PREPARATION OF PANI/GO/MOF-Fe_3O_4 NANOCOMPOSITE VIA SOL-GEL METHOD FOR REMOVAL METHYL ORANGE AND NAPROXEN SODIUM

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by

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LIST OF SYMBOLS

%	**Percentage**
°C	Degree Celsius
Co	Initial concentration
Ce	Equilibrium concentration
cm	Centimetre
ΔG°	Gibbs free energy
ΔH°	Change in enthalpy
KL	Langmuir isotherm constant
KF	Freundlich isotherm constant
m	Mass
min	Minutes
mm	Milimetre
nm	Nanomitre
qe	Equilibrium adsorption capacity
qmax	Maximum adsorption capacity
sec	Seconds
ΔS°	Change in entropy
T	Temperature
T	Time
μm	Micrometre
V	Volume

LIST OF ABBREVIATIONS

Abbreviation	Description
AC	Activated carbon
BET	Brunauer-Emmett-Teller analysis
DI	Deionized water
DLD	Delay line detector
ECs	Emerging contaminants
FTIR	Fourier Transform Infrared Spectroscopy
Fe_3O_4	Magnetic oxide
GO	Graphene oxide
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
HPLC	High-Pressure Liquid Chromatography
MO	Methyl Orange
MOF	Metal-organic framework
Mg L^{-1}	Milligram per litre
NAP	Naproxen Sodium
NSAID	Non-steroidal anti-inflammatory drug
PANI	Polyaniline
PFO	Pseudo-first-order
pHPZC	Point zero charge
Ppm	Parts per million
PSO	Pseudo-second-order
PhACs	Pharmaceutically active chemicals
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
USM	Universiti Sains Malaysia
UV	UV-visible spectrophotometer
WHO	World Health Organization
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction Analysis

PENYEDIAAN KOMPOSIT NANO PANI/GO/MOF-FE_3O_4 MELALUI KAEDAH SOL-GEL BAGI PENYINGKIRAN METIL JINGGA DAN NATRIUM NAPROXEN

ABSTRAK

Pelepasan pewarna industri dan pencemar baru (ECs) ke dalam sumber air menjadi kebimbangan alam sekitar yang serius. Dalam kajian ini, satu kaedah sintesis yang mudah dan kos efektif telah digunakan untuk mensintesis nanokomposit PANI/GO/MOF-Fe_3O_4 untuk penjerapan pewarna industri: methyl orange (MO) dan pencemar baharu naproxen natrium (NAP) daripada air sisa. Teknik pencirian, termasuk FTIR, XRD, SEM, dan TGA, telah digunakan untuk mengenal pasti morfologi dan kestabilan terma nanokomposit terhasil. Keputusan parameter fisio-kimia (seperti pH, masa sentuhan, dos penjerap, kepekatan bahan terjerap, dan suhu) menunjukkan penjerapan yang optimum. Kajian terhadap model Langmuir dan Freundlich mendedahkan bahawa model Langmuir lebih sesuai menggambarkan tingkah laku penjerapan dengan pekali penentuan yang tinggi (R^2=0.999 untuk MO dan 0.998 untuk NAP). Selain itu, dapatan kajian kinetik mengesahkan penubuhan model pseudo-orde pertama dengan keserasian yang baik dengan keputusan eksperimen (R^2=0.998 untuk MO dan 0.994 untuk NAP), menunjukkan dominasi fizisorpsi. Model tindak balas pseudo-orde kedua juga memberikan kesesuaian yang munasabah (R^2=0.965 untuk MO dan 0.958 untuk NAP). Analisis termodinamik menunjukkan sifat eksotermik (ΔH^o= -17.72 kJ mol^{-1} bagi MO dan -28.28 kJ mol^{-1} untuk NAP) dan spontan (ΔG^o= -3.877 kJ mol^{-1} bagi MO dan -5.416 kJ mol 1 bagi NAP) bagi pewarna dan ECs. Nanokomposit PANI/GO/MOF-Fe_3O_4 menunjukkan kapasiti penjerapan yang cemerlang bagi MO (239.78 mg g^{-1}) dan NAP (40.64 mg g^-

^{1}). Selain itu, kemudahan pemulihan dan kebolehkitaran nanokomposit sehingga 4 kitaran meningkatkan kelestarian dan sifat mesra alamnya, menawarkan pendekatan yang berdaya maju untuk menangani cabaran alam sekitar dalam rawatan air sisa industri. Keberkesanan penjerapan yang ketara oleh nanokomposit magnetik PANI/GO/MOF-Fe_3O_4 menonjolkan aplikasinya yang boleh digunakan untuk rawatan air sisa yang mengandungi pewarna dan bahan anti-radang.

PREPARATION OF PANI/GO/MOF-FE3O4 NANOCOMPOSITE VIA SOL-GEL METHOD FOR REMOVAL METHYL ORANGE AND NAPROXEN SODIUM

ABSTRACT

Discharging industrial dyes and emerging contaminants (ECs) into water resources has become a severe ecological and public health hazard, evidenced by measurable contaminant levels in wastewater and their adverse impacts on aquatic life and human health. In this study, a simple synthesis method (in-situ polymerization) has been employed to synthesize PANI/GO/MOF-Fe_3O_4 nanocomposite for the adsorption of industrial dye: methyl orange (MO) and an emerging contaminant, naproxen sodium (NAP), from the wastewater. The PANI/GO/MOF-Fe_3O_4 nanocomposite was chosen for its unique combination of high adsorption capacity (239.78 mg g^{-1} for MO and 40.68 mg g^{-1} for NAP), and facile magnetic recovery (up to four cycles) compared to alternative materials. Characterization techniques, including FTIR, XRD, SEM, and TGA, have been used to identify the nanocomposite's morphology and thermal stability. The results of physio-chemical parameters such as pH (6 for both MO and NAP), contact time (90 min for MO and 60 min for NAP), adsorbent dose (25mg for both MO and NAP), adsorbate concentration (200mg L^{-1} for MO and 30 mg L^{-1} for NAP) and temperature (25°±2 for both MO and NAP) were used to check the optimal adsorption condition. The studies of Langmuir and Freundlich's models revealed that the Langmuir model better describes the adsorption behavior with high determination coefficients (R^2=0.999 for MO and 0.998 for NAP). Moreover, the kinetic studies confirmed the establishment of a pseudo-first-order model with good agreement with the experimental results

(R^2=0.998 for MO and 0.994 for NAP), indicating the dominance of physisorption. Thermodynamic analysis indicated exothermic (ΔH^o= -17.72 kJ mol^{-1} for MO and -28.28 kJ mol^{-1} for NAP) and spontaneous (ΔG^o= -3.877 kJ mol^{-1} for MO and -5.416 kJ mol^{-1} for NAP) nature of dye and ECs. The PANI/GO/MOF-Fe_3O_4 nanocomposite exhibited outstanding adsorption capacities for MO (239.78 mg g^{-1}) and NAP (40.64 mg g^{-1}), surpassing many previously reported nanocomposites such as chitosan/PVA/zeolite nanofiber (153 mg g^{-1} for MO), Zn/Al-LDO (181.9 mg g^{-1} for MO), Fe_3O_4@graphene nanocomposite (10.6 mg g^{-1} for NAP), and activated carbon electrode (20.3 mg g^{-1} for NAP), confirming its superior affinity and dual-functionality for diverse emerging contaminants. Furthermore, the nanocomposite demonstrated ease of recovery and maintained reusability for up to 4 cycles under the tested conditions, enhancing its sustainability and eco-friendliness and offering a viable approach to combat the environmental challenges of industrial wastewater treatment. The significant adsorption efficacy of PANI/GO/MOF-Fe_3O_4 magnetic nanocomposite underscores its potential in treating dye and anti-inflammatory-containing wastewater remediation

CHAPTER 1

INTRODUCTION

1.1 Background of study

1.1.1 Significance of Clean Water and Emerging Contaminants

Clean water is essential to sustain various industrial, biological, and agricultural activities (Chen et al., 2023). It is the most prevalent substance on the planet and covers 71% of Earth's surface (Wang & Peng, 2010). The World Health Organization (WHO) reported that over 2.2 billion human beings do not have access to drinkable water worldwide (Ismail & Go, 2021). Around 1.8 million people die yearly from waterborne infections because of the consumption of contaminated water (Manetu & Karanja, 2021). Furthermore, wastewater contains different contaminants, such as emerging contaminants (ECs), including personal care products (PCP), pharmaceuticals, industrial chemicals, and insecticides (Ahmed et al., 2021). The term "emerging contaminants" refers to newly identified pollutants that pose unpredictable environmental risks and have the potential to cause significant harm (Rathi et al., 2021). Significant progress has been made in detecting organic contaminants in industrial waste streams, including developing novel analytical techniques in the last century to identify recently found and developing toxins (Khan et al., 2022).

1.1.2 Presence and Impact of Emerging Contaminants in Wastewater

The ECs observed concentration in the wastewater ranging from 1 ng L^{-1} to 100 ng L^{-1} (Rout et al., 2021a). Consumption of EC-contaminated water severely affects normal body functions. These contaminants cause health problems such as gastrointestinal disease, cancer, and other hormonal disturbances (Yadav et al., 2023). Pharmaceutical waste (such as antibiotics, anti-inflammatories, anxiolytics, anti-virals, Antifungals, etc.) is considered one of the most important categories of concern for environmental pollutants. PhACs and PC pollutants do not disintegrate quickly and remain in the environment for prolonged periods due to their sturdy structure. Environmental PCs' quantified amounts (ranging from 1 to 39 ng mL^{-1}) have recently been identified as potentially hazardous to the ecosystem (Rivera-Utrilla et al., 2013). Naproxen (NAP) is the pharmaceutical drug widely utilized as a non-steroidal anti-inflammatory drug (NSAID) that is frequently encountered in aquatic environments (Baratta et al., 2022; Mohd Hanafiah et al., 2022; Wojcieszyńska & Guzik, 2020). Unfortunately, NAP and its by-products are toxic to all living organisms (Feng et al., 2023). Thus, developing an effective ambi-functional adsorption method that can potentially treat EC using a single nanocomposite adsorbent has become mandatory.

1.1.3 Existing Treatment Techniques and Prominence of Adsorption

Physical, chemical, and biological techniques can be used to treat ECs containing wastewater. So far, many methods such as membranes (Eskikaya et al., 2023), natural treatment (Khan et al., 2023), photocatalytic (Suresh et al., 2023), advanced oxidation (Fu et al., 2023), and adsorption (Gomes et al., 2016) have been used for removing the ECs containing water. Due to their high cost and technical constraints, only a few of these procedures are recommended despite having a high decolorization efficiency. Adsorption is the most popular technique for removing or reducing ECs from aqueous solutions because of its ease of application and inexpensive cost (Mustafa et al., 2022). The adsorption using polymers such as polyaniline (PANI) and activated carbon has shown significant pollutant removal efficiency (Ravindiran et al., 2023; Zare et al., 2018). Several materials, including activated carbon (Manimegalai et al., 2023), PANI (M. Khan et al., 2022), graphene oxide (GO) (Zubair et al., 2024), metal-organic framework (MOF) (Khan et al., 2023), and carbon nanotube-based composite (Ates et al., 2017), have been utilized to treat wastewater.

1.1.4 Advantages of Magnetic Polymer-Based Nanocomposites for ECs Removal

Moreover, the adsorption has some disadvantages regarding regeneration capacity, such as quick saturation and the lack of ability to adsorb the contaminants after desorption (Patel, 2021; Shang et al., 2020). Therefore, the current research focuses on incorporating magnetic nanoparticles (Fe_3O_4) into polymer-based adsorbents to prepare PANI/GO/MOF-Fe_3O_4 magnetic nanocomposites. GO offers a large surface area and functional groups (such as carboxyl and hydroxyl), enabling π-π interactions and hydrogen bonding with organic molecules (Tang et al., 2018). MOF improves adsorption selectivity and capacity by providing customized pore architectures and chemical functions (R. B. Lin et al., 2021). Compared to traditional materials such as activated carbon (AC) and carbon nanotubes (CNT), PANI/GO/MOF-Fe_3O_4 nanocomposite presents superior adsorption performance due to its well-defined surface functionalities, including π–π interactions, hydrogen bonding, electrostatic attractions, and metal-ligand coordination, arising from the integration of PANI, GO, MOF, and Fe_3O_4 components. Due to the highly adjustable surface area of the PANI/GO/MOF-Fe_3O_4 composite, different contaminants may be selectively adsorbed based on their chemical characteristics. The PANI/GO/MOF-Fe_3O_4 composite presents a unique combination of magnetic recoverability with improved adsorption capacity and selectivity towards NAP and MO. Both NAP and MO are examples of negatively charged contaminants that interact electrostatically with positively charged sites provided by the PANI component of the composite. Utilizing eco-friendly nanocomposites like PANI/GO/MOF-Fe_3O_4 to remove wastewater pollutants can substantially benefit developing nations, particularly those facing serious water contamination issues. Several studies have demonstrated that nanomaterials like PANI/GO/MOF-Fe_3O_4 offer efficient solutions for wastewater treatment, particularly suitable for regions lacking advanced infrastructure. For instance, Cordova Estrada et al. (2021) emphasized the practical utility of magnetic nanocomposites for dye elimination in resource-constrained environments, owing to their facile separation and regeneration capabilities. Similarly, Kaya and Yağmur (2020) reported the efficient adsorption performance of polymer-based materials under mild conditions, reinforcing their potential use in decentralized systems common in developing countries.

The current work presents a comprehensive study on the synthesis, characterization, and adsorption performance of a novel PANI/GO/MOF-Fe_3O_4 magnetic nanocomposite. This material was systematically investigated for its potential to remove methyl orange (MO) and naproxen (NAP) from contaminated water. Through its multifunctional surface chemistry, enhanced structural stability, and magnetic recoverability, the composite demonstrates promising applicability for practical wastewater treatment, particularly in addressing emerging contaminants in environmentally and economically constrained system.

1.2 Problem Statement

Traditional adsorbents such as activated carbon, silica, and chitosan, while widely studied, exhibit critical drawbacks in treating emerging contaminants (ECs), including poor selectivity, low regeneration efficiency, and limited interaction mechanisms. Single-component nanomaterials like pristine graphene oxide, MOFs, or conducting polymers often suffer from aggregation, structural instability, and weak pollutant affinity in complex wastewater matrices. Furthermore, commonly used synthesis techniques such as sol-gel, melt blending, and physical mixing typically result in inhomogeneous dispersion and poor interfacial contact between composite constituents, ultimately reducing the functional performance and durability of the resulting adsorbents. These shortcomings in both material properties and synthesis approaches hinder the development of robust and efficient adsorbents.

Various materials such as activated carbon, zeolites, silica, and polymer-based composites have been extensively explored for the removal of emerging contaminants (ECs) from wastewater. However, these materials frequently exhibit low structural stability, poor regeneration efficiency, and significant leaching of active components, which can lead to secondary contamination. For instance, carbon-based adsorbents, while effective initially, tend to lose adsorption capacity over repeated cycles due to weak bonding and surface degradation. Similarly, polymer-only or MOF-only systems often suffer from limited recyclability and poor magnetic recovery, making them inefficient for practical deployment. Moreover, widely used synthesis approaches like sol-gel and co-precipitation methods typically result in non-uniform dispersion of nanoparticles and weak interfacial interactions, which further compromise the long-term performance and stability of the adsorbents.

Existing studies on adsorption mechanisms often overlook how operational parameters such as pH, contact time, adsorbent dosage, and temperature influence adsorption efficiency under realistic environmental conditions. Many reported materials show inconsistent or poorly understood behavior when exposed to variations in these physicochemical parameters, limiting their predictability and scalability for practical applications. Moreover, batch adsorption studies often lack comprehensive optimization, which leads to suboptimal design of treatment systems and an incomplete understanding of adsorbent–adsorbate interactions under varying environmental stresses. Additionally, despite growing concerns over material sustainability, limited efforts have been made to evaluate the regeneration potential of adsorbents beyond a few cycles, and those that have, often report significant loss in adsorption efficiency. These gaps emphasize the need for a thorough investigation into how different environmental and operational parameters affect the adsorption behavior and stability of multifunctional nanocomposites.

1.3 Objectives of the study

The study project aimed to achieve the following objectives to address the problem statement:

1. To synthesize PANI/GO/MOF nanocomposite adsorbent using the chemical method.
2. To synthesize iron oxide-based PANI/GO/MOF-Fe_3O_4 nanocomposite via the hydrothermal method to prevent adsorbent release as a secondary pollutant by controlling leaching during application, and to characterize the composite using advanced analytical techniques such as SEM, XRD, FTIR, TGA, XPS, BET, etc.
3. To determine the adsorption behaviour of the adsorbent based on physicochemical parameters such as pH, contact time, adsorbent dose, adsorbate concentration, and temperature, and to investigate the reusability or regeneration of PANI/GO/MOF-Fe_3O_4 magnetic nanocomposite adsorbent.

1.4 Scope of the study

This study focuses on the synthesis, characterization, and application of a multifunctional PANI/GO/MOF- Fe_3O_4 nanocomposite for the effective removal of naproxen (NAP) and methyl orange (MO) from contaminated water systems. The approach integrates materials with distinct properties to overcome the limitations of conventional adsorbents such as poor selectivity, low reusability, and high production costs. The chemical in situ polymerization method was selected for synthesizing the PANI/GO/MOF composite due to the limitations of other fabrication techniques such as sol-gel, solution casting, and melt blending, which often result in poor dispersion, weak interfacial bonding, or agglomeration of components. In contrast, the chemical in situ polymerization technique enables direct polymer growth in the presence of GO and MOF precursors, ensuring homogenous distribution, enhanced structural integrity, and improved functional group availability. This method also allows better control over morphology and facilitates strong π–π and electrostatic interactions essential for contaminant binding.

To incorporate magnetic functionality, Fe_3O_4 nanoparticles were synthesized via the hydrothermal method. This method was chosen over co-precipitation or thermal decomposition because it produces highly crystalline, uniform, and thermally stable nanoparticles with minimal aggregation and enhanced magnetic properties. Importantly, hydrothermal synthesis reduces the risk of Fe ion leaching, a known limitation in many iron-based adsorbents, thus preventing secondary pollution and ensuring environmental compatibility. Characterization of the composite and its components was performed using FTIR, XRD, TGA, SEM, BET, and XPS to assess structural, morphological, thermal, and surface properties. BET and XPS were specifically used for the final nanocomposite to understand surface functionality and porosity, which are critical for adsorption efficiency.

Adsorption experiments were designed to examine the impact of pH, adsorbent dose, initial pollutant concentration, and contact time. The pH range (2–10) was selected to simulate typical wastewater conditions; extreme values were excluded to avoid structural degradation observed in pretests. The adsorbent dose (0.025–0.125 g) was optimized to capture the point at which additional material no longer contributed to significant adsorption improvement. Initial concentration ranges for MO (50–400 mg L^{-1}) and NAP (10-50 mg L^{-1}) were based on reported levels in real effluents. Contact times were selected based on kinetic screening to ensure equilibrium within practical durations. The applicability of the material was validated using real textile wastewater to ensure effectiveness beyond synthetic laboratory systems. Kinetic, isotherm, and thermodynamic modeling (PFO, PSO, Langmuir, Freundlich, ΔH^o, ΔS^o, ΔG^o) were employed to interpret the adsorption mechanism, rate, and feasibility. This structured methodology and the selection of synthesis techniques were driven by performance gaps in previous materials and methods, ensuring the composite's efficiency, stability, and reusability for real-world wastewater treatment applications.

CHAPTER 2

LITERATURE REVIEW

2.1 Emerging Contaminants

ECs are a large group of artificial compounds that have only recently been identified as serious water contaminants. However, they have been in the water for a long time (Khan et al., 2022). According to the United States Geological Survey (USGS-6), ECs are chemical substances that are not constantly tracked in the environment, yet have a significant potential to impact human health and the environment, even in very low quantities (Sondhi et al., 2023). Pharmaceutically active compounds (PhACs), personal care products (PCPs), endocrine-disrupting chemicals (EDCs), biocides/regulated compounds (RCs), industrial chemicals, surfactants, and artificial food preservatives are the primary categories of synthetic substances that are crucial for modern societies worldwide (Singh et al., 2022). These compounds have recently been detected in groundwater and surface water, classifying them as uncontrolled pollutants in the ecosystem and presenting significant environmental risks (Sultan et al., 2024). ECs are found in wastewater streams ranging from ng L^{-1} to g L^{-1} (Zahmatkesh et al., 2023).

2.1.1 PhACs

PhACs a class of emerging contaminants (ECs), have raised considerable concern in recent decades due to their implications for human health and safety (Alkarim et al., 2023). Even at trace concentrations (ng L^{-1}), PhACs can accumulate in the human body through the food chain, particularly via aquatic organisms, leading to adverse effects such as genetic mutations (Bebianno & Garcia da Fonseca, 2020), reproductive issues (Caliman & Gavrilescu, 2009), genetic damage (Ortúzar et al., 2022), and the development of cancer (Mishra et al., 2023). Primary sources of PhACs include hospitals, animal excrement, research endeavors involving medicinal substances, and the release of expired medication into the environment (Narwal et al., 2023). Hospitals are the primary suppliers of medications that are leaked into the environment. Hospital water use typically ranges from 400 to 1200 liters per bed per day (Majumder et al., 2021). The effluent discharged from hospitals comprises pathogens, pharmaceutical residues and metabolites, drug conjugates, radioactive elements, and other substances. It has been observed as the most commonly identified active pharmaceutical ingredient (API) in river streams, with a presence in 62% of the 1052 sampling sites examined across 258 rivers globally (Fatimazahra et al., 2023). An overview of pharmaceutical active contaminants (PhACs), their sources, environmental concentrations, and associated health impacts is summarized in Table 2.1.

Table 2.1 Overview of Pharmaceutical Contaminants (PhACs), their environmental concerns, sources and health impacts.

PhAC	Environmental Concentration (ng/L)	Primary Source	Health Impact	Reference
Diclofenac	10–1200	Hospitals, domestic waste	Toxic to aquatic organisms; renal failure in fish	Fatimazahra et al., 2023
Ibuprofen	20–2800	Households, industrial discharge	Reproductive toxicity; liver and kidney damage	Bebianno & Garcia da Fonseca, 2020
Naproxen	15–1300	Hospital wastewater, expired drugs	Genotoxicity, endocrine disruption	Ortúzar et al., 2022
Carbamazepine	50–1500	Hospitals, domestic waste	Neurotoxicity,	Mishra et al., 2023

			bioaccumulation	
Sulfamethoxazole	30–500	Animal excrement, hospitals	Antibiotic resistance, immunotoxicity	Narwal et al., 2023
Ciprofloxacin	5–850	Pharmaceutical industries, hospitals	Genetic mutations, cytotoxic effects	Caliman & Gavrilescu, 2009

2.1.2 PCP

PCPs are used to improve the quality of everyday life and include a broad array of items such as shampoos, lotions, detergents, hair dyes, lipsticks, cosmetics, creams, bath soaps, dental products, toothpaste, sunscreens, fragrances, and other household essentials. (Benny et al., 2024). In recent decades, the production and use of Pharmaceuticals and Personal Care Products (PPCPs) have risen markedly. Their extensive usage, improper disposal, and insufficient treatment of urban wastewater have contributed to the contamination of aquatic environments by PCPs and their derivatives. (Khalid & Abdollahi, 2021; Kumar et al., 2023). Releasing the waste from PPCPs into the water causes harmful consequences on plants, animals, and humans, including genetic damage, mutation, and ecological toxicity (Ziylan-Yavas et al., 2022).

Furthermore, the fate and concentration of these compounds in the environment are influenced by various physicochemical properties, including the n-octanol/water partition coefficient (Kow), degradation rate, and organic carbon normalized sediment/water partition coefficient (Koc) (Narayanan et al., 2022). Additionally, factors such as waste stream flow and usage patterns of these compounds can vary by region and season and play a role in determining their release (Ogbeide et al., 2018).

A summary of commonly detected PCPs, their active ingredients, environmental implications, and concentrations reported in aquatic environments is provided in Table 2.2.

Table 2.2 Summary of Common PCPs, Their Ingredients, Environmental Impact, and Reported Concentrations

Compound Type	Active Ingredients	Environmental Concern	Detected Concentration (ng/L)	References
Shampoo	Sodium lauryl sulfate	Aquatic toxicity, skin irritation	3000	Benny et al., 2024
Toothpaste	Fluoride	Bioaccumulation, dental fluorosis	1500	Ziylan-Yavas et al., 2022
Sunscreen	Benzophenone-3	Endocrine disruption, coral bleaching	2500	Khalid & Abdollahi, 2021
Fragrance	Synthetic musks	Persistent in environment, bioaccumulation	1800	Narayanan et al., 2022
Hair Dye	Paraphenylenediamine	Toxicity to aquatic organisms	2200	Ogbeide et al., 2018

2.1.3 Endocrine-disrupting chemicals (EDCs)

Endocrine-disrupting chemicals (EDCs) disrupt the endocrine system's normal functioning, typically by imitating or obstructing the actions of natural hormones. EDCs can be found in a wide range of products, including plastics, insecticides, and personal care items. Although certain EDCs may have advantages in commercial settings, such as increasing the shelf life of products or promoting agricultural productivity, their extensive release into water bodies presents substantial environmental and health hazards (Ghosh et al., 2022; Hahladakis et al., 2018). EDCs have the potential to interfere with the reproductive and developmental functions of fish and other living things in aquatic environments, resulting in population decreases and disturbances in the overall balance of the ecosystem. Moreover, the presence of EDCs in water supplies or consumer goods has been associated with a range of detrimental health consequences in humans (Stiefel & Stintzing, 2023). These include reproductive abnormalities, hormonal disturbances, and an elevated susceptibility to some types of cancer. Therefore, it is essential to comprehend the origins, routes, and consequences of EDCs to reduce their harmful effects on aquatic ecosystems and human well-being (Zhou et al., 2019).

2.1.4 Biocides

Biocides, commonly referred to as regulated compounds (RCs), are a diverse group of chemicals that are specifically formulated to manage or eliminate detrimental organisms (Macedo et al., 2023). These chemicals offer significant benefits across various sectors such as agriculture, healthcare, and water treatment by effectively inhibiting microbial growth and preserving product quality (Andrés et al., 2022). However, their widespread use has raised concerns about their discharge into aquatic environments, where they can persist and accumulate, posing risks to both ecological systems and human health (Mendoza et al., 2022). Biocides have been linked to harmful effects on aquatic organisms, leading to ecosystem disturbances and deterioration of water quality (Martins et al., 2018).

Furthermore, the potential effects of these substances on human health, such as their toxicity and ability to accumulate in food chains, require strict regulatory actions and advanced treatment methods to reduce their impact on the environment (Zahoor et al., 2023). Table 2.3 presents key findings from recent studies on the sources, environmental impact, and toxicological concerns of biocides and textile-derived pollutants. On the other hand, the pathways and sources through which emerging contaminants enter aquatic environments are illustrated in Figure 2.1.

Table 2.3 Summary of biocides, their applications, and environmental Impacts.

Biocide Type	Application	Environmental Concern	Detected Concentration (µg/L)	References
Triclosan	Personal care, toothpaste, soaps	Endocrine disruption, persistence	0.1–2.3	Macedo et al., 2023
Chlorhexidine	Mouthwash, disinfectants	Aquatic toxicity	0.01–0.45	Martins et al., 2018
Benzalkonium chloride	Surface disinfectants, antiseptics	Antibiotic resistance	0.2–1.1	Zahoor et al., 2023
Isothiazolinones	Industrial cooling systems	Skin sensitization	0.05–0.6	Andrés et al., 2022
Glutaraldehyde	Hospital disinfectants	High aquatic toxicity	0.03–0.9	Mendoza et al., 2022
Phenolic compounds	General disinfectants	Bioaccumulation potential	0.2–2.0	Martins et al., 2018
Silver ions	Wound dressings, coatings	Toxic to aquatic life	0.01–0.05	Zahoor et al., 2023
Chlorine dioxide	Water disinfection	Reactivity and residual toxicity	0.5–5.0	Macedo et al., 2023

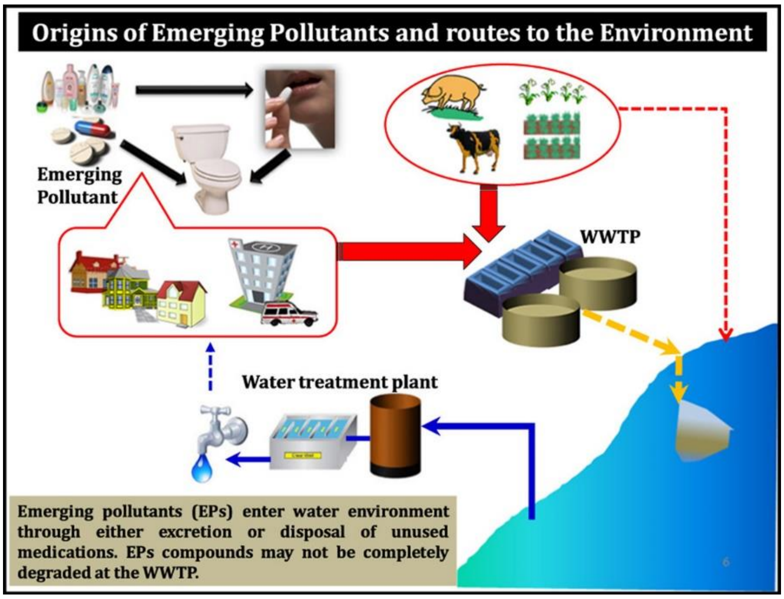

Figure 2.1 Different sources and discharging of emerging contaminants into water bodies (Gogoi et al., 2018)

2.2 Techniques for Emerging Contaminants Remediation

The remediation of ECs has been carried out using several methods, such as adsorption, membrane, advanced oxidation, biological treatment, chemical precipitation, and physical treatments. Because of the complexity of the contaminants and the environmental systems in which they are present, each strategy for removing or degrading ECs has unique benefits and mechanisms. These strategies are described in brief below.

2.2.1 Adsorption

The term adsorption refers to a phenomenon that occurs on surfaces when a solid (the adsorbent) attracts molecules or ions from a liquid or gas (the adsorbate) (Mahmood Aljamali et al., 2021). Adsorption is a prominent physical treatment method that relies on the exceptional surface area of adsorbents to be effective. The adsorption technique effectively removes many organic, inorganic, and hazardous pollutants. On the other hand, adsorption capability is influenced by factors such as the size of the pollutants, their concentration, temperature, molecular mass, and other chemical parameters (F. Yu et al., 2019). However, EC molecules can be adsorbed onto the surface of an adsorbent through many forces, including hydrogen bonding, electrostatic interactions, van der Waals forces, and hydrophobic interactions. Adsorbents typically have porous structures, enhancing the overall surface area available for adsorption and facilitating quicker fluid flow. Adsorption is a cost-effective and uncomplicated technique to eliminate dyes from water and wastewater. To understand how different materials adsorb ECs, researchers typically employ parameters like the Freundlich adsorption isotherm (K_F) and Langmuir maximum adsorption capacity (q_{max}) (Ansari et al., 2012).

Adsorption can be classified into two types: physical adsorption and chemisorption, also known as activated adsorption (Wang & Guo, 2020). Physical adsorption occurs when the adsorbent and adsorbate surface bind together due to non-specific van der Waals forces. On the other hand, chemisorption involves the formation of ionic or covalent bonds through chemical processes (Agboola & Benson, 2021). Physical adsorption is a reversible process that is less selective. In contrast, chemisorption is more selective and irreversible (Gunawardene et al., 2022). Considering the versatility and simplicity of adsorption, it remains a widely adopted technique for EC removal, especially in resource-limited settings. In my opinion, the future of adsorption lies in developing multifunctional, regenerable adsorbents that combine high surface area with tailored surface chemistry for targeted contaminant capture. This will be essential for addressing the growing complexity of emerging pollutants in real wastewater matrices. Several studies have demonstrated the effectiveness of adsorption in removing emerging contaminants using diverse materials, as summarized in Table 2.4.

Table 2.4 Selected adsorption-based studies for emerging contaminant removal, highlighting adsorbent materials, target pollutants, maximum adsorption capacities, and operational parameters.

Adsorbent	Contaminant	Adsorption Capacity (mg/g)	Contact Time (min)	Reference
Activated Carbon	Ibuprofen	45.2	120	Wong et al., 2018
GO/Fe_3O_4 Nanocomposite	Methyl Orange	56.5	90	Wu et al., 2021
Chitosan Composite	Naproxen	39.8	150	Verma et al., 2023
PANI/ZnO	Diclofenac	42.1	100	Shaterian et al., 2020
MOF-5	Paracetamol	33.7	120	Samal et al., 2022
Biochar	Tetracycline	47.6	110	Rajput et al., 2024
GO/Alginate	Levofloxacin	50.3	130	Tunioli et al., 2023

2.2.2 Membrane technique

Membrane technology involves a physical process that filters contaminants through a membrane based on their size and properties (Othman et al., 2022). Hydrostatic pressure surrounding the membrane is the primary driving force for this filtration. Although membrane-based separation is a commonly used method for removing contaminants, there is a growing trend in this field to combine frequent upgrades, inclusions, and exclusions to ensure more efficient contaminant removal (Cevallos-Mendoza et al., 2022).

Various membrane filtration technologies exist, each characterized by a unique range of pore sizes (Tu et al., 2021). Microfiltration (MF) has a pore size ranging from

0.001 to 0.1 µm, ultrafiltration (UF) has a pore size less than 0.001 µm, nanofiltration (NF) has a pore size ranging from 1 to 10 nm, and so on (Gul et al., 2021). NF membranes extract ECs from polluted water through molecular solubility and diffusion, steric hindrance, hydrophilic-hydrophobic forces, and electrostatic repulsions. The use of a semipermeable membrane also aids in the removal of particles smaller than 1 nm in reverse osmosis (RO) (Chogani et al., 2020). Liu et al., (2023) applied membrane technology to the remediation of newly discovered TrOCs. Hydrostatic pressure is crucial for several membrane functions, including water transport and the retention of particles with large molecular weights. Although UF and MF membranes were utilized in several trials to remove ECs, the removal efficiencies were inadequate. (C. N. Rani & Karthikeyan, 2022) found NF treatment of ECs with 60% elimination efficiency for diclofenac and naproxen. Despite the advancements in membrane technologies, challenges such as membrane fouling, high operational costs, and limited efficiency for low-molecular-weight ECs persist. The integrating membrane systems with complementary techniques like adsorption or advanced oxidation could offer more robust and effective solutions. Moreover, further material innovation is needed to enhance selectivity and permeability without compromising durability. The membrane technique for the wastewater treatment has been illustrated in Figure 2.2.

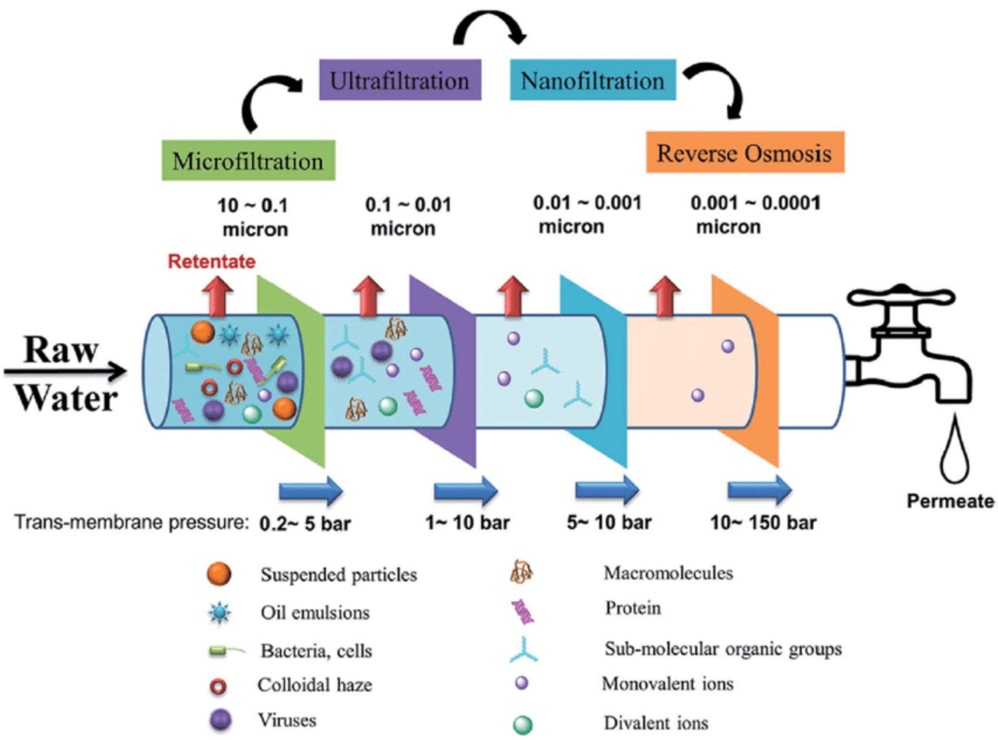

Figure 2.2 Pressure-driven membrane filtration technologies applied in water treatment, highlighting pore size distributions and typical contaminants retained by microfiltration, ultrafiltration, nanofiltration, and reverse osmosis membranes. Reproduced with permission from Selatile et al. (2018).

2.2.3 Advanced Oxidation Processes

The Advanced Oxidation Process (AOP) is a promising method for the treatment of wastewater containing tenacious organic pollutants (Mukherjee et al., 2023). This is attributed to the capacity of this mechanism to employ reactive radicals of hydroxyl species. The reactive radical source differs in each kind of advanced oxidation method (Wang & Wang, 2020). The conventional oxidation procedure may not always effectively decompose the organic chemicals found in wastewater. As a result, the enhanced oxidation method has been developed, simultaneously utilizing highly reactive hydroxyl molecules as free radicals in oxidation processes (Kumari & Kumar, 2023). Advanced oxidation techniques such as photo-Fenton, photocatalysis, and solar-driven processes are employed in wastewater treatment. A comparative overview of these AOPs, including their principles, target contaminants, operational conditions, and limitations, is presented in TABLE 2.5 to highlight their applicability and performance in wastewater remediation.

Table 2.5 Overview of key AOP techniques used for emerging contaminant removal, including mechanisms, catalyst types, benefits, and limitations.

AOP Technique	Mechanism	Catalysts/Materials Used	Advantages	Limitations	References
Photocatalysis	Catalyst activation by UV/sunlight to generate hydroxyl radicals (•OH) that oxidize pollutants.	TiO_2, ZnO, g-C_3N_4, Ag/TiO_2, $BiVO_4$	Highly effective, sunlight-activated, reusable catalysts, low operating cost.	Limited visible light response, catalyst separation/recovery issues.	Garrido-Cardenas et al. (2020), Priyadarshini et al. (2022)
Photo-Fenton	Fenton's reagent (Fe^{2+}/H_2O_2) under UV irradiation accelerates •OH production.	Fe^{2+}, Fe_3O_4, H_2O_2, UV light	Strong oxidizing ability, effective for antibiotics and dyes, operates at ambient conditions.	Sludge generation, narrow pH range (2.5–4), high H_2O_2 cost.	Phoon et al. (2020), O'Dowd & Pillai (2020)
Hybrid AOPs	Combines AOPs with biological, membrane, or adsorption processes for enhanced degradation.	TiO_2 + membrane, Fe_2O_3 + biological sludge	Enhanced treatment efficiency, energy saving, good for complex wastewater.	Complex design, higher maintenance, integration cost.	Rekhate & Srivastava (2020), Pimenov et al. (2022)

2.2.4 Chemical treatment technologies

Chemical wastewater treatment systems have the potential to efficiently eliminate several classes of ECs based on factors such as the specific compounds being targeted, the type of wastewater being treated, and the operating circumstances (Saidulu et al., 2021). For instance, polar medicines and beta blockers have shown varying efficiency in biological processes (Rezaei et al., 2022). Hence, it is imperative to investigate chemical treatment methods as viable alternatives to discover appropriate polishing processes to eliminate ECs further (Viancelli et al., 2020). These technologies can be roughly categorized as oxidation procedures in which extremely reactive chemical species are used in an aqueous phase.

Oxidation reactions have mainly been employed as a supplementary measure rather than a complete replacement for conventional methods, such as the remediation of ECs (Rajput et al., 2024). Chemical oxidation of ECs from wastewater requires chemical agents, including ozone, chlorine, hydrogen peroxide, and combinations of these oxidants, including transition metals and metal oxides-based catalysts in the so-called Advanced Oxidation Processes (AOPs) (Singh & Mishra, 2021). Furthermore, many energy sources, including solar energy, UV–vis radiation, electric current, gamma radiation, and ultrasound, are also employed. In AOPs, the oxidation reactions of environmentally hazardous substances (ECs) rely on generating highly reactive free radicals, specifically hydroxyl radicals (Zhang et al., 2023). These hydroxyl radicals are crucial in transforming pollutants into less toxic molecules and are more easily broken down by biological processes. The primary objective of chemical oxidation is to completely transform contaminants into carbon dioxide, water, nitrogen, and other minerals through mineralization (Khan et al., 2023). The rate constants for most reactions involving hydroxyl radicals in a water-based solution typically range from

106 to 109 M^{-1} s^{-1}. The polarity and number of functional groups of pharmaceuticals can be altered through chemical oxidation processes, which impact their usefulness in organisms (Williams et al., 2002). The chemical treatment process for wastewater can be effectively visualized through a schematic process flow diagram illustrating sequential chemical treatment stages, as shown in FIGURE 2.3.

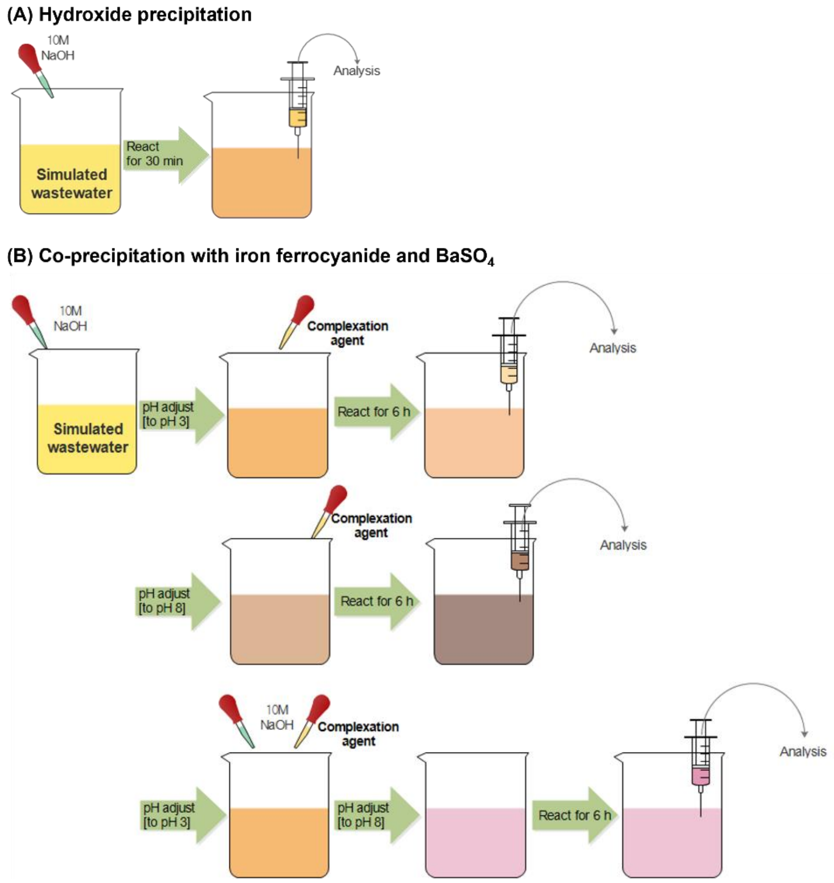

Figure 2.3 Schematic process flow diagram illustrating sequential chemical treatment, Maengkyo et al. (2023).

Chemical treatment, especially oxidation-based methods, holds considerable promise for removing recalcitrant emerging contaminants that are not effectively treated by biological processes. Its success largely depends on the chemical nature of the pollutants and the wastewater composition. Selecting suitable oxidants and operating conditions is essential to ensure efficient degradation and minimize the formation of harmful by-products.

2.2.5 Biological treatments

Biological treatment eradicates ECs through the utilization of various biological organisms or techniques. The objective of this treatment is to provide a systematic method for the efficient elimination of byproducts (Shahi Khalaf Ansar et al., 2023). Biological treatment is extensively utilized due to its superior cost-effectiveness compared to chemical or physical treatments. This therapy utilizes a typical cellular mechanism and relies on nematodes, bacteria, or other organisms to decompose organic waste (Sharma et al., 2023). Typically, these treatments occur during the later stages of the treatment process and focus on effectively eliminating pollutants through biodegradation. Due to the inhibitory effects of toxic pollutants, bacteria are often aided by the mechanism of co-metabolism to boost their proliferation and facilitate the breakdown of the ECs.

Physical therapy output items frequently undergo biological treatment as a meticulous form of treatment (Muter et al., 2017). This method offers several advantages, including low operational cost, environmental compatibility, and effective degradation of a wide range of biodegradable organic contaminants. It is particularly suitable for large-scale treatment systems and produces minimal secondary pollution. However, its efficiency can be limited by the presence of toxic or persistent compounds, and it often requires longer treatment durations and precise environmental control to sustain microbial activity. FIGURE 2.4 illustrates the configurations of two biological treatment technologies, Anaerobic Baffled Reactor (ABR) and Anaerobic Filter (AF) commonly applied for decentralized wastewater treatment, offering enhanced sedimentation, biogas recovery, and filtration efficiency

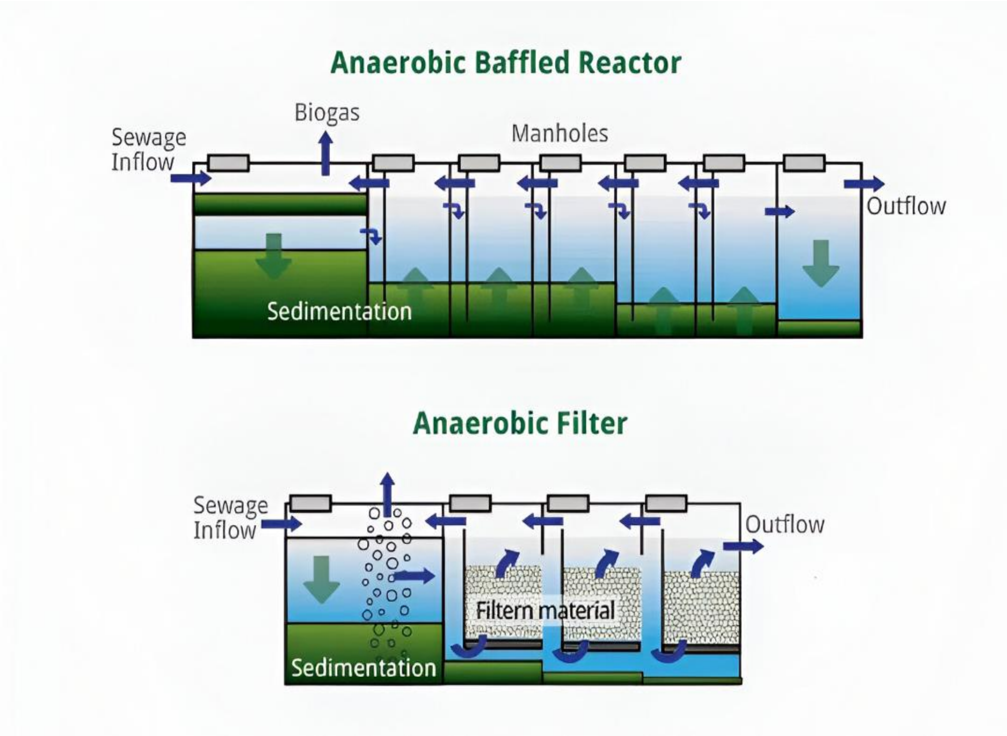

Figure 2.4 Biological technique for wastewater treatment. Adapted from Green.org (2024).

The biological treatment presents a practical and sustainable option for large-scale EC removal, particularly for biodegradable compounds. Its low cost and minimal environmental impact make it attractive, but its efficiency may be hindered by toxic or persistent pollutants and the need for controlled operational conditions to maintain active microbial populations.

2.3 Role of Natural Adsorbents in Emerging Contaminant Removal

Several studies have examined various adsorbents to remove ECs from wastewater. Extensive research has been conducted on removing ECs from various environmental sources, including wastewater sludge, sediments, soil, aroma materials, pesticides, and human medications (Rasheed et al., 2019). Industrial and PPCP pollutant removal immunochemical procedures are currently available. Activated carbon (Agrawal et al., 2017), biochar (Xiang et al., 2020), activated hydrochars (Azzaz et al., 2020), carbon nanotubes (Yadav & Srivastava, 2017), metal-organic