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Modified Zeolite as Purification Material in Wastewater Treatment: A Review

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ABSTRACT

Natural zeolite is a hydrated aluminosilicate substance that has excellent ion exchange and adsorption properties and is environmentally and economically friendly. This review describes the current application and modification of zeolite in wastewater treatment using acid and surfactants, zeolite composites (such as zeolite membranes), permeable reactive barriers and photocatalysts. The properties of zeolite as well as the regeneration and desorption of cast-off zeolite are briefly reviewed. Modifications are made to improve the capability of zeolite in wastewater treatment facilities. Furthermore, this review proposes the integration of zeolite and other available technologies to treat emerging pollutants in wastewater. Different types of zeolite (natural and synthetic zeolite of different origins) are compared, and their properties are evaluated. Different type of pollutants and treatment methods involving zeolite are also discussed. Zeolite is enhanced to solve the problem of various pollutants in wastewater.

Keywords: zeolite properties; wastewater treatment; zeolite composite, modification; regeneration

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INTRODUCTION

Growing population, shrinking water resources, and increasing pollution from industrial and household effluent activities have rendered polluted water resources even more critical. Water purification of wastewater from industries and household has gained favourable attention for many years [1,2]. Wastewater treatment aims to extract pollutants from water resources. Water pollutants, such as soluble and insoluble heavy metals and organic matter may be highly toxic and carcinogenic to humans and the aquatic environment [3]. Methods currently available to limit pollutants and dissolved toxins include ultrafiltration [4], advanced separation of oil–water [5], use of hydrocyclones [6], chemical clarification [7] and gas flotation [8].

Natural and synthetic zeolite is widely used as adsorption and filtering material to purify water and wastewater. Zeolite is used in decolourisation, detoxification, disinfection, separation, and concentration of water and gas mixture to remove harmful constituents [1,9]. Zeolite is also used to treat various types of pollutants in wastewater, especially metal ions, ammonia, nitrates, phosphates, hydrocarbons, oils and organic matter [10] as well as pathogenic bacteria [11,12] odour compounds [13,14] and colour pigment dye waste from the textile industry [15,16].

Zeolite mainly consists of hydrous alumino-silicate minerals with aluminium and silicon in the form of oxides (AlO_4 and SiO_4). The three-dimensional tetrahedral crystalline porous material with cage-like structure (Figure 1) has substantial cation exchange capacity (CEC), large internal and outer surface areas and pore size ranging from 3.0 Å to 10 Å [17]. The two categories of zeolite are naturally occurring zeolites and synthetically manufactured (synthetic) zeolites, which have a regular and microporous arrangement for industrial use. Synthetic zeolite is produced using various substances, such as natural clay minerals and agricultural wastes, including corn cob or rice husk [18,19].

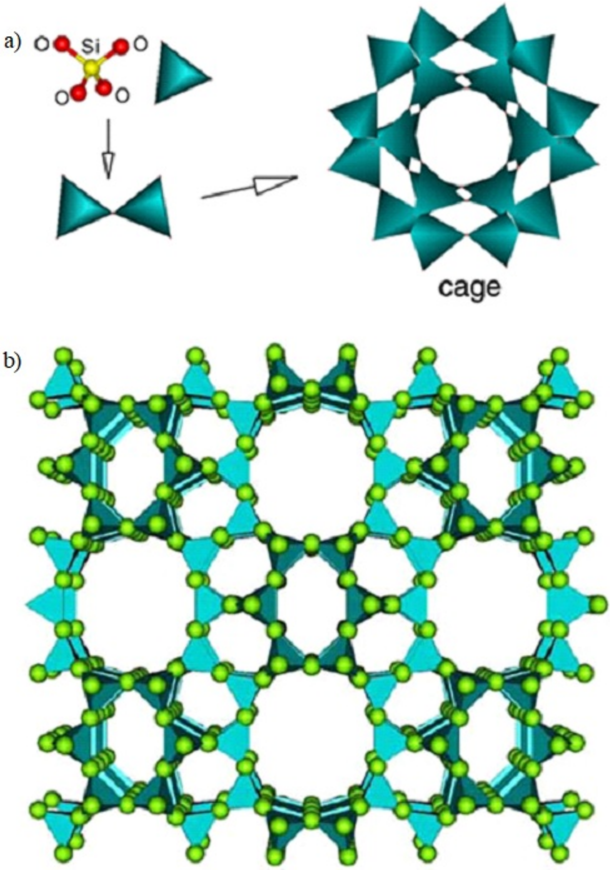

Figure 1: Crystal Structures of Zeolites: (a) Primary Building Units (PBUs) and Secondary Building Units of Zeolite; (b) Chemical Model of a Complex Zeolite Structure (Source by Moshoeshoe *et al.* [20])

In nature, several types of zeolite exist and clinoptilolite is among the most common. Other natural zeolites are mordenite, phillipsite and chabazite (Table 1). The properties of natural zeolite vary depending on their origin; particle size affects their potential for adsorption, and selectivity varies according to zeolite types [21].

Table 1: Different Varieties of Natural Zeolite's Cation Exchange Capacity (CEC) (Source by Moshoeshoe *et al.* [20])

Zeolite type	Ratio of SI/Al	Primary cation	CEC (meq/g)
Analcime	1.5 - 2.8	Na	3.6 - 5.3
Chabazite	1.4 - 4.0	Na, K, Ca	2.5 - 4.7
Clinoptilolite	4.0 - 5.7	Na, K, Ca	2.0 - 2.6
Heulandite	4.0 - 6.2	Na, K, Ca, Sr	2.2 - 2.5
Mordenite	4.0 - 5.7	Na, K, Ca	2.0 - 2.4
Philipsite	1.1 - 3.3	Na, K, Ca	2.9 - 5.6
Laumontite	1.9 - 2.4	Na, K, Mg	3.8 - 4.3
Natrolite	1.2 - 1.7	Na	2.9 - 3.2
Erionite	2.6 - 3.8	Na, K, Ca	2.7 - 3.4
Faujasite	2.1 - 2.8	Na, K, Mg	3.0 - 3.4
Ferrierite	4.9 - 5.7	Ca	2.1 - 2.3

Synthetic and natural zeolites are efficient adsorbents and ion exchangers due to their simplicity and low cost [22]. Ion exchange capacity CEC confers zeolite with a wide range of selectivity and capacity to isolate substances based on differences in molecular sizes and shapes [23–25].

A high CEC value enables zeolite to be used in wastewater treatment. Adsorption of heavy metals by ion exchange in minerals could occur within the interlayer or in the pores of zeolite. Zeolite can absorb a high amount of heavy metals due to their skeleton and lamellar structure, which provides numerous sites for adsorption [26].

The CEC of natural zeolite (Table 1) occurs owing to an imbalance in surface charges caused by the zeolite's partial replacement of Si^{4+} by Al^{3+}.The sites and negative charges are exchangeable by H^+ or alkali and/or alkaline-earth cations, which are often neutralised for acidic zeolite [17, 21, 27].

Higher substitution of Si^{4+} by Al^{3+} in the crystal lattice reduces the Si/Al ratio and raises the negative charge of the zeolite, altering the CEC and selectivity. The low ratio of Si/Al generates high CEC because significant number of cations are needed for balancing the negative charge of zeolite [17, 21, 28, 29]. For example, the ratio Si/Al for natural zeolite or clinoptilolite generally ranges from 4 to 5.5 [29, 30]. Moreover, differences in granule size and zeolite type influences the chemical and physical features of zeolite.

Water pollutants require a wide range of treatment methods because of their complexity. Traditional approaches, such as biological and physical techniques, are still helpful for wastewater treatment but are not economically attractive and require complex processes [31, 32]. Many new pollutants, such as emerging pharmaceutical contaminants, persistent organic pollutants and engineered nanomaterials, have been identified as a waste product in aquatic systems. Conventional techniques in wastewater treatments include physical, chemical and biological methods have certain limitations [33–35].

Stringent disposal regulations have reduced allowable contaminants in waste streams. For economic and technological reasons, only a few wastewater management techniques (Figure2) are widely employed in the industrial sector [36–38]. This phenomenon has encouraged industry players to seek alternative treatments that have minimal investment and higher efficiency and are cheaper to operate, easy to maintain and sustainable [35]. However, innovative and economically viable wastewater treatment technologies with high efficiency remain to be developed [1, 39,40].

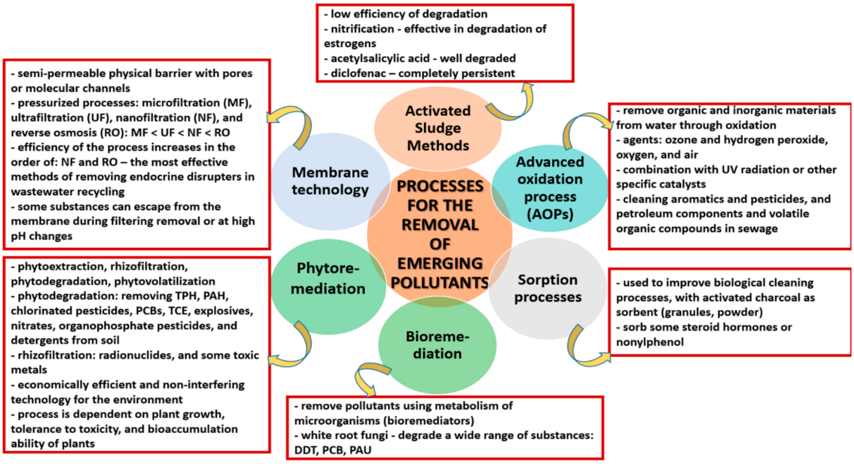

Figure 2: Pollutant-Removal Technologies (Source by Vasilachi *et al.* [41]*)*

Pollutants should be classified and treated based on their type and properties. A substantial amount of these pollutants are found in industrial wastewater; the industrial sector uses large amounts of water and produces substantial wastewater containing minerals and organic pollutants [1]. This paper reviews different methods for purifying wastewater by using zeolite and modified zeolite. This review will also discuss current trends on modification and the advantage of modified materials compared with other adsorbents. A brief overview of the regeneration of zeolite for reusing is also presented.

ZEOLITE ADSORPTION

Adsorption allows easy, simple and minimal design of wastewater treatment process and has a broader application to provide highly effective water pollution control even at trace level compared with other traditional wastewater treatments [1,39,42]. Adsorption is economically practical because it employs relatively low-cost materials, such as natural zeolite, whereas synthetic ion-exchange resins are costly for large-scale systems. Removing pollutants by using zeolite is a more economical technique compared with electrochemical treatments, such as chemical precipitation and reverse osmosis [3].

In the United States, one tonne of natural zeolite costs between $ 50 and $ 300 [43], or $0.03 and $ 0.12 per kilogramme [44]. The ease of operation, high performance and relatively low cost make natural zeolite economical and enticing in water treatment applications. In contrast to clays, natural zeolites are particles with size of millimetres or larger and does not exhibit shrink-swell behaviour. Zeolite has superior hydraulic properties and is thus suitable for filtration systems. Zeolite also has higher mechanical strength and thermal stability than the other adsorbents [45].

NATURAL ZEOLITE MODIFICATION

The low adsorption of natural zeolite limits its widespread use as an absorbent [46, 47]. Natural zeolite is typically modified to improve its adsorption efficiency in wastewater through various chemical and physical treatments and by incorporation into various composite materials and membranes. Researchers have explored the enhancement of natural zeolite via surface modification to improve its ability and effectiveness for treatment of water effluent [48].

Chemical modification includes the use of acids, salts and cationic surfactants [25, 49, 50]. The properties of zeolite vary due to differences in the elements of natural and synthetic zeolites. Clinoptilolite zeolite is hydrophilic in nature because of its high aluminium content [51].

ACID TREATMENT

Acid treatment by acid leaching or dealumination is often used for treatment of zeolite and an effective form of modification to surface treatment and surfactant alteration [52]. Exposure to certain acids, for example hydrochloric acid, nitric acid, sulfosalicylic acid, and acetic acid would cause the decationisation of ions and dealumination without compromising the integrity of zeolite structure [53].

Acid leaching is also used for post-synthesis alteration of synthetic zeolites to expel Al from the structure and increase the Si /Al molar ratio. Acid leaching also helps increase the mesoporosity of zeolite necessary for the passage of large molecules [54]. Acid pretreatment increase the affinity to neutral compounds such as surface-active amines. In adsorption sites on the external surface of H^+ of natural clinoptilolite, the protonated amine molecules are stronger anions than the quaternary ammonium salt cations [55, 56]. The treated zeolites would be more receptive to anions and nonpolar organic pollutants than the untreated zeolites. [57].

SURFACTANT-MODIFIED ZEOLITE

Surfactants are frequently employed to alter the surface characteristics of zeolite depending on its use and type of contamination. Saturation of natural zeolite using quaternary ammonium surfactants, for example dodecyltrimethylammonium (DDTMA), didodecyldimethyl ammonium bromide (DDAB), tetradecyltrimethylammonium (TDTMA), and hexadecyltrimethylammonium bromide (HDTMA), generates a surfactant-modified zeolite [58]. This method modifies the surface properties of hydrophilic zeolite to bind to hydrophobic organic compounds [59].

Surfactant tail groups attached to zeolite may change its natural hydrophilic properties to hydrophobic and retain a broad spectrum of pollutants. Surfactant-modified zeolite is commonly utilised for heavy metal extraction and removal, as well as Surfactant-modified zeolite is commonly utilised for heavy metal extraction and removal, dyes; phenol and 4-chlorophenol, volatile organic compounds (benzene, ethylene, toluene) and xylene natural organic compound (tannic, humic, and fulvic acids) and pharmaceutical products, such as ibuprofen, antibiotics (norfloxacin and moxifloxacin), diethylamine, diclofenac and diclofenac sodium as well as aromatic hydrocarbons (anthracene, fluoranthene, fluorene, phenanthrene, pyrene)[10, 25 ,28, 51, 52, 58, 60, 61].

However, using surfactant for zeolite modification has some disadvantages. Certain ions that interchange on the surface of zeolites bind tightly; as a result, removing the ions for zeolite regeneration is challenging owing to high surfactant adhesion on the zeolite surface and repulsion of surfactant head groups and incoming metallic cations [61]. Zeolite's surface characteristics influence its interaction and effectiveness in removing contaminants from wastewater. Negatively charged non-modified zeolites exhibit a high affinity for cationic surfactants and exchangeable cations, but unable to perform anion exchange. By exposing zeolite to cationic surfactants, its exterior surface charge could be altered from negative to positive. The surfactant would provide a functional group to the zeolite surface, increasing the adsorbent's efficiency. This process substantially changes the surface and allows zeolite to execute anion exchange and increase organic compound adsorption through the formation of hydrophobic and electrostatic forces [62–64]. This interaction produces a high organic carbon content on the exterior surface while preserving a large portion of the inner-surface cation exchangeability. Large organic cations can easily interchange with native counter ions on the zeolite's outer shell [61].

The interaction between zeolite and surfactant is based mostly on sorption on the outer surface of the three-dimensional zeolite framework. Nevertheless due to the large surfactant molecules, ECEC is employed as base for preparation of surfactant-modified zeolite [36]. The hydrophobic tails of the surfactant molecules unite to form a double sheet if the surfactant concentration in the solution exceeds the ECEC, (Figure 3) [36, 65].

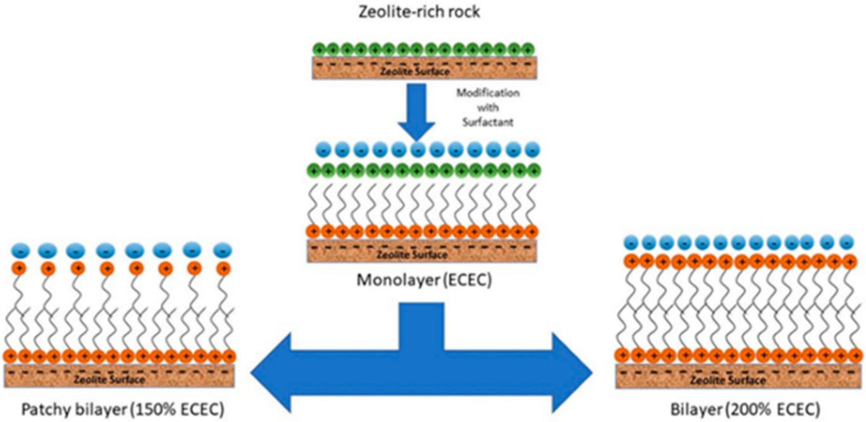

Figure 3: Double-Layer Formation and Anion Adsorption on the Zeolite Surface (Source by de Gennaro *et al.* [66])

Treatment and modification greatly increase the average pore diameter, total pore volume and surface area of the original zeolite due to increasing Si/Al ratio [67, 68]. Ion exchange occurs when the ion is withdrawn from an aqueous solution and substituted by another cation or anion [69]. Brunauer–Emmett–Teller (BET) analysis conducted by various research group to access the change in surface area, total pore volume, pore size. The modification of natural zeolite has shown to increase the surface area up to 10 times, total pore volume, pore size via thermal, acid (HCI) or alkaline (NaOH) treatment [70].

ZEOLITE COMPOSITES

An emerging technology of using zeolite for wastewater treatment involves the incorporation of a nanomaterial to form zeolite composites to improve the adsorption aptitude and capability. Zeolite, chitosan and biochar are utilised for nutrient removal [45]. The synergy between zeolites and other materials has been investigated for the eradication of pollutants from wastewater. For example, zeolites modified with nanomaterials, such as magnetic iron oxide (Fe_3O_4) and chitosan, would improve the relinquishment of mercury in liquid hydrocarbon. The modified zeolites with iron oxide nanoparticles and chitosan effectively removed mercury with 63%–66% effectiveness [71]. Badeenezhad [44] and his group proved that natural zeolite (clinoptilolite) can effectively remove methylene blue dye from aqueous solutions. Moreover, natural zeolite can effectively and rapidly remove ions of heavy metal such as Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} from polluted water [72, 73]. Synthetic and natural zeolites doped by metal ions are gaining popularity as effective catalysts for the hydrogen peroxide oxidation of pigments and textile effluent [such as methylene blue (MB)][74, 75]. Methylene blue oxidation is catalysed by natural zeolite-based silver and magnetite nanocomposites; in the study, zeolite was impregnated with 5.5 wt. percent Fe and 6.4 wt. percent Ag in the form of magnetite nanoparticles and in the form of silver oxide and metallic silver nanoparticles with a size of 32, 42, and 20 nm respectively. Physical adsorption was found to play a role in the elimination of methylene blue [75]. Figure 4 shows the scanning electron microscope (SEM) and transmission electron microscope (TEM) micrographs of natural zeolite-based silver and magnetite nanocomposites for the methylene blue catalytic oxidation in water [75].

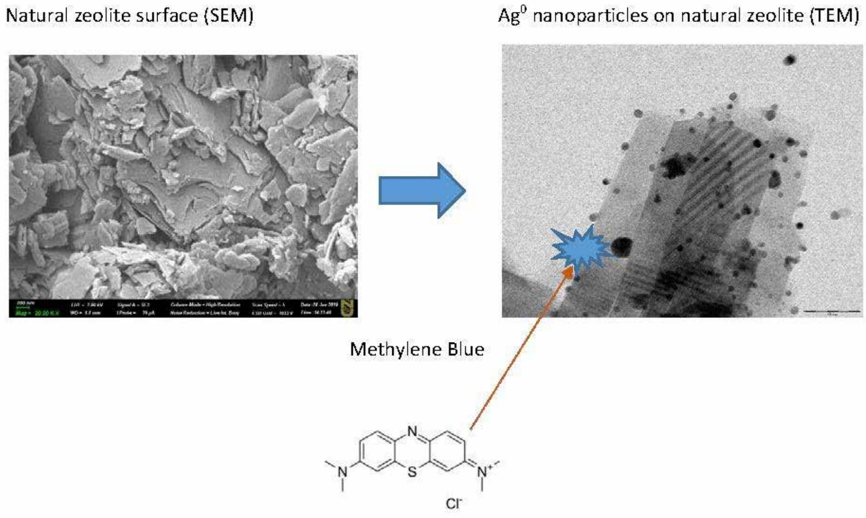

Figure 4: Micrograph (SEM and TEM) of Natural Zeolite-Based Silver and Magnetite Nanocomposites (Source by Kuntubek *et al*. [75])

Surface-modified zeolite and zeolite-based composites have increased performance than non-modified zeolite. For example, polyethene glycol is used for zeolite surface alteration [76], and zeolite is used in the composite to obtain biopolymer-based biosorbent (polysaccharide). Composite products are primarily formed based on the concept of combining two or more components that display adjusted properties compared with individual features [77]. This synergistic mixture retains all the intriguing qualities of specific components and overcomes the significant disadvantages of each part. Different modified zeolite-based composites have been manufactured to improve the adsorption performance of zeolite. Various methods, such as photocatalytic degradation, membrane separation and synthetic polymeric material application, are used in synergy with zeolite for wastewater treatment. Table 2 lists some examples of the use of different types of zeolite for different types of wastewater and their efficiency for treatment.

Table 2: Type of Zeolite and Pollutants in Wastewater

Zeolite type	Type of pollutant	Removal %	References
Natural zeolite, pre-treated with 1 mol/L of NaCl, and separately modified with surfactants	Polycyclic aromatic hydrocarbons (anthracene, fluoranthene, fluorene, phenanthrene,	>93%	[58]
Synthetic zeolites (Zeolite1-6)	Pb ion Cd ion Cr ion	100% 98.4% 100%	[11]
Natural clinoptilolite	Ammonium	84–88%	[78]
ZnO/zeolite pellets (concurrent photocatalysis and adsorption)	Caffeine (in dark)	60%	[79]
	Caffeine (under UV)	100%	
Turkish zeolite altered with quaternary ammonium	F ion	85%	[80]
Acid-activated zeolite samples and conditioning with NaCl	Ammonium nitrogen	100%	[81]
Natural zeolite	palm oil mill effluent residue	69.72%	[82]

Fe(III)-modified zeolite-alginate beads (FeA)	Pb ion	80%	[84]
Natural zeolite - clinoptilolite and its acid-modified counterpart	Residual antibiotics pollution (moxifloxacin and norfloxacin)	30 %-70 %	[52]
Acid-modified (1 M H_2SO_4) clinoptilolite	Gd(III) ion	70%	[85]
Faujasite modified with graphene oxide (GO)	Methylene blue (MB)	93% - 99%	[86]
Australian natural clinoptilolite zeolite treated with concentrated H_2SO_4 and coated with graphene oxide	Cd ion	71% - 78%	[87]
Synthetic nano-zeolites with graphene oxide (GO)	Ca ion	98%	[88]
Modified zeolite with magnesium (Mg-zeolite)	Pb ion Cd ion Cu ion	>98% >98% >98%	[89]
Zeolite modified by integrating calcinations with MgO	Ammonia	73.4%	[90]
NaCl-modified zeolite	$NH4^{+}$-N PO_4^{3-}-P	92.13% 90.3%	[91]

INTEGRATION OF ZEOLITE WITH OTHER ADSORBENTS

Natural zeolite particles are loaded with graphene oxide to improve the adsorption properties. The zeolite performance can be enhanced by the integration of the material with other adsorbents, such as graphene oxide.

A composite composed of faujasite zeolite and graphene oxide composite disks was investigated as a regenerable pollutant adsorber that maintains its properties upon rejuvenation. Faujasite zeolite with well-dispersed reduced graphene oxide (GO) comprised of micropores from the crystalline framework of faujasite and meso/macropores from the accumulated graphene sheets and faujasite particles exhibits increased adsorption capacity compared with the individual materials [86]. Zeolite and graphene could also find synergy in other wastewater application with zeolite modified with magnetic graphene oxide. Electrostatic interactions, hydrophobic interactions and hydrogen bonding are responsible for GO and its synergistic relationship to zeolite. Dealumination of zeolite, which involves cleaning followed by acid therapy as well as partial thermal deoxygenation of GO, can improve hydrophobic interactions. This method resulted in a tenfold increase in surface area (from 10.55 m^2 g1 to 117.96 m^2) and a threefold reduction in pore diameter (from 30.68 Å to 81.91 Å) [87].

Wastewater treatment using composite biosorbents commonly comprise biopolymer made of polysaccharides, such as cellulose (cell) and its derivatives, chitosan (CS) and alginate (Alg). The integration of small quantities of zeolites into the polysaccharide matrix contributes to a major increase in the mechanical efficiency and thermal and chemical stability of the composite biosorbents. Composite biosorbents have additional characteristics, such as biodegradability, biocompatibility, antibacterial behaviour and chelating property, due to the nature of the biopolymer matrix. Chitosan (CS) modified using zeolites such as clinoptilolite and synthetic zeolite (zeolite Na-A synthesised from fly ash) Na-A was examined for its practical use in removing heavy metal ions from polluted water and wastewater [92, 93]. Zeolite acts as inorganic fillers into biosorbent (polysaccharides) composites, which are more effective in treating wastewater [92, 94, 95]. The sorption properties of the chitosan composite modified with clinoptilolite show 9 wt.% to 20 wt.% improved loaded capacity for Cu^{2+} ion removal compared with cross-linked chitosan because clinoptilolite microparticles enhance the approachability of the ion to the chitosan functional group network [92]. Additionally, the ions adsorbed onto the composite could be readily desorbed by a low concentration of hydrochloric acid (HCl) without affecting the integrity of the biosorbents [92, 96, 97].

In another study, zeolite synthesised from fly ash was modified with monolayer chitosan on the external surface for treatment of humic acid, phosphate and ammonium. The chitosan layer developed on the surface of the zeolite and non-zeolite oxide fraction (Fe_2O_3, Al_2O_3 and CaO) provide necessary forms for the retention of organic humic acid, anionic phosphate and cationic ammonium. The experimental works showed enhanced affinity towards humic acid and improved adsorption for phosphate compared with non-modified zeolite, with highest adsorption abilities of 31.6 and 4.05 mg/g, respectively [98].

Zeolite is integrated into several variety of membrane, for-instance such as reverse osmosis (RO), membrane bio-reactor, high-performance ceramic microfiltration (MF) membranes utilising natural zeolite powder and permeable reactive barriers [59, 99, 100] Composite films fabricated using zeolite as a filler could act as an active layer for reverse osmosis membrane. Zeolites are capable of delivering critical desalination characteristics while also being possibly tolerant of incoming water, which can easily clog polymer membranes and resist relatively economical cleaning techniques. Two kinds of zeolite, hydrophilic FAU and hydrophobic MFI, were employed, each with variable wetting characteristics. Salt ions were completely rejected by both zeolite membranes.

Recent advances in polymer-based membrane research have centred on examining various types of nanocomposite membranes including nanofillers, such as zeolite, to improve membrane efficacy [101]. Reverse osmosis (RO) utilises a semipermeable membrane is used to remove ions, pollutants, and bigger particles. Inorganic membranes, which primarily consist of zeolites, have higher resistance to a mixture of feed water and rough cleaning methods.

MEMBRANE BIOREACTOR (MBR) TECHNOLOGIES

The effectiveness of zeolite for controlling the fouling of membrane for wastewater treatment in fixed-bed membrane bioreactor was also studied [102]. Membrane bioreactor (MBR) technologies integrate biological wastewater treatment with micro/ultrafiltration. Membrane fouling is the principal downside of operating MBR systems because soluble and tiny particles infiltrate the membrane and, along with other organic and inorganic matter, are absorbed into the membrane pores, thereby decreasing the permeate volume [103]. Zeolite could minimise membrane fouling by incorporating additional processes, such as adsorption or coagulation with MBR, to improve permeability and reduce membrane resistance. Zeolite serves as an absorber for soluble organic compounds, enabling sludge to be added to the substance to reduce the possibility of direct contact with colloids/soluble matter and membrane. Zeolite membrane bioreactor creates considerably low trans-membrane pressure and less soluble microbial products due to adsorption and bio-layer adherence to the membrane surface [102].

CERAMIC MICROFILTRATION

The hybrid process of ceramic microfiltration with natural zeolite powder offers other methods, such as adsorption and ion exchange, to improve permeation flux and total organic carbon rejection for the remediation of oily wastewater to 99.9%. The use of natural zeolite powder as an adsorbent and in the framework of mullite and mullite–aluminium membranes in freshly produced membranes can lower the cost of manufacturing. The performance of this membrane is better than the microfiltration standard for all membranes, except for mullite-aluminium membranes. The hybrid approach improves the quality of output water, decreases membrane fouling, is more energy-efficient and environmentally friendly, and needs lower capital and operational costs [104].

PERMEABLE REACTIVE BARRIERS (PRBS)

The most efficient and potential remediation technology is permeable reactive barriers (PRBs) packed with adsorption materials; however, refining reactive materials remains a significant obstacle in the production of successful PRB technology. Recent research reveals that composite adsorbent construct of zeolite-supported nanoscale/microscale zero-valent iron is an functional and favourable reactive substance for obliteration of Cd(II), Pb(II) and As(III) from aqueous solution in permeable reactive barriers [105, 106]. Using zeolite as a reinforcing agent for the framework improves the dispersibility of zero-valent iron particles and synthetic zeolite [106].

Nano-/micro-scale zero-valent iron with a large specific surface and a micro-porous structure is an effective adsorbent of metal irons. Altering the zeolite surface by coating with iron or iron oxides can improve the adsorption potential of zeolite for metals, and the zeolite-iron mixed framework has synergistic effects on improving the adsorption ability of composites for heavy metals. Moreover, modifying the zeolite surface by coating with iron or iron oxides can improve the adsorption potential of the zeolite for metals; the zeolite-iron mixed solution has synergistic effects on enhancing the adsorption sensitivity of the composite for heavy metals.

ZEOLITE PHOTOCATALYSTS

Adsorption or coagulation does not eradicate or remove contaminants entirely. These contaminants are simply concentrated [40]. Photocatalysis is an interesting approach to eradicate emerging pollutants by oxidation at ambient temperature and pressure. Photocatalytic processes could be performed for wastewater remediation with adsorbent by doping the adsorbent material with metal semiconductor. Integrating these materials would help achieve the adsorption and decomposition of toxic compounds by irradiation from ultra-violet (UV) and visible light [35, 40]. Adsorbents and photocatalysts must be compatible in order for the nanocomposite to be highly reusable and stable. A hybrid UV system with the semiconductor material and zeolite for wastewater treatment was investigated [107]. The unique properties of zeolite, which is biocompatible, mechanically resistant, inert and capable of lower recombination of the electron–hole process, would significantly contribute to pollutant adsorption and swift recombination of photogenerated electrons in a hybrid adsorbent–photocatalyst application [40]. The adsorption capability of the hybrid adsorbent-photocatalyst of zeolite and semiconductor materials could be further enhanced by increasing the surface area and incorporating nanomaterial adsorbents, such as graphene and graphene oxide. This process would increase the pollutant's concentration on the photocatalytic surface and promote the active sites for photocatalytic activity.

Semiconducting materials, such as zinc oxide and titanium oxide, are employed in photocatalyst techniques because of their capacity to absorb light and produce reactive oxygen species (ROS), which are essential for pollutant degradation [108]. Adsorption and photocatalysis are two different processes used to treat various types of wastes, such as heavy metals and pharmaceutical wastes. The most frequently investigated compound for photocatalyst application is titanium dioxide (TiO_2), a non-toxic, biologically safe, readily usable and inexpensive metal oxide [109–111]. With its unique framework of Al-O units, zeolite could be integrated as an adsorbent into the photocatalytic composite.

DESORPTION AND REGENERATION OF ZEOLITE

Zeolite offers a formidable advantage compared with other adsorbents because of its tunable physicochemical properties and the possibility of being regenerated without significant loss of performance at relatively low temperatures [112]. Once the potential for the adsorption of zeolite has been depleted and reach the saturation point, zeolite could be disposed or reused. Potential reuse options of saturated zeolite are considerable options for viable use of zeolite in the industry for wastewater treatment. Disposal of zeolite into a landfill site depends on the material adsorbed, which may contain nutrients, and zeolite could be exploited for agricultural purposes, such as fertilizer or soil conditioner [113]. However, when estimating the benefits of using zeolite in other sectors, such as agriculture, the possible accumulation of unwanted pollutants, e.g. heavy metals, should be considered [114, 115]. Moreover, heavy metals and organic waste inside wastewater could be recovered through the regeneration of the used zeolite to prevent hazardous chemicals from being released into the environment [116].

Regeneration of zeolite by chemical processing is an option. However, pollutant desorption is required to make the process more cost-effective and environmentally acceptable. Several regeneration methods, including wet air oxidation as well as chemical and thermal regeneration, are applicable [117]. Zeolite exchangeable ionic sites could be regenerated simply by washing it with another strong cation solution because the ions exchanged on the zeolites are loosely held [118, 119]. Chemical regeneration can be conducted using chemical saturation of brine and salts, such as alkali sodium chloride solution (NaCl) [120] and potassium chloride (KCl) [85] and sodium hydroxide (NaOH) [121] and via saturation of mineral acids by using sulfuric, hydrochloric [85], nitric, acetic and ethylenediaminetetraacetic acids, which are chelating agents [122]. The use of NaCl solution has been carried out to regenerate and replace contaminants, such as ammonium ion, from exhausted zeolite, so the vacant sites can be used for another ammonium ion exchange [123]. The process is essential for the recovery and removal of nitrogen from wastewater. Optimal NaCl should be used under neutral pH [124]. The combination of 1 M KCl and 1 M HCl acidified to pH 4.0 was used to desorb Gd(III) from zeolite [85]. Organic desorption from the zeolite surface by using stearyldimethylbenzylammonium chloride (SDBAC) was investigated under different pH levels of aqueous solutions and ionic strengths over certain periods [65].

Nevertheless, no quantitative data on the renewability of zeolite is available in the literature. In this regard, more research is needed to address the principal shortcomings of zeolite in alkaline chemical regeneration as well as the sustainability of zeolite.

Zeolite regeneration by ozone has been explored for ammoniacal nitrogen removal. However, ozone did not fully recover the adsorption ability of saturated zeolite given that the zeolite performance efficiency decreased by approximately 18%. For phosphate or phosphorus contaminant, ozone shows promising potential for zeolite regeneration methods that allow the use of zeolite for few adsorption cycles [125]. Physiochemical and mechanical regeneration can also be used to regenerate exhausted zeolite by the evolution of Fenton-like reaction, thermal treatments, solvent extraction, photolysis, mechanical shaking and air stripping [123, 126]. All these methods, however, are costly. Another alternative is to use the combination of adsorbent and photocatalyst materials, a new technology that can eliminate contaminants' complete mineralisation of adsorbed species. [127]. For example, a study by Fanourakis *et al.* [35] showed that the combination of clay-based adsorbent (made of zeolite) could be utilised to treat emerging pharmaceutical contaminants by photocatalysis with the combination of nanomaterials (graphene or carbon nanotube) and adsorbent materials.

CONCLUSION

The review reports the capability of zeolite in wastewater treatment. The efficacy of wastewater treatment methods is determined by the final discharge requirement and the type of pollutant to be treated. A variety of approaches and techniques are being investigated by industry and academe to discover a new way to handle wastewater more directly and safely. Natural zeolite has the ability to absorb pollutants, and its properties and capability could be further improved with further modification such as via modification such as acid and surfactant as well as hybrid system. Many studies were conducted on the use of zeolites as adsorbents in water and wastewater treatment, their properties and potential alteration of natural zeolites. Research and application of zeolites are still active and critical areas that merit consideration and deliver exciting prospects. The review has shown that specific modification on zeolite improved the adsorption as well as the treatment strategies that would cover larger spectrum of pollutants in waste-water. Various technologies and methods are still being investigated by companies and academe to find a novel solution towards a more simple and efficient wastewater treatment.

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