published by

EQA - International Journal of Environmental Quality
ISSN 2281-4485 - Vol. 65 (2025): 25-34
Journal homepage: https://eqa.unibo.it/

Zeolites as versatile material for sustainable water purification: a review

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Article info
Received 8/9/2024; received in revised form 14/9/2024; accepted 19/9/2024
DOI: 10.6092/issn.2281-4485/20297

Abstract
Water contaminants are prevalent in various sources and this poses high risks to the environment as well as human health thereby increasing the need for an efficient sustainable water management. Zeolites are a special type of crystalline aluminosilicate minerals that possess rich frameworks of interconnecting channels and cages. They have exceptionally high cation exchange capacities and has drawn much attention as suitable adsorbent material for the elimination of different types of pollutants in water systems. Besides the use in water purification, zeolites are also used environmentally as filters of toxicants and as sources of nutrition to crops. Zeolites have multiple functions in commercial and environmental processes because of their structural and chemical characteristics. They can act as requisite catalysts, adsorbents, and ion exchangers due to the broad applicability in commercial and environmental processes across industries. This review aims at examining the use of zeolites in different water purification processes with the view of explaining the nature/extent of adsorption properties and ion exchange of the material. The effectiveness of various kinds of zeolites, such as clinoptilolite, chabazite, etc is presented with special reference to the removal of heavy metals, ammonia, organic contaminants, and operation of desalination. Furthermore, the review provides an account of the limitations and comparison with other technologies.

Keywords
Zeolites, Water Treatment, Heavy Metals, Ammonia, Organic Contaminants, Desalination.

Introduction

Zeolites are aluminium silicate minerals, having the characteristics of a crystalline structure, and are used as catalysts or adsorbents (Costa et al., 2012). They are recognized for their well-defined microporous, strong acid activity, selective adsorption properties and thermal and chemical stability (Roth et al., 2015). Such minerals consist of a virtually three-dimensional anionic framework with an atomic ratio O:(Al + Si) = 2, which makes them special group properties (Byrappa & Yoshimura, 2012). Zeolites are useful because of their practical uses that greatly influence the economy. In different sectors, zeolites can work as catalysts and adsorbent materials. With development in zeolite synthesis methods, new types of zeolites have been obtained including mesoporous single crystals and hierarchical materials to broaden their use (Byrappa & Yoshimura, 2012; Roth et al., 2015). Furthermore, protection of the environment as well as enhancing food production has been achieved through utilization of zeolites in the sense that it is able to adsorb toxic substances and in agriculture, it is

DOI: 10.6092/issn.2281-4485/20297

used to provide nutrients (Adamović et al., 2011). Zeolites are useful in various aspects and perform a number of functions in all industries. They are either used as catalysts, adsorbents, or ion exchangers due to their structural and chemical characteristics that help them outperform other materials in various industries such as environmental cleanup (Adamović et al., 2011; Byrappa and Yoshimura, 2012; Costa et al., 2012; Roth et al., 2015).

Types of zeolites commonly used in water treatment

Zeolites are characterized by microporous structure; widely used for water treatment because of the pronounced high cation exchange capacity and selectivity by channel dimensions (Krstić, 2021). Natural zeolites such as clinoptilolite, chabazite, and mordenite are commonly used in water treatment (Rashed & Palanisamy, 2018). These zeolites are selected according to the ability of its interaction with various from water making separation of heavy metals and ionic species possible (Koshy and Singh, 2016).

Although natural zeolites possess useful properties for water treatment, they may not be pure and hence are often not employed for numerous applications because of alterations in the structure in the process of purification (Costa et al., 2012). Various types of synthetic zeolites exceeding two hundred have been reported to be applicable in water treatment procedures (Rashed & Palanisamy, 2018). These synthetic varieties are that they can be engineered for a certain end use or purpose; the synthetic variants perform better than their natural counterparts. Conclusively, among the natural zeolites clinoptilolite, chabazite, and mordenite are widely used in water treatment while synthesis zeolites are also in increasing use due to the fact that they can be synthesized to exact requirements and contain no impurities (Costa et al., 2012; Rashed & Palanisamy, 2018). Figure 1 entails the mechanism and applications of zeolites in water treatment.

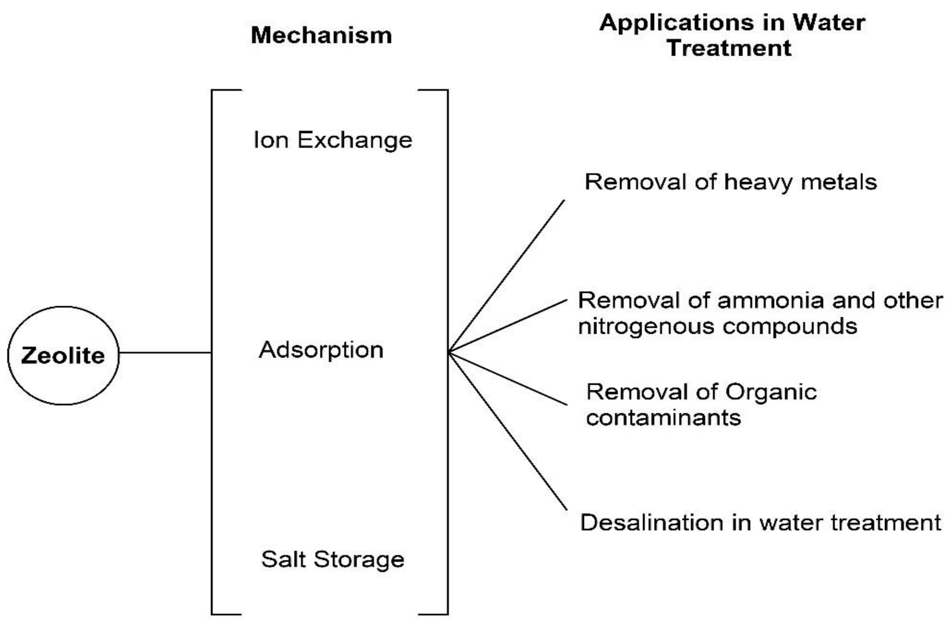

Figure 1
Mechanism and applications of zeolite in water treatment

Clinoptilolite. Clinoptilolite is a type of naturally zeolite with a three-dimensional aluminate-silicate structures and possesses ion exchange and adsorption properties (Pabiś-Mazgaj et al., 2021). Clinoptilolite can be made up of aluminium, silicon, oxygen, and other cations including sodium, potassium, and calcium. Its composition can vary depending on where it comes from and how it is treated (Adam et al., 2023; Hernández-Beltrán & Olguín, 2007). It is extracted from beds of volcanic tuff. Its properties can be improved for a particular application by using techniques like ion exchange and acid treatment (Hernández-Beltrán & Olguín, 2007; Sadeghi et al., 2016). Clinoptilolite is widely utilized in water treatment because of its ability to remove contaminants through ion exchange and adsorption including pollutants like ammonia (Adam et al., 2023; Chmielewská, 2016), heavy metals (Ferronato et al., 2015) and even radio-active materials like strontium-90 (Sadeghi et al., 2016). Studies on the adsorption of

DOI: 10.6092/issn.2281-4485/20297

arsenic from groundwater have also been conducted (Camacho et al., 2011). The high surface area, exchangeable cation content, and negative charge at neutral pH of clinoptilolite make it an extremely excellent water treatment material (Adam et al., 2023).

Chabazite. Chabazite or $Ca[Al_2Si_4O_{12}]{\cdot}6H_2O$ is made of an oxygen-bonded framework of tetrahedra of silica (SiO_4) and alumina (AlO_4) with calcium cations opposing the negative charge (Aono et al., 2020; Das and Sengupta, 2023). Chabazite can be produced by processing the natural mineral using alkaline hydrothermal methods. To increase the ion-exchange potential of chabazite, it must be treated with an alkaline solution at high temperatures. Interzeolite conversion is another process used to create chabazite. This technique uses zeolites, such as faujasite, as sources of aluminum (Dang et al., 2021). Chaba.zite's adsorption and ion-exchange properties make it a popular choice for the removal of pollutants like ammonium in water and wastewater treatment processes (Das and Sengupta, 2023; Gounder et al., 2021). Additionally, chabazite can be recycled and used again in cyclic adsorption-desorption processes (Das and Sengupta, 2023).

Mordenite. Mordenite or $(Na,Ca,K)_4(Al_8Si_{40}O_{96})$.28 H_2O comprises of a framework of silica (SiO_4) and alumina (AlO_4) tetrahedra linked by oxygen atoms, with sodium, calcium, and potassium cations balancing the negative charge. Mordenite is usually prepared using hydrothermal synthesis method. Conventional methods involve utilizing silica and alumina sources like rice husk ash, silica gel, metakaolin and coal fly ash together with an alkaline solution. Organic templates such as tetraethylammonium (TEA^+) cations, glycerol, ethylene glycol and polyethylene glycol have been employed to alter the mordenite framework and characteristics. Mordenite has been investigated for water treatment applications as a result of its high surface area, pore volume, and ion exchange capacity. Mordenite has exhibited efficiency in removing heavy metal ions like lead (Pb^{2+}) from aqueous solutions by means of adsorption and ion exchange processes (Narayanan et al., 2020).

Mechanisms of water purification using zeolites

Ion Exchange. Zeolite can exchange the ions present in them with that of ions present in the water. This action is dependent upon may factors like the geo-chemical properties of zeolites, pH of the solution, concentration, co-existing anions, valency, surface change and the condition of the experiment. Ion exchange is one of the most effective methods for the removal of metals ions such as magnesium, calcium and sodium from water (Margeta et al., 2013; Mkilima et al., 2022; H. Wang et al., 2020). Ion exchange pathway including zeolites are based on the capability of these minerals to exchange their constituent cations with the ones in an aqueous solution. Zeolites which are crystalline, hydrated aluminosilicates, possess a framework of $(Si,Al)O_4$ tetrahedra. The aluminum in the structure gives a negative charge. This charge is balanced by cations situated inside the zeolite's cavities and channels (Dyer, 2005; Pabalan and Bertetti, 2001). The structural composition and the solvating particle zeolite ratio (z) can affect the selectivity of zeolites. Zeolites with a $z<2$ preferentially absorb lithium, $z<3$–4 favour sodium and z value of 5–6 exhibit a preference for larger cations (Bobonich, 1990). The higher ion exchange potential and rate of ion exchange of mordenite makes it more effective than clinoptilolite for reducing sodium ions in saltwater (Wajima, 2013). The mechanical strength and ion exchange potential of synthetic zeolites are important for their practical use in water treatment (Guida et al., 2020). Water molecules present in the zeolite's voids also affect the exchange of cations. This process can be slow in zeolites with narrow-pored frameworks (Dyer, 2005). The free energy of solvation of cations in zeolites is lower as compared to their hydration. This in turn affect the ion exchange selectivity and the redistribution of water between the solid and liquid phases (Bobonich, 1990).

Adsorption. Zeolites can adsorb contaminants such as heavy metals, organic compounds and other impurities from water. This property is due to their large surface area and pore capacity. Some of the factors that contribute to this property are pollutant content, water pH, and zeolite composition. Adsorption is an important technique for removing contaminants such as heavy metals, pharmaceuticals and dyes from water (Krstić, 2021; Margeta et al., 2013; H. Wang et al., 2020). Adsorption mechanisms of zeolites in water purification primarily include ion exchange and molecular adsorption processes. Zeolites are microporous aluminosilicate minerals and exhibit a outstanding affinity for diverse pollutants. This is due to their special structure di-

DOI: 10.6092/issn.2281-4485/20297

stinguished by channels and cavities. Ion exchange is a primary mechanism around neutral pH where zeolites exchange their inherent cations (such as Na^+, Ca^{2+}, K^+, Mg^{2+}) with contaminants like ammonium ions in water. This selectivity can be affected by the ionic concentration and the accessibility to competing ions. At high ammonium levels Ca^{2+} may turn into the predominant ion for adsorption over Na^+. Molecular adsorption which involves the physical adsorption of molecules onto the zeolite surface can be crucial particularly in alkaline conditions where it can inhibit ion exchange (Lin et al., 2013). Zeolites can be made more selective and have a higher adsorption capacity by employing several techniques. By adding NaCl or silver nanoparticles, the surface shape is altered and the availability of exchangeable ions is increased (Lin et al., 2013; Ruíz-Baltazar et al., 2024). Zeolites can also be combined with other substances, such as magnetic nanoparticles, to make reuse and separation simpler. This could increase the viability of water filtration methods. (Sossou et al., 2024). Molecular simulations and computational analysis have been used to predict how pollutants may interact with zeolites. This can assist in selecting the right zeolite varieties for particular contaminants (Fischer, 2020).

Salt storage. Zeolites have the ability to retain salt ions inside of their framework structure, which lowers the water's overall salt content. Water that has been salted with sodium and other minerals can be used for irrigation and other purposes by using zeolites to reduce the salt content (Mkilima et al., 2022; H. Wang et al., 2020). Zeolites are well known for their involvement in water especially in the context of desalination and heavy metal cleanup. This is due to their distinctive physicochemical characteristics. (Abdelwahab and Thabet, 2023; Al Ghazawi and Al Diabat, 2022). The primary methods by which these microporous materials works are ion exchange and adsorption. Both of which are essential to their capacity to retain ions throughout the purification of water. Zeolites' ability to exchange ions is primarily responsible for their salt storage mechanism. Negatively charged alumino-silicate frameworks found in zeolites' natural structure draw and retain positively charged ions, or cations, such sodium, potassium, and magnesium (Tahraoui et al., 2021). The cations in the zeolite structure can be swapped with other cations from the saline water. This is also applicable to those that contribute to the salinity or hardness of the water. Zeolites can be replenished for subsequent use due to the reversible nature of this exchange process. (Shahmirzadi et al., 2018). Moreover, another important aspect of salt storage is zeolites' adsorption capacity. The adsorption of salt ions from water is facilitated by the porous structure of zeolites which offers a vast surface area. Plasma treatment has been demonstrated to greatly raise the specific adsorption capacity for salts in ultralong carbon nanotube-based zeolite membranes and can improve the efficacy of zeolites (Yang et al., 2013).

Applications of zeolites in various water treatment processes

Removal of heavy metals. Zeolites have been thoroughly researched and used in water treatment procedures to eliminate heavy metals. Heavy metals pose a serious threat to the environment because of their toxicity and persistence (Abdelwahab and Thabet, 2023; Buzukashvili et al., 2024; Chen et al., 2020; Kozera-Sucharda et al., 2020; Senila and Cadar, 2024; Sossou et al., 2024; Velarde et al., 2023; Yuna, 2016). The ion-exchange and adsorption characteristics of zeolites are what make them desirable for their ability to effectively remove different types of heavy metal ions from contaminated water sources (Abdelwahab and Thabet, 2023; Yuna, 2016). Zeolites' ability to remove heavy metals can differ depending on their structure, origin, and whether they are manufactured, modified, or natural. It has been claimed that natural zeolites, such as clinoptilolite, are effective at removing metals like nickel, mercury, arsenic, cadmium, and chromium (Velarde et al., 2023). Modified and synthesized zeolites frequently exhibit better sorption performance and cation exchange capabilities when compared to their natural counterparts (Kozera-Sucharda et al., 2020; Yuna, 2016). Modifications may involve treatments with metallic, surfactant and acid/base/salt reagents (Velarde et al., 2023). In order to make the process more economical magnetic nanoparticles have also been studied for possible integration into zeolites. This would provide for the simple separation and reuse of the adsorbents. Zeolites are an adaptable and efficient remediation method for heavy metals in water treatment systems. Their versatility makes it viable to create customized adsorbents that can resolve specific problems with water contamination. The fabrication of new zeolite forms that give high removal efficiency and the potential for regeneration and reuse (including those made from coal fly ash or

DOI: 10.6092/issn.2281-4485/20297

created through 3D printing) further increases their application potential (Buzukashvili et al., 2024; Khalil et al., 2021). Zeolite modification and synthesis methods are constantly evolving which highlights their significance in environmental sustainability and protection (Chen et al., 2020; Senila and Cadar, 2024).

Removal of ammonia and other nitrogenous compounds. There has been a lot of research done on the use of zeolites to remove nitrogenous compounds, such ammonia, from water. Zeolites are perfect for this because of their ion exchange properties. This property enable them to adsorb ammonium ions (NH_4^+) from aqueous solutions in a preferred manner (Hanusová, 2014; Rahmani et al., 2004). The regeneration process and the presence of competing cations are two factors that can impact how well zeolites remove ammonia. Clinoptilolite has a high ion exchange capacity and can be effectively regenerated using sodium chloride (NaCl) solutions. It can continue to work well even after multiple cycles (Rahmani et al., 2004). Magnetic zeolites generated from fly ash (MZL) have shown promising results like robust adsorption of ammonia nitrogen and the added benefit of being readily separated from water by high-gradient magnetic separation (HGMS) (Sugawara et al., 2016). Selective ion exchange capabilities and potential for effective regeneration make Zeolites a feasible choice for the removal of ammonia and other nitrogenous chemicals in water treatment. Zeolites can be altered to improve their adsorption capabilities and make it easier to integrate them into other water treatment procedures. Examples of these modifications include adding them to PVDF membranes or alkali alteration. (Huang et al., 2024; Rohani et al., 2021). The removal process can be accelerated and a more all-encompassing approach to regulating nitrogenous impurities in water can be provided by combining zeolite-based ion exchange with additional treatment techniques such biological nitrification or electrochemical oxidation (Almutairi & Weatherley, 2015; Li et al., 2009).

Removal of organic contaminants. Organic contaminants include volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and other petrochemicals (Muir et al., 2017). The transformation of zeolites with inorganic salts, organic surfactants or metals improves their adsorption capacity making them more efficient in purifying water (Muir et al., 2017; S. Wang and Peng, 2010). By combining magnetic nanoparticles with zeolites, magnetic zeolites can be made more cost-effective and convenient for water treatment applications by effectively eliminating contaminants. These zeolites can be easily separated and reused (Sossou et al., 2024). Zeolites can be synthesized using various methods such as hydrothermal synthesis. Their adsorption mechanisms include chelation, surface adsorption, diffusion, electrostatic interaction, and complexation (Dehmani et al., 2023). Zeolites are a flexible and cost-effective solution for removing organic pollutants from water. They can be used to treat a variety of aquatic pollutants considering their special physicochemical qualities and capacity to improve and alter their performance. Their applicability and sustainability in water treatment procedures are further emphasized by their capacity for regeneration and reuse, especially in the case of magnetic zeolites (Krstić, 2021; Sossou et al., 2024).

Desalination in water treatment

Heavy metals and ionic species are among the contaminants that are removed from water by using zeolites, microporous aluminosiliceous minerals with high ion exchange capabilities (Koshy & Singh, 2016). They are good in adsorbing and eliminating pollutants from water because of their distinct pore properties and surface area. Zeolites can be used in desalination to treat saline waters, like those found in mines, by effectively eliminating ions like barium and radium (Chałupnik et al., 2013). This is especially important for areas with plenty of salty water sources that are unfit for human consumption because of dissolved minerals and salts. It's interesting to note that although zeolites are good at eliminating certain ions, the publications that are linked do not specifically address their ability to desalinate water by eliminating common salts like sodium chloride. They may, however, be able to enhance existing desalination procedures by concentrating on impurities that are challenging to eliminate using traditional techniques, as evidenced by their ability to treat water that contains high concentrations of particular ions. Zeolites are useful because they can remove a variety of impurities from saline fluids, which makes them useful in the water treatment process, including desalination. They are appropriate for applications that require the targeting of particular ionic species due to their great efficiency in ion exchange. Zeolites are widely used to remove certain ions from saline waters, however their application in broad-spectrum desalination is not covered in the context given (Chałupnik et al., 2013; Koshy and

DOI: 10.6092/issn.2281-4485/20297

Singh, 2016).

Limitation in water treatment

Zeolites, being hydrous aluminosilicates, are well known for their use in water treatment because of their ion-exchange and adsorptive qualities. Their application is restricted, though. Zeolites may not be able to completely remove all sorts of pollutants from water, which is one of the main problems with their selectivity to certain contaminants. In addition, the existence of competing ions may affect the function of zeolites and lower their water purification effectiveness. Another noteworthy observation is that although zeolites are advantageous in the treatment of multivalent ions in water, their use is more complicated in the case of organic contaminants or microbes. This is due to the possibility that zeolites lack the essential characteristics to interact with these pollutants in an efficient manner (A Al Dwairi and E Al-Rawajfeh, 2012). Additionally, zeolites can regenerate after saturation, which can be energy-intensive and not necessarily feasible for large-scale applications (Bülow & Micke, 1996).

Recent advancements and novel zeolite materials for water treatment

Exploration of natural zeolites and zeolite composites for the removal of heavy metals from contaminated water sources has marked recent breakthroughs in zeolite materials for water treatment. These developments are essential considering the environmental risks linked to heavy metal pollution and how it affects ecosystems and human health (Abdelwahab and Thabet, 2023). Zeolites have been found to be efficient and financially feasible sorbents for the filtration of water due to their high cation exchange capacity, low cost, and superior thermal stability. Their ability to selectively exchange ions due to their microporous nature makes them very useful for the treatment of wastewater and water (Krstić, 2021). New zeolite materials have been created via post-synthetic alterations to improve their properties for particular tasks, even though natural zeolites are still functional. These alterations extend the properties of zeolites beyond those imposed by synthesis conditions by changing the atomic structure, micropore level, crystal and particle levels, among other things (Valtchev et al., 2013). Research has examined the impact of binders and peptizers on the microporous structure of zeolite compositions, emphasizing the significance of sample preparation for textural analysis (Maraeva et al., 2020).

Comparison of zeolites with other water treatment technologies

Natural zeolites are used in water treatment systems and have been blended with organic and polymeric components to create water-purifying nanocomposite polymers. Numerous uses for environmental protect-tion are possible with these materials (Margeta and Vojnović, 2011). On the other hand, oxidation, adsor-ption, coagulation, filtration, and disinfection are just a few of the procedures used in conventional water treatment systems. Reverse osmosis (RO), membrane filtration (MF), ultrafiltration (UF), nanofiltration (NF), and other membrane technologies are empha-sized as chemical-free substitutes for conventional techniques (Scott, 1995). Zeolites are part of a wider range of technologies that are effective in treating water. Membrane technologies, especially those in conjunction with enzymatic reactions, have demonstrated promise in eliminating endocrine disrupting chemicals (EDCs) from water. One prominent exam-ple of such a technology is the oxidation of a broad variety of substrates by laccase enzymes (Singh et al., 2018). Sustainable green material synthesis, which emphasizes the use of carbon-based materials, biopo-lymers, and nanomaterials with lower environmental impact and potential for water remediation, has also received attention (Hassan and Saleh, 2024).

Future prospects and challenges in zeolite-based water treatment

The promise of advanced materials including membrane technology, biochar, green-synthesized nanoca-talysts, chitosan-based hydrogels, and nanomembra-nes to address water contamination challenges is un-derlined. These materials have advantages including selectivity, high surface area, and small environmental impact (Chelu et al., 2023; Nasrollahzadeh et al., 2021; Osman et al., 2024; Singh and Verma, 2023; Tripathy and Gupta, 2023). However, it is accepted that there are difficulties during manufacturing and disposal, in-cluding material stability, fouling, energy efficiency, cost-effectiveness, and potential environmental implications (Osman et al., 2024; Satyam and Patra, 2024; Tripathy and Gupta, 2023).

Declaration

The authors declare that there is no conflict of interest.

DOI: 10.6092/issn.2281-4485/20297

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