Sustainable environment through using porous materials: a review on wastewater treatment

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Abstract

Porous materials play an important role in creating a sustainable environment by improving wastewater treatment's efficacy. Porous materials, including adsorbents or ion-exchangers, catalysts, metal-organic frameworks, composites, carbon materials, and membranes, have widespread applications in treating wastewater and air pollution. This review examines recent developments in porous materials, focusing on their effectiveness for different wastewater pollutants. Specifically, they can treat a wide range of water contaminants, and many remove over 95% of targeted contaminants. Recent advancements include a wider range of adsorption options, heterogeneous catalysis, a new UV/H_2O_2 procedure, ion exchange, Fenton oxidation, membrane activities, ozonation, membrane bioreactor, electrochemical treatment, wet air oxidation, and a carbon capture methodology utilising various porous materials. A particular focus for innovative research is on developing technologies to synthesize porous materials and assess their performance in removing various pollutants from wastewater at varying experimental conditions. Porous materials can be essential in designing wastewater treatment systems to address the critical environmental issues of water stress and safe drinking water worldwide.

Keywords: Sustainable environment, Porous materials, Wastewater treatment, Adsorption, Catalyst, Membrane

1 INTRODUCTION

The progress of any country is contingent on the available resources, whether they are used for production, distribution, or consumption. Natural resources–particularly water – are being used at an escalating rate, creating shortages and issues of pollution that must be addressed for long-term sustainability. Using one key natural resource, such as water, impacts other parts of the biosphere; thus, addressing pollution and contamination in one resource can positively impact other natural resource systems. The United Nations has identified clean water and sanitation as one of its central Sustainable Development Goals, noting that progress toward safe, sanitary access to water must increase fourfold to reach the goal of universal clean water access by 2030.[1] Chemical engineering and other fields involved in manufacturing processes can play an important role in reducing contamination to alleviate worldwide water stress so that this goal can be met. Chemical engineering and related fields now emphasise enhancing substance treatment, manufacturing and chemical disposal processes as a part of rehabilitating water systems and preserving them for future generations. Such research began after Anastas et al.'s initial publication of "green chemistry" in 1998, bringing the field's attention to the need to reduce hazardous substances in chemical processes. Therefore, emerging sustainable materials and related industrial developments are paramount for ensuring water resource access and quality over the long term. One key sustainable material, and the focus of this review, is porous materials.

Porous materials' applications can contribute to greener water management and alleviate water stress by reducing hazardous materials' impact on the water supply. It is advantageous as an adsorbent due to its large surface area, making it highly efficient for various industrial purposes. Different porous constituents are currently discovered and developed, categorized based on their leading structural materials: carbon-containing, oxygen-based, organic polymer-based, nanoparticle-containing, ionic liquid-based, and composite material-based adsorbents. One key structural aspect is the material's pores, which shape the function of the materials. Porosity is the most effective property of solids that affects their validation for a specific application. This property varies based on the synthesis method, circumstances, and their precursors. Materials' porosity could be intrinsic or extrinsic, which is a unique property that

might predominate in several natural and synthetic materials. These are classified as organic, inorganic, and hybrid organic-inorganic materials, and each is characterised by different pore sizes. According to the International Union of Pure and Applied Chemistry (IUPAC), porosity is classified into three types based on diameter:

(i)   Microporosity (pore diameter < 2 nm)

(ii) Mesoporosity (pore diameter 2–50 nm)

(iii) Macroporosity (pore diameter > 50 nm[2]

Porous solids may have only one porosity level or more. Multi-level solids are typically known as hierarchically porous materials.[3] The porosity of the used solid material can limit any application by restricting the species diffusion from/into the internal surface area and active sites. So far, porous materials have been synthesized to have multi-level porosity to cope with this problem.[4] Multi-level porosity can solve this problem by interconnected micro-meso-macropores that control highly efficient diffusion and interchange properties and exhibit great potential in nanotechnology, energy transformation and cell rehabilitation. These multi-level solids are eco-friendly because of their capability to separate CO_2 from other gases via gas-solid interactions. Thus, eco-friendly crude initiatives are applied at modest production conditions and linked to the most critical industries and applications. [5,6]

This present review article sheds light on porous materials' critical role in the current wastewater treatment techniques. It explains how they contribute to sustaining safe water resources. Good quality, inexpensive with large surface areas and a range of treatment competencies has been developed as innovations in sustainable approaches to water treatment. This review paper outlines the latest development in using porous materials in water treatment. It discusses the different feedstock-based porous materials and their applications for wastewater treatment in the context of sustainable development, with a specific focus on new porous materials that can optimize the treatment process and enhance the functionality of relevant wastewater treatment technologies.

2 WASTEWATER TREATMENT

Wastewater is released from different discharges to the water bodies. It can contain contaminants that cause severe problems to both human and aquatic life. Water can be polluted by various wastes such as salts, radioactive elements, heavy metals, organic pollutants, dyes, oil spills, and pharmaceutical wastes. Population growth and industrial expansion both raise water demand. This demand creates an exigence to find feasible methods for reusing polluted water safely.[7] Different treatment technologies have been developed to remove these contaminants. Effective options for porous materials are in high demand for these technologies because, recently, it has shown enhanced contaminant segregation compared to others associated with acceptance capacities and selectivity due to their versatile functionality. Several characteristics make porous materials important for wastewater treatment. These aspects are summarized below in the Table 1.

TABLE 1 Characteristics of porous materials

Characteristics of porous materials as	Relevance of features in wastewater treatment	References
Adsorbent - Pore size distribution forming the porosity of the adsorbent. - Microporosity, mesoporosity, and microporosity forming the external and internal large surface area and contributing to the high adsorption capacity. - The external surface containing variable functional groups such as carboxyl, carbonyl, phenol, quinone, lactone, etc. - Chemical complexity if chemisorption occurs.	- The adsorption performance of the adsorbent for the pollutants depends on the pore size distribution and the surface functional groups. - The adsorption mechanism depends on the chemical properties of the adsorbent surface and the pollutant's nature.	**8**
Ion-exchanger - Pore size distribution forming the porosity of the adsorbent. - Microporosity, mesoporosity, and microporosity forming the external and internal large surface area and contributing to the high adsorption capacity. - The internal surface containing the ions or cations to be exchanged. - The external surface containing variable functional groups if the exchanger is made as composite of organic and inorganic materials. - Chemical complexity only if chemisorption occurs.	- The exchange performance depends on the convenience of the pore size and porosity level of the exchanger to the size of cations of the metals to be removed. - The ion-exchange mechanism depends on the structure and surface-chemical properties of the exchanger and the polluting metal properties. Therefore, engineering a convenient porous ion-exchanger determines the removal performance.	**8**
Catalyst - Pore size distribution and internal large surface area contributing to the high catalysis performance. - The catalyst porosity and shape selectivity. - The internal surface containing the active sites for catalysis.	High porosity and large internal surface area accommodating the active elements which leads to high catalysis performance.	**9**

• Catalyst stability under harsh treatment conditions, especially for heterogeneous Fenton type catalysts based on porous supports such as zeolites, mesoporous silicas, clays, etc.	• An extra motivation for utilizing solid Fenton catalyst is providing the potential stabilization of the less stable reduced Fe(II) or Cu(I) oxidation states by a suitable (porous) support.	
Membrane i. Membranes include adsorption and filtration such as electrospun membranes: • High porosity, specific surface area, and easy regeneration make the membranes talented materials for uptaking the contaminants from aqueous solutions. • The engineered layered structure on the porous fibers offers more adsorption sites, special charges, and functional groups which increase the capacity and rate of adsorption. ii. Porous MF, UF, and MD membranes where the rejection is based on the size exclusion and electrostatic charge effects. • The pore size and porosity of the membrane for the selective portioning of the uncharged pollutants by size exclusion (pore sieving). But for ionic species, the rejection is affected by the size exclusion and electrostatic interactions. • Other surface properties including membrane surface roughness and surface wettability raised from the membrane's porosity.	• High porosity, large specific surface area, and high pore size uniformity, are expected to make the membranes effective materials for wastewater treatment. • Effectively promoting the separation flux. • The separation efficiency and antifouling of the membrane can also efficiently be improved through composing special wettability on the membrane's surface. • The adsorption and pore-blocking of the membrane is the main reason for fouling during the treatment of dye polluted wastewaters.	**10, 11**

Below are the most common methods that utilize porous materials for treating wastewater:

2.1 Membrane filtration

Research emphasis on wastewater is increasing due to the importance of removing contamination and reusing water. Additionally, this process is related to environmental concerns and contributes to a greener society. Because membrane separation techniques involve low costs, lesser energy consumption, clean, feasible, and flexible design systems with high-quality water with reduced area requirement,[12] they are crucial to developing effective green technologies for wastewater treatment. A pressure gradient, concentration gradient, temperature gradient, and electrical current lead to the membrane-based separation depending mainly on the presence of a porous membrane (semipermeable membrane), as shown in Figure 1.
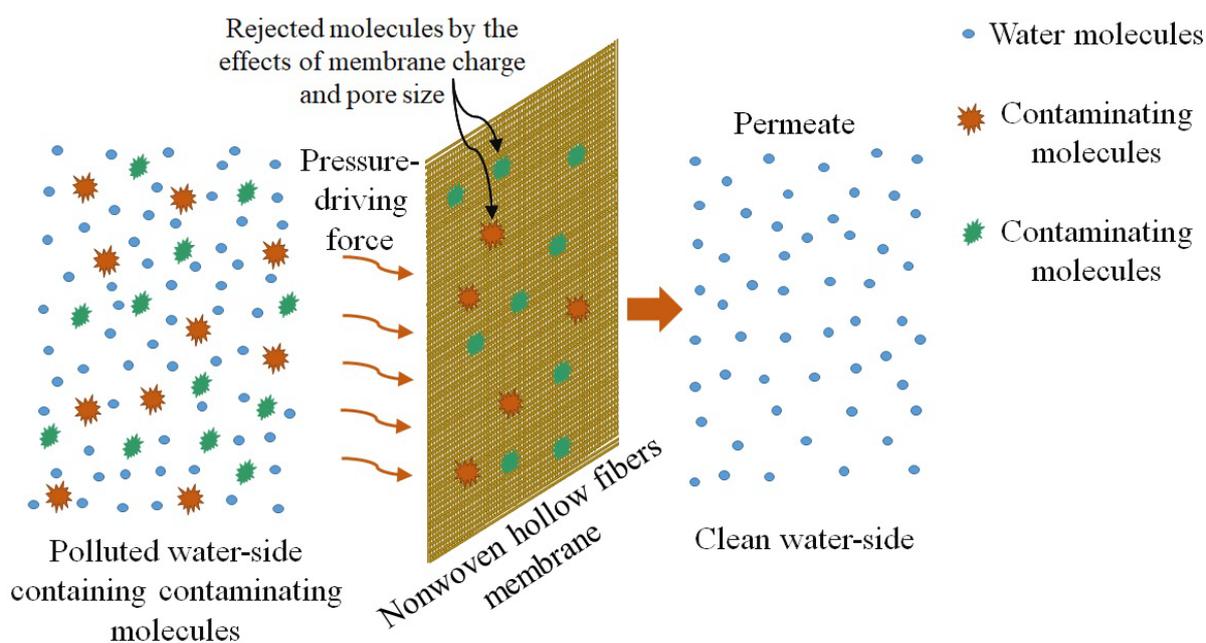

FIGURE 1 Wastewater treatment by membrane separation

Membranes can be one of the following four major types, which are categorized based on the rate of treatment:

i.   microfiltration (MF) membrane with screens particles of 0.1–0.5 mm
ii. ultrafiltration (UF) membrane with screens particles of 0.005–0.05 mm
iii. nanofiltration (NF) membrane with screens particles of 0.0005–0.001 mm,

iv. reverse osmosis (RO) membrane with molecular size below 10 molecular weight cutoff (MWCO).[13,14]

MF and UF are low-pressure, vacuum, immersed driven membranes; NF and RO are high-pressure operated membranes. Usually, the treatment process includes the electrodialysis (ED) membrane, electrodeionization (EDI) membrane and electrodialysis reversal (EDR) membrane for periodic changes of the polarity as a water-softening process which are nothing but an electrical current-driven membrane treatment progression. Hence, selecting a proper membrane process is based on the blend present in the water and the domine of terminated effluents. For example, pressure-driven membrane techniques are used for industrial wastewater treatment and natural water for household and drinking needs.[14] The structure of a membrane is crucial for its characteristics and separation process because it specifies the operational parameters and the implementation of the filtration process. Semi-permeability is the most critical property of the membranes, which permits selective passage and retention of the species. This property determines the membrane action based on its structure and succeeding characteristics like permselectivity, hydrophilicity or hydrophobicity properties.[15] Membranes can be categorized based on their structure, as shown in Figure 2. The possible structures are: dense, porous (symmetric or asymmetric), and composite.[16] Dense homogeneous polymer membranes are commonly made from a solution by solvent evaporation or by extrusion of a melted polymer. Due to their low permeate flow, these membranes can be practically used when synthesized with highly absorbent polymers like silicone.[16] The asymmetric membranes integrate the property of a high permeate resulting from a relatively thin selective top layer, with the underlying porous structure providing proper mechanical stability.[17] The symmetric membranes can also be either isotropic or anisotropic. Isotropic membranes have uniform physical structure and composition, broadly used for microfiltration. Microporous isotropic membranes have relatively high permeation fluxes. When these are non-porous, which have a much tighter cell structure preventing ease of flow, ultimately reducing the permeation fluxes due to their minimized application. Therefore, their application is minimal. Furthermore, anisotropic membranes are non-uniform membranes with different compositions and structures. They have a thin selective layer supported by a thick, highly absorbent layer. The thin-film composite membrane, which consists of a dense top layer covering a porous structure, was introduced as an alternative to the asymmetric membrane.[17]

The different types of membranes used in the water treatment were highly influenced by the materials, pore sizes and applications (Table 2).
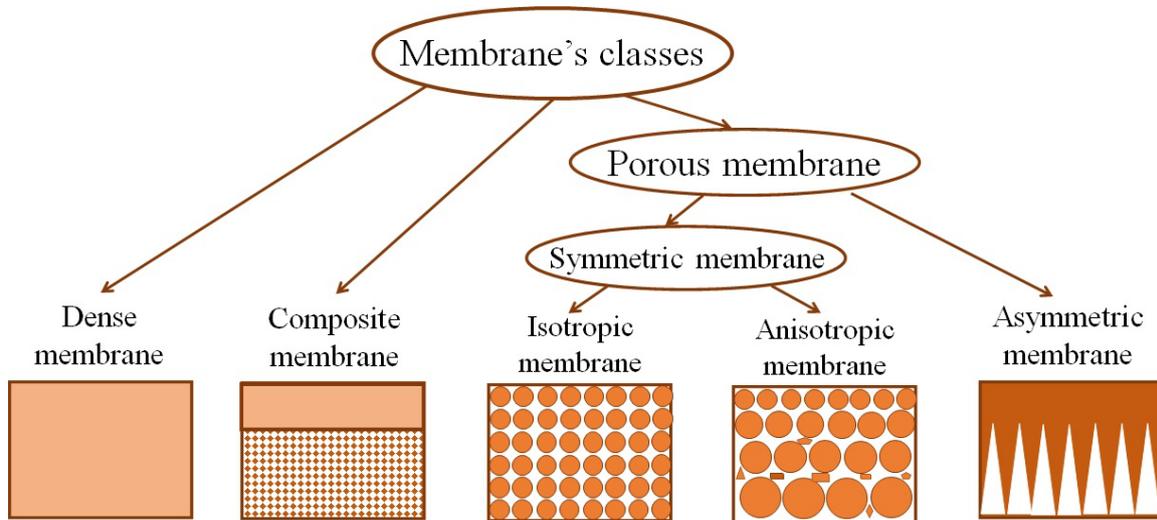

FIGURE 2 Classification of membranes based on morphology, adapted from[15,16]

TABLE 2 Classification and usability of membranes

Classification	Use in water treatment	Effectiveness	References
Dense membrane	• Most of the applications of polymeric nanofiltration membranes. • Separation of organic-water mixtures by pervaporation. • Dense type nanofiltration membranes are employed in separation (multivalent) ions from a solvent and relatively small organic compounds. • Separating salts from dye solutions. • The extraction of the natural products presenting in highly concentrated form via separation of acids from sugar solutions.	• To achieve separation on a molecular scale, a relatively dense membrane is required. • The quite low permeate flow across the membrane because it is important to keep a minimal thickness to allow the mechanical stability for a membrane.	**18**
Composite membrane or Thin film composite membrane	• Wide employment for wastewater reclamation • Desalination of brackish and sea water, • The purification and separation of chemical and biological species.	• The most important advantage of a composite membrane is the possibility of optimizing the top layer and the support. • Achieving the desired permeability and selectivity combined with owning mechanical strength and excellent compression resistance through optimizing both the top selective layer and bottom porous substrate. • This type of membrane has a mechanical strength membrane arising from supporting the thin selective layer by a strong support layer. • These membranes are engineered to consist of two or more highly selective polymeric layers which being coated as a dense ultrathin layer on a one or more porous support layer (sublayer),	**19**

		which is often an ultrafiltration membrane serving as a support. This is reflected in presenting selective separation by a durable membrane. • Reducing the overall transport resistance.	
Isotropic membrane	• Dialysis • Electrodialysis • To some degree, in microfiltration	• The merit of having a uniform structure throughout the entire membrane thickness i.e. uniform pore size or nonporous. • The possibility of increasing the permeation rate and reducing the total resistance of the mass transfer through optimizing the reduction in membrane thickness.	**20**
Anisotropic membrane	Likewise its work as an asymmetric membranes, they are mostly used in the pressure driven membrane processes like: • In reverse osmosis • Ultrafiltration • Microfiltration	Having the same unique features of asymmetric membranes which are: • High fluxes i.e. high permeate flow per unit area • Credible mechanical stability equipping a quite superfine selective layer. • This kind of membrane provides various ranges of effective separation properties depending on the nature of the material been used for preparation or the pore size in the skin layer (top layer). This is because the skin layer (porous layer) is responsible for membrane selectivity and the resistance to the mass transfer.	**21**
Symmetric membrane	This kind of membrane gathers the applications of isotropic and anisotropic membrane, including: • Reverse osmosis • Ultrafiltration • Microfiltration	• Uniform physical structure and composition to provide the required selective separation and permeation rate. • If they are microporous isotropic membranes, they allow comparatively high fluxes relative to that given by nonporous (dense) membranes	**22**

	• Dialysis • Electrodialysis	which have extremely limited application because of their low permeation fluxes. They showed wide applications as microfiltration membranes. • If they are anisotropic membranes, their non-uniform porosity over the membrane area allows high permeablity	
Asymmetric membrane	This kind of membrane with random pore sizes is widely applied in microfiltration separation such as employment of most ceramic membranes which have an asymmetrical membrane structure for oily water purification.	• Allowing reasonable permeating flux when compared to symmetric membranes because the flux determining top layer of the asymmetric membrane can be very thin. • The high possibility of enhancing the separation properties of the membrane by changing the preparation parameters of specifically the thin top layer.	**23**

Currently, most available membranes are asymmetric. Various techniques are applied to synthesize the thin-film composites, which include a slightly complex procedure with numerous steps to control the materials' pore size.[16,17] Currently, these membranes are synthesized from different polymers, commonly using the "phase-inversion" method to fabricate asymmetric structures. Therefore, this method is significantly utilized to produce polymeric membranes helpful in treating various pollutants in wastewater. However, several techniques such as interfacial polymerization, track–etching, stretching, and electrospinning other than phase inversion are also applied in the industry to fabricate the membranes.[16] With due respect, the gas separation industry favours polymeric membranes due to their more straightforward fabrication methods and lower costs. Its main drawback was lower stability in organic solvents above 200°C temperature. However, the membranes were fabricated using poly(oxindolebiphenylylene) included higher thermal stability up to 500 °C in its oxidative environment.[24] Also, the glassy polymers showed the enhanced capability to separate gases like carbon dioxide and hydrogen at higher temperatures (250 °C). As well as VTEC polyimide films remain robust and bendable after numerous thermal runs up to 400 °C.[25] Consequently, membranes synthesized by applying inorganic materials are required higher temperatures for operation. They can be prepared from microporous ceramics, alumina, metals, zeolites, and carbon. Also, they can be made from dense metals, such as palladium, which permit the selective diffusion of tiny molecules like helium and hydrogen.[17] These different types of membranes are commercially used for wastewater treatment. Current studies are being conducted to evaluate their relative performances. Membranes containing both the polymeric texture and inorganic materials are called mixed matrix membranes (MMM). MMMs are membranes that combine the merits of polymeric membranes and inorganic materials. A critical value is metal oxides, which effectively reject pollutants from wastewater.[26] Various inorganic additives have been included in the synthesized MMM for wastewater to upgrade the overall membrane operation, i.e. improved permeation, fouling resistance and separation capabilities.

Wastewater frequently contains dyes, particularly from an area with textile or cosmetic processing plants. Removing dyes from wastewater is critical because many organic dyes are highly toxic and carcinogenic and pose significant health risks.[27] Deploying inorganic coagulants is one approach to removing dyes from wastewater. However, it generally requires high chemical dosages of the coagulant and produces large quantities of sludge; thus, this

process is high-risk, high-cost, and environmentally uncertain. Different approaches to using porous materials within dye-related wastewater treatment can offer better outcomes. Removing dyes from water can be achieved using different types of membranes. For example, Alsalhy et al.[28] used ZnO nanoparticles (0.025-0.03 wt.%) added to a casting solution of poly(phenyl sulfone) (PPSU). The membrane's porosity was changed by creating a layer of finger-like pores nearby the support layer and spongelike pores close to the layer adjacent to the membrane's top surface. As a result, it enhanced the fabricated membrane's porosity, which typically influenced the pure water's hydrophilicity and permeability, crucial for dye separation from aqueous solutions. Another approach by Ghadhban et al.[29] involved preparing a membrane by blending 19.2% PPSU and 0.8% polyethersulfone (PES), which could increase average roughness and porosity. It also improved pure water's permeability by 25% by reducing the contact angle. It can potentially remove dye (Drupel Black NT) to 96.62% from a feed solution with a dye concentration of 50%. The UF MMM's capability might be enhanced to remove dyes (acid black and rose Bengal) by incorporating graphene oxide nanoparticles (GO-NPs) in a casting solution with PES. Typically, the GO-NPs are imposed to change the fabricated MMM's structural morphology by altering their porosity, reducing the contact angle and increasing the flux, indirectly enhancing the dye's rejection and antifouling properties and improving long-term operation from 14 to 26 days.[30]

Dye-contaminated water has also been studied with inorganic membranes. For example, considered the ceramic-supported carbon membrane bioreactors and GO membrane bioreactors were applied to remove azo dye mixtures containing tri azo direct blue 71 dye, diazo reactive black 5 dye, and monoazo acid orange 7 dye from the aqueous solution. Also, these membranes were used to remove other dyes that do not belong to the azo family, such as ethylene blue dye and Rhodamine B dye, from aqueous solutions. The conductive property of the GO membrane surface resulted in a more efficient and higher color removal of all dye solutions than ceramic-supported carbon membrane bioreactors at a wide range of feed concentrations and permeated flux.[31] Other researchers[32] fabricated a continuous compact membrane bioreactor consisting of ceramic-supported GO membrane (CSGoM). They used it for anaerobic bio-decolourization of diazo reactive black 5, monoazo acid orange 7, and triazo direct blue 71 from aqueous solutions. The biodecolorization for all azo dye solutions was steady irrespective of the feed concentration at low permeate flux. While at higher permeate flux and feed concentration, the decolorization marginally decreased to 93% for monoazo

solution, 85% for diazo solution, and 81% for triazo solution. Overall, it is clear that removing dyes using polymeric membranes was more efficient than inorganic membranes in terms of the dye's rejection percentage. Still, its performance is relatively weak in acidic, polluted media.

Another key polymer option for wastewater treatment is hyper-cross-linked porous polymers (HCPs). HCP porous materials are biodegradable, and they have a high surface area. These HCPs are effective for removing dye as well as organic and inorganic contaminants, toxic metal ions, and nutrients.[33] The benefits of HCPs include a wide array of surface areas and energy efficiency options, particularly when a continuous flow synthesis is used.[34] Therefore, selecting a suitable additive to the polymeric material is essential because it improves dyes' separation performance from aqueous solutions. Similarly, the surface nature of the fabricated membrane determines its function in removing specified ions and salts from water. Hence, altering the used precursors in fabrication could change the membrane's porosity, hydrophilicity, and surface charge. For example, PES was used to fabricate micellar-enhanced UF (MEUF) for studying the removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions from wastewater in the presence of sodium dodecyl sulfate (SDS) as an anionic surfactant at a wide pH range of 1-12.[35] PES is the most used polymer because studies show that moderated hydrophilic polymers in fabrication membranes effectively remove heavy metals. Accordingly, PES was utilized by Hadi et al.[13] to fabricate three hollow fibre membranes with different levels of PES content and investigate its influence on the morphological structure of the produced membrane as well as the removal performance of toxic metal ions (Cd^{2+} and Pb^{2+} ions individually). The higher PES content membrane had a smaller pore size, narrow pore size distribution, and larger thickness. This membrane gave the maximum rejection of Cd^{2+} ions (78%) and Pb^{2+} ions (99%) from a single solution containing 10 ppm of metal ions and pH of 6.5 for Cd^{2+} ions and 6 for Pb^{2+} ions. Also, the membrane with high PES content performed better in the removal process than the other fabricated membranes when they were used to removed^{2+} ions, Co^{2+} ions, and Pb^{2+} ions from binary and ternary aqueous solutions.[36] Adding hydrophilic porous inorganic to organic membranes can enhance the produced membranes' structural properties, and it is another approach to removing heavy metal ions. Improving these structural properties positively impacts wastewater filtration. Zeolites with a low silica-to-alumina ratio can be excellent inorganic membrane additives to remove heavy metal ions. Abdullah et al.[37] removed 97% chromium ions using a membrane containing 0.8% NaY zeolite and 15% PES from a solution containing 150 ppm of chromium ion at a pH of 6 and trans-

membrane pressure of 1 bar. Similarly, 90.2% removal of 137Cs from actual nuclear liquid waste was achieved by applying a PES membrane prepared with 0.15% NaY at pH 7.5,[38] likely using 0.9% NaX zeolite in 20%wt. A modified PES UF membrane yielded the highest rejection of Pb^{2+} ions (97%). This rejection figure was obtained by creating a new porous structure within the MMM's texture, increasing the porosity, and reducing the contact angle of the prepared MMMs.[39] These studies showed that using the same polymer but changing the additive or the concentration of the additive and the polymer can produce a membrane that can be used for different functions. For example, a cellulose triacetate (CTA) membrane was applied in the forward osmosis (FO) process to treat industrial wastewater resulting from the tanning plant containing Cr^{3-}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+.[40] FO using PPSU NF fibres was also applied to desalinate saline water.[41] The PPSU amount and fabrication conditions affected the porosity and thickness of the produced fibres, which were reflected during desalination in a highly concentrated NaCl solution. Increasing the amounts of PPSU reduced the specific reverse flux of salt.

Even when the treatment method changes, the polymeric membranes and MMMs have proven their performance in eliminating ions and complex salts from water. Another desalination case involved using ZSM-22 nano additives embedded PES membranes texture to desalinate modelled brackish water made of $MgCl_2$ and NaCl. Adding high porous ZSM-22 nano additives to the membrane mixture improved the membrane permeability and anti-fouling properties.[42] The poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) flat sheet membranes by phase inversion were used for membrane distillation (MD). The findings showed that the high polymer concentration (15 wt.%) sharply reduced the permeation and salt rejection by decreasing surface pore size and increasing membrane thickness. Also, adding lithium chloride to the casting solution positively impacted the membrane's porosity and pore size. Still, it negatively impacted the membrane's mechanical properties.[43] Therefore, the successful removal of salts and ions can be achieved by optimizing the most critical factors affecting the porosity: the internal structure and the surface charge of the prepared membrane. Inorganic membranes have also been applied in treating effluents containing salts. The ceramic tubular MF membrane consisting of alumina (70%), yttria (5%), and zirconia (25%) were used for the simultaneous removal of humic acids, different heavy metals and high NaCl concentrations.[44] The difficulty here is that heavy metal ions at high salinity levels sharply increased the retention of humic acids. However, it was slightly affected by the trans-membrane

pressure. Similarly, a tubular ceramic made of a layer of TiO_2 coating porous alumina support (0.9 nm TiO_2 NF membrane) as a model NF membrane was used to understand the rejection mechanism of several negatively charged salts.[45] The rejection mechanism of these solid porous membranes is highly dependent on the Donnan effect based on the charge density and electrostatic interactions between ionic solutes. Finally, that positively alters the matrix's fixed electric charges and could work with negatively and positively charged membranes.

As the pollutant water is an admixture of various organic and inorganic species, the separation by membrane technology has also been developed to remove organic pollutants. For example, polyvinyl chloride/functionalised multi-walled carbon nanotube (PVC/F-MWCNT) membranes and PVC/GO membranes were improved to enhance their capability to remove chemical oxygen demand (COD) from actual petroleum wastewater. The membranes fabricated with 0.12 wt% of GO and F-MWCNT showed improved porosity, tensile strength, and contact angle. The PVC/F-MWCNTs membrane achieved a higher COD rejection of 88.9%.[46] Also, the antifouling property of a PPSU flat sheet membrane was improved by embedding it with tungsten oxide and graphene oxide (GO-$WO_{2.89}$) and it showed high permeation flux when it tested in the removal of bovine serum albumin (BSA) from water.[47] Therefore, these improvements to the GO-$WO_{2.89}$ membranes improve the pure water permeability and contaminants removal. Moreover, organic compound elimination using a modified electro membrane bioreactor (EMBR) fabricated with the sponge-like property of the MWCNTs was found to perform better than a nanotube-coated sponge–MBR (NSMBR).[48] Conclusively, the porosity and the pore's shape change according to the type and concentration of the polymer and the concentration and nature of the additive. Turning the pore shape to figure-like, primarily by adding the oxides in some way, increases the hydrophilicity, and the correspondent permeates flux. Also, an addition to the casting solution to prepare an MMM or co-polymer membrane will create new functions which can influence the pollutants' retention and reduce the resultant membrane's antifouling property. Therefore, any alteration in the membrane's precursors will impact the outcome of a process wherein a porous membrane is used and thus influence the wastewater treatment holistically. Unlike solid inorganic membranes, utilising polymeric membranes becomes inconvenient when applications must work at elevated temperatures and under harsh conditions. Such conditions require reasonable mechanical and thermal stability. Solid inorganic membranes provide the necessary stability because of the advantages of resisting extreme chemical cleanup, higher temperature and

corrosion resistance, long life, and autoclavable. Several inorganic membranes which vary in type and porosity have been evaluated,[17] such as asymmetric microporous α-alumina tubes whose inside surface contains 40–100 Å pores. The outside surface contains 100,000 Å pores. Other oxides or polymerization–pyrolysis products may contain microporous glass tubes and pores. Silica hollow fibres have 3–5 Å pores. Porous glass, ceramic, or polymeric materials are coated by a dense, thin film (only a few μm thick) of palladium metal. Others, like pyrolyzed carbon, sintered the metal and zirconia on sintered carbon. They are classified as membranes with excellent pores, i.e. less than 10 Å, and thus satisfactory for gas mixture separation. In contrast, membranes with larger pores (i.e. larger than 50 Å) are necessary to separate solid particles from aqueous solutions consisting of small molecules or large molecules. Some of these inorganic membranes have met various applications, treating effluents containing undissolved matter, oil and different organics. For example, oily wastewater treatment was studied using a ceramic MF membrane in a dead-end filtration system. This membrane achieved a maximum oil rejection of 99.7% and a reduced permeate flux of 17.2 l/m^2.h at an oil feed concentration of 1200 mg/L.[49] Comparable fluxes and separation factors with a trade-off between separation and high flux were achieved using zeolite membranes. These are prepared from A zeolite, mordenite, and clinoptilolite and implemented to separate ethanol dehydration, cyclohexane, and phenol removal from water.[50] Zeolite membranes are preferable to other solid inorganic membranes due to their outstanding molecular sieve property. They allow selective separation rather than the retention of molecules on the porous barrier. Therefore, selecting the most suitable membrane for a given wastewater situation is complicated. The optimal selection depends not only on the nature of the pollutant(s) but also on the porosity and other membrane properties, such as the fabrication of materials, preparation method, and the separation process. Wastewater treatment is a dynamic process, and so is the selection of porous materials.

2.2   Adsorption

Adsorption is one facet of wastewater treatment for which porous materials are particularly relevant. Adsorption is a process of phase transfer in which chemical species enrich a solid surface from a fluid phase.[51] Adsorption is essential in wastewater treatment because of its high-quality treated outputs, flexibility in operation and design, and possible process reversibility.[52] These characteristics mean that adsorbents can be regenerated via an appropriate desorption method;[53] thus, adsorption is environmentally friendly. Adsorption in wastewater

treatment uses solid surfaces (adsorbents) to uptake ions or molecules (adsorbate) from a solution. The solid surfaces interact with species in the adjacent aqueous phase via the active rich likely heterogeneous sites because of their specific electronic and spatial characteristics. Figure 3 shows a typical schematic diagram of the adsorption process.
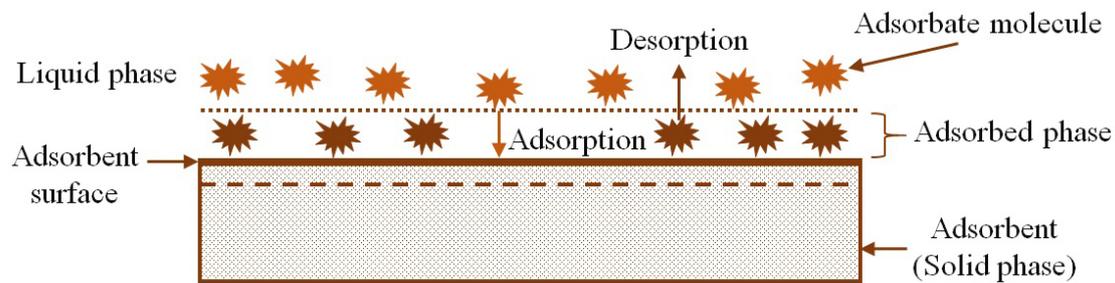

FIGURE 3 The concept of adsorption, adapted from[51]

Any change in the liquid phase properties, such as pH, temperature, and concentration, causes adsorbed species to be released from the adsorbent surface back into the liquid phase in a reversible process known as desorption. Because adsorption is a surface process, the surface area of adsorbents is the most important factor in determining the quality of the adsorbents and adsorption. Their porosity determines the surface area of the adsorbents because pore walls create the internal surface area. The pore walls form large interior surfaces because of the porosity of the adsorbent. The surface areas for the engineered adsorbents are in the range of 10^2-10^3 m^2/g as they are typically highly porous materials. The external surface is usually less than 1 m^2/g.[51,54] The typical microporous adsorbents such as silica gel, activated carbon, alumina, and zeolites were mentioned. Thus, several effectively designed adsorbents have favourable properties such as hydrophilicity, hydrophobicity, pore size, and surface area. These natural and as-prepared adsorbents are widely used in treating wastewater contaminated with different ions, dyes, organic compounds, and pharmaceuticals.[55,56]

There is a significant body of research on removing harmful ions from water using different adsorbents. Overall, this research shows that designed adsorbents have advantages over natural adsorbents. The removal of Cr^{3+} from tannery effluent was investigated by Rahman et al.[57,58] whereas Cr^{6+} ions from aqueous solutions were studied using Ulva compressa L. biosorbent[59] and Stipa tenacissima L. biosorbent[60] in a batch system. Ulva compressa L. achieved an elimination rate of 96%. However, only 90% was recorded using Stipa tenacissima L. biosorbent at optimum conditions. Also, the removal of Cr^{6+} ions from aqueous solutions was

conducted using a designed mesoporous powdered-activated carbon prepared from Peganum harmala seeds. The removal efficiency of Cr^{6+} ions reached 99% due to the high specific surface area of the designed adsorbent (442.986 m^2/g).[61] In addition, other designed adsorbents were used for metal ions adsorption,[62–67] also with chitosan/Fe^{3+} hydroxide to remove Nd ions from aqueous solutions[68] or non-crystal hydrated calcium silicate gel for Pb^{2+} ions removal from an aqueous solution. The latter achieved a removal efficacy of about 90% due to its moderate surface area of 128 m^2/g.[69] All the present studies with the designed adsorbents suggested and confirmed higher removal efficiency, even with a tiny dose, than the natural adsorbent, which generally required larger amounts with a lesser removal percentage. Different adsorbents can efficiently remove dyes, antibiotics, and organic compounds from aqueous solutions.[55, 70–76] One option for efficient removal is magnetic nanocomposite adsorbents. A $FeNi_3@SiO_2@CuS$ adsorbent prepared for the adsorption of methylene blue dye from the aqueous solution achieved a maximum removal efficiency of 85.21%.[77] Similarly, a carbon cross-linked Y zeolite nanocrystals composite was fabricated with a surface area of 176.44 m^2/g and a pore volume of 0.0573 cm^3/g to be used for the removal of methyl violet dye from aqueous solutions; and it attained high removal efficiency at normal temperature and pH.[78] Other low-cost adsorbent options are those prepared from waste precursors. Polyvinyl alcohol-glutaraldehyde cross-linked hydrogel beads are a low-cost adsorbent used to absorb Congo red dye from model industrial effluent.[79] Likewise, cellulose microfibers prepared from the recycled newspaper were used to remove basic textile dye BY28 from aqueous solutions.[80] During the adsorbent synthesis to remove a specific dye, the focus was on creating the functional group that attracted the pollutant on the adsorbent surface. Notably, the dye class is one of the important keys to adsorption. This is because the dyes of different classes (acidic dyes, basic dyes etc.) have different natures, which influence the interference of their molecules with the adsorption layer.

Furthermore, engineered adsorbents have been widely used in the studies of removing pharmaceuticals from aqueous solutions by adsorption, and such adsorbents are highly effective. For example, a mesoporous pumice-derived silica aerogel was applied with a specific surface area of 407 m^2/g for ibuprofen adsorption from an aqueous medium.[81] Another magnetic $PAC@Fe_3O_4$-MN nanoparticle with a surface area of 594.5 m^2/g was used for the adsorption of ciprofloxacin from an aqueous medium.[82] Mesoporous-activated carbon formulated from Azolla filiculoides fern was utilized to remove ampicillin from pharmaceutical

wastewater with maximum efficiency of 96.84%.[83] The adsorption of ciprofloxacin from an aqueous solution was conducted using an amine-functionalized MCM–41 mesoporous silica nanoparticle, which included a specific surface area of 524 m^2/g, and reached 99.25% removal proficiency.[84] Ciprofloxacin was also efficiently adsorbed from aqueous solutions using a hierarchically porous composite from ZSM-5 zeolite nanocrystal-coated carbon with a specific surface area of 739 m^2/g.[85] A biochar prepared from the fibre residue of palm oil with a surface area of 835.3 m^2/g was used for the adsorption of cephalexin from aqueous solutions.[86] A comparison among these studies shows that treating wastewater polluted with pharmaceuticals can be efficiently performed using engineered adsorbents with a removal percentage above 96%. To achieve this effectiveness, the key factors controlling the process are the surface charge, porosity, and, thus, the surface area of the adsorbents. Adsorption has also been applied to treat water polluted with other organic compounds such as organic acids, phenol, etc. For instant, humic acid was removed by adsorption using barberry stem powder and carbonized barberry stem (ash).[87] Phenol was removed from aqueous solutions by adsorption using agricultural waste (Ceratophyllum demersum L.) with a removal efficiency of 94.7%.[88] Also, the engineered adsorbent mesoporous MWCNT coated with $CoFe_2O_4$ nanoparticles (MWCNTs/$CoFe_2O_4$) was used for the adsorption of bisphenol A from wastewater with a removal efficiency of 99%.[89] These approaches were as effective with organic compounds as the pharmaceutical contaminants, showing that they can be multifunctional.

Multiple aspects of the porous materials must be accounted for when incorporating different adsorbents to remove harmful materials from contaminated water. Cost and efficacy are two significant factors to consider. Bio-adsorbents derived from natural waste can be effective though they have removal rates at the lower end of the acceptable range; their advantage is cost-effectiveness. On the other hand, the engineered adsorbents provide a very high removal efficacy. Still, they are expensive to create and use in wastewater treatment.

2.3   Ion-exchange

Ion exchange is the frequently used separation and purification technique for polypeptides, proteins, polynucleotides, nucleic acids, other charged biomolecules, and metal cations. The ion exchange method is still the backbone for numerous food, chemical, pharmaceutical, petrochemical, power industries and water reuse processes. The ion exchange method is advantageous because of its high capacity, simplicity, controllability, widespread applicability,

and high resolving power. The success of this technology requires understanding the basic principles of ion-exchange and suitable applications for a specific-treated feed. The capacity of ion-exchange materials can limit the key parameters of ion-exchange, as well as the nature, forms and functions of ion-exchangers, ions/cations to be separated, pH and temperatures of the solutions containing the ions/cations.[53,90] The working principle of ion exchange depends on exchanging ions in the insoluble porous solid material (ion-exchanger) with ions in the liquid phase. The ion-exchanger contains mobile cations or anions in fixed ion-exchange sites that exchange with a stoichiometric number of the same charge ions when interacting with aqueous solutions. Ion exchangers can also be cation or amphoteric ion exchangers, which exchange anions and cations together.[91–95] Figure 4 shows a schematic diagram of the principle of ion-exchange work.
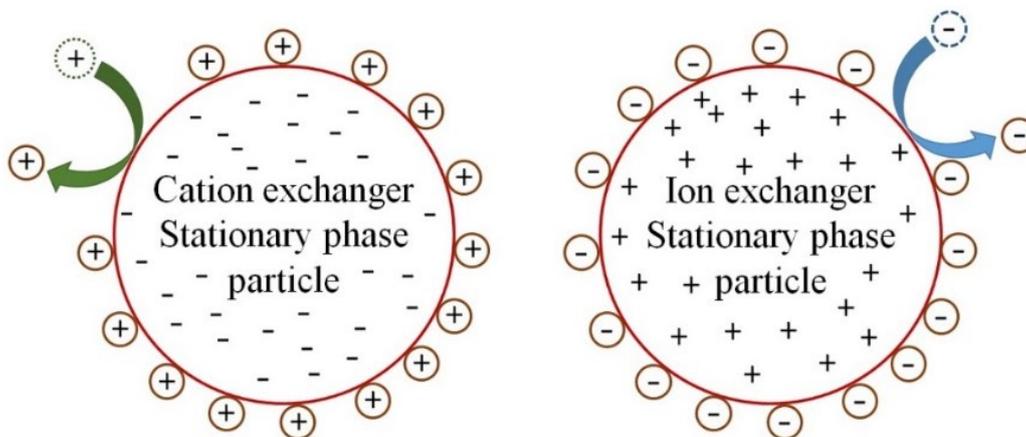
FIGURE 4 Ion-exchange on both cationic and ionic exchangers

Ion-exchange technology has been extensively used to remove different pollutants from wastewater, such as heavy metals.[96] Ion-exchangers can be either natural or synthetic solid resin. Also, they can be either natural or synthetic zeolite with a low silica-to-alumina ratio. Natural organic ion exchangers are of limited use because they often make exchanges in an acid solution. This means that their exchanging groups are ionized under acidic conditions. In contrast, the weaker carboxylic and phenolic groups are not ionized. Also, they change the colour of the treated solutions, and their features are hard to reproduce because controlling the treatment they are given is difficult. Natural inorganic ion-exchangers such as clays and natural zeolites are often used for backfilling or isolating radioactive waste disposal sites due to their ion-exchange properties, easy workability, and low permeability.[97–102] However, this type cannot generally work for column operation as their physical properties limit the flow through

the bed. However, synthetic organic and inorganic ion-exchangers are preferred because they have superior physical and chemical stability. Also, they are produced using a controlled method. Therefore, they have well-distributed functional groups, more uniform particle size and cross-linking degree.[103] In contrast to the above options, zeolites are the most used ion-exchanger in the field of wastewater treatment among all types because of their unique porous structure, favourable surface area, availability of mobile cations in their structure, and chemical and mechanical stability.[104] Zeolites are microporous crystalline aluminosilicates with a three dimensions open framework structure consisting of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra in their pores and channels.[105] Zeolites have been used in different forms to remove heavy metal ions from water by ion-exchange. The purely synthesized zeolites were used in numerous studies dealing with heavy metal removal with high removal percentage.[106] For example, 4A zeolite was used to remove Pb^{2+} and Ni^{2+} ions from aqueous solutions by ion-exchange. Also, the removal of Ni^{2+} ions from aqueous solutions was studied using the synthesized NaX zeolite and NaY zeolite in a batch system, and 99% removal was achieved.[107] Similarly, NaX zeolite and NaY zeolite were prepared from waste aluminium foil as an alumina source and used to remove Cd^{2+}, Cu^{2+} and Hg^{2+} ions from aqueous solutions.[108]

Moreover, another trend has emerged in synthesising microporous zeolitic ion-exchangers. It aims to synthesise them as hierarchically porous structures to perform better in ion-exchange and wastewater treatment applications. In this case, zeolites will be distributed over another inert porous support or the structure of the microporous zeolite itself but need to be modified to attain different porosity levels. For example, a hierarchically porous NaX zeolite/date stones carbon and a NaX zeolite/diatomite were applied for Mn^{2+} removal by ion-exchange.[109] Also, a 4A zeolite/carbon composite was prepared via hydrothermal treatment and applied to remove Fe^{3+} ions and Ni^{2+} ions from aqueous solutions by ion-exchange.[110] In addition, nanosized 4A zeolite/hazelnut shells and nanosized 4A zeolite/cherry stones were prepared by modifying the carbon surface with a diallyl dimethyl ammonium chloride (PDDA) solution. The resultant ion-exchange composites were examined in removing Cu^{2+} ions from aqueous solutions.[111] A comparison between conducting the ion-exchange using pure zeolite and the hierarchically porous ion-exchangers demonstrates that zeolite performed better during ion-exchange with large capacity when it was used as a composite with other porous support. The large ion-exchange capacity was obtained due to the reduction of mass transfer resistance for the diffusion of the ions.

The same results were obtained when the hierarchically porous ion-exchangers were used for radioactive ions removal from aqueous solutions. For example, nanosized natural clinoptilolite/date stones carbon was prepared by conditioning the carbon using diallyl dimethyl ammonium chloride solution. The resultant ion-exchange composite was applied to remove Cs^{2+} ions from aqueous solutions.[112] Also, natural clinoptilolite/date stones carbon and synthesized clinoptilolite/date stones carbon were used to remove Sr^{2+} ions from aqueous solutions.[113] Furthermore, hierarchically porous 4A zeolite/almond shells carbon and 4A zeolite/walnut shells carbon were prepared by a hydrothermal treatment to remove Co^{2+} ions from aqueous solutions.[114] Choosing the proper ion-exchanger to deduct a specified pollutant must be optimized because the ion-exchange process is influenced by the nature of the pollutant, solution pH, solution temperature, and other factors, alongside the features of the ion exchanger itself. This is because the solution pH greatly influences the structure of the ion-exchangers and, thus, their performance. Moreover, the solution temperature affects the hydration radius of the cations or ions to diffuse through the ion-exchanger pores.

2.4   Catalytic oxidation

Catalytic oxidation is a group of wastewater treatment technologies belonging to advanced oxidation processes. It depends, in the first place, on the presence of a catalyst, no matter the source of the oxidant. As part of advanced oxidation processes, catalytic oxidation uses hydroxyl radicals or sulfate radicals as the eventual reactive oxidizing agent to remediate the organic contaminants in wastewater. Also, they are highly active and novel ways to increase the speed of the oxidation process. Advanced oxidation process includes catalytic wet peroxide oxidation, electrochemical oxidation, supercritical water oxidation, gamma-ray, X-ray and electron beam-based processes, microwave/hydrogen peroxide, sonolysis, photocatalysis, ozone-based processes, ferrioxalate-mediated processes, Fenton and photo-Fenton processes, UV-hydrogen peroxide processes.[115–117] The processes that use porous solid catalysts are catalytic wet air oxidation, catalytic wet peroxide oxidation, photocatalysis oxidation either solar photocatalysis or UV photocatalysis, heterogeneous catalytic wet hydrogen peroxide oxidation, sonophotocatalytic oxidation, heterogeneous catalytic ozonation, and sonocatalysis. Transition metal oxides coated on porous supports are well-known active catalysts in such catalytic reactions. The CuO catalyst supported by Al_2O_3 and SiO_2 is an example of such a catalyst. It was used to remove by catalytic wet air oxidation in a trickle bed reactor.[118,119]

These catalysts are favoured because of their rigidity and strength during the catalytic reactions rendering a low pH medium. Similarly, a heterogeneous catalyst (PVP$_2$-Cu(II) catalyst) was used to oxidise phenol with hydrogen peroxide in a batch reactor. It converted 64% phenol, which is considered a promising outcome for phenol oxidation under harsh conditions.[120] The magnetic Fe$_3$O$_4$ particles were another promising option of catalysts used for the catalysis of ozonation of drugs (sulfamethoxazole) by the ozone oxidation power. This catalyst's magnetic property encourages its function in catalysis even if it is not the core of the whole process.[121]

Activated carbon has been extensively used for the catalytic oxidation of the pollutants in wastewater due to its large specific surface area and relatively low cost when prepared from an abundant precursor. For example, activated carbon was used to catalyse diethyl phthalate oxidation ozonation and Fenton-like oxidative removal of phenol from aqueous solutions.[122,123] Also, in other studies, the activated carbon-supported the active part of a catalyst used in the catalytic oxidation of the pollutant. For example, phenol's catalytic wet peroxide oxidation-aqueous solutions use zero-valent iron-supported modified activated carbon catalysts.[124,125] Obtaining a high oxidation rate in these reactions was attributed to the large surface area offered by activated carbon. Despite this large surface area, its oxygenated groups on the surface could play an essential role in adsorption. Thermal treatment at higher temperatures reduced the oxygenated surface groups. Hence, activated carbon collapses and increases pore sizes, decreasing its adsorption capacity. Other combinations of active compounds were also used as porous catalysts for the oxidative removal of the organic compounds, including drugs and dyes, using different oxidants. For instance, sludge carbon/TiO$_2$ nanocomposites were used as heterogeneous catalysts for bisphenol A removal by catalytic ozonation and catalytic wet air oxidation.[126] For dye oxidation, MWCNT was applied for the catalytic oxidation of methyl orange dye in aqueous solutions.[127] Also, GO loaded with TiO$_2$, Fe$_3$O$_4$, and TiO$_2$/Fe$_3$O$_4$ as heterogeneous catalysts in the ozonation process to remove ibuprofen from aqueous solutions.[128]

Moreover, the porous catalysts have been involved in catalytic oxidation induced by sonication or irradiation to remove pharmaceuticals in wastewater. For example, cobalt ferrite nanocomposite loaded onto graphene was used as a sonophotocatalyst for the degradation of diazinon,[129] heterogeneous modified sodium vermiculite iron-rich clay was used for electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton oxidation treatment process

for removal of diazo dye from aqueous solutions.[130] Additionally, silver oxide anchored on Y zeolite (Ag$_2$O@Y Zeo) was used for the removal of Ranitidine as a contaminant of emerging concern by simultaneous adsorption-photodegradation induced via simulated sunlight irradiation.[131] Nickel ferrite/chitosan/Bi^{3+} oxyiodide nanocomposite was used for the removal of metronidazole from aqueous solutions by photocatalytic oxidation using simulated sunlight,[132] MWCNT loaded with CuNiFe$_2$O$_4$ nanoparticles was used for the removal of ampicillin from aqueous solutions using photocatalytic oxidation,[133] and FeNi$_3$@SiO$_2$@ZnO magnetic nanocomposite was used for the removal of tamoxifen from aqueous solutions by photocatalytic oxidation. [134,135] When treating water polluted by different dyes, the presence of a suitable porous catalyst in the oxidative treatment was influential using other oxidants, mainly when the treatment process is induced by irradiation and sonication sources. In this area, TiO$_2$ nanoparticles/GO nanocomposite achieved 100% removal of orange 7 dye in the sonophotocatalytic oxidation using UV light. [136] Also, TiO$_2$–zeolite Y was used for the photooxidation process of methyl orange dye in water.[137] MWCNT loaded with CoFe$_2$O$_4$ nanoparticles was managed for the sonophotocatalytic oxidation process to remove acid blue 113 dye from aqueous solutions.[138] Likewise, the catalytic oxidation of other organic pollutants in the presence of a solid porous catalyst is vital to proceed with the oxidation induced by photoirradiation and sonication. For example, core/shell magnetic zinc oxy-sulfide nanocomposite coated with sulfonated polyindole is used for photocatalytic H$_2$ production. Bisphenol A degradation,[139] FeNi$_3$@SiO$_2$@TiO$_2$ nanoparticles were applied to photocatalytic oxidation of the humic acid in aqueous solutions.[140] Psphotungstic acid-based magnetic nanocomposite was employed for photocatalytic bacterial inactivation of pathogenic E. Coli bacterium.[141] The common idea of the studies mentioned above is the presence of a sustainable porous catalyst provides the required area for a particular reaction. It has a regenerable property since the presence of the oxidant, sonication, and irradiation to eliminate the pollutants are valueless unless there is a proper catalyst.

2.5   Electrochemical reactions

In wastewater treatment, an electrochemical reaction is a branch of advanced oxidation reactions that necessitates the presence of electrodes in the reactor. All methods in the previous section can be used for this branch of reactions as long as they are coupled with electrodes. The advantage of such a reaction is the in situ production of at least one of the required chemicals for the oxidation process, such as the Fenton reaction, for example, in an electrochemical

reactor.[142] Herein, this article will deal only with applying electrochemical reactions involving a porous media, catalyst, or electrode. Several approaches to electrochemical reactions for wastewater treatment have been studied. For the electrochemical production of H_2O_2, single-atom Pt on titanium carbide and titanium nitride nanoparticles catalysts were prepared. The support was suitable for conducting the surface reaction and as single-atom anchoring sites.[143] Another example was a single-atom catalyst made of platinum supported on titanium nitride nanoparticles for hydrogen peroxide production in the electrochemical oxygen reduction of formic acid and methanol.[144] Also, a high H_2O_2-producing capacity metal-carbon composite doped with Fe and N was used in an electro-Fenton system to oxidise phenol in aqueous solutions.[145] The magnetic porous catalyst was another promising choice for catalysts used in electrochemical reactions. The mesoporous magnetite Fe_3O_4 nanoparticles catalyst was cast-off to treat a real washing machine effluent using four electrochemical advanced oxidation processes, namely catalytic electro-Fenton and catalytic electro-Fenton in the absence and presence of peroxymonosulfate to generate both hydroxyl and sulfate radicals.[146] A well-designed compact porous Cu-Zn alloy having a macroscopic interconnected porosity was used as cathodes for the cathodic reduction of nitrate.[147] Chalcopyrite as a sustainable catalyst was applied to remove cephalexin from aqueous solutions by a heterogeneous Fenton-based electrochemical oxidation process and heterogeneous photoelectro-Fenton with UVA light.[148] Another trend in the electrochemical reaction is to raise the generation of highly reactive hydroxyl radicals by fabricating porous electrodes or meshes on which the redox reactions occur. As an example of increasing the production rate of the highly reactive hydroxyl radicals (H_2O_2), a hierarchically porous carbon catalyst (used as a catalytic electrode) was used for the degradation of triethylamine, n-hexadecene, 2,6-di-tert-butyl-4-methylphenol, dibutyl phthalate, and atrazine by electro-Fenton.[149] Also, mesoporous ZnO/CuO nanocomposite cathodes were applied to remove the methylene blue at galvanostatic conditions by a Fenton-like reaction.[150] Moreover, Cu-Zn-TiO_2 microporous nanotube array polymetallic nanoelectrode was prepared for the electrochemical removal of nitrate.[151] Similarly, Ti/SnO_2-Sb_2O_3/α, β-PbO_2 electrode was used for the electrochemical oxidation of methylisothiazolinone.[152] Moreover, bifunctional electrocatalytic filter anodes were examined for the simultaneous removal of particulate contaminants and refractory dissolved organic from natural wastewater.[153]

Utilizing electrochemical membranes has been applied in the oxidative degradation of pollutants in wastewater. Such porous reactive membranes provide in situ generation of the reactive radicles with selective retention of molecules. In some applications, they eliminate the need for catalysts. Porous titanium suboxide and Pd-Cu doped Ti_4O_7 (Pd-Cu/Ti_4O_7) reactive electrochemical membranes were used for the electrochemical oxidation of antibiotic sulfamethoxazole with adding no catalyst.[154] Also, the bismuth-doped tin oxide-deposited reactive electrochemical membranes were utilized to oxidise atrazine, clothianidin, and terephthalic in agricultural water. The synthesized reactive electrochemical membranes had high removal efficiency (complete mineralization) for atrazine, clothianidin, and terephthalic acid at 3.5 V/SHE because of improving the $OH^\bullet$ production.[155] Other similar interventions have been tested as well. For example, the electrocatalytic reduction of NO_3 was conducted using porous reactive electrochemical membranes in the form of Pd-Cu/reactive electrochemical membrane and Pd-In/reactive electrochemical membrane.[156] Likewise, the nanostructured TiO_2 meshes were used to degrade carbamazepine in real secondary wastewater effluent by electrochemical photocatalytic oxidation.[157] Therefore, providing a surface with an appropriate porosity to eliminate pollutants from wastewater successfully is the key to efficient and cost-effective electrochemical reactions. Successfully, a three-dimensional electrochemical system was introduced to the AOP by electrochemical reactions, which remarkably decreased the applied voltage and effectively eliminated the organic contaminants present in low ionic strength wastewaters. This system comprised a composite wire mesh anode containing blue TiO_2 nanotubes covered by SnO_2-Sb_2O_3, a proton exchange membrane, and a stainless-steel wire mesh cathode. A reduction of 75.7% of the applied voltage and 73% of electrical efficiency per log order for 0.001 M Na_2SO_4 was obtained by using this 3-D system.[158] Therefore, when using an electrochemical oxidation reaction, it is necessary to find porous catalysts, electrodes, and membranes whose properties support the high formation of the reactive radicles degrading the pollutants in low voltage usage conditions. This effective, synthesized media is sustainable and can be regenerable, making the pollutants treatment process feasible.

2.6 Hybrid treatment technology

Hybrid treatment technology involves coupling two treatment methods to effectively remove a specific pollutant or simultaneously remove several contaminants in the same effluent. For example, membrane technologies can be combined with electrochemical advanced oxidation

processes (EAOPs) for wastewater treatment. Similarly, ion exchange or adsorption can be coupled with membrane technologies. In this case, the properties of the membranes or the other media together determine the possible application(s). The electrical conductivity of a membrane is significant if the filtration is coupled with electro-catalysis, photoelectro-catalysis, electro-chemical anodic oxidation, and electro-Fenton.[159] In sections 2.4 and 2.5, some examples were given about implementing such methods for removing some pollutants from water to explain the essential roles of catalysts and membranes as porous media. Some new trends in using these porous media in hybrid technologies are explored herein.

An example of using a porous media in catalytic pollutant oxidation coupled with photoelectron-effect is the hierarchically nanostructured ZnO/Ag composite photoelectrodes. This hybrid combination was utilized for the methyl orange dye's photoelectrocatalysis oxidation with 100% degradation.[160] In this case, the synthesized composite served as a catalyst and an electrode in the dye treatment process. Similarly, thin-film mats of porous electrospun fibres of TiO_2 have been applied as porous media for coupling absorption-photocatalytic degradation to remove methylene blue from water.[161] Also, in successive adsorption and photocatalytic degradation, $FeNi_3@SiO_2@ZnO$ nanoparticles were also enhanced for penicillin removal from aqueous solutions.[162] These produced nanoparticles worked as an efficient porous media holding dual functions: adsorption and catalysis. Capacitive membrane deionization (MCDI) is an inexpensive method for brackish water desalination that involves reversible electrosorption involved with high surface area and porous electrodes paired; with an ion-exchange membrane. This is a clear example of hybrid treatment technology, which couples the treatment with ion-exchange and membrane separation. For such a process, sulfonated pentablock copolymer (sPBC) could be used as a cation-exchanger coating a membrane for brackish water desalination.[163] The advantages of hybrid treatment technologies are that they can treat multiple contaminants simultaneously. Still, because many types of wastewaters involve multiple pollutants, hybrid treatment technologies are essential to the porous materials landscape. Different pollutants or contaminants in the water aim to remove using porous materials. Highly effective metal ions or waste-related toxic pollutants are required to remove from the water (Table 3) because the heavy metal in wastewater significantly threatens human health if untreated appropriately. It persists as an uphill task from the biological and environmental standpoint because of its dangerous consequences on health and the environment. It looks like activated carbon exhibits higher cost-effectiveness for utmost

heavy metals. Cyclodextrin-based porous polymer, Zeolite A, birch bark, cork, glass wool, polyurethane foam and graphene oxide was also used for removal purposes. However, novel materials still demonstrate potential as future adsorbents because of their distinctive physical and chemical characteristics that could attain a higher adsorption capacity for water treatment.

3 CONCLUSIONS AND FUTURE PERSPECTIVES

Porous materials play an important role in effective wastewater treatment and thus contribute to conserving and repairing water resources. A wide range of porous materials have been evaluated through research to determine their effectiveness for individual pollutants. Some porous materials, particularly hybrid ones, have been explored in effluents with multiple contaminants. Because wastewater from industrial and household use is often contaminated with more than one type of pollutant, further exploration of how porous materials perform in situations with multiple contaminants will be advantageous. It can accelerate their applicability to real-world use. New porous materials have led to advances in the production of environmentally-friendly wastewater treatment. Porous materials can be made from various organic or inorganic sources, such as powder, pellets and membranes, in different structures and forms. Porous materials can be utilized significantly for treating wastewater contaminated with organic pollutants, heavy metals, drugs and antibiotics, oil and dyes. The key aspects were discussed when selecting the appropriate porous material for a given application.

There are technical and more significant challenges to using porous materials in wastewater treatment. However, all wastewater treatment advances face social, cultural, and economic challenges, particularly where water sources are shared among nations with differing financial priorities and variable attention to environmental concerns. Economic considerations also apply in developing countries. Around 4.2% of wastewater is treated effectively, whereas, in high-income countries, 74% is treated. Further, wastewater treatment plants in developing countries often operate below capacity. There is a lack of access to compelling technologies, including porous materials and the infrastructure necessary to put innovative technologies into use in developing countries, meaning that wastewater continues to cause significant harm to human and environmental health. Research on wastewater technologies should also consider how they can be adapted for contexts of limited resources, in addition to the current assumption that they will be used in an optimal wastewater treatment infrastructure. Overall, porous

materials can contribute to adequate wastewater treatment and improve water safety for human consumption and sustainable environmental management.

TABLE 3 The applications of porous materials for removing pollutants from water.

Porous materials as adsorbent	Pollutant	% Removal Capacity	References
Amorphous porous SiO_2	Oil	100	**164**
Carbon-based poly porous materials	Heavy metals like Pb, Cd, Cr, Cu, As, Nitrogen and phosphorus	—	**165**
Crystalline porous SiO_2	Congo red	99.8	**164**
Lime mud	Pb^{2+}	96	**166**
	Cd^{2+}	---	
	Zn^{2+}	99	
	Cu^{2+}	28	
	Cr^{6+}	93	
	Ni^{2+}	---	
Activated carbon	Dichloromethane	98.3	**167**
	1,1,2-Trichloroethane	86.3	
	Carbon tetrachloride	99	
	Tetrachloroethylene	91.6	
	Hexachlorobenzene	95.1	
	Trichloroethylene	94.7	
	Amoxicillin	93	**168**
	Ranitidine hydrochloride	99.16	**169**
	Paraquat	13	**170**
	Cu^{2+}	16	

	Carbamazepine	84	
	Tetracycline	36	
	Bisphenol A	96	
	2,4-Dichlorophenol	86	
Cyclodextrin-based porous polymer	Bisphenol A	80	**170**
	2,4-Dichlorophenol	72	
Pillar[n]arene-based porous polymers, n=5	Paraquat	97	**170**
	Cu^{2+}	88	
	Carbamazepine	90	
	Tetracycline	66	
	Bisphenol A	96	
	2,4-Dichlorophenol	82	
Pillar[n]arene-based porous polymers, n=6	Paraquat	96	**170**
	Cu^{2+}	93	

	Carbamazepine	96	
	Tetracycline	76	
	Bisphenol A	98	
	2,4-Dichlorophenol	79	
Digested raw bark	Pb^{2+}	96	**166**
	Cd^{2+}	---	
	Zn^{2+}	99	
	Cu^{2+}	28	
	Cr^{6+}	93	
	Ni^{2+}	---	
SBA-15	Methylene Blue	99.1	**171**
	Safranine T	83.6	**172**
Zeolite A	Pb^{2+}	99.9	**166**

	Cd^{2+}	99.9	
	Zn^{2+}	99.8	
	Cu^{2+}	99.9	
	Cr^{6+}	---	
	Ni^{2+}	99.8	
MCM–41	Methylene Blue	94	**173**
	Yellow dye	92	**174**
	Crystal violet	98	**175**
	Pb^{2+}	99.9	
	Cd^{2+}	99.9	
	Zn^{2+}	99.8	
Zeolite A	Cu^{2+}	99.9	**166**
	Cr^{6+}	---	
	Ni^{2+}	99.8	

Birch bark	Petroleum derivatives	60–85.3	176
	n–alkanes	92–98	
Cork	Petroleum derivatives	60–80.2	
	n–alkanes	90.3–95.2	
Glass wool	Petroleum derivatives	72.3–87.1	
	n–alkanes	94.7–97.1	
Polyurethane foam	Petroleum derivatives	75.3–80.7	
	n–alkanes	85.4–95.7	
Waste rubber tire	Pb^{2+}	96	166
	Cd^{2+}	---	
	Zn^{2+}	---	
	Cu^{2+}	99.9	
	Cr^{6+}	---	
	Ni^{2+}	87	

Graphene oxide	Safranine dye	97.78	177
Graphene oxide nanoplatelets	Ibuprofen	98.17	178

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