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Recent advances in wastewater treatment technologies: Innovations and new insights

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Abstract

Wastewater often contains toxic organic pollutants that can have adverse effects on human health and aquatic life upon exposure. Rapid urbanization and technological advancements have led to the growth of various industries, such as agriculture, petrochemicals, pharmaceuticals, and biotechnology, all of which consume substantial amounts of water and generate complex wastewater compositions during the manufacturing process. As a result, large volumes of these wastewaters are difficult to treat due to the wide variation in composition, including dyes, pharmaceutical waste, organic matter, residual contaminants, and hazardous or inhibitory substances. Conventional wastewater treatment methods have been increasingly challenged and are often failing to meet the required criteria. Consequently, there is a pressing need for innovative, cost-effective, and environmentally sustainable solutions, which has accelerated the development of advanced wastewater treatment technologies. This review article first outlines the role of technology in wastewater treatment. Then, it provides an overview of the recent advances in removing various pollutants such as organic compounds, heavy metals, pharmaceutical, and pesticides from wastewater and strategies that enhance efficacy, affordability, and sustainability. Finally, the use of artificial intelligence (AI) and machine learning for process monitoring and optimization is explored. Ultimately, this review aims to provide a comprehensive overview of the current state of wastewater treatment technologies and their potential to contribute to a more sustainable future by integrating new insights from recent research.

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Keywords

Wastewater treatment
Artificial intelligence (AI) and machine learning
Advanced oxidation processes
Pollutants removal and chemical treatment

1. Introduction

Water is a vital resource for industrial processes as well as human survival, but it is seriously threatened by pollutants from both human activity and natural events [1,2]. Water pollution has been made worse by the growing world population, industrialization, rapid urbanization, and the far-reaching effects of climate change [3,4]. This has caused ecological harm, particularly from fertilizers released into water bodies. Water resources have been severely strained by these combined forces, leading to both qualitative and quantitative limits [5]. Although the lack of clean water is a major issue in developing countries, pollution from cities and industrial operations causes ongoing shortages of drinkable water supplies in even highly developed industrialized nations [6]. Through the release of extremely hazardous and non-biodegradable effluents, the high-water needs of different industrial sectors contribute to ecosystem challenges and environmental deterioration [7]. One of the most important challenges of the twenty-first century is addressing the effects of worldwide water scarcity [8,9]. Substances including pesticides, pharmaceutical waste [10], Organic and inorganic contaminants, antibiotics, heavy metal leaching into water bodies, herbicides, Spilled oil, eutrophication of water bodies, analgesics and dyes, are important sources of water pollution [11]. These pollutants may build up and seriously damage the environment [12]. For example, they may eutrophicate waterbodies, which may eventually have an impact on aquatic ecosystems. A significant level of oxygen demand and extreme toxicity can result from contaminants invading water bodies, which can damage aquatic life systems and the quality of the water [13]. To lessen the persistent harm that these toxins cause to both the environment and people, remediation is necessary. Therefore, cutting-edge, affordable, environmentally responsible, and highly effective wastewater treatment techniques are essential [14]. Many treatments, including membrane process, physio-chemical, flocculation, biological, absorption/adsorption, coagulation, sedimentation, physical and chemical treatment, filtration and oxidation processes, were created and put to the test in experiments to address these problems [15,16]. However, their primary disadvantages are excessive energy consumption, ineffective treatment, a tendency to foul, and treatment techniques that are limited to eliminating a specific pollutant [17]. Moreover, organic contaminants and heavy metals cannot be effectively removed from wastewater by current treatment methods [18,19]. The procedures are labor-intensive, inefficient, sluggish, and costly due to the need for large systems, infrastructure, and engineering expertise, in addition to their chemical and operational demands [20]. Due to its exciting and promising mechanism, which allows for the complete degradation of various contaminants into simpler chemicals, most researchers are currently interested in the advanced method of photocatalytic degradation [21,22]. Photocatalysis, a process that uses light to accelerate a photoreaction via a photocatalyst, offers an innovative approach to degrade contaminants in wastewater [23,24]. Moreover, Metal-Organic Frameworks (MOFs) are highly efficient adsorbents offering excellent selectivity and adsorption capacity for removing heavy metals from water. MOF-based adsorption has been proven cost-effective and efficient in removing a wide range of water pollutants such as heavy metals, organic dyes, and persistent organic compounds due to its favorable physical and chemical properties [25].

The latest developments in new wastewater treatment technology are examined in this overview. Presenting a thorough overview of the most recent developments in wastewater treatment with a focus on the potential of innovative strategies to meet sustainable water management goals is the aim. Furthermore, a promising area that has the ability to completely transform how we handle and lessen environmental issues is the nexus of wastewater treatment, machine learning, and artificial intelligence (AI). Therefore, the research emphasized that by improving the efficacy, precision, and automation of wastewater treatment operations, the incorporation of AI technology offers a new paradigm for tackling these issues. This assessment attempts to inform policymakers, researchers, and industry professionals about the most promising approaches to tackling the intricacies of wastewater treatment by utilizing the latest technological advancements.

2. Removal technology of contaminated water

The majority of the wastewater produced by the oil and gas field production and exploration process is known as produced water (PW), and it comprises a variety of hydrocarbons in free, dispersion, and dissolved forms [26]. PW contains a complex mixture of inorganic and organic substances, including waxes, radionuclides, dissolved oxygen, formation solids, dissolved and dispersed oil, heavy metals, treatment chemicals, dissolved gases, salts, and microorganisms. Gas and oil fields produce 250 million barrels of water a day, of which more than 40 % is released into the environment worldwide [27]. This release of PW poses a serious risk to surface, soil, and subsurface water contamination due to inadequate treatment. As a result, a variety of technologies which fall into the categories of biological, chemical, and physical methods are used to purify PW. Technologies like coagulation, membrane separation, chemical oxidation, microbial degradation, filtering, and electrochemical oxidation could be effective in removing pollution from the environment. These methods do, however, have certain drawbacks, including high expense, the production of secondary pollutants, and inefficient removal [28]. Adsorption has been presented as an environmentally friendly, economical, and cost-effective method for the purification and reclamation of produced water. It is thought to be one of the most important traditional techniques for this purpose, and it includes the removal of biological, organic, and inorganic pollutants [29]. It can take the place of other established techniques for treating wastewater pollution. Its versatility allows it to be applied in a multitude of ways. Its removal efficiency exceeds 99 %, and it is simple to separate the desired compounds from a diluted solution. It is also resistant to harmful substances and can be readily recovered from the adsorbed materials using a variety of techniques, including desorbing agents, leaching with the use of chemical reagents, biological processes, and thermal treatment [30]. Many adsorbents, including zeolites, activated carbons, activated alumina, and inexpensive materials like peat, limestone, and rice husk ash, can be employed in the adsorption process. Among adsorbents, activated carbon is said to be the most used. Amorphous, microcrystalline, and non-graphical solid, AC has a high surface-to-volume ratio, high mechanical stability, high light stability, high thermal stability, porous and solid structure, and high purity. Furthermore, AC can be used as an adsorbent to remove ions and organic contaminants from wastewater due to its high capacity for adsorption of various species [31]. Innovative wastewater treatment techniques include a variety of techniques such as electrocoagulation, hybrid approaches, nanotechnology, membrane technology, and the production of ozone via water electrolysis or corona discharge. These technologies' main objective is to remove harmful pollutants and toxins from wastewater, including bacteria, viruses, heavy metals, hormones, medications, synthetic colors, and flame retardants. Chemical, Physical, and biological techniques include coagulation–flocculation, electrochemical oxidation, membrane filtration, solvent extraction, ion exchange, precipitation, adsorption [32], catalytic oxidation, and photodegradation are used in this process, as illustrated in Fig. 1. The incorporation of nanoparticles into these techniques has effectively removed a number of pollutants. Nevertheless, the high energy consumption of these technologies can result in high expenses.

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Fig. 1. Cutting-edge wastewater treatment technologies.

3. Removal of organic compounds

Aquatic environments contain a wide variety of organic contaminants. These pollutants can be divided into groups such as hydrocarbons, plasticizers, organohalides, surfactants, dyes, and phenolic compounds [33]. These organic contaminants are difficult for water to break down, poisonous, potentially carcinogenic, and chemically stable. An early commitment was made by Frank and Bard to the photodecomposition of cyanide in water on TiO_2 [34]. After that, Carey reported that TiO_2 under UV light could catalyze the degradation of polychlorinated biphenyls, which laid the groundwork for future photocatalysis research [35]. The oxidative decomposition function of semiconductor photocatalytic materials for organic pollutants was formally proposed by Ollis et al. shortly after they discovered that halogenated organic compounds, such as trichloroethylene and trichloromethane, would induce photocatalytic oxidative decomposition in a TiO_2-sensitized system [36]. This discovery propelled the field of organic pollution research into one of the busiest. A variety of semiconductors, including TiO_2, ZnO, Fe_2O_3, C_3N_4, and bismuth-based semiconductors, have generally proven to be effective in breaking down a broad spectrum of organic pollutants into easily biodegradable or less toxic compounds, which are then further mineralized into innocuous CO_2 and H_2O [37].

3.1. Petroleum hydrocarbons

Oil is a highly valued resource used in the manufacturing of numerous chemicals and energy [38]. On the other hand, carelessness in the extraction, transportation, processing, storage, and consumption phases can result in severe and often irreversible environmental contamination [39]. A complex mixture of hundreds of different molecules, mostly hydrocarbons, make up crude oil. It is discovered that crude oil contains negligible amounts of many elements, including nitrogen (0 %–0.5 %), sulfur (0 %–6 %), oxygen (0 %–3.5 %), and some metals [40]. Compounds with solely carbon and hydrogen in their structure are known as aromatic hydrocarbons, or aromatics, and they are all harmful to the central nervous system [41]. Furthermore, oil pollutants are seen as a major hazard to both human health and the environment because of their toxicity, mutagenicity, and carcinogenicity [42]. Among the naturally occurring compounds of crude oil and gasoline are petroleum hydrocarbons, such as benzene, toluene, ethylbenzene, and xylene [43]. These compounds are frequently found in surface and subterranean water due to industrial activities, particularly the handling of petrochemicals, reservoir leaks, or improper waste disposal procedures [44]. The activities and regular efficiency of the refinery may be impacted by the high concentrations of oil compounds and active sludge, which cannot be efficiently removed by methods based on standard wastewater treatment processes [45]. The processes used for removal should not produce hazardous secondary pollutants in addition to wastewater at the maximum amount permitted for release into the environment. For additional purification, the sewage filtration by coagulation and dissolved air flotation (DAF) flocculation output can be moved to a biological reactor. While advanced coagulation techniques like flocculation and electrocoagulation are more sophisticated than traditional physical and chemical techniques, their main drawback is the massive amounts of hazardous sludge that are frequently resisted and cannot be recovered. Large amounts of petroleum compounds can be isolated using physical separation techniques, and in certain situations, these compounds can be recycled using a variety of techniques [46]. The main drawback of these techniques is their high energy consumption as well as the frequent obstructions and clogging of various instruments and equipment. The goal of water reuse can be further achieved by third-party refinement by employing techniques like enhanced oxidation, reverse osmosis, and nano-filtration. Adsorption is a life-saving technique that works with minerals and high-quality materials that can be combined with inexpensive materials and adsorbents. In addition to reducing the amount of sludge produced, the process cost can be decreased by combining the adsorption process with one of the more sophisticated techniques. Multiple reports from different groundwater sources have led to the identification of multi-ring aromatic hydrocarbons. Notable is the relationship with industry (Fig. 2).

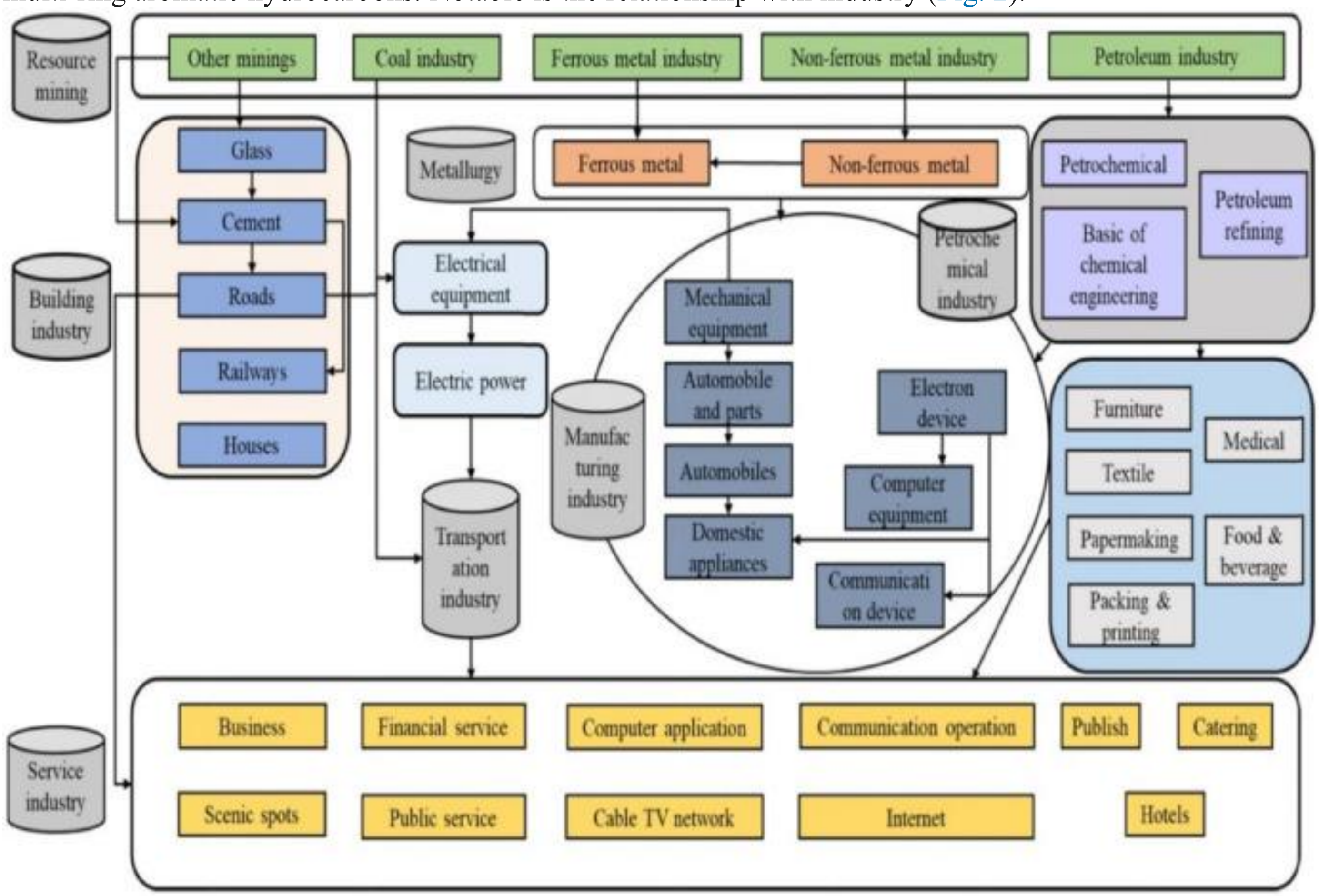

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Fig. 2. The relationships of the petrochemical industry and other industries. Redistributed under the International Creative Commons Attribution 4.0 License, CC-BY Ref. [47]. Copyright 2020, MDPI.

In environmental management, removing petroleum hydrocarbons from water is crucial, especially in areas impacted by oil spills, industrial discharges, or runoff from petroleum-related activities [48]. The amount of water that needs to be treated, the kind and concentration of hydrocarbons present, financial considerations, and regulatory requirements all have a part in the technology that is chosen to remove petroleum hydrocarbons from water. In order to attain the best outcomes, a variety of techniques are frequently used. In order to guarantee that the water fulfills safety and environmental criteria following treatment, it is imperative to conduct ongoing monitoring and evaluation of treatment efficiency. It is possible to efficiently remove these contaminants from water by using a variety of treatment techniques [49]. Below is a summary of some typical methods.

3.1.1. Physical methods

Adsorption: Water containing petroleum hydrocarbons can be extracted using adsorbents such as activated carbon. Hydrocarbon molecules are drawn to the adsorbent's surface during the process. Fluids are recovered by use of sorbents, materials, or mixes of insoluble materials during adsorption, physical attachment, or both. Adsorbents need to be waterproof and capable of absorbing oil molecules [50]. Adsorbents are frequently employed to remove the final oil trap, even though they can be the only cleaning solution for minor leaks. Adsorbents also have the advantage of slowing down the layer's playback speed and aiding in its cleaning. The three main categories of debris are mixed organic, natural, and organic. Carbon monoxide, nitrogen, sawdust, dry grass, maize wood, feathers, and other mostly carbon-readable materials are examples of natural organic adsorbents. Although organic adsorbents have the ability to absorb up to 15 times the weight of their oil, there are several drawbacks to using them. Certain organic adsorbents have a tendency to absorb water almost as much as they do oil. The absorbent drowns as a result of this. Particles like sawdust, which is challenging to gather after being distributed across the water's surface, are lost by many organic adsorbents [51]. Oil can be absorbed by natural mineral adsorbents up to 20 times their weight. Similar to organic adsorbents, mineral absorbers are widely available in large quantities at a reasonable cost. The water's surface does not employ these kinds of adsorbents. Human-made materials that mimic plastics, including polyurethane, polyethylene, and polypropylene, are examples of combined absorbents. These materials are intended to absorb liquids on their surface and are often used in sponge form. Additional compound absorbents include rubber and shrink-bonded polymers, which absorb liquids on their solid structures and cause absorbent materials to inflate. Up to 70 times their weight in oil can be absorbed by most composite adsorbents [52]. When choosing adsorbents to clean up leaks, one should take into account the characteristics of both the absorbent and the types of oil. Light petroleum products enable faster oil absorption. Additionally, thicker-layered oils adhere to surfaces more successfully. When retrieving sealing materials, lighter oil with less viscosity is easier to handle than heavier oil with more viscosity, which leads to secondary contamination. Even though adsorption techniques for wastewater treatment have advanced remarkably, there are still certain obstacles and restrictions that must be overcome. Adsorption capacity, selectivity and non-specific binding, material degradation and stability, adsorbent recovery and reusability, economic viability, and regulatory and environmental issues are the six categories into which these limits can be divided. The ensuing subsections go into greater information about each of these categories. The efficacy and efficiency of adsorption methods for treating wastewater are determined by their adsorption capacity. The amount of adsorbate that a specific mass of adsorbent can absorb under particular circumstances is known as its adsorption capacity. The characteristics of the adsorbent (such as surface area, porosity, and functional groups), the adsorbate (such as polarity, concentration and molecular size), and the adsorption conditions (such as contact time, pH, and temperature) all affect the adsorption capacity (Fig. 3).

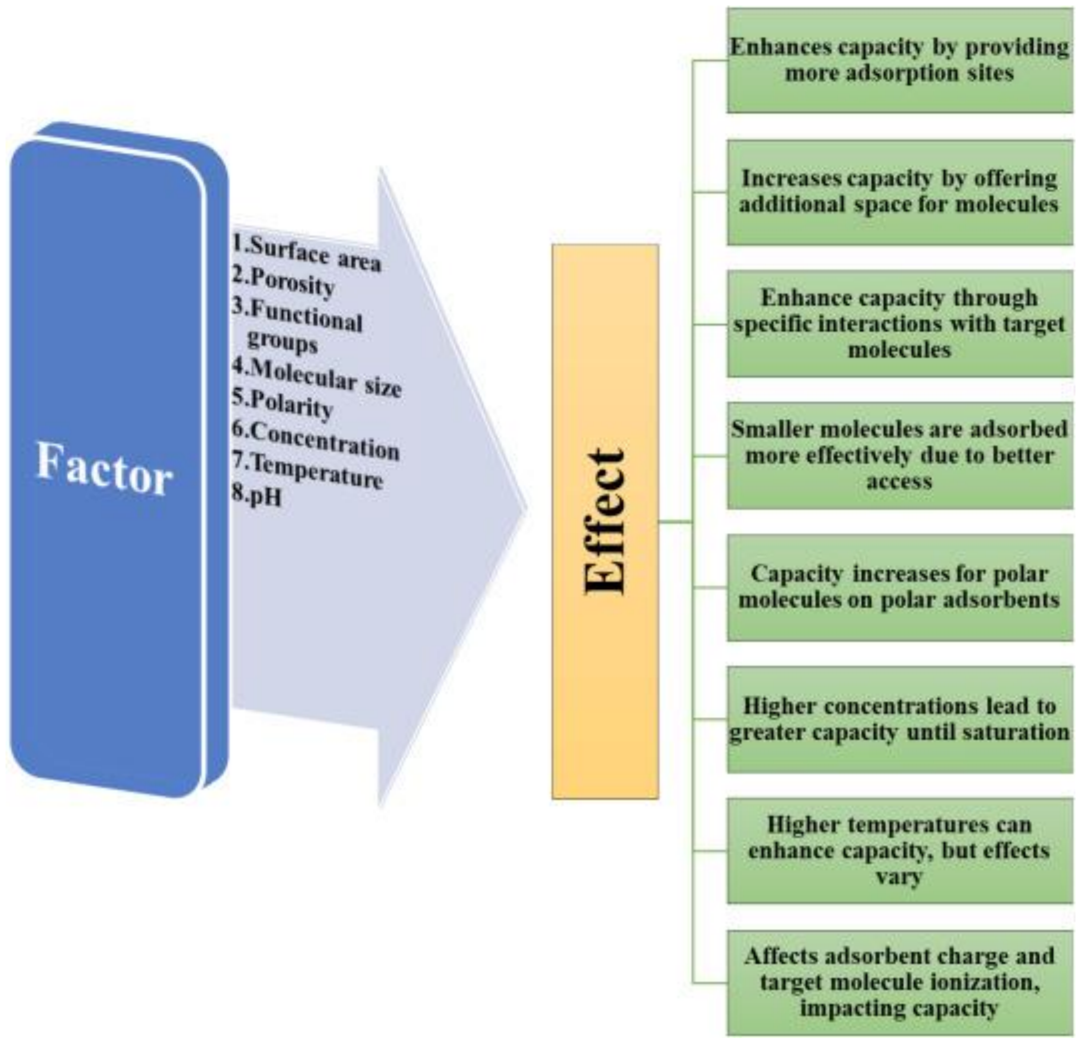

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Fig. 3. Adsorption capacity-influencing factors and their consequences.

Modified natural clay (MC), according to Dawood et al., is a promising, environmentally benign, and scalable adsorbent for enhanced water filtration. The study offers a novel and sustainable method of purifying water by removing nitrate ions and dangerous organic pollutants using thermally stable natural clay. The process combines thermal regeneration and adsorption to guarantee excellent removal efficiency and reusability. Pharmaceutical substances (phenazopyridine and tetracycline), industrial colors (methyl orange and methylene blue), and nitrate ions are among the pollutants under investigation. These substances were chosen based on their toxicity, persistence, and resistance to standard treatment techniques. High removal efficiency were found in batch adsorption studies carried out under ideal conditions (pH ≈ 4, 25 °C, and pollutant concentrations between 10 and 40 mg/L). These efficiencies ranged from 84 %

to 93 % for organic pollutants and 89 % for nitrate. MC was characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) to ascertain its compositional and structural characteristics, which could account for its adsorbent capabilities (Fig. 4). The crystalline structure of these minerals was validated by the XRD examination, which gave a clear picture of the MC's mineralogical makeup. Additionally, the MCs were enlarged in the SEM pictures, which offered crucial details about their size, shape, composition, and crystallography.

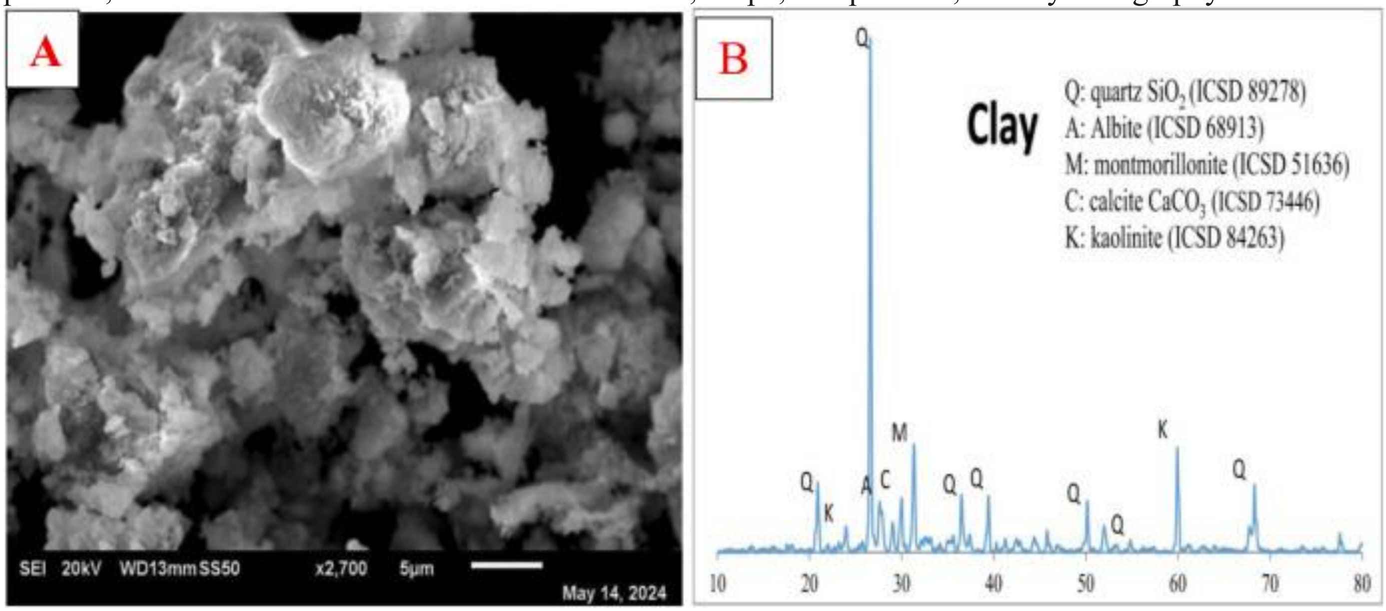

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Fig. 4. a) X-ray patterns of diffraction for natural calcined clay. b) SEM images of the MCs.

Future studies should concentrate on improving the conditions for thermolysis, evaluating the technique on actual wastewater, and extending its use to a wider variety of newly discovered pollutants. This method offers a realistic and long-term means to reach clean water targets more broadly.

Moreover, Kan et al. demonstrated that releasing adsorbed micro-organic pollutants is more detrimental than coming into direct contact with goldfish, and that carboxylated multi-walled carbon nanotubes can cause damage to the liver and gills of goldfish. According to recent research, carbon nanotubes can stop the growth of rat cardiomyocytes and are more hazardous to animals than asbestos and quartz. Further impeding the broad application of carbon nanotubes are their tendency to aggregate in water, which makes recycling challenging, and their rising production costs. Because of its huge specific surface area and abundance of pore channels, graphene makes it easier to remove impurities quickly. According to Xu et al., graphene removed bisphenol A (BPA, $C_{15}H_{16}O_2$) far more efficiently than other carbon compounds. According to Chen et al., graphene treated with amino acids exhibited the greatest ability to adsorb sulfamethoxazole. Graphene, however, has been shown in experiments to have strong biomagnification effects. It damages biological metabolism and accumulates in organisms through the food chain [54]. High concentrations of graphene were discovered in the intestines of freshwater snails and zebrafish by Lu et al. and Su et al. The blood and cells were exposed to the deposited graphene, which disrupted biological metabolism. Existing studies have demonstrated that graphene poses a possible harm to humans, despite the paucity of information regarding graphene's impacts on humans (Fig. 5).

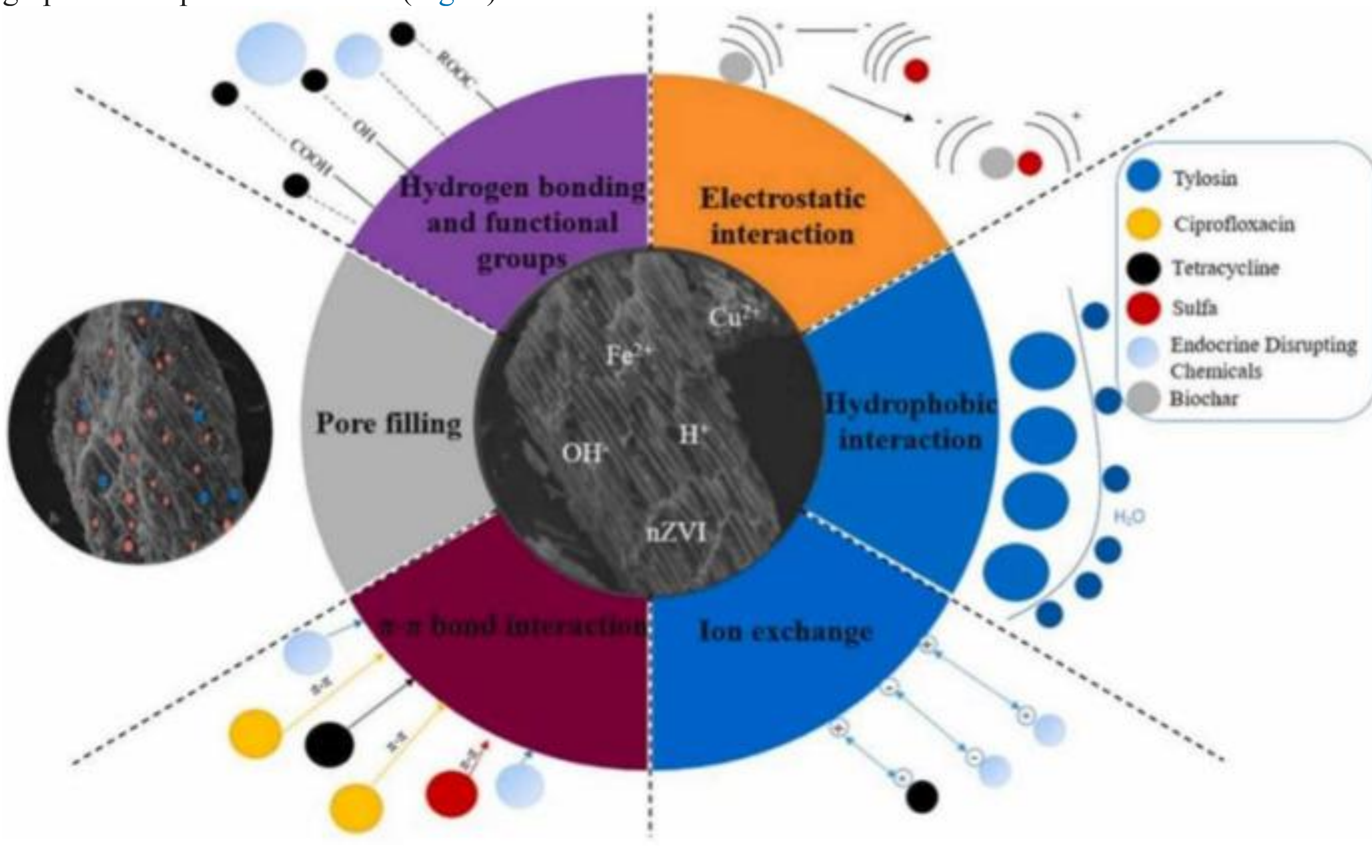

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Fig. 5. Mechanism of micro-organic contaminants adsorption through bioactive carbon. Reprinted with permission from Ref. [55]. Copyright [2023], Elsevier.

3.1.2. Chemical methods

Advanced oxidation processes (AOPs): Petroleum hydrocarbons are broken down into less hazardous chemicals by strong oxidants like hydrogen peroxide or ozone, which are used in advanced oxidation processes (AOPs) [56]. This technique works well for handling complicated hydrocarbon mixtures. Moreover, AOPs produce hydroxyl radicals (OH•), which are effective at oxidizing stubborn pollutants. OH• has a high standard oxidation potential of up to 2.80 V and a high pace of reaction when compared to typical oxidants such as potassium permanganate, oxygen, chlorine, ozone, or H_2O_2 [57]. Therefore, when OH• reacts with both inorganic and organic solutes, large rate constants can be reached. Generally speaking, AOPs use the abilities of various oxidants to break down dangerous pollutants by transforming them from their reduced forms to their ultimate safe oxidized forms. In order to mitigate the negative effects on the environment caused by the principal pollutants being disposed of in the aquatic ecosystem, this process mineralizes and breaks down the contaminants into innocuous materials [58]. Despite the fact that these systems employ various oxidants, they all often produce radicals in the same way. These procedures have a great potential to remove contaminants from water that are difficult for biological approaches to eliminate. Strong OH•/oxidants form and, in the best-case scenario, these radicals interact with the targeted pollutants to convert them to carbon and water are the two primary phases of AOPs. H_2O_2 is created when two OH• contact, as the equation below illustrates:(1)$OH\cdot + OH\cdot \rightarrow H_2O_2$

The two main advantages of AOPs over other alternatives are (i) their strong disinfectant characteristics, which make them useful in many situations, and (ii) their ability to destroy organic pollutants on their own. For example, successful treatment might require extra steps such catalytic oxidation if methyl tert-butyl ether was removed through stripping [59]. Nevertheless, AOPs eliminate organic contaminants directly, negating the requirement for additional chemical treatments. AOPs are impacted, nevertheless, by the production of unwanted oxidation byproducts. Slow reaction rates of these oxidation byproducts would cause a delay in mineralization and unintended buildup. Additionally, some AOPs result in the formation of inorganic compounds, such as when ozonation converts bromide to bromate. These inorganic substances obstruct the oxidation reactions and interfere with AOPs. These substances scavenge the OH•, which are intended to eliminate and destroy the relevant pollutants. Consequently, the problem of radical scavengers and the possibility of generating undesirable intermediate derivatives from the oxidized forms of contaminants must be addressed. pH affects the concentration of the radical and the acid-base equilibrium involving the production of OH•. AOP systems that are effective should be designed and built with two important factors in mind. First, the chemical dosage, which will raise costs and could lead to the development of byproducts [60]. Second, it's important to take into account reactor configuration and contact duration, which are frequently decided upon while doing a pilot research as opposed to a lab-scale experiment. The effectiveness of the pollutants in question degrading is also influenced by the quality of industrial wastewater and other operational factors. It is well known that the majority of organic materials will react with the added radicals very away. The degree of turbidity in industrial wastewater affects the water's ability to absorb UV light, which in turn affects system effectiveness [61].

3.1.3. Biological methods

Bioremediation: This organic process makes use of microorganisms (fungi and bacteria) that may break down petroleum hydrocarbons into less toxic compounds. By introducing particular microbial strains or nutrients to encourage microbial growth, bioaugmentation or biostimulation can improve bioremediation [62]. Numerous studies have demonstrated that in both aquatic and terrestrial ecosystems, microorganisms (bacteria, yeasts, and fungi) play a major role in the breakdown of polluting compounds, including hydrocarbons. Hydrocarbons should be able to be accepted as primary substrates by selective microorganisms [63]. These microbes must be able to manufacture enzymes that can speed up the hydrocarbon digestion process and ensure that any toxic byproducts they make don't harm the environment. However, no microbe can entirely distribute crude oil on its own. During the process of distilling crude oil, a number of forward chain reactions occur in which particular microbes target petroleum molecules first. The intermediate chemicals produced by this method will require the usage of a different class of microbes. Carbon from pollution can be used as a source of energy by local native microorganisms, or LMOs, in the ground and subsurface waters of oil locations. These microorganisms have adapted to these conditions over time. The contaminants are transformed into end products (carbon dioxide and water) by these microorganisms. Like other remediation procedures, bioremediation is believed to be a viable strategy for overcoming all the challenges involved in successfully remediating petroleum hydrocarbons. But it also has significant drawbacks, like the incapacity to entirely clean up and eliminate PWHCs from polluted soils. Some hydrocarbons in petroleum waste hydrocarbon (PWHC) polluted soils can disintegrate entirely, whereas others defy the natural process of degradation and are non-biodegradable due to the persistent nature of some of the chemicals present. Similarly, this approach might not work well for saturated subsurface cleanup (in anoxic circumstances). Furthermore, PWHC contamination of groundwater cannot be prevented by this strategy [64].

3.1.4. Electrochemical methods

Electrocoagulation is an electrochemical method that has been shown to be successful in wastewater treatment and purification. Despite the process's great efficiency and environmental friendliness, significant capital and operational expenses have made its industrial applicability less than hopeful [65]. The principal disadvantages of electrical and chemical coagulation include the generation of vast amounts of toxic sludge that is unrecoverable and frequently repelled. Petroleum sludge's elemental makeup includes Fe, P, Pb, Cu, Zn, Ca, Mg, Cd, K, Cr, and N. Petroleum sludge is a complicated combination that contains varying amounts of waste oil, wastewater, sand, and mineral particles. Petroleum businesses produce significant amounts of sludge, which is a major source of environmental contamination. Oily sludges are classified as hazardous waste under the Environment Protection Act and Hazardous Wastes Handling Rules. Even if de-oiled, these sludges cannot be disposed of in landfills unless they are completely remediated. Sludges produced by the petroleum industry accumulate in crude oil tanks, refinery product tanks, desalters, and other locations during oil production and processing. Sludges with recoverable oil less than 40 % are classified as low oil content sludge [66]. These sludges must be treated and rendered harmless before disposal. The efficacy of the electrocoagulation process (ECP) is often assessed for the treatment of petroleum-contaminated groundwater and expressed as the total petroleum hydrocarbon (TPH) extracted by electrode materials (mostly aluminum, iron, and steel). The highest TPH elimination was accomplished by adopting steel-iron as the anode-cathode electrode configuration. In most cases, batch and continuous trials demonstrated that the ECP could effectively remove TPH from water, making it a potential technology for treating petroleum-contaminated groundwater [67]. An example of the above is a published study that used an electrocoagulation technique to remove turbidity from petrochemical wastewater. The batch experiments were carried out with different values of current density, NaCl concentration, and electrolysis time, and the maximum turbidity removal effectiveness was 97.43 %. In addition, another study looked into the treatment of gas refinery oily wastewater with electrocoagulation using aluminum electrodes, and gas chromatographic analysis of raw and treated wastewater revealed that most normal hydrocarbons (nearly 99 %) were removed during the process [68]. Verma et al. studied coagulation-flocculation as a pretreatment method for pure terephthalic acid (PTA) wastewater. The influence of various inorganic and organic coagulants on wastewater treatment was investigated using wastewater collected from an effluent treatment plant's flow equalization tank. The settling and filtering properties of the sludge were also investigated [69]. The jar tests demonstrated that the wastewater was best treated when 3000 mg/L ferric chloride was added at pH 5.6. At optimal conditions, the wastewater's COD was decreased by 75.5 %. Gravity filtration of the treated wastewater revealed that adding cationic polyacrylamide (175 mg/L) to ferric chloride coagulation increased filtration properties while decreasing specific cake resistance. Another significant contribution was made by El-Ashtoukhy et al., who investigated the use of electrocoagulation to remove phenolic compounds from oil refinery waste effluent using an electrochemical reactor with a fixed bed anode made of randomly oriented Al raschig rings packed in a perforated plastic basket located above the horizontal cathode [70]. The study found that the optimal conditions for phenolic compound removal were current density = 8.59 mA/cm^2, pH = 7, NaCl concentration = 1 g L^{-1}, and temperature = 25 °C. After 2 h, 100 % of the phenol component was removed from genuine refinery wastewater at a concentration of 3 mg/L. In comparison to other cell designs utilized in prior experiments, the novel anode design of an electrocoagulation cell allowed for higher efficiencies while using less energy. Saeedi and Khalvati-Fahlyani's work also described the treatment of oily effluent from gas refineries using electrocoagulation with aluminum electrodes [71]. The efficacy of chemical oxygen demand (COD) removal was investigated by varying electrode distance, initial pH, sodium sulfate (Na_2SO_4) as a supportive electrolyte, polyaluminum chloride dose as a coagulant aid, and current density. The findings demonstrated that increasing the current density, polyaluminum chloride, and, to a lesser extent, Na_2SO_4 dosage improves COD removal efficiency. The findings also revealed that 97 % of COD can be eliminated under optimal operating circumstances. Using Na_2SO_4 as a supporting electrolyte reduces specific electrical energy consumption from 19.48 kWh (kg COD removal) $^{-1}$ to 11.057 kWh (kg COD removal) $^{-1}$. Gas chromatographic study of raw and processed wastewater found that the electrocoagulation technique eliminated over 99 % of typical hydrocarbons [72].

Recently**,** Membrane methods are increasingly being used to treat industrial and municipal wastewater due to their simplicity, versatility, and increased energy efficiency [73]. These procedures can be divided into four categories based on the pore size of the membrane used: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis. MF, UF, and NF membranes remove pollutants with sizes of 100–1000, 5–100, and 1–5 nm, respectively [74]. Several recent research have reported the treatment of industrial wastewater using membrane methods. For example, RO and NF effectively removed Cu^{2+} and Cd^{2+} from synthetic wastewater. RO removed 98 % and 99 % of Cu^{2+} and Cd^{2+}, respectively, while NF removed around 90 % of both. Another study indicated that RO removed 99.5 % of Cu^{2+} and Ni^{2+}. Galambos et al. investigated the chemical oxygen demand (COD) removal effectiveness of RO and NF in treating food sector wastewater. This study employed two samples of wastewater with baseline COD levels of 9500 and 1160 ppm. The RO permeate has a COD of less than 125 $mgO_2\ L^{-1}$, making it suitable for disposal into natural waters. The study did not look at the energy requirements involved with the treatment processes. Polymer-supported ultrafiltration (PSU) has been studied for the treatment of synthetic wastewater containing heavy metals [75]. Prior to filtering, Barakat and Schmidt added carboxyl methyl cellulose (CMC), a water-soluble polymer, to complex the cationic forms of heavy metals such as Cu^{2+}, Ni^{2+}, and Cr^{3+}. The study found that a high pH (≥7) promoted the formation of CMC-heavy metal complexes, precipitation, and size-exclusive removal of metal hydroxides. In many circumstances, changing the solution pH is found to be a significant step in heavy metal rejection since high pH can cause the precipitation of heavy metal hydroxides, which can subsequently be filtered out using UF membranes. Juang and Shiau examined the removal of Cu^{2+} and Zn^{2+} from synthetic wastewater with chitosan-enhanced membrane filtration. The inclusion of chitosan in the feed solution increased metal removal by 6–10 times, which is due to the amino group in chitosan acting as a site for metal binding. Other water-soluble metal-binding polymers used to remove heavy metals include diethylaminoethyl cellulose and polyethyleneimine (PEI). Minerals can also help to remove heavy metals from the membrane reactor. Adding 10 g L^{-1} vermiculite at pH = 8 removed more than 99 % of Pb^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. As a result, the combined sorption-UF process with appropriate pH adjustment (>7) can be used as a pre-treatment stage to remove heavy metals from industrial wastewater, such as metal plating. Adsorbents can improve heavy metal removal efficiency in membrane processes. Malamis et al. (2010) employed adsorbents such bentonite, vermiculite, and clinoptilolite to remove Cu^{2+} from activated sludge permeate at a concentration of 317 mg/L. Adsorption with 10 and 20 g L^{-1} bentonite or vermiculite (pH: 5.5) followed by ultrafiltration resulted in Cu^{2+} removal efficiencies ranging from 93.8 to 96.8 to 99.4 %. Ultrafiltration alone could only remove 59.4–78.3 % of Cu^{2+}, demonstrating the better effectiveness of adsorbent-enhanced UF systems. The use of zeolite and bentonite reduced fouling, however vermiculite did not have any antifouling effects. In a follow-up work, Katsou et al. studied the removal of Ni^{2+} using a combined adsorption and UF system [76]. At a pH of 6, a batch UF unit with an initial Ni^{2+} concentration of 320 mg/L achieved removal efficiencies of

65.3 and 80 % using 15 g L^{-1} of bentonite and vermiculite, respectively. Membrane methods have also been utilized to treat saline industrial effluent with significant organic content. For example, suspended solids (SS) and colloidal COD were reduced from seafood-processing wastewater through initial concentration using a UF system, followed by protein recycling for use in fish meal manufacturing. Turano et al. used MF and centrifugation to remove up to 80 % SS and 90 % COD from olive oil mill effluent. It is worth mentioning that, while RO is the most efficient at removing heavy metals from wastewater, it is not as extensively used as other membrane processes such as MF, UF, or NF due to its high energy requirements. Furthermore, the aerobic environment might encourage the production of metal oxides, which can prematurely foul RO membranes, needing regular membrane replacements [77].

3.2. Phenolic compounds

Phenols in wastewater come from a variety of industrial operations, including refineries, paint manufacturing, medicines, and petroleum production. They are highly soluble in water, extremely poisonous, and physiologically recalcitrant [78]. The bulk liquid is the primary reaction site in the photocatalytic process for breaking down phenol and its chlorophenol and nitrophenol derivatives, and the attack of hydroxyl radicals on the cyclic carbon produces a variety of oxidation intermediates. The primary intermediates generated during the photocatalytic degradation of phenol have been identified as hydroquinone, catechol, and p-benzoquinone [79]. The reaction's intermediates, including chlorohydroquinone, 4-chlorocatechol, and resorcinol, are eventually transformed into acetylene, maleic acid, carbon monoxide, and carbon dioxide [80]. Chlorophenols are moderately hazardous water contaminants that are thought to be carcinogens. The primary byproducts found during photocatalytic degradation include 4-nitrocatechol, benzoquinone, hydroquinone, and certain organic acids. Pharmaceuticals, coke operations, resin production, plastics, paint, pulp, paper, and wood goods. The release of these substances without treatment may pose substantial health concerns to humans, animals, and aquatic systems [81]. Phenol has been recognized as a priority pollutant by both the United States Environmental Protection Agency (EPA) and Canada's National Pollutant Release Inventory. To ensure a sustainable environment, international regulatory authorities have set strict phenol discharge limitations. For example, the EPA has established a water purity criterion of less than 1 ppb for phenol in surface water [82]. Toxicity limits are typically between 9 and 25 mg/L for both humans and aquatic life. Phenol has serious health consequences that can be both immediate and chronic. Long-term exposure can cause irregular breathing, muscle weakness, tremors, stupor, and respiratory arrest in humans at deadly dosages. Human skin, eyes, and mucous membranes get irritated when exposed to phenol. Chronic phenol exposure can cause anorexia, weight loss, diarrhea, vertigo, salivation, and dark urine coloration [83]. Animals with chronic phenol exposure have irritation in their gastrointestinal and central nervous systems, as well as their liver, kidney, and cardiovascular tissues. Animal studies have indicated that fetal body weight decreases, growth retardation occurs, and the offspring develop abnormally [84]. As a result, phenolic compound-contaminated wastewater must be treated before to discharge. This paper describes both standard and sophisticated approaches for extracting phenols from industrial effluent. Conventional methods for phenol removal include steam distillation, liquid-liquid extraction, adsorption, solid-phase extraction, wet air oxidation, catalytic wet air oxidation, and biodegradation. Advanced phenol removal technologies include electrochemical oxidation, photo-oxidation, ozonation, UV/H_2O_2, Fenton reaction, membrane processes, and enzymatic treatment [85].

3.2.1. Distillation

Distillation procedures for phenol removal from water are all variations of steam distillation, hence there is an energy need that must be satisfied cheaply. The methods can be destructive or non-destructive, with the latter allowing for the recovery of phenolics [86]. Steam or azeotropic distillation, which is based on phenol's relative volatility, can filter water containing phenol contaminants. In another study, an aqueous phenol solution was directly introduced into a novel steam plasma torch (steam plasma jet treatment), and the phenol was rapidly decomposed in the thermal plasma jet, resulting in the production of hydroxyl radicals and the oxidative degradation of organic pollutants in aqueous solutions. In the liquid phase, phenol produced pyrocatechol, hydroquinone, maleic acid, butanedioic acid, and muconic acid, with H_2, CO, and CO_2 as the main gaseous products. Steam thermal plasmas have high enthalpy and activity, while also being eco-friendly, making them attractive in the field of environmental cleanup [87].

3.2.2. Adsorption and extraction

Adsorption and extraction procedures for phenol removal from water are successful at concentrations ranging from trace to percent, depending on the cost (including energy) of utilizing and reusing the necessary secondary material, adsorbent, or extractant. Activated carbon is the most widely used and extremely effective adsorption technology [88]. It is expensive, but has been demonstrated to be successful at removing trace organic pollutants. As a result, new options are being developed, including chemical modification of activated carbon, impregnation with nanoparticles, different sources of carbon, different activation methods, and substitution with low-cost biosorbents, such as lignocellulose and chitin/chitosan, which are promising alternatives to remove phenolic compounds [89].

3.2.3. Phenol removal by membrane processes

Membrane technologies are dependable and cost-effective for treating phenol, with numerous benefits including low power consumption, high-quality effluent, a small footprint, and easy scaling up with membrane modules [90]. However, membrane fouling can occur as a result of particles and colloids in the feed streams. The most important membrane methods for removing phenols from wastewater include extractive membrane bioreactors and hollow fiber membranes; photocatalytic membrane reactors; high-pressure membrane processes like nanofiltration, reverse osmosis, and pervaporation; and membrane distillation [43].

3.2.4. Extractive Membrane Bioreactors (EMBR) and hollow fiber membranes

An EMBR combines an aqueous-aqueous extractive membrane technique with biodegradation to effectively remove phenol in wastewater. Loh et al. created composite hollow fiber membranes with varying amounts of polydimethylsiloxane (PDMS) infiltration by applying a layer of PDMS to a polyetherimide (PEI) hollow fiber substrate for phenol removal. Praveen and Loh studied how hollow fiber membranes impregnated with trioctylphosphine oxide (TOPO) may remove phenol from wastewater. The advantages of this technique include a compact design and adjustable equipment configuration, making it useful in the field of environmental engineering [91].

3.2.5. Photocatalytic Membrane Reactors (PMRs)

PMRs are hybrid reactors that combine photocatalysis with a membrane separator, which serves as both a simple barrier for the photocatalyst and a selective barrier for the molecules being destroyed. It is required to remove photocatalyst particles from treated water following degradation [92].

3.2.6. Reverse Osmosis (RO) and Nanofiltration (NF)

RO is a membrane-based demineralization technology for separating dissolved particles, particularly ions, from aqueous solutions, whereas NF is commonly used to remove organic contaminants, inorganic salts, color, and hardness from aqueous solutions. NF is suited for use in front of a RO unit to reduce RO pressures caused by organic materials [40].

3.2.7. Pervaporation (PV)

PV has recently gained popularity as an alternate method of removing low volatile organics from wastewater. PV's distinguishing features include low energy consumption, no secondary contamination, great efficiency, and ease of operation. Water and volatile organic compounds are typically concentrated on the feed and permeate sides of the membrane, with the permeate compound evaporating at the same time. Membranes such as PDMS, urethane polymers, and poly(ether block amide) (PEBA) membranes have been employed to remove phenol. Previous studies revealed that PV using a PEBA 2533 membrane could be an alternate method for extracting phenol from wastewater streams. In comparison to PDMS and zeolite-filled PDMS membranes, this membrane demonstrated high phenol selectivity [93].

3.2.8. Membrane Distillation (MD)

The MD method is a non-isothermal membrane-based separation that competes with existing technologies such as RO, which are limited by osmotic pressure. Mohammadi et al. also investigated phenolic wastewater treatment by vacuum membrane distillation (VMD) utilizing the Taguchi optimization approach. The procedure involved using a 0.22 µm pore size polytetrafluroethylene (PTFE) membrane. The MD method has two significant drawbacks: membrane fouling and pore wetting [94].

3.2.9. Chemical oxidation

Chemical oxidants destroy aqueous phenols. The methods have low reagent and energy costs and operate under mild conditions (temperature and pH), typically in the parts per million range or more. The most frequent chemicals used in oxidative wastewater treatment include ozone, chlorine, chlorine dioxide, chloramines, ferrate [Fe (VI)], and permanganate [Mn (VII)]. Permanganate and ferrate have been widely studied and employed due to their strong reduction potential [95].

3.2.10. Electrochemical oxidation

Electrochemical oxidation is an alternate destructive treatment for aqueous phenols that requires no reagents but incurs equipment and energy expenditures. As previously discussed by Martinez-Huitle et al. and Tasic et al., electrochemical oxidation processes are classified as direct or indirect oxidation [96]. Adsorption of contaminants onto the anode surface is the mechanism of direct or anodic treatment. Anode materials include Pt, PbO_2, SnO_2, IrO_2, and BDD (boron-doped diamond), which have been extensively studied. Treatment efficiency is influenced by parameters like as current density, pH, anode material, and electrolyte composition. Phenol degradation follows pseudo first-order kinetics, and the process's effectiveness is measured by apparent current efficiency, electrochemical oxidation index, or instantaneous current efficiency [5]. Indirect oxidation uses intermediary redox reagents to transfer electrons between the electrode and the pollutant, preventing pollutants from clogging the electrodes. Chloride ions promote phenolic compound elimination by forming Cl_2 or ClO^- in electrochemical oxidation of active chlorine [13].

3.2.11. Advanced Oxidation Processes (AOPs)

AOPs are a collection of procedures that share the ability to produce hydroxyl radical (OH•) in situ, which is capable of mineralizing most organics, including phenolics. The AOPs discussed below, UV/H_2O_2, Fenton, wet air oxidation, and ozone, are all applicable to a wide concentration range of phenolic target chemicals [54].

3.2.12. Phenol removal by UV/H_2O_2 treatment

The integration of microwave (MW) irradiation with UV/H_2O_2 treatment has proven to be an effective enhancement for the removal of phenol from wastewater. This hybrid approach

significantly accelerates reaction kinetics, reduces energy activation, minimizes equipment footprint, simplifies operational procedures, and increases overall treatment efficiency. The synergistic effect of microwave-assisted UV/H_2O_2 treatment enhances the oxidative degradation of phenol by promoting hydroxyl radical generation and improving mass transfer processes.
For instance, the application of microwave irradiation at 2.5 GHz in conjunction with a UV/H_2O_2 system has demonstrated a substantial improvement in phenol degradation. This combined technique leads to more efficient mineralization, although it necessitates a higher dosage of H_2O_2 to achieve complete breakdown of organic pollutants. The introduction of MW energy not only accelerates the decomposition of H_2O_2 into reactive hydroxyl radicals but also enhances the overall oxidation process. As a result, the conversion of phenol and the total organic carbon (TOC) removal efficiency have been observed to increase by up to 50 % compared to conventional UV/H_2O_2 treatment alone.
These findings highlight the potential of MW-assisted advanced oxidation processes (AOPs) as a promising method for wastewater treatment, particularly for the removal of refractory organic contaminants like phenol. Further research into optimizing MW parameters, H_2O_2 concentration, and reaction conditions could enhance process efficiency while reducing energy consumption and operational costs.

3.2.13. Fenton and Fenton-like treatment

The Fenton reagent, which consists of H_2O_2 and ferrous ions at low pH, is an AOP that can oxidize aromatic contaminants. Iron II interacts with hydrogen peroxide to produce iron III and hydroxyl radicals. In an acidic environment, hydrogen peroxide regenerates iron (III) into Fe (II). In addition, there are Fenton-like, photo-Fenton, and electro-Fenton enhancing techniques.

3.2.14. Wet Air Oxidation (WAO) and Catalytic Wet Air Oxidation (CWAO)

Wet air oxidation (WAO) can be used to treat toxic organic wastewater that is resistant to biological treatment using either high temperature and high pressure (WAO) or a combination of high temperature, high pressure, and catalysts (CWAO). In this process, oxidizable organics such as phenol and phenolic compounds in water are mixed with gaseous oxygen (normal air or oxygen alone) at temperatures ranging from 150 to 400 °C and pressures ranging from 2 to 40 MPa. The concentration of oxygen in water is significantly higher than at atmospheric pressure, and the water remains liquid. The oxidation reactions in WAO convert phenolic chemicals into less harmful end products such carboxylic acids, carbon dioxide, and other tiny molecular weight molecules.

3.2.15. Biological treatment

Biological therapy is the most regularly used treatment for aqueous phenols, and as such, it is frequently used as a baseline or reference method to evaluate the other procedures discussed below. The treatment is a low-cost, easy-to-design, and low-maintenance approach for converting phenolic solutions into simple end products.

3.2.16. Enzymatic treatment

Enzymatic therapy, which draws inspiration from biological treatment, employs a biocatalyst, or enzyme, to perform a transformation on phenolic chemicals, resulting in their removal from water. The procedure can offer substantial advantages (including cost-effectiveness) over traditional biological and chemical therapies, as long as the enzyme in question is available as a commodity at a reasonable price.

3.3. Removal of dyes

Due to their toxicity and color, dye pollutants found in industrial wastewater have garnered a lot of attention [97]. Significant pollution has been produced by the disposal of these dye pollutants in a number of locations across the world. In particular, since dyes may be visible to the human eye in water, even minimal concentrations of them as little as 1 ppm for some colors can be considered a serious toxin in the water system [98]. Since more than 10,000 industrially available colors are practically used in many different industries, including tanneries, paints, rubber, plastics, textiles, paper, paints, cosmetics, and leather goods, they could potentially be very polluting [99]. Worldwide, more than 700,000 t of dyes are produced each year; of these, 12 % are wasted during processing or manufacturing, and 20 % of these lost dyes end up polluting the environment. Aquatic organisms are seriously threatened by many industrially produced water contaminants. In addition, dyes can cause gastrointestinal distress, nausea, vomiting, diarrhea, and inflammation in both people and animals [100]. In industrial operations, more than 100,000 commercially available dyes are necessary for a variety of products. Most dyes, including methyl orange (MO), methylene blue (MB), and rhodamine B (RhB), are soluble in water, not easily biodegradable, and may be detrimental to the environment [101]. Ag@AgCl@MIL-100(Fe)/CCF was produced by Duan and colleagues using in situ synthesis of MOF and carboxymethylation of cotton fabric used as a scaffold. Strong oxidizing hydroxyl radicals are produced during the photocatalysis process by the reaction of photogenerated electrons with O_2, and superoxide ions are produced by the reaction of photogenerated h^+ and H_2O. Because of their potent oxidizing ability, these radicals end up being the ones responsible for the destruction of MB dye [102]. Excellent recyclability and exceptional simultaneous removal efficiency of the soluble dyes were found using photocatalysts. Nguyen et al. documented the effects of TiO_2/ZnO/rGO composites on the deterioration of MB, RhB, and MO and postulated the pathways and processes of degradation when exposed to UV light. In addition, when compared to the individual materials, the heterojunction of TiO_2/ZnO/rGO materials can demonstrate outstanding photocatalytic practical application, stability, and recyclability [103]. This is explained by the dye's high adsorption capacity, broad surface area, narrow bandgap, and enhanced charge carrier separation efficiency [104]. According to Pan et al., compared to pure α-$AgVO_3$ and $BiFeWO_6$, the $BiFeWO_6$/α-$AgVO_3$ composite with 1 wt percent of $BiFeWO_6$ may considerably contribute to increased RhB elimination [105]. The SnO_2-MoS_2 nanostructures demonstrated a significant improvement in photocatalytic degradation of MB and RhB in comparison to pure MoS_2 or SnO_2 [106]. This improvement in photocatalytic degradation was responsible for the high specific surface area and improved absorption of visible light. Smith et al. concentrated on the morphology of ZnO immobilization on PALFs and the photocatalytic efficacy of ZnO/PALFs in the removal of wastewater containing Congo red, which is dependent on their morphology [107]. Under UV/vis irradiation, the catalyst demonstrated a high performance (>95 %) and reusability for Congo red degradation [108].

4. Removal of heavy metals

Heavy metal ion removal from wastewater is critical for maintaining a clean environment and protecting human health [109]. Heavy metals are elements with atomic weights ranging from 63.5 to 200.6 with specific gravity greater than 5.0. Heavy metal wastewaters are increasingly being discharged into the environment, directly or indirectly, as industries such as metal plating, mining, fertilizer, tanneries, batteries, paper, and pesticides develop rapidly, particularly in developing countries [110]. Heavy metals, unlike organic pollutants, are not biodegradable and accumulate in living organisms [111]. Many heavy metal ions are hazardous or carcinogenic.

Toxic heavy metals of special significance in industrial wastewater treatment include zinc, copper, nickel, mercury, cadmium, lead, and chromium [112]. Zinc is a trace element that is vital to human health. It is critical for the physiological functioning of living tissue and regulates numerous metabolic processes. However, excessive zinc consumption can result in serious health concerns such as stomach cramps, skin irritations, vomiting, nausea, and anemia. Copper plays a crucial role in mammalian metabolism [113]. However, excessive copper absorption causes major toxicological problems, such as vomiting, cramping, convulsions, and even death. Nickel levels beyond the critical level may cause major lung and kidney difficulties, in addition to gastrointestinal distress, pulmonary fibrosis, and skin dermatitis [114]. Nickel is a proven human carcinogen. Mercury is a neurotoxin that can damage the central nervous system. Mercury in high amounts impairs pulmonary and kidney function, causing chest discomfort and dyspnoea. Minamata Bay is a prominent case of mercury poisoning. The US Environmental Protection Agency has categorized cadmium as a potential human carcinogen. Cadmium offers serious health concerns. Chronic cadmium exposure causes renal failure, and excessive amounts of exposure can end in mortality. Lead can affect the central nervous system [115]. Lead can also harm the kidneys, liver, and reproductive system, as well as basic cellular and brain activities [116]. Toxic symptoms include anemia, sleeplessness, headaches, dizziness, irritability, muscle weakness, hallucinations, and kidney damage. Chromium exits the aquatic environment primarily in two states: Cr (III) and Cr (VI). Overall, Cr (VI) is more hazardous than Cr (III). Cr (VI) impacts human physiology, accumulates in the food chain, and causes significant health concerns ranging from minor skin irritation to lung cancer (Table 1) [117]. Faced with increasingly rigorous laws, heavy metals are now environmental priority pollutants and one of the most serious environmental issues. As a result, hazardous heavy metals should be removed from wastewater in order to safeguard both people and the environment [118]. Several described approaches were used to remove heavy metal ions from various wastewater sources. These treatments could be classed as adsorption, membrane, chemical, electric, and photocatalytic [119].

Table 1. The maximum permissible limits, and Health effect and of heavy Metal.

Heavy Metal	Permissible Limits (USEPA) µg/L	Permissible Limits (WHO) µg/L	Health Hazards
Lead	6	10	Kidney problem, Central Nervous System Damage, loss of appetite, anemia, high blood pressure, suspected carcinogen, diminishing IQ, cause sterility, and muscle and joint pains

Heavy Metal	Permissible Limits (USEPA) µg/L	Permissible Limits (WHO) µg/L	Health Hazards
Arsenic	*	500	Gastrointestinal effects, skin, producing liver tumors, and carcinogenic
Copper	*	3000	Insomnia, diarrhea, irritation of nose, eyes, mouth, headache, dizziness, and stomachache, liver damage, and convulsions,
Mercury	0.03	1	Neurological disorder, Severe muscle pain, eyes and muscle membrane, dermatitis, anorexia and corrosive to skin, Neurotoxin, Kidney dysfunction, and circulatory disorder
Chromium	50	50	Allergic dermatitis, producing lung tumors, and suspected human carcinogen
Cadmium	10	3	Cause lung fibrosis, dyspnea and weight loss and carcinogenic
Nickel	200	20	Kidney Damage, reduced lung function, cancer of lungs and nasal sinus, causes chronic bronchitis, dermatitis, gastrointestinal disorder, and lung
Chromium	50	50	Allergic dermatitis, producing lung tumors, carcinogen, Nausea, and diarrhea
Zinc	*	5000	Neurological symptoms, anemia, causes short-term illness called "metal fume fever" and restlessness, depression, nausea, and skin irritation
Arsenic	*	500	Carcinogenic, skin, gastrointestinal effects and producing liver tumors

4.1. Adsorption-based separation

Adsorption-based separation technologies are successful at removing heavy metal ions from wastewater [120]. The adsorption mechanism is defined by the physicochemical properties of adsorbent and heavy metals and operating conditions (i.e., adsorbent amount, temperature, adsorption time, initial concentration of metal ions and pH value). The general mechanism of adsorption–desorption process with its terminologies is illustrated in Fig. 6. This approach employs a variety of adsorbents, including natural materials (such as activated carbon and clay), synthetic polymers, and sophisticated nanomaterials (such as graphene oxide) [47]. Functionalization improves the efficiency of these adsorbents by increasing their binding capacity for certain metals [121]. Recent advancements include the integration of adsorption with other treatment methods to increase overall efficiency, as well as the development of smart materials that respond to environmental changes [122]. While pilot studies have showed successful real-world applications, issues like as adsorbent saturation, regeneration, and economic feasibility persist [123].

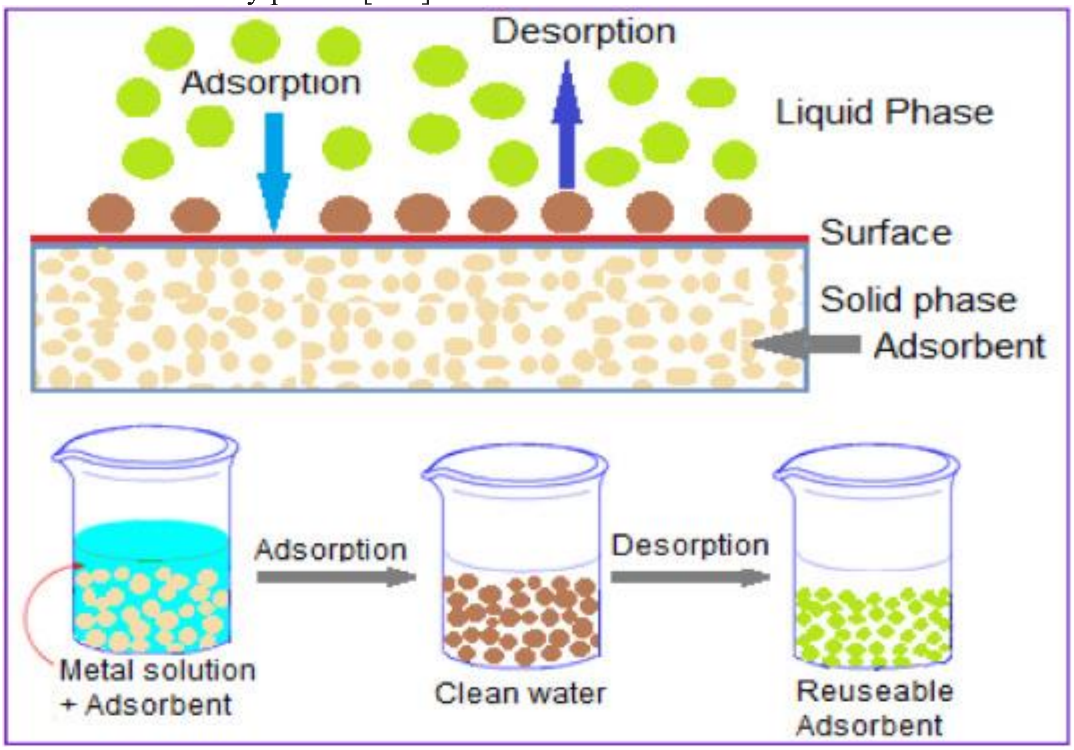

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Fig. 6. The mechanism of metal ions adsorption–desorption process in water. Redistributed under the International Creative Commons Attribution 4.0 License, CC-BY from Ref. [124]. Copyright 2021, MDPI.

4.1.1. Carbon-based adsorbents

Carbon-based adsorbents, such as activated carbon, biochar, and graphene oxide, have emerged as promising materials for extracting heavy metal ions from wastewater [125]. Their large surface area, porous structure, and customizable surface chemistry increase their adsorption capability for different metals including as lead, cadmium, and mercury. Activated carbon is commonly utilized due to its high adsorption capabilities and availability, however biochar generated from biomass provides an environmentally friendly option with added soil health benefits. Graphene oxide's unusual structure allows for great selectivity and quick adsorption rates [126]. The most often used methods of modification to improve pore structure, mechanical strength, adsorption capacity, thermal stability, and specific surface area are sulfuration, oxidation, and nitrogenation. They are mostly dependent on the adsorbent materials, which can occasionally be highly costly. The cost of the adsorbent should therefore be taken into account while selecting the best adsorbents. Challenges include regenerating adsorbents for reuse and developing cost-effective production methods. Ongoing research focuses on improving these materials and developing hybrid techniques that combine carbon-based adsorbents with other treatment technologies to improve the efficiency and sustainability of heavy metal removal from wastewater [127].

4.1.2. Chitosan-based adsorbents

Chitosan (CS), a chitin-derived biopolymer, has emerged as an efficient adsorbent for the removal of heavy metal ions from wastewater. Its natural abundance, biodegradability, and non-toxicity make it an environmentally benign option. Chitosan-based adsorbents can successfully absorb heavy metal ions by mechanisms such as ion exchange, chelation, and electrostatic attraction due to the presence of amino and hydroxyl functional groups [128]. pH, temperature, and contact time all have a major influence on adsorption efficiency. Combining chitosan with other materials, such as nanoparticles or activated carbon, can improve its adsorption and regeneration capability. Because chitosan (CS) has hydroxyl (–OH) and amino (–NH2) groups, it is a naturally occurring adsorptive polymer with high affinity for contaminants found in wastewaters. Its inadequate mechanical strength and weak stability, in spite of its distinctive qualities, render the regeneration ineffective [129]. Additionally, the poor porosity, low surface area, resistance to mass transfer, and high crystallinity of CS make its utilization as a powder or flake difficult. To get around these problems, structural and chemical changes have been suggested. Chemically modifying CS with cross-linking creates a bridge between the functional groups and polymer chains, giving CS strength [130]. This strategy, however, lowers uptake. Overall, chitosan-based adsorbents provide a long-term and efficient solution for cleaning heavy metal-laden wastewater, helping to safeguard the environment and recover valuable resources [131].

4.1.3. Mineral adsorbents

The use of mineral adsorbents such as activated carbon made from minerals, zeolites, and clays in wastewater treatment is growing as a means of eliminating heavy metal ions [132]. These materials are good in capturing pollutants because of their special qualities, which include large surface area, ion-exchange capacity, and chemical stability. Mineral adsorbents can successfully bind heavy metals through the adsorption process, which often involves mechanisms including ion exchange, surface adsorption, and complexation [133]. They can be severely impacted by variables like pH, temperature, and the presence of competing ions. Furthermore, their effectiveness can be increased by making changes to increase the adsorption capacity, such as activating acid or forming composites with other materials. All things considered, mineral adsorbents offer an affordable and environmentally friendly way to remove heavy metals from wastewater while also adhering to legal requirements [134]. The use of natural minerals might be more affordable. After a few cycles, the removal efficiency could, however, drop. Consequently, many modification techniques have been put forth to improve the removal effectiveness of such adsorbents, including calcination and impregnation. Nevertheless, these changes add to the process's expenses and introduce fresh chemical agents into the environment. Grafting functional groups could create multipurpose, environmentally friendly adsorbents that can be used to treat a range of wastewater kinds. Innovative low-cost and high-performance adsorbents could be developed through the manufacture of clay adsorbents based on one-dimensional nanotubes and two-dimensional nanosheets [135].

4.1.4. Magnetic adsorbents

An inventive method for removing heavy metal ions from wastewater is the use of magnetic adsorbents. Iron particles are housed in a particular type of material matrix called a magnetic adsorbent (typically magnetic nanoparticles, such as Fe_3O_4) [136]. The foundation material may consist of biomass, carbon, polymers, CS, or starch. These materials combine the benefits of easy separation using an external magnetic field with a high adsorption capacity. They are typically made of iron oxides or modified magnetic nanoparticles. Heavy metals can be effectively bound by the adsorption process, which includes mechanisms including complexation, ion exchange, and electrostatic attraction [137]. The concentration of the starting metal, contact time, and pH are important variables that affect their performance. Magnetic adsorbents can be functionalized or have their surfaces altered to improve their capacity and selectivity for particular heavy metals. Because of their ease of recovery and repurposing, they represent an economical and sustainable wastewater treatment solution that also enhances water quality and complies with regulations [138].

4.1.5. Biosorbents

An environmentally beneficial method of extracting heavy metal ions from wastewater is to use biosorbents, which are made from natural sources including algae, microbial biomass, and agricultural waste. These materials efficiently bind heavy metals by a variety of methods, such as complexation, ion exchange, and adsorption [139]. The concentration of metal ions, pH, temperature, and contact time are important variables that impact the efficiency of biosorption. By making changes, the biosorbents can be made more selective and capable of attaching to particular metals [140]. Pollutants and the surface of the biosorbent can generally interact via electrostatic contact, aggregation, microprecipitation, complexation/coordination, ion exchange, reduction, or oxidation. The ionization of functional groups on the biosorbent surface and the charge density of the biosorbent surface are influenced by the pH of the solution. Cations are nearly stable at low pH levels and can form bonds with the surface of the biosorbent [141]. However, the solubility of metal cations reduces and a precipitation event may occur at higher pH values. Because it provides more available sites for biosorption, the amount of biosorbent has a significant impact on the removal efficiency. Because of bond rupturing, a drop in Gibb's free energy, and a decrease in solution viscosity, the biosorbent capacity may rise at higher temperatures. These factors improve the biosorbent active sites and raise the frequency of collisions (mobility and kinetic energy) between the biosorbent and metal ions, which results in a higher affinity [142]. Utilizing biosorbents encourages waste valorization by repurposing organic materials in addition to offering a sustainable approach to treating contaminated water. They are an appealing solution for dealing with heavy metal contamination while promoting environmental sustainability due to their low cost and biodegradability [143].

4.1.6. Metal-organic frameworks adsorbents

Because of their large surface areas, adjustable porosity, and functionalizable structures, metal-organic frameworks (MOFs) are becoming increasingly popular as extremely efficient adsorbents for the removal of heavy metal ions from wastewater [144]. These crystalline materials can have different functional groups added to them to improve their adsorption capabilities. The metal ions in them are coupled to organic ligands. The development of customized frameworks that can selectively absorb particular heavy metals, such lead, cadmium, and arsenic, even at low concentrations, is the result of recent developments in MOF synthesis.

The performance of their adsorption is affected by temperature, pH, and the presence of competing ions. MOFs are a sustainable alternative for treating wastewater since they have the capacity for regeneration and reuse [145]. The most common method for creating metal-organic frameworks (MOFs) is reticular synthesis, which involves forming a strong binding between metal ions and organic linkers. Thousands of MOFs were proposed by researchers [146]. It was observed that the majority of the costly and hazardous organic ligands utilized to create numerous MOFs Because of their facile integration of functional groups and hydrolytic-thermal stability, such as amine, carboxylic, hydroxyl, and oxygen, or by applying the cross-linking process, the zirconium-MOFs family (such as UiO-66) is a potential nanostructure material for sorption applications. Even with MOFs' intriguing properties and strong ability to extract heavy metal ions, certain target metals cannot enter their micropores, which are minuscule pores. The majority of them are also not very stable in water [147]. Although MOFs including Cu, Fe and Mn have been created, the majority of them have poor chemical stability [148]. Consequently, more study is required to fine-tune the structure of MOFs and scale up these materials for use in industrial wastewater applications. In addition, it is important to suggest and implement various functionalization techniques in order to improve the stability and sorption kinetics of MOFs. Their potential as an environmentally benign remedy to heavy metal contamination is positioned by their ability to be customized for specific uses. MOFs are anticipated to be essential in developing wastewater treatment methods as research progresses [149].

4.2. Membrane-based filtration and separation

The removal of heavy metal ions from wastewater has gained significant attention due to the increasing adoption of membrane-based filtration methods. These methods are favored for their high selectivity, efficiency, and seamless integration into existing treatment systems [151]. Utilizing semi-permeable membranes, they enable the separation of pollutants based on size, charge, or chemical affinity. Advances in nanofiltration and reverse osmosis membranes have significantly improved the selective rejection of heavy metal ions such as lead, cadmium, and mercury. One of the key innovations in this field includes the development of hybrid membranes incorporating functionalized polymers or nanoparticles to enhance adsorption and improve selectivity [152]. The effectiveness of membrane filtration is influenced by factors such as operating parameters, including temperature and pressure, as well as membrane pore size. To address challenges such as membrane fouling and limited lifespan, surface modifications and

advanced cleaning techniques are being explored [153]. Ongoing research continues to focus on enhancing membrane durability and reducing operational costs, making membrane-based filtration a promising and sustainable approach for heavy metal removal in wastewater treatment.
Recent advancements in membrane-based techniques have extended beyond conventional filtration, incorporating novel approaches for enhanced heavy metal ion removal. Electrodialysis is one such technique that effectively eliminates heavy metal ions from wastewater by driving ion transport through selective ion-exchange membranes under the influence of an electric field. This method offers high efficiency and reduced energy consumption compared to traditional approaches [154]. Another innovative approach is the use of membrane bioreactors (MBRs), which combine biological treatment with membrane filtration. MBRs utilize microorganisms capable of bioaccumulating or transforming contaminants, while membrane separation retains biomass and facilitates metal removal [155].

Nanofiltration and ultrafiltration techniques rely on membranes with specific pore sizes to selectively reject heavy metal ions while allowing smaller molecules to pass through. Recent advancements in membrane materials, such as graphene oxide and polymer composites, have significantly improved both selectivity and permeability [156]. Ultrafiltration (UF) operates at low transmembrane pressure (TMP), and since its membrane pores may be larger than heavy metal ions, additives can be used to increase ion size for more effective removal. Two primary approaches, polymer-enhanced ultrafiltration (PEUF) and micellar-enhanced ultrafiltration (MEUF), have been developed to address this limitation. Additionally, nanofiltration (NF) targets solutes with molecular weights greater than 200 Da and particles within the 0.0005–0.007 μm range, positioning it between UF and reverse osmosis (RO) processes. NF membranes are composed of polymer composites with multilayer thin films containing negatively charged chemical groups. Anti-fouling NF membranes have been successfully developed using CeO_2/Ce_7O_{12} and PES through phase inversion, demonstrating extraction efficiencies between 94 % and 98 % for Fe^{3+}, Al^{3+}, Co^{2+}, Cd^{2+}, Cu^{2+}, and humic acid [157].

Hybrid systems further enhance heavy metal removal efficiency by integrating membrane filtration with other treatment methods such as adsorption or advanced oxidation processes. For example, combining membrane filtration with activated carbon or biochar significantly improves overall pollutant removal [158]. Additionally, surface modification of membranes through the incorporation of functional groups or nanomaterial coatings enhances selectivity and reduces fouling, further optimizing performance in heavy metal removal applications [159].

4.3. Chemical-based separation

Chemical techniques are well-established and frequently used to remove heavy metals from wastewater. The chemical-based techniques, such as ion exchange, electrochemical techniques, advanced oxidation processes (AOPs), coagulation, and precipitation, will be covered in this section [160]. Significant threats to the environment and human health arise from wastewater contaminated with heavy metals. Chemical-based separation approaches have shown promise in effectively eliminating these dangerous ions in recent times.

Precipitation is one such method, where chemicals are added to wastewater, reacting with heavy metal ions to generate insoluble compounds that can be filtered out. Sulfides and lime ($Ca(OH)_2$) are common reagents [161]. Chemical precipitation, also known as coagulation precipitation, is one of the most well-established and successful processes and is widely employed in industry. To aid in the sedimentation of dissolved metal ions, it transforms their shape into solid particles. Through co-precipitation, pH modification, or electro-oxidizing potential change, the coagulant (reagent coagulation) precipitates metal ions. The removal of sediments typically follows [162]. Hydrogen precipitation is easy to use, affordable, and pH-tunable, making it a popular method. To create insoluble metal hydroxide precipitates, a hydroxide is added to the agitated wastewater.

Ion exchange is another technique that uses resins to bind heavy metal ions from the wastewater in a specific manner. The removal efficiency of some metals can be improved by tailoring the procedure [163]. Chemical coagulation, where coagulants such as aluminum sulfate are introduced to wastewater, facilitates the clumping of heavy metals into larger particles that are easily extracted by filtration or sedimentation [164]. The agglomeration of destabilized particles is known as flocculation, whereas coagulation refers to the instability of colloids by negating the forces that keep them apart. Aluminum, ferrous sulfate, and ferric chloride are traditional coagulants used to neutralize ion charges. With the aid of a flocculant, such as polyaluminum chloride (PAC), polyferric sulfate (PFS), polyacrylamide (PAM), or other macromolecule flocculants, flocculation joins the particles to form large agglomerates. Although PE was regarded as one of the most useful flocculants, the sludge created may be toxic. Most flocculants are synthetic and not biodegradable [165]. Advanced oxidation processes (AOPs) produce reactive species capable of oxidizing heavy metals, simplifying their removal and separation. Electrochemical techniques allow for the reduction and deposition of heavy metal ions onto electrodes using electrochemical cells, facilitating their removal from the solution [166]. Current studies underscore the significance of tailoring these techniques to particular wastewater compositions, improving efficacy, and cutting expenses. To increase removal rates and sustainability, combining these methods with nanomaterials or bioadsorbents is also being investigated. Chemical-based separation remains a crucial field of study for reducing heavy metal contamination in wastewater, protecting the environment, and producing cleaner water supplies [167].

4.4. Electric-based separation

Electric-based separation is among the most effective methods for eliminating heavy metal ions from wastewater, particularly through electrochemical approaches [168]. These methods leverage electricity to facilitate metal removal and purification. One such approach is electrocoagulation, which uses an electric current to generate coagulants in situ. These coagulants agglomerate and destabilize heavy metal ions, making it easier to remove them through filtration or sedimentation. Another method is electrodeposition, where heavy metal ions are reduced and deposited onto electrodes upon the application of a voltage. This technique allows for the selective recovery and recycling of metals such as copper, nickel, and lead. Additionally, electrodialysis employs ion-selective membranes and an electric field to effectively concentrate and remove heavy metal ions from wastewater [169]. In an electrochemical system, electrons move from the anode (positive side), where oxidation occurs, to the cathode (negative side), where reduction takes place. These simultaneous chemical processes, known as redox (reduction-oxidation) reactions, facilitate the removal of metals and contribute to water purification. Recent advancements have focused on optimizing electrode materials and configurations to enhance efficiency while minimizing energy consumption. Furthermore, researchers are exploring the integration of renewable energy sources into these systems to improve sustainability. Overall, electric-based separation presents a viable and efficient solution for mitigating heavy metal contamination in wastewater [140].

4.5. Photocatalytic-based separation

Among these new, sophisticated oxidation technologies, photocatalysis is well-liked and shows promise in a number of domains [150]. A schematic illustration illustrating the fundamentals of the photocatalytic process can be found in Fig. 7. Photocatalysts typically feature semiconductor architectures. If the energy of a photon in the incident light is greater than or equal to the bandgap energy between the semiconductor valence band (VB) and the conduction band (CB), electrons (e^-) in the valence band may jump to the CB and may leave a positively charged hole (h^+) on the VB when the semiconductor material is exposed to light. When treating heavy metals, this pair of h^+ and e^- might migrate to the semiconductor's surface and go through a series of oxidation and reduction reactions, which are represented by the conversion of various valence states [151]. The wide bandgap's high energy requirements for incident light and the readily recombinant nature of photogenerated carriers (e^+ and h^+) are the primary limiting factors in the photocatalysis process. The greatest research has been done on TiO_2, the most common photocatalyst. Its broad bandgap, however, is only sensitive to UV light [152]. As a result, more photocatalysts with appropriate and effective bandgaps have been created and put to use. Examples of these include ZnO, C_3N_4, and bi-based catalysts [153]. Numerous studies on photocatalysis for the treatment of organic wastewater, water splitting for the creation of hydrogen and oxygen, and nitrogen fixation are now in progress. The generated active species have strong redox capabilities and don't create more pollution because photocatalysis only needs light as an energy source. Using it for redox in water treatment is quite possible [154].

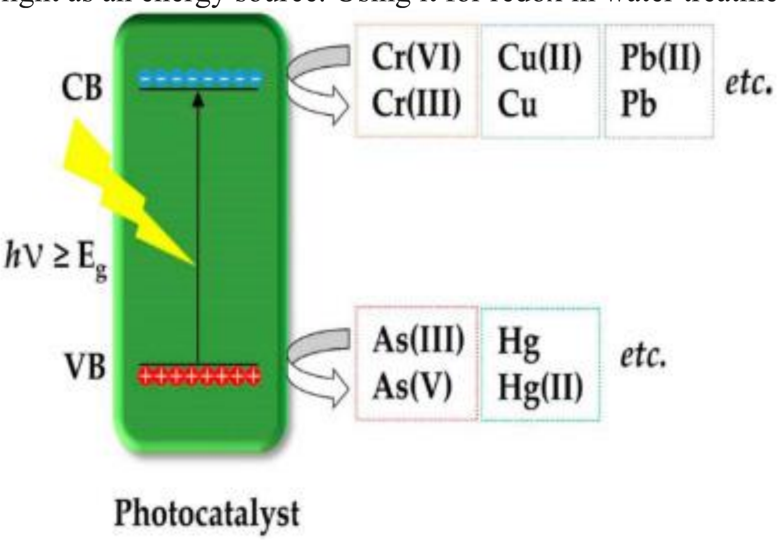

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Fig. 7. Schematic diagram of photocatalytic treatment of heavy metals. Redistributed under the International Creative Commons Attribution 4.0 License, CC-BY from Ref. [155]. Copyright 2020, MDPI.

Photocatalysis process involves three important phases: charged carrier photogeneration, charged carrier separation and diffusion to the photocatalyst surface, and a redox reaction on the photocatalyst surface (Fig. 8) [156]. Using an outdoor dual sun photocatalytic approach with flat plate collector, 93.5 % Cu^{2+}, 99.6 % Fe^{3+}, and 99.4 % Zn^{2+} were extracted from the wastewater effluents of actual soil washing. With simulated ultraviolet (UV)–solar TiO_2 photocatalysis, ethylenediamine-N, N′-disuccinic acid (EDDS), and Cu^{2+} have been removed from wastewater (0.2 mM EDDS and 0.2–1.4 mM $CuSO_4$), achieving 100 % conversion efficiency at a 24 % mineralization degree. In another study, maximum removal efficiency of 41 % Cu^{2+}, 100 % Fe^{3+}, 100 % Zn^{2+}, and 100 % EDDS were obtained using a synthetic soil washing solution (3.6×10^{-1} mM EDDS, 8.0×10^{-2} mM Cu^{+2}, 1.0×10^{-1} mM Fe^{+3}, and 8.0×10^{-2} mM Zn^{+2}). Utilizing a synthetic rhodium/antimony co-doped TiO_2 nano-rod and titanate nanotube (RS-TONR/TNT) exposed to visible light, the Zn^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, and organic pollutant were recovered from wastewater with 70 and 80 % degradation efficiency for dye and Bisphenol A, respectively. When everything is said and done, photocatalytic-based separation is a potential method for effectively treating heavy metal-polluted wastewater, promoting resource recovery and environmental sustainability [157].

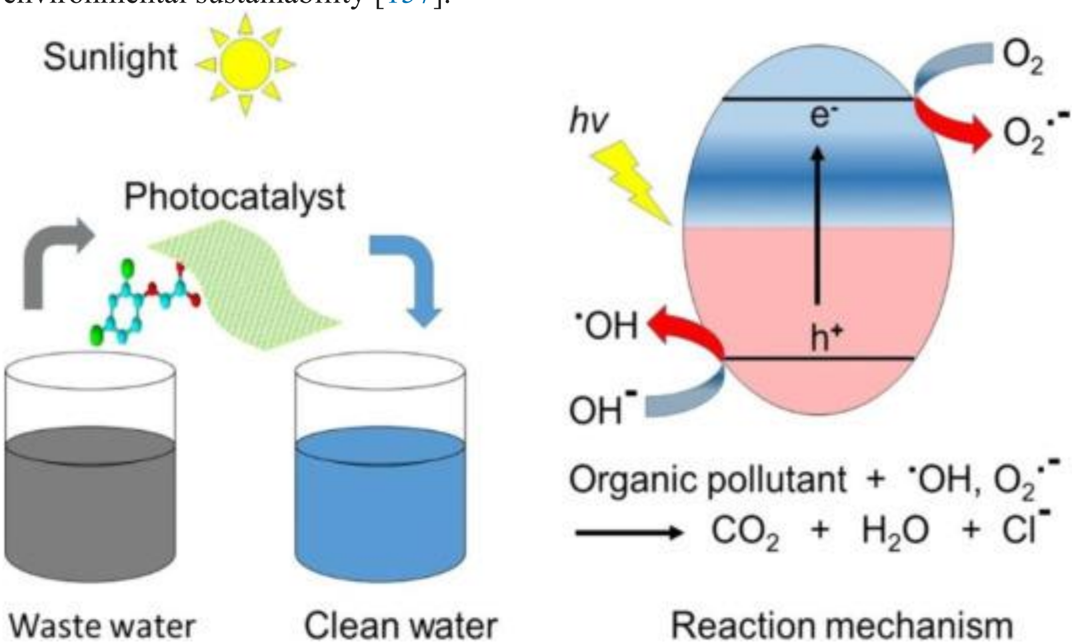

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Fig. 8. Diagram illustrating the principle of semiconductor photocatalysis for wastewater treatment. Redistributed under the International Creative Commons Attribution 4.0 License, CC-BY from Ref. [158]. Copyright 2020, Sage.

5. Removal of pharmaceutical

Due to their detrimental effects on the ecosystem, pharmaceutical compounds (PCs), a growing pollutant, have drawn more attention in recent years [158]. In contrast, typical treatment techniques like air stripping, flocculation, reverse osmosis, etc., have limitations when it comes to handling these kinds of compounds [159]. Heterogeneous photocatalysis is among the most effective techniques among all of these for breaking down harmful chemicals like antibiotics [160]. In actuality, individuals will be directly exposed when they eat contaminated fish or plants that have already been irrigated when pharmaceutical residues from untreated wastewater containing numerous harmful medications are dumped into the environment (Fig. 9). Man will always be a victim of his own acts as long as we have not discovered answers or experienced cutting-edge therapies for the removal of hazardous pharmaceutical residues [161].

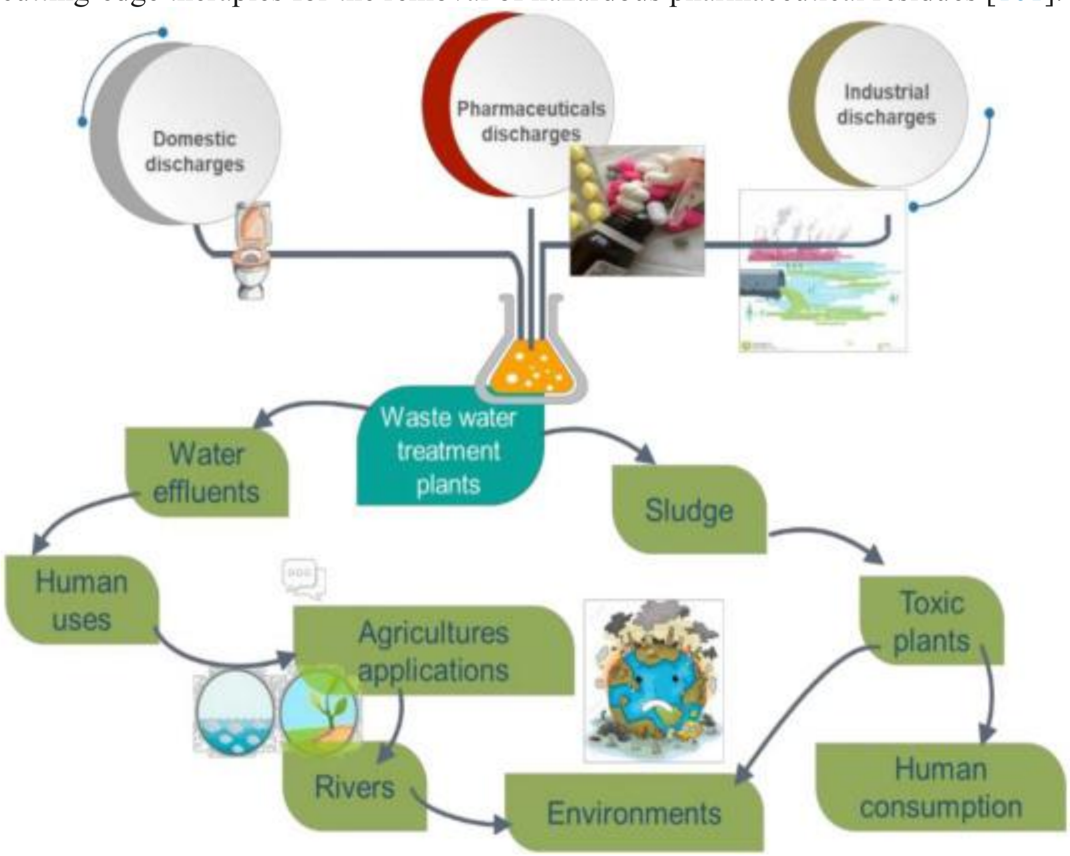

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Fig. 9. Sources of pharmaceutical contamination. Redistributed under the International Creative Commons Attribution 4.0 License, CC-BY from Ref. [162]. Copyright 2021, MDPI.

The issues of environmental pollution and public health hazards have drawn attention to the removal of heavy metal ions from wastewater, especially when it comes to pharmaceutical pollutants [163]. Current strategies concentrate on using cutting-edge treatment techniques like.

5.1. Adsorption techniques

By using biochar, activated carbon, or new nanomaterials that can bind pharmaceutical residues and heavy metals efficiently, removal efficiency can be increased. Solid adsorbent adsorption has the potential to be one of the most effective methods for treating a variety of pharmaceutical product-containing fluids and wastewaters [164]. As a more affordable option for wastewater treatment, there have been great studies on the use of carbon materials to eliminate pharmaceutical contaminants. Adsorbents can be divided into two categories: natural and synthetic. Charcoal, clays, clay minerals, zeolites, and ores are examples of natural adsorbents [165]. These natural materials have a great deal of potential to alter and eventually improve their adsorption capacities. In many cases, they are also widely available and reasonably priced [166]. Adsorbents made from home and industrial waste, sewage sludge, polymeric adsorbents, and agricultural products and waste are known as synthetic adsorbents [167]. The porosity, pore structure, and adsorbent surface nature of each adsorbent are unique attributes. Fruit waste, date nuts, coconuts, used tires, bark and other tannin-rich materials, sawdust, rice husk, fly ash, petroleum waste, fertilizer waste, blast furnace slag, sugar industry waste, chitosan and seafood processing waste, algae, peat, clays, red mud, zeolites, sediment and soil, ores, etc. are just a few of the wastes that are used [168]. There are three primary ways to look at the way advanced materials are now being used to remove PPCPs from wastewater: activated carbon (AC), clays, and biochar. Thermo-responsive gel, magnetic nanoparticles, and molecularly imprinted polymers (MIPs) are some other more contemporary materials that have also been reported; but, in comparison, they still lack development and case studies [169].

5.2. Bioremediation

A sustainable method that uses microorganisms that can bioaccumulate heavy metals while breaking down pharmaceutical contaminants. Because of their diverse metabolic capacities, bacteria play a major role in the biosphere, supporting the metabolic cycles that are essential to all life on Earth [170]. Scholars are exploring the possibility of various microorganisms breaking down pharmaceuticals and personal care products (PPCPs) into environmentally acceptable monomers, which may provide a new and alternative method of removing pharmaceutical residues from the environment [171]. Technologies that use sludge (aerobic, activated, or granular) have proven to be particularly effective in treating municipal wastewater, mostly due to the bacterial populations involved. A study assessing the effectiveness of eliminating pharmaceutical products like atorvastatin, caffeine, paracetamol, xylazine, trimethoprim, sulfamethoxazole, naproxen, fluoxetine, diclofenac, clarithromycin, carbamazepine, atenolol, azithromycin, erythromycin, ketoprofen, metoprolol, erythromycin, ciprofloxacin, valsartan, simvastan, and losartan using activated sludge in Latvia in municipal wastewater revealed that these pharmaceutical contaminants were biodegraded by Nitrospirae, Actinobacteria, Verrucomicrobia, Firmicutes, Acidobacteria, Proteobacteria, Chloroflexi, and Bacteroidetes [172]. Furthermore, certain taxa and species that are engaged in the elimination of pharmaceutical substances such metoprolol, venlafaxine, fluoxetine, alprenolol, propranolol, bisoprolol, gemfibrozil, salbutamol, norfluoxetine, and 17β-estradiol have shown clearance efficiencies of 90 % or greater [43].

5.3. Advanced Oxidation Processes (AOPs)

AOPs offer intriguing advantages for the successful remediation of emerging contaminants, such as the high removal efficiency of antibiotics and their proven adaptable application among the many treatment strategies developed to destroy efficiently persistent developing compounds [173]. It's interesting to note that these procedures were found to be the most economical methods for cleaning up waters tainted with drugs that dissolve poorly in water. Treatment methods including ozonation, photodegradation, electro-Fenton, and others are hindered by high energy costs, high operational expenses, and the creation of byproducts that need further funding [174]. Generally speaking, AOPs are defined by the in-situ formation of low-selectivity highly reactive oxygen species, such as anionic superoxide radicals (O_{2-}), hydroxyl radicals (HO°), H_2O_2, and O_3, which provide full mineralization pathways to CO_2, H_2O, and inorganic acids. Under certain operational conditions, these procedures are environmentally favorable. One of the most widely used AOPs, the Fenton process is thought to be a viable treatment method for effectively removing a number of pharmaceutical active components and enhancing wastewater's biodegradability. Though direct H2O2 breakdown or photo-reduction of Fe^{3+} to Fe^{2+} could result from the inclusion of a light source in this process, it is possible to further boost the OH radical rate. It has also been claimed that the photo-Fenton technique is an effective way to treat actual wastewater with high levels of organic content in complicated matrix systems. One of the most widely used AOPs in recent times is the electro-Fenton (EF) procedure, which uses the conventional Fenton's reaction to electrocatalytically produce OH radicals. Nevertheless, expensive energy and reagent expenses are required to make up for the subpar performance brought on by water turbidity, even though (AOP) is one of the best treatments for the removal of developing chemicals. Its application as a supplemental treatment in urban wastewater treatment plants is still uncommon primarily because of this (Carré et al., 2018). Furthermore, when the goal is the quasi-complete mineralization of treated solutions, AOPs become more expensive overall since this operation requires longer electrolysis times, which result in large electrical energy consumption [175].

5.4. Conventional treatments

In recent decades, the growing number of drugs in the environment has become a major problem. These substances can endanger aquatic ecosystems and human health as they find their way into wastewater systems through human and veterinary use [176]. Consequently, environmental scientists and wastewater treatment facilities now place a high priority on the efficient removal of pharmaceuticals during wastewater treatment [177]. This paper investigates the efficacy of common treatment techniques used in wastewater management in eliminating pharmaceutical pollutants. Pharmaceuticals are made to have biological effects on the body. This includes over-the-counter, prescription, and veterinary pharmaceuticals. Nevertheless, after consumption, they frequently infiltrate wastewater systems and exit the human body unmetabolized. There are worries over the persistent nature of these emergent pollutants in treated effluent and their possible ecological effects because conventional wastewater treatment procedures were not initially intended to address them [178]. Three phases of wastewater treatment are usually involved: primary, secondary, and tertiary. Every one of these phases contributes to lowering the number of contaminants, including medications. Primary treatment is the initial step in treating wastewater, and its goal is to get rid of big particles and particulate matter from the water. This procedure involves sedimentation to enable heavier materials to sink to the bottom of a tank and screening to remove debris. Primary treatment is usually useless against dissolved drugs, which can readily pass through this step, even though it is effective in eliminating bigger particles and organic waste. The focus of secondary treatment is on organic materials that is degrading biologically. The most popular technique is an activated sludge process, in which organic contaminants are eaten by microorganisms [179]. These microbes can biodegrade certain medications, but many drugs are resistant to biological breakdown because of their chemical structures. Antibiotics and some synthetic medications, for instance, might not significantly alter following subsequent therapy. Other techniques, such trickling filters, are also not very good at removing pharmaceuticals since they focus more on organic debris than particular pollutants. As an extra polishing step, tertiary treatment is used to improve the quality of treated effluent. This phase could entail a number of procedures, including chemical and filtration treatments. Certain dissolved substances and leftover particle debris can be removed using membrane filtering or sand filters. Certain medications can be broken down by chemical processes like ozonation or chlorination, but they can also result in toxic byproducts that increase the risk to the environment [180]. Because these substances are complex, total medication elimination remains a challenge for conventional tertiary therapies, despite their best efforts. The precise chemical structure of each medicine determines how efficient the clearance is, and this variation is substantial. The difficulties presented by medicines are emphasized by the shortcomings of traditional wastewater treatment techniques [181]. Numerous substances exhibit persistence and resistance to common chemical and biological therapies. Consequently, a considerable number of pharmaceuticals may still be present in treated effluent and end up being released into rivers, lakes, and oceans. The situation is further complicated by the increasing range of medicinal products. Every day, new medications are created and released into the market, frequently without thorough evaluations of their effects on the environment or how well they remove impurities from wastewater treatment systems already in place [182].

5.5. Electrocoagulation process

The potential harm that medications can cause to human health and aquatic ecosystems has made their presence in wastewater a significant environmental concern [201]. Conventional wastewater treatment methods often fail to efficiently remove these pollutants, highlighting the need for innovative technologies [202]. One such promising approach is electrocoagulation (EC), a process that utilizes electrical currents to remove impurities from wastewater. This paper examines the electrocoagulation process, highlighting its advantages over traditional treatment methods and its effectiveness in removing pharmaceuticals.

Electrocoagulation is a physical-chemical treatment process that uses electrical currents to destabilize and aggregate suspended particles, colloids, and dissolved pollutants in wastewater

[203]. The process involves sacrificial anodes, typically made of iron or aluminum, which dissolve during treatment and release metal ions into the solution. These ions interact with contaminants, leading to the formation of micro-flocs that can be easily removed through filtration or sedimentation. Studies have shown that electrocoagulation is an effective method for removing a wide range of pharmaceutical pollutants from wastewater [204]. Research indicates that EC can significantly reduce the concentration of pharmaceuticals commonly found in wastewater, including antimicrobials, analgesics, and anti-inflammatory drugs.
Several factors influence the effectiveness of electrocoagulation. The type of pharmaceutical present in the wastewater plays a critical role, as different medicines have varying levels of clearance efficiency due to their distinct chemical compositions and properties. For instance, hydrophobic drugs are generally easier to remove compared to hydrophilic drugs [169]. Operating conditions such as pH, retention time, and current density are also crucial to the efficiency of the electrocoagulation process. By optimizing these parameters, the removal of specific pharmaceuticals can be improved [205]. Additionally, the choice of electrode material impacts the process's overall efficiency and the generation of coagulants. Aluminum electrodes, for example, have shown promising results in the removal of certain pharmaceuticals.
Electrocoagulation presents a viable alternative for removing pharmaceuticals from wastewater due to its high removal efficiency and minimal chemical usage [206]. This method is especially attractive for addressing the growing concern of pharmaceutical pollution in water bodies. As research continues to optimize operating conditions and improve system design, electrocoagulation has the potential to significantly enhance wastewater treatment processes and protect aquatic ecosystems from pharmaceutical contaminants. Adopting this advanced technology could pave the way for more environmentally sustainable wastewater management strategies in the future [207]. The advantages and disadvantages of various treatment processes for pharmaceutical removal are summarized in Fig. 10.

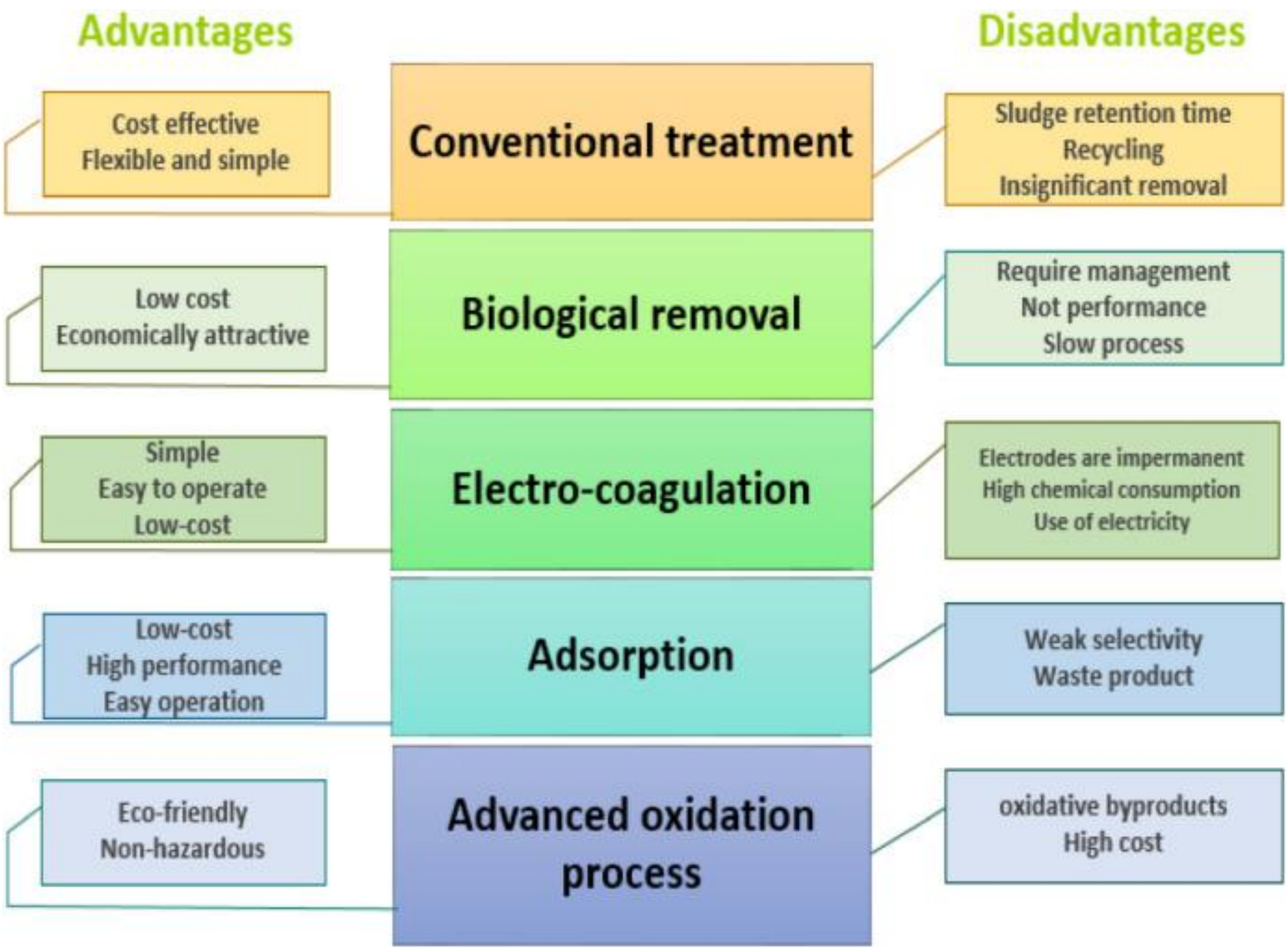

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Fig. 10. Advantages and disadvantages of different treatment process for the removals of pharmaceuticals. Redistributed under the International Creative Commons Attribution 4.0 License, CC-BY from Ref. [162]. Copyright 2021, MDPI.

6. Removal of pesticides

In addition to their application in preventing degradation during storage or transportation, pesticides are employed as ripening regulators, fruit thinning agents, defoliants, desiccants, and growth regulators [183]. Nevertheless, one of the main causes of water contamination is also pesticide use. Every pesticide has harmful side effects and is carcinogenic. Pesticides are biologically resistant and harmful. Pesticides, even small amounts, can linger and have a significant effect on both human health and the ecosystem [184]. Because semiconductor photocatalysis offers chemical stability and anti-biodegradation properties, it has also been used in the pesticide degradation industry. The majority of the semiconductor materials used in photocatalytic pesticide degradation are found in different metal oxides (such ZnO and TiO_2). Mesoporous Ag/Ag_2O-TiO_2 p-n heterojunction was used to photocatalytically degrade the herbicide dimethenamid-P in the presence of visible light [185]. Pesticides primarily enter the aquatic system through three routes: (a) the agricultural zone, where they are widely used for pest control to protect crops from pests; (b) the waste products of companies that produce pesticides; and (c) residential use. Herbicides, insecticides, rodenticides, fungicides, and plant growth regulators are examples of pesticides [186]. Excessive and uncontrolled use of pesticides can contaminate waterways through agricultural runoff, endangering aquatic life as well as human health. The World Health Organization (WHO) states that, except for dieldrin, heptachlor, epoxide aldrin, and heptachlor, which have an acceptable range of 0.3 ppm, the maximum allowable level of any individual pesticide and the total amount of pesticides in drinking water are 0.1 and 0.5 ppm, respectively. Human digestive, dermatological, cancerous, neurological, endocrine, reproductive, and respiratory issues can all be brought on by excessive pesticide exposure. Ensuring clean drinking water and safeguarding aquatic habitats require the removal of pesticides from water [187]. A combination of techniques designed to address the particular pesticide types present and the intended use of the treated water is frequently necessary for the effective removal of pesticides from water. For sure safe and clean water supplies, these treatment techniques must be improved by ongoing research and technological developments. Pesticide-contaminated water can be successfully treated using a variety of techniques. Furthermore, MOFs' enhanced porosity, customizable pores, and simplicity of production have attracted a lot of attention. Most frequently, π–π interactions, ion exchange, H-bonding, acid–base interactions, and electrostatic interactions are used in the method of removing harmful substances using MOFs. In the adsorption process, electrostatic interactions between oppositely charged MOFs (adsorbents) and surface charges on pollutants (adsorbates) are essential. Fig. 11 describes the adsorption mechanisms of MOFs in the removal of pollutants from wastewater. Here are a few of the most popular methods.

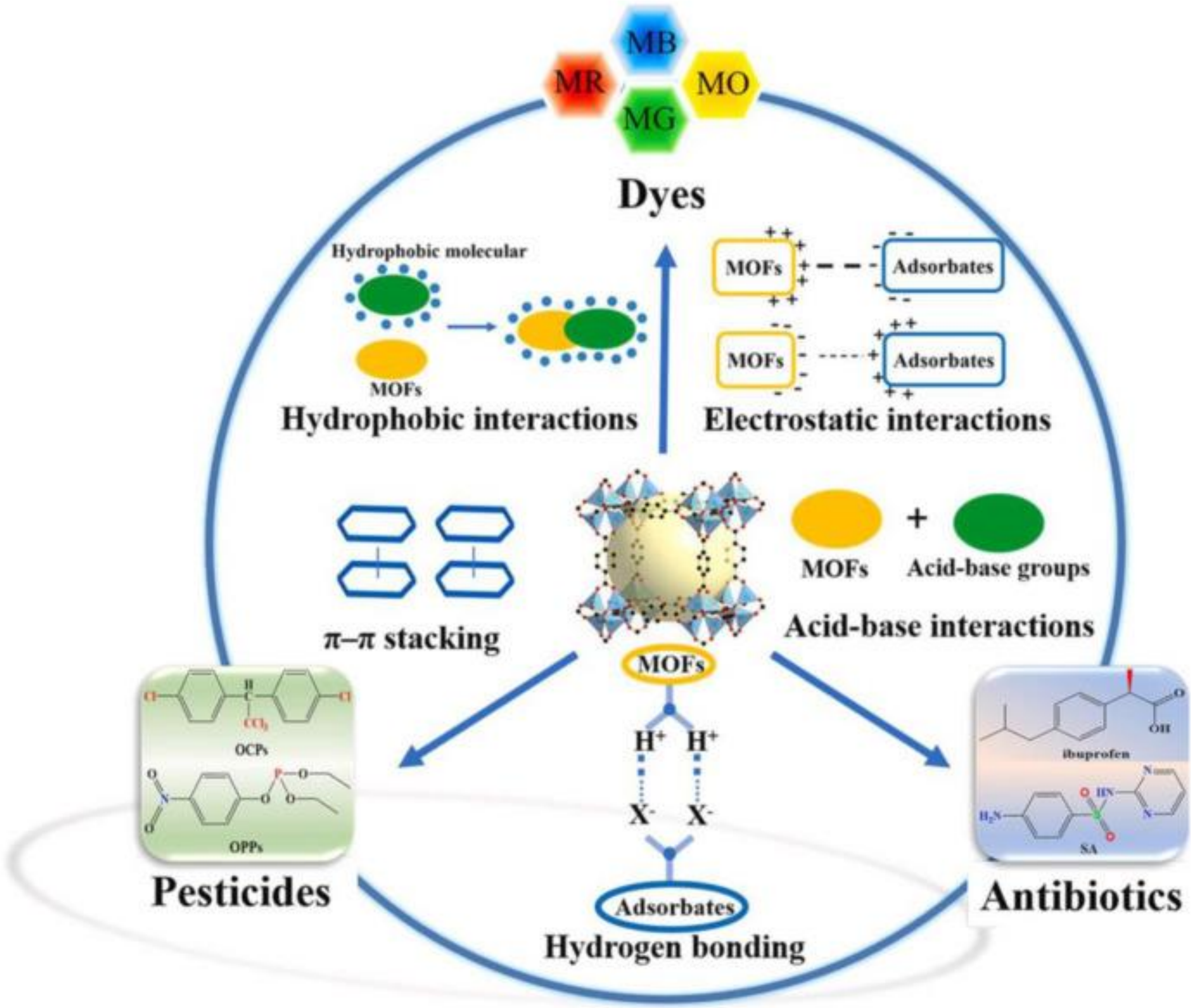

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Fig. 11. The MOFs' adsorption processes. Redistributed under the International Creative Commons Attribution 4.0 License, CC-BY from Ref. [188]. Copyright 2023, ACS.

6.1. Physical methods

A type of treatment approach where the use of physical forces is predominant is known as a physical unit operation [189]. The physical methods category includes not only adsorption but also membrane-filtration techniques including electrodialysis, reverse osmosis, and nanofiltration. The screening, mixing, flocculation, sedimentation, flotation, and filtration processes are commonly employed in the industry. In addition, the physical approach refers to methods that are solely physical in nature and do not involve any significant chemical or biological alterations in order to enhance or treat wastewater. Another way to characterize adsorption is as an equilibrium separation technique that works well for decontaminating water [190].

6.2. Chemical methods

When it comes to treating wastewater, chemical unit procedures are identical to physical treatment in that no microorganisms are used. Chemical treatment is a type of treatment where pollutants are removed or converted through the addition of chemicals or through other chemical reactions [191]. The chemical treatment processes of precipitation, adsorption, and disinfection are a few examples. Industrial wastewaters are frequently treated chemically since microorganisms are not always able to effectively eliminate the contaminants present in them [192]. Moreover, the procedure includes flocculation-inducing chemicals like calcium, iron, or aluminum added to the dye effluent. The procedure has also made use of other agents. To improve the procedure, the two in combination may also be introduced. Strong oxidants that break down pesticides into less hazardous compounds include hydrogen peroxide, ozone, and chlorine. For certain pesticide chemicals, Advanced Oxidation Processes (AOPs) are very effective because they produce hydroxyl radicals. Furthermore, the addition of coagulants can aid in the agglomeration of pesticide particles, which can then be eliminated by filtration or sedimentation [193].

6.3. Phytoremediation

Pesticides from tainted water can be absorbed by some plants and broken down by them. This technique makes use of the ways that plants naturally eliminate or stabilize contaminants. An eco-friendly and sustainable way to treat contaminated water with plants is called phytoremediation. This method makes use of some plant species' innate capacity to absorb, gather, and occasionally break down contaminants such as pesticides, heavy metals, and organic chemicals [194].

6.4. Electrochemical treatment

Electrochemical treatment refers to the use of electrochemical methods to purify contaminated water and wastewater [220]. This approach represents a powerful and versatile technique for addressing water pollution, offering an effective means to treat a wide spectrum of contaminants. Due to its efficiency, adaptability, and ability to handle various pollutants including heavy metals, organic compounds, and microorganisms electrochemical treatment has become a crucial component of modern water management strategies. As technological advancements continue, future improvements in efficiency, cost-effectiveness, and scalability are expected, broadening its applicability in both industrial and municipal settings. By leveraging chemical processes driven by electrical energy, electrochemical treatment provides an innovative and sustainable solution for water purification [221].

Electrochemical treatment involves several fundamental mechanisms that contribute to contaminant removal. One of the primary processes is electrolysis, wherein an electric current is passed through contaminated water. This current establishes an electric field via submerged electrodes (anodes and cathodes), facilitating electrochemical reactions that degrade or remove pollutants [222]. A key mechanism in electrochemical treatment is oxidation-reduction (redox) reactions. At the anode, oxidation reactions generate reactive species such as chlorine and hydroxyl radicals, which effectively oxidize and degrade organic pollutants. Concurrently, reduction reactions at the cathode facilitate the precipitation of metal ions, aiding in their efficient removal from the water [223]. Another widely used process is electrocoagulation, in which metal hydroxides are generated at the anode. These coagulants aggregate suspended particles and contaminants into larger flocs, simplifying their removal through sedimentation or filtration. This method is particularly effective in treating wastewater containing suspended solids, oils, and heavy metals. Electrodeposition is another essential electrochemical technique used to extract heavy metals from water. Through reduction reactions occurring at the cathode surface, metal ions are deposited in solid form, allowing for their selective removal and potential recovery for reuse [224]. Additionally, electrochemical treatment can enhance Advanced Oxidation Processes (AOPs), wherein certain systems generate strong oxidants such as hydrogen peroxide or ozone. These highly reactive oxidants facilitate the breakdown of complex organic contaminants, significantly improving the degradation of persistent pollutants [225].

Overall, electrochemical treatment continues to evolve as a promising water purification technology, offering sustainable and energy-efficient solutions for industrial and municipal wastewater management. Ongoing research focuses on optimizing electrode materials, reducing energy consumption, and integrating hybrid systems to enhance treatment efficiency and economic feasibility.

7. Application of AI and ML

Human water consumption makes wastewater management a complicated topic, and traditional wastewater management techniques have drawbacks of their own. Wastewater management is undoubtedly a benefit of AI, which has been applied in a variety of applications to improve results, but with its own set of drawbacks [195]. With AI combined with the internet of things (IoT), the automation, regulation, control, and many other complex parts of a wastewater management entity would be made simpler. Human error and risks would also be significantly reduced. The use of artificial intelligence and machine learning in wastewater treatment is a noteworthy innovation with several benefits. AI and ML algorithms are making wastewater treatment processes more precise, accurate, convenient, sophisticated, cost-effective, and time-efficient. Data analysis, forecasting models, and wastewater treatment procedures can be managed more effectively thanks to AI and ML. Beyond conventional treatment techniques, these technology advancements are employed for analysis, estimation, and energy optimization. Artificial intelligence (AI)-based systems are able to anticipate discharge quality, provide operational recommendations, and monitor the biological and chemical characteristics of wastewater [196]. The use of AI in water and wastewater management is demonstrated by five main applications: water treatment control, predictive energy optimization, wastewater modeling, prompt response, and wastewater treatment optimization (Fig. 12). These applications demonstrate how AI improves water resource management sustainability, efficiency, and energy consumption. The application of AI and ML to water treatment offers a number of opportunities as well, such as process automation and big data interpretation. Real-time analysis of large data, the identification of patterns and anomalous beauty, and the development of treatment strategies that would enhance results should all be possible with these technologies. Advanced water treatment plant technologies that use AI and ML will improve water quality and efficiency while also lowering operational costs. AI and ML also aid in predictive analysis, which shows a model for maintenance before it fails and schedules it according to specifications [197]. A predictive method like these aids in reducing downtime, extending service life, and preserving the appropriate level of treatment process efficiency.

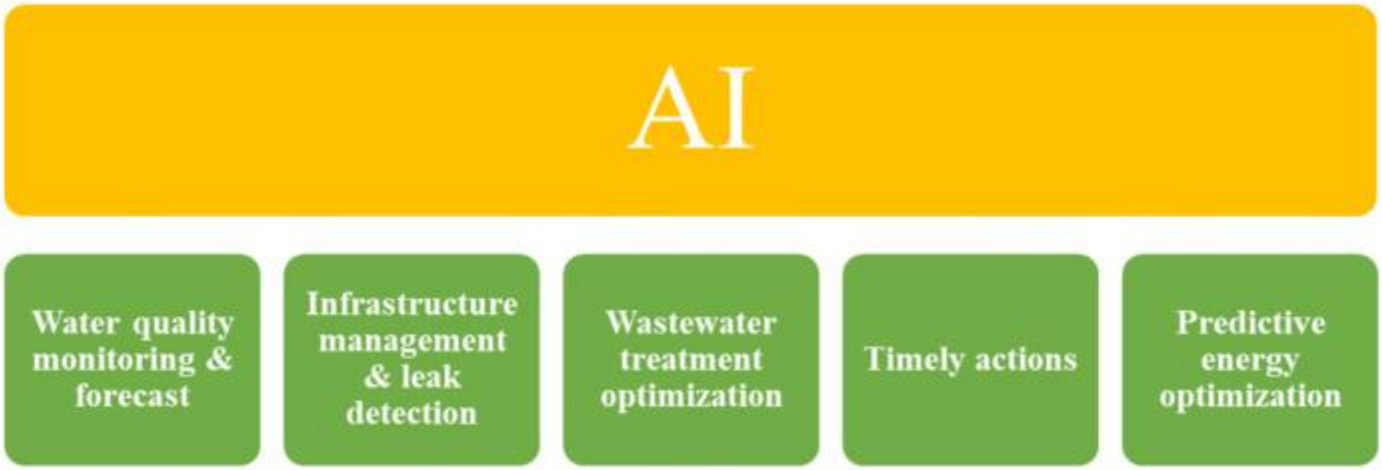

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Fig. 12. Application of AI and ML in waste water treatment.

8. Future prospects

Wastewater management is a pressing issue as the world struggles with growing urbanization, industrialization, and population density. Heavy metals, microplastics, and pharmaceuticals are just a few of the complex contaminants found in modern effluents that are difficult for traditional wastewater treatment technologies to handle. Within this framework, novel technologies are developing to transform wastewater treatment processes, with one potentially promising avenue being nanotechnology. Hence, nanotechnology, artificial Intelligence and other emerging technologies to improve wastewater treatment were recommended future technologies for wastewater treatment.

Nanotechnology: Nanotechnology focuses on the manipulation of matter at the atomic and molecular scale, typically within the range of 1–100 nm. This field offers significant potential for enhancing the efficiency of pollutant removal processes, particularly in wastewater treatment. The promise of nanotechnology lies in the high surface area to mass ratio characteristic of nanoparticles. There are three primary methods for applying nanotechnology in wastewater treatment: utilizing individual nanoparticles, incorporating them into powder or granular forms, and integrating them into membranes or polymers. In the context of permeable reactive barriers and photocatalysts, individual zero-valent iron particles, palladium-coated iron particles, and palladium-coated gold nanoparticles show considerable promise. Nanoscopic materials such as carbon nanotubes and alumina fibers, when wrapped around a carbon block filter structure, as well as TiO_2/Al_2O_3 membranes and carbon nanotubes embedded in zeolite filtration membranes, are also effective in eliminating water contaminants. Nanotechnology offers several key applications in wastewater treatment. Nanofilters, made from materials such as carbon nanotubes and graphene oxide, enable the selective removal of water pollutants. These advanced membranes demonstrate exceptional permeability and selectivity, effectively separating contaminants while minimizing fouling. Additionally, in advanced oxidation processes (AOPs), nanoparticles serve as catalysts to accelerate the breakdown of pathogens and organic pollutants. For instance, titanium dioxide nanoparticles, when activated by UV radiation, generate reactive oxygen species that degrade harmful substances in wastewater. Furthermore, specifically engineered nanoparticles can adsorb certain pollutants, including heavy metals and pharmaceutical residues. This tailored approach allows for the efficient removal of contaminants even at low concentrations.

Artificial Intelligence and Machine Learning: Artificial intelligence (AI) and machine learning (ML) have the potential to revolutionize decision-making and operational efficiency in wastewater treatment. By analyzing large-scale treatment plant data, these technologies enable real-time monitoring of water quality parameters, optimization of chemical dosages, and predictive maintenance. AI can enhance the overall effectiveness of treatment facilities and reduce operating costs by automating repetitive tasks and providing valuable insights. Given the global challenges of pollution and water scarcity, efficient wastewater treatment has become increasingly crucial. Traditional methods often struggle to cope with the volume and complexity of pollutants in modern effluents. In this context, AI and ML technologies are making a significant impact, offering opportunities to improve the sustainability, reliability, and efficiency of wastewater treatment operations. This essay explores the applications, benefits, and future prospects of AI and ML in this critical field. One of the key applications of AI and ML in wastewater treatment is process optimization. AI algorithms can adjust operational parameters such as chemical dosing, aeration rates, and flow management by analyzing real-time data from sensors deployed in treatment plants. This dynamic adjustment can help reduce energy consumption and chemical usage, while simultaneously enhancing treatment efficiency.
Another important application is predictive maintenance. Many machines and equipment in wastewater treatment plants require regular maintenance. AI can forecast when equipment is likely to malfunction or need servicing by analyzing historical performance data. By implementing predictive maintenance strategies, facilities can reduce maintenance costs, extend equipment lifespan, and minimize downtime.

Quality monitoring is another critical aspect of wastewater treatment, and AI-powered systems excel in this area. These systems can monitor various parameters such as turbidity, pH levels, and the presence of specific pollutants. Through real-time trend or anomaly detection, AI can alert operators to take prompt corrective actions, thus improving regulatory compliance and ensuring water quality.

In addition to these applications, AI and ML can optimize data management processes. Wastewater treatment generates vast amounts of data from sensors, laboratory tests, and operational logs. AI and ML can automate the collection, processing, and reporting of this data, ensuring that decision-makers have access to timely and accurate information while saving time.

Resource recovery is also an area where AI can make a significant impact. AI can optimize processes for extracting valuable resources, such as nutrients and energy, from wastewater. For example, machine learning algorithms can identify the optimal conditions for biogas production or nutrient recovery, supporting a circular economic approach in wastewater treatment.

Overall, AI has the potential to significantly enhance the efficiency of wastewater treatment operations through real-time process optimization. This leads to reduced operating costs and improved pollutant removal. Additionally, AI-driven insights allow operators to make well-informed decisions based on data rather than intuition or experience, resulting in better adherence to environmental standards and more effective management practices.

Decentralized Treatment Systems: Particularly in rural or rapidly urbanizing areas, decentralized wastewater treatment systems provide a flexible substitute for typical centralized facilities. Large-scale infrastructure is not necessary when using technologies like modular treatment units and built wetlands, which may be installed at the place of usage. By recycling nutrients and reusing water, these systems not only lessen the strain on centralized plants but also advance resource recovery.

9. Conclusion

A major problem for humanity is water shortage, which is caused by things like population growth and the effects of climate change. Wastewater treatment becomes a critical step in protecting human health and the ecosystem at large. However, initiatives to improve water quality and treatment struggle to keep up with our communities' rapid expansion. The problem of water shortage is made worse by human activities that have complex effects on water supplies, such as changing the landscape and introducing contaminants. The paper covered the latest developments in wastewater treatment technologies. Efficiency, environmental compatibility, cost-effectiveness, selectivity, and resource recovery are all areas where each technique has special advantages. Implementing wastewater treatment facilities that are suited to these needs is required due to variations in wastewater properties, local site-specific factors, and treatment aims. Combining different treatments is typically necessary because a single technique is frequently insufficient to meet the goals of treatment. It was made abundantly evident that in order to purify produced water to a level that permits safe reuse rather than re-injection into water disposal wells, integrated systems comprising various technologies are necessary. Fouling, material degradation, and maintainability are frequent issues that still need to be resolved, and they have an impact on sustainability and the rate at which pollutants degrade. Moreover, the advent of novel technologies, such as nanotechnology, AI, and decentralized systems has improved our capacity to identify and eradicate a broad spectrum of pollutants. Real-time monitoring and treatment process optimization are made possible by the integration of smart technologies, such as IoT and AI, which lowers operating costs and improves performance. These innovations not only tackle the pressing issues of environmental contamination and water scarcity, but they also advance the ideas of the circular economy by recovering important resources like energy and nutrients. Generally, to create a reliable treatment process for this kind of water, the choice of combination treatment technologies should be a major focus area from both a theoretical and experimental perspective.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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