmosphere and may also be used as an indicator. It can also be used in gamma-ray dosimeters since its color diminishes with radiation strength (Rajhans et al. 2020). Prolonged dye contact with the skin or eyes might cause severe irritability due to the dye's extreme toxicity and when consumed it can cause nausea, vomiting, and diarrhea (Lade et al. 2015). CR dye displays different types of toxic effects including skin-related, environmental, microbial, yeast, bacterial, algal, and protozoan toxicity that exhibits genotoxic and cytotoxic effects with the ability to produce genetic alterations and cancer (Rajhans et al. 2020).

Over the decades, wastewater has been treated using diverse approaches like photocatalysis (Jorfi et al. 2016, Khan et al. 2023b), ultrafiltration (Hoslett et al. 2018, Yin et al. 2019), electrochemical processes (Islam et al. 2023), adsorption (Ukanwa et al. 2019, Burchacka et al. 2021), etc.

RESEARCH ARTICLE

Surface Modification of Activated Carbon through Bacterial Adsorption and its Effect on Cadmium Removal from Aqueous Solution

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Abstract: Introduction/Objectives: The increasing contamination of water sources by pathogenic microorganisms and heavy metals necessitates the development of multifunctional adsorbents capable of addressing both simultaneously. In this study, fish scale-derived activated carbon (FSAC) was used to remove *Staphylococcus aureus* and *Klebsiella pneumoniae* through a column adsorption technique. Subsequently, FSAC pre-adsorbed with *S. aureus* (FSAC-M) was utilized in a batch adsorption experiment for the removal of cadmium (Cd).

Methods: Bacterial removal was monitored via colony-forming units (CFU mL⁻¹) at 10-minute intervals, while Cd adsorption was evaluated using isotherm, kinetic, and thermodynamic analyses.

Results: Both bacterial strains were effectively removed, with FSAC-M exhibiting a higher adsorption capacity ($q_m = 6.51 \text{ mg g}^{-1}$) than FSAC ($q_m = 5.43 \text{ mg g}^{-1}$) for Cd adsorption owing to the presence of microbial surface functionalities. The adsorption followed the Langmuir isotherm ($R^2 = 0.996$ for FSAC-M; 0.988 for FSAC), indicating monolayer adsorption. Although the kinetic data fit the pseudo-second-order model ($R^2 = 0.997$ for FSAC-M; 0.995 for FSAC), thermodynamic results indicated an endothermic, spontaneous, and predominantly physisorptive process ($\Delta H = 16.33\text{--}16.99 \text{ kJ mol}^{-1}$), with positive ΔS values reflecting increased randomness at the solid-solution interface.

Discussion: Microbial pre-adsorption introduced additional binding sites and surface interactions, enhancing FSAC's affinity for both biological and chemical contaminants.

Conclusion: FSAC effectively adsorbed *S. aureus* and *K. pneumoniae* in a column setup, while FSAC-M demonstrated notable Cd removal in batch mode. The adsorption conformed to isotherm and kinetic models, with thermodynamic results indicating a spontaneous and temperature-dependent process, highlighting the applicability of FSAC for multifunctional water treatment.

Keywords: Activated carbon, adsorption, bacteria, heavy metal, wastewater treatment, fish scales.

1. INTRODUCTION

Water forms the foundation of all life on Earth, as numerous biological functions in living organisms depend on it. However, limited access to safe and potable water has become a pressing global issue [1, 2]. Extensive environmental pollution has further contributed to the contamination of water sources with inorganic, organic, and biological pollutants. The World Health Organization (WHO) reports that nearly 80% of wastewater is released into natural water bodies without proper treatment. The presence of pathogenic microorganisms in both treated and freshwater supplies poses a serious threat to human health worldwide.

Pathogenic microorganisms present in treated and untreated drinking water represent a major global health concern. It is estimated that approximately 485,000 deaths occur annually due to diseases caused by the consumption of microbially contaminated water. Such waterborne illnesses include cholera, dysentery, typhoid, typhoid fever, and polio [3]. *Staphylococcus aureus*, a gram-positive bacterium and a leading cause of food poisoning, can contaminate drinking water and is associated with various infections including skin infections, endocarditis, and sepsis [4, 5]. The detection of *S. aureus* in water sources is particularly concerning due to its pathogenic potential and its well-documented resistance to multiple antibiotics [6]. Likewise, *Klebsiella pneumoniae*, a gram-negative bacterium, is linked to severe clinical conditions such as pneumonia, bacteremia, meningitis, and infections of the liver, urinary tract, and gastrointestinal tract, and

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LETTER

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An environmentally benign synthesis of Tetrabutylphosphonium tribromide (TBPTB) – a versatile and efficient phase transfer reagent for organic transformations

Visekhono Kuotsu^a, Vevosa Nakro^a, Imkong Yanger^a, Tsenbeni N. Lotha^a, Ketiyala Tzudir^a, Upasana Bora Sinha^b and Latonglila Jamir^a

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ABSTRACT

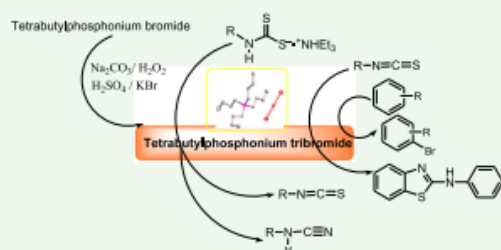
Tetrabutylphosphonium tribromide (TBPTB), a mild and versatile reagent, has been synthesized following an environmentally benign protocol. The new reagent possesses inherent phase transfer properties which facilitates organic reactions in aqueous medium. Thermal stability of the reagent which enables organic reactions under microwave irradiation and recyclability of the spent reagent are special attributes of the new reagent. These properties collectively provide an opportunity for facile, practical, and eco-friendly synthesis of a wide range of pharmaceutically significant and specialty organic compounds such as bromo-organics, isothiocyanates, cyanamides and 2-aminobenzothiazoles in excellent yields on-water under microwave irradiation.

ARTICLE HISTORY

Received 14 October 2019
Accepted 3 May 2021

KEYWORDS

Tetrabutylphosphonium tribromide; phase-transfer reagent; aqueous reactions; microwave reactions



Introduction

With the advent of green chemistry since the nineties, there has been a continuous effort towards environmental benignity, which, among others has led to the synthesis of numerous chemical reagents. While these efforts have resulted in tremendous advancements in addressing chemical toxicity, it has on the other hand, lead to an overload of new chemical compounds. Therefore, in order to work towards environmental protection in a holistic manner, it becomes important to identify the essential traits in a reagent and therefore plan the design in a way that these features are incorporated in the reagent. In line with this, it was envisaged that developing a reagent that could perform multiple chemical transformations would be superior to those that were

reaction specific. On the other hand, with the increase in negative focus towards organic solvents in chemical synthesis, there is an effort to perform chemical reactions in aqueous medium (1–3). However, the most important limiting factor is the insolubility of the reagents and substrates in water. This is where the need for phase transfer reagents is realized and has been considered an important property in the development of the new reagent.

A while ago, the first phosphonium tribromide reagent, Ethyltriphenylphosphonium tribromide (ETPPTB) has been developed by our group and its reactivity has been studied (4). In continuation of our efforts to study this class of reagents, it has been realized that further work is required in terms of development of a range of such reagents and studies of its properties.

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 Supplemental data for this article can be accessed <https://doi.org/10.1080/17518253.2021.1929511>.

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Valorizing pig hooves for activated carbon production with efficient Methyl green adsorption, DFT insights and bacterial removal via bio-adsorbent column

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ABSTRACT

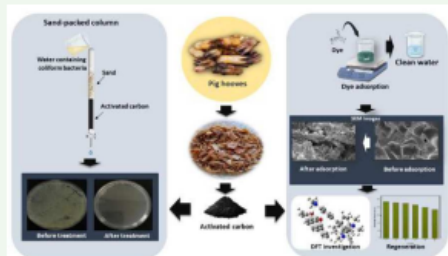
This study describes the use of a novel activated carbon (AC) adsorbent produced from pig hoof waste for the effective removal of Methyl Green (MG) from aqueous solutions. The AC, synthesized through KOH activation, boasts a substantial surface area of 334.031 m²/g and a total pore volume of 0.007 cm³/g. Comprehensive characterization was performed using proximate and ultimate (CHNS) analysis, BET, SEM, TEM, EDX, XRD, FT-IR, XPS, TGA, particle size analysis, zeta potential and zero-point charge (pH_{ZPC}). Adsorption data fit the Langmuir isotherm model exceptionally well ($R^2 = 0.99$) indicating monolayer adsorption and followed pseudo-second-order kinetics implying chemisorption. The thermodynamic studies revealed that the adsorption of the MG dye is a spontaneous and endothermic phenomenon. Density Functional Theory (DFT) computations elucidated the adsorption mechanism, highlighting the critical role of oxygen functional groups. The AC's unique properties enabled the development of a bio-adsorbent carbon column capable of removing *Escherichia coli* and *Staphylococcus aureus* from raw water samples with a 99% removal efficiency. The study also explored the potential for AC regeneration, demonstrating its versatility and sustainability for various applications. This research not only presents an efficient method for dye removal but also underlines the significance of repurposing waste materials, thereby supporting waste reduction and promoting eco-friendly practices for long-term environmental solutions and pollutant mitigation.

ARTICLE HISTORY

Received 6 May 2024
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KEYWORDS

Carbon adsorbent; dye; environmental remediation; theoretical modeling; wastewater treatment



1. Introduction

Dyes from a variety of sectors, including paper manufacturing, printing, electroplating, food and artistic industries, have emerged as substantial contributors to water contamination (1). Notably, synthetic dyes are non-biodegradable compounds that are resistant to variables such as heat, light, chemicals, and oxidizing agents. As a result, the dumping of synthetic dyes has raised serious health and environmental concerns. This is mostly owing to the dyes' intrinsic mutagenic, carcinogenic, or poisonous qualities that negatively impact

both human health and the aquatic environment (2). Cationic dyes such as Methyl green (MG) are one of the earliest synthetic dyes produced that are more toxic as compared to non-ionic and anionic dyes due to their intricate structure, characterized by aromatic rings that confer high optical and physicochemical stability (3). It is also a histochemical stain for DNA and its complex with DNA is used as an experimental substrate for the determination of deoxyribonucleases. The MG-DNA complex can be disrupted by drugs that target DNA as their bioreceptor. This displacement of MG has

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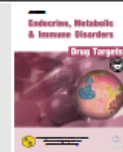
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RESEARCH ARTICLE



Sustainable Synthesis of Guanidine Derivatives and Computational Assessment of their Antidiabetic Efficacy



Imkongyanger Ao¹, Kikoleho Richa², Tsenbeni N. Lotha¹, Ketiyala Ao¹, Lemzila Rudithongru¹, Vevosa Nakro¹, Vimha Ritse¹, Nima D. Namsa³, Pranay Punj Pankaj⁴, Upasana Bora Sinha⁵ and Latongli Jamir^{1,*}

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Abstract: Background: Type 2 Diabetes Mellitus (T2DM) represents a significant and pressing worldwide health concern, necessitating the quest for enhanced antidiabetic pharmaceuticals. Guanidine derivatives, notably metformin and buformin, have emerged as pivotal therapeutic agents for T2DM management.

Aims: The present study introduces an efficient one-pot synthesis method for the production of symmetrical guanidine compounds and subsequently, their evaluation as potential T2DM agents.

Methods: This synthesis involves the reaction of isothiocyanates with secondary amines, employing an environmentally friendly and recyclable reagent, tetrabutylphosphonium tribromide (TBPTB). In order to understand the mechanics of ligand-protein interaction, ADME/Toxicity, and drug-likeness aspects, in silico studies were incorporated.

Results: An efficient and easy method for synthesis of guanidine compounds has been devised. Comprehensive assessment of the biological activity of the synthesized guanidine compounds, specifically in the context of T2DM, has been rigorously conducted.

Conclusion: Computational analyses have unveiled their substantial potential as promising antidiabetic agents. Results highlight the relevance of these compounds in the ongoing pursuit of novel therapeutic solutions for T2DM.

Keywords: Guanidine, antidiabetic agents, Type 2 diabetes mellitus, computational studies, tetrabutylphosphonium tribromide, compounds, therapeutics.

1. INTRODUCTION

Diabetes Mellitus (DM), as marked by persistently increased glucose levels with severe cardiovascular complications, nerve damage, ocular issues, and renal dysfunction, remains a serious global health concern. Among its forms, type 2 diabetes mellitus (T2DM) is prevalent, afflicting approximately 422 million individuals worldwide, with an alarming annual mortality rate of 1.5 million [1]. Such escalating prevalence, coupled with the chronicity, high fatality, and disability rates associated with T2DM, underscores the urgent need for advanced pharmaceutical interventions and improved healthcare systems to combat this ailment. In this context, organic compounds featuring the guanidine functional group, such as metformin, buformin, and phenformin, have demonstrated substantial efficacy against T2DM. The essential role of guanidine fragments in these compounds for their hypoglycemic activity was first established by Ishikawa, Koasasayama,

and their collaborators [2-4]. Subsequently, several research groups recognized and continued to build upon these established findings [5-8]. Fig. (1) illustrates selected compounds containing the guanidine moiety with proven antidiabetic potential [8]. Table 1 highlights the mode of action and adverse effects of some similar commonly known drugs [9-18].

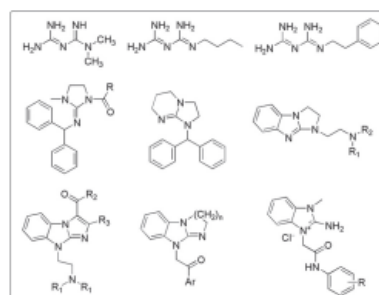


Fig. (1). Examples of some anti-T2DM guanidine compounds.

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Climate Change Impact and Traditional Adaptation Practices in Northeast India: A Review

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Abstract

The review explores the intricate traditional knowledge (TK) nurtured by the diverse indigenous communities of Northeast (NE) India, emphasizing on their adaptive strategies amidst the region's evolving climate patterns. NE India faces a multitude of climate change-induced risks, including earthquakes, landslides, flash floods, and thunderstorms/lightning, highlighting the critical role of indigenous knowledge in mitigating these challenges. Through generations of experience, indigenous cultures have amassed a treasure trove of traditional ecological knowledge, particularly pertinent in NE India's context. Given the region's vulnerability to climate change impacts, these indigenous practices are indispensable. The review provides an in-depth analysis of these aspects, shedding light on recent climate change impacts, prevalent issues, and the indigenous adaptation strategies in NE India. Recognizing the significance of indigenous knowledge in climate change adaptation, the review stresses the importance of integrating it with scientific knowledge to enhance adaptation effectiveness. It extensively covers various aspects of traditional farming systems, watershed governance, the preservation of biodiversity, and traditional medical practices in NE India. However, the region faces challenges from growing development, the industrial revolution, and devastation, emphasizing an urgent need to document, evaluate, and preserve indigenous cultures' traditional ecological knowledge (TEK).



Article History

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Keywords

Adaptation;
Climate change;
Indigenous People;
Northeast India;
Traditional knowledge.

Introduction

Climate change has emerged as a major concern in the modern world as per strong scientific and

socioeconomic study findings. It is now recognized as one of the foremost global concerns, given its potential impacts on various aspects, including

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Environmentally benign synthesis of unsymmetrical ureas and their evaluation as potential HIV-1 protease inhibitors via a computational approach

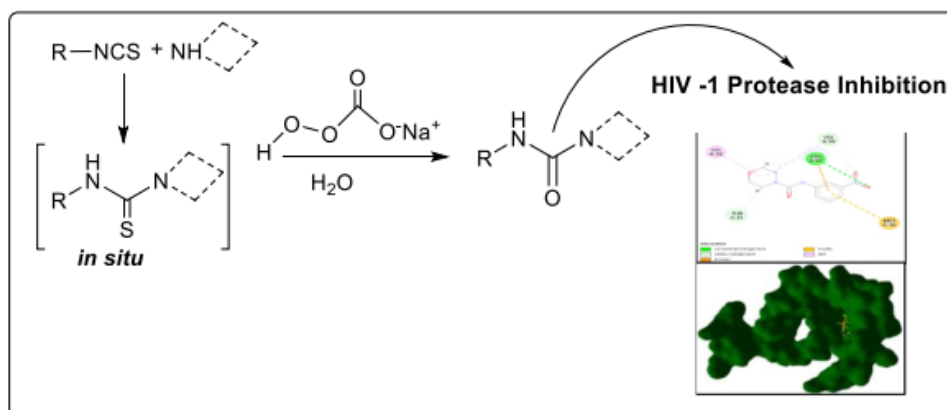
Tsenbeni N. Lotha¹ · Kikoleho Richa² · Viphrezolie Sorhie¹ · Ketiyala¹ · Vevosa Nakro¹ · Imkongyanger¹ · Vimha Ritse¹ · Lemzila Rudithongru¹ · Nima D. Namsa³ · Latonglila Jamir¹

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Abstract

The present work reports the cost-effective, high yielding and environmentally acceptable preparation of unsymmetrical ureas from thiocarbamate salts using sodium percarbonate as an oxidant. Efficacy of the unsymmetrical ureas as potential human immune deficiency virus (HIV-1) protease inhibitors has been evaluated via in silico approach. The results revealed interactions of the urea compounds at the active site of the enzyme with favorable binding affinities causing possible mutations hindering the functioning of the enzyme. Further computational assessment of IC₅₀ using known references satisfactorily authenticated the inhibitory action of the selected compounds against HIV-1 protease. Added to the easy synthesis of the ureas following an environmentally benign protocol, this work may be a valuable addition to the ongoing search for drugs with better efficacy profiles and reduced toxicity against HIV.

Graphical abstract



Keywords Urea · HIV-1 protease inhibitors · In silico · Molecular docking

Introduction

Urea and its analogues are one of the most widely explored compounds that have found diverse utility as agrochemicals like herbicides, insecticides, chemical fertilizers [1], other biologically active plant products [2], pharmaceuticals [3],

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Experimental and theoretical insights on biomass-derived activated carbon for the removal of aniline blue and malachite green dyes

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Abstract

In recent years, the combination of experimental and theoretical studies to elucidate adsorbate-adsorbent interactions has gained significant attention. In this context, the research focuses on the adsorption of two cationic dyes, Aniline Blue (AB) and Malachite Green (MG), using activated carbon (AC) derived from pig hooves biomass (PHB) as a green adsorbent. The AC exhibited a BET surface area of 334.031 m²/g and an average pore volume of 0.007 cm³/g. Under optimized conditions, the removal efficiencies for AB and MG were exceptionally high, reaching 99.3% and 99.16%, respectively, with Langmuir model providing the best fit. Kinetic data were well described by a pseudo-second-order model for both dyes, with a high coefficient of determination (R^2 close to unity), low chi-square (χ^2), and Root Mean Square Error (RMSE). Thermodynamic analysis revealed the adsorption process as spontaneous and endothermic. Density functional theory (DFT) simulations confirmed the experimental results, indicating the adsorption of AB and MG onto AC was highly favorable. Amongst the analyzed oxygen functional groups, carboxyl group had the most significant impact on adsorption with the most negative adsorption energies. Regeneration studies demonstrated that the AC could be reused for up to six cycles, suggesting its reusability. These results highlight the efficient adsorption of both dyes onto the AC, in agreement with isothermal adsorption observations, making it a promising solution for wastewater treatment applications.

Keywords Green Adsorbent · Dyes · Pig Hooves Biomass · DFT · Regeneration

1 Introduction

Water pollution from dyes is a major environmental issue, with the dyeing process generating significant wastewater containing harmful substances like heavy metals, organic chemicals, and salts. These effluents contaminate water sources, posing risks to public health and aquatic ecosystems [1]. Around 0.7 million tons of 10,000 dyes are produced globally each year, leading to their accumulation in waterways and terrestrial environment. These synthetic dyes form suspended particulates and sludge, now classified as micro-pollutants [2]. Dye pollution is persistent and challenging to break down, posing a severe threat to aquatic ecosystems by altering water color, depleting dissolved oxygen, limiting sunlight penetration, and disrupting the ecological balance [3]. Even at low concentrations, dyes diminish the aesthetic

quality of water bodies, highlighting the need for effective removal methods [4].

Various treatment approaches, including ozonolysis [5], UV irradiation [6], adsorption [7], photocatalysis [8], membrane filtration [9], and biological processes [10], have been employed. Of these, adsorption is especially advantageous, offering an efficient, cost-effective and straightforward technique that generates no toxic by-products, making it well-suited for a wide array of applications. Several classes of adsorbents are available, including carbon nanotubes, activated carbon, hydrogels, nanocellulose, nanofibers, pillared clays, nanocomposites, and polymer-based materials [11–14]. Amongst these, activated carbon (AC) has garnered considerable attention owing to its versatility across various industries, including gas and air purification. AC is widely utilized for wastewater treatment, purification, and decolorization due to its high surface area, defined pore structure, and presence of electron-donating functional groups on its surface. These functional groups contribute to its superior performance in removing a wide range of contaminants, rendering AC highly effective for diverse applications in water pollutant treatment [15–18].

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A MICROWAVE ASSISTED ENVIRONMENTALLY BENIGN PROTOCOL FOR PREPARATION OF ESTER COMPOUNDS AND COMPUTATIONAL EVALUATION OF THEIR ANTIMICROBIAL EFFICACY

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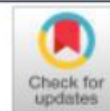
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(Received 18 October 2023, Revised 17 November 2023, Accepted 30 November 2023)

ABSTRACT : This paper reports on an enhanced, economical, effective, and ecologically safe synthesis of esters using a direct condensation method between carboxylic acids and alcohols under microwave radiation. The process is catalyzed by molecular iodine. Using an *in-silico* technique, the synthetic esters were assessed for their antibacterial properties and found to be suitably effective against a variety of significant microorganisms. A theoretical analysis of the biological features of the ester compounds under investigation, along with their environmental friendliness, substrate diversity, ease of use and high yields of the synthetic technique, may shed some light on the compounds' potential as anti-microbial agents.

Key words : Esterification, molecular iodine, catalyst, antimicrobial, *in silico*.

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INTRODUCTION

Over time, research on creating novel and effective synthesis processes for esters has progressed. This is due to the fact that esters are used in many common applications such as bulk chemicals, fine chemicals, medications, plasticizers, food preservatives, perfumes, cosmetics and chiral auxiliaries. In the food processing industries, ester compounds are commonly used as fruit flavors, to emulsify milk products, to reduce viscosity in chocolates and for other purposes. Additionally, esters are essential building elements for reactions that include polymerization (the opening of a lactone's ring), polycondensation, or macro lactonization. (Larock, 1989; Otera, 2003; Cai *et al.*, 2022; Xue *et al.*, 2023; Cinar and Topal, 2022).

Therefore, our group has previously investigated the utilization of catalytic quantity of ETPPTB for the esterification of acetic acid with various alcohols in an effort to design a system that is straightforward yet effective and metal free (Otera, 2003). Molecular iodine (I₂) was thought to successfully replace the role of Br₂ in the reaction since the working mechanism requires

ETPPTB as the source of Br₂, which really pushes the reactions forward. When considering alternatives to ETPPTB, we anticipated that substituting molecular I₂ would provide a more accessible and economical option. This also applies to using any other tribromide reagent.

Also, in a further greening improvisation of our earlier methodology, we have attempted the replacement of reflux conditions with microwave irradiation, which has also effectively reduced the time of reaction. Furthermore, a significant quantity of acid was used in our previous work (Jamir *et al.*, 2011) as a solvent and reagent (1 mmol alcohol to 1 ml acetic acid). We have reduced the amount of acetic acid by 75% in this attempt by using water as the solvent medium.

The present methodology is expected to be a more acceptable alternative in terms of environmental benignity, ease of execution and cost effectiveness as compared to the likes of using R₂SnO (Steliou *et al.*, 1980), diorgano tin chloride (Otera *et al.*, 1991), TiCl(OTf)₃ (Izumi *et al.*, 1995), TiCl₂(ClO₄)₂ (Otton *et al.*, 1988), Hf(IV) and Zr(IV) salts (Ishihara *et al.*, 2000), La(OTf)₃ (Barrett and Braddock, 1997), Ce(OTf)₃ (Iranpoor and Shekariz,



ENVIRONMENTAL INTIMACIES FROM INDIA'S NORTH EAST

PSYCHO-SOCIAL IMPLICATIONS
FOR PRO-ENVIRONMENT BEHAVIOUR

Edited by
Indranee Phookan Borooah, Bidita Das
and Sabiha Alam Choudhury

Chapter

Climate Impact in North East India

By Tsenbeni N Lotha , Ketiyala , Vevosa Nakro ,
Latonglila Jamir 

Book [Environmental Intimacies from India's North East](#)

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Urkunde

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Bezeichnung:

Ein System zur Synthese von Aktivkohle aus tierischen Bioabfällen zur
Entfernung kationischer Farbstoffe

IPC:

B01J 20/30

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Die Präsidentin des Deutschen Patent- und Markenamts



Eva Schewior

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Urkunde

über die Eintragung des
Gebrauchsmusters Nr. 20 2024 101 249

Bezeichnung:

Ein Aktivkohlen-Produktionssystem unter Verwendung tierischer Abfälle

IPC:

C01B 32/312

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13.03.2024

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09.04.2024

Die Präsidentin des Deutschen Patent- und Markenamts



Eva Schewior

München, 09.04.2024



Urkunde

über die Eintragung des Gebrauchsmusters Nr. 20 2024 101 576

Bezeichnung:

Ein System zur umweltfreundlichen Synthese von
Tetrabutylphosphoniumtribromid (TBPTB) und organischen Verbindungen durch
das Reagenz

IPC:

C07F 9/54

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(57) Abstract :

The invention is a process and method for employing activated carbon obtained from fish scales which is processed with potassium hydroxide for the adsorption of Congo red dye. Elemental analysis, XRD, SEM, FT-IR spectroscopy, BET surface area analysis, CHN analysis, and zero-point charge are among the characterization techniques used. The overall pore volume of the synthesized carbon is 0.119 cm³/g, and its BET surface area is 150.049 m²/g. Temperature, initial dye concentration, and contact time all has an impact on the adsorption process; the adsorption data are well described by the Freundlich model. Pseudo-second-order thermodynamic study indicates spontaneity and exothermicity in the process. Fish scale-derived activated carbon showed promise as a reusable carbon over a period of six cycles, suggesting that it might be used as an adsorbent to remove Congo red dye.

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