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ORIGINAL ARTICLE

A Review on Development of Porous Aluminosilicate-Based Zeolite Adsorbent for Heavy Metal Pollution Treatment

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ABSTRACT – Heavy metal contamination endangers human health and has been identified as a global issue. The rising concentration of heavy metals in industrial and domestic wastewater has prompted the quest for effective technologies and treatments to remove them. Zeolite is a promising material for eliminating heavy metals from diverse sources that pollute wastewater. Zeolite is a crystal comprised of hydrated aluminosilicates of alkali and alkaline earth metals in a three-dimensional crystal network composed of easily controllable SiO_4^{4-} and AlO_4^{5-}. This review focuses on the critical analysis of the application of several zeolites for the adsorption of heavy metals from wastewater, namely Cd(II), As(III and V), Cr(III and VI), Cu(II), Pb(II), Ni(II), Mn(II), and Hg(II). The results of heavy metal removal reported by zeolites are summarized, and the chemical modification of zeolites with acid/base/salt reagents, surfactants, and metal reagents has been investigated, compared, and discussed. The adsorption/desorption capabilities, systems, operational parameters, isotherms, and kinetics of zeolites are then explained and compared.

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INTRODUCTION

Heavy metal pollution is a global environmental problem because the increase in environmental pollution is directly proportional to the increase in industrialization, urbanization, and the use of various chemical compounds in various fields. This heavy metal pollution has become the center of attention because of its harmful effects on living things and the environment. Heavy metals can pollute the environment through natural processes such as soil erosion, forest fires, volcanic eruptions, and biogenic processes [1]. Besides natural processes, heavy metal pollution also comes from anthropogenic sources, where anthropogenic sources are the main factor causing increased heavy metal pollution. Anthropogenic sources of heavy metal pollution, such as industrial, mining, agricultural, and domestic activities, are illustrated in Figure 1 [2]. These activities produce wastewater containing heavy metal ions such as Cd(II), As(III and V), Cr(III and VI), Cu(II), Pb(II), Mn(II), Ni(II), Pb(II), and Hg(II).

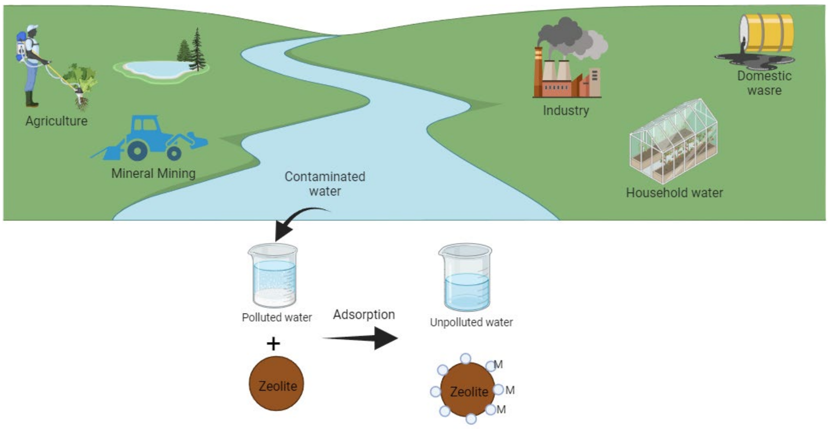

Figure 1. Illustration of heavy metal pollution and adsorption process with zeolite

Heavy metal characteristics, including toxicity, non-biodegradability, biological accumulation in the human body, and their carcinogenic nature, threaten the environment and human health [3], [4]. One of the consequences of the accumulation of Cu metal ions in the human body is causing extreme mucosal disorders, liver damage, and nervous system disorders [5]. Therefore, it is very important to remove heavy metal pollutants from domestic or industrial wastewater effectively. There are three methods for removing heavy metals: chemical, physical, and biological [6]. Chemical methods such as coagulation, chemical precipitation, solvent extraction, electrochemical reduction, and flotation are usually used to treat wastewater that contains heavy metals. Physical methods, such as adsorption, ion exchange, and membrane technology, have been carried out to treat heavy metal waste [7]. Biological methods for

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reducing heavy metals in water usually use microorganisms. Various microorganisms such as *Escherichia coli*, *Neopestalotiopsis clavispora*, *Beauveria bassiana*, and *Metarhizium anisopliae* are reported to be effective as bio-adsorbents of heavy metals [8]. However, these methods require high costs and complex processes and produce secondary waste such as sludge [9]. The adsorption method is currently considered effective and simple for treating heavy metal waste. The adsorption method is most widely applied because it is relatively easy to use, economical, and efficiently removes heavy metals at low concentrations, especially in the 1–100 mg/L range. Various materials such as polyacrylamide, alumina, activated carbon, chitosan, clay, and zeolite have been used for heavy metal adsorption. Of these various materials, activated carbon is the most efficient as an adsorbent compared to other materials. However, activated carbon has high production and regeneration costs, so using activated carbon as an adsorbent is considered uneconomical.

As shown in Figure 1, the adsorption process can be defined while the ions or molecules can attract on the surface of materials, and their interaction of the adsorption process can be classified into two mechanisms. The first is physical adsorption (physisorption), and the second is chemical adsorption (chemisorption). The physisorption mechanism based on the physical interaction between the adsorbate and the adsorbent surface allowed the Van der Walls force or electrostatic mechanism for its interaction. On the other hand, the chemisorption mechanism was associated with the stronger interaction between adsorbate and adsorbent; it can be classified as the formation of chemical bonding; either a covalent bond or coordination bond was suitable for this characteristic. Based on the thermodynamic approach, adsorption enthalpy for physisorption around 20–40 kJ/mol was lower than the chemisorption enthalpy value of 80–240 kJ/mol. The adsorption mechanism approach can be applied to many types of porous material; chemisorption and physisorption mechanisms can be found in several porous materials that have properties as ion exchangers or by some surface modification or functionalization to create the charge on the adsorbent surface.

On the other hand, zeolite has a special attraction for researchers because of its characteristics. Zeolites are a group of hydrated aluminosilicate minerals of alkali and alkaline earth metals in a three-dimensional crystal network composed of silica (SiO_4^{4-}) and alumina (AlO_4^{5-}) tetrahedral with four oxygen atoms in each rectangular corner [10]. Zeolite can be found in nature, resulting from hydrothermal processes in alkaline igneous rocks. This mineral can be found in cracks or cracks in rocks. In addition, zeolite can be produced from volcanic activity, which contains much silica [11]–[14]. Zeolite is an attractive material because of its manageable physicochemical properties. More than 200 types of zeolites have been discovered and reported, with pore diameters ranging from 0.25 to 1 nm [15]. Research related to zeolite for adsorbents experienced a significant increase yearly in the 2001–2022 range, as shown in Figure 2. In Figure 2, it appears that in 2001, publications related to the use of zeolite as heavy metal adsorbents were less than 500 publications, but in 2020, it reached more than 3000 publications, which is an increase of up to 6 times. Zeolites' characteristics and properties have drawn attention due to their efficacy in adsorbing heavy metals because they act as molecular sieves. An exhaustive evaluation of prior studies on heavy metal removal on zeolites has been conducted [16]–[18]**.** Researchers are currently more interested in zeolite's adsorption capacity in the adsorption of a particular heavy metal of interest. This review article discusses the adsorption capabilities of various natural synthetic and modified zeolites for Cd(II), As(III and V), Cr(III and VI), Cu(II), Pb(II), Ni(II), Mn (II), and Hg(II). Furthermore, the best conditions for process parameters such as pH, contact time, adsorbent dosage, initial concentration, and temperature were identified. Therefore, this article will review the state-of-the-art zeolite as an adsorbent for various heavy metals, including natural, synthetic, and modified zeolite.

Based on the data of publications since 2000, it exhibited that zeolite as a porous adsorbent was widely used and developed for wastewater or heavy metal removal. There are some advantages of zeolite as an adsorbent compared to other porous materials: (I) Zeolite can be synthesized to form a different framework that can be applied for various applications, which means that the chosen zeolite type based on their application or proposed from researchers; (II) the pore size of zeolite can be designed into various forms, such as micropores, mesopores, or hierarchical pores. Hierarchical pores can be defined as materials with two types of pores, for example, micropores and mesoporous structures into zeolite; (III) zeolite had a high specific surface area, and it was easy to create the charge on the zeolite surface due to the presence of ion exchanger into zeolite structure. Surface charge can be formed as negative or positive charge via surface functionalization. This mechanism allowed the zeolite to adsorb the pollutant via chemisorption and physisorption. Hence, the dual adsorption mechanism into porous zeolite enhanced the adsorption capacity and their performance for heavy metal removal; (IV) zeolite synthetic can be synthesized using natural resources such as kaolin, silica sand, red mud, clay, risk husk ash, and many more. Then, the by-products from coal combustion, such as fly ash and bottom ash, have been used for raw materials in zeolite synthesis. Many sources of raw materials for the synthesis of zeolite can reduce the cost of production.

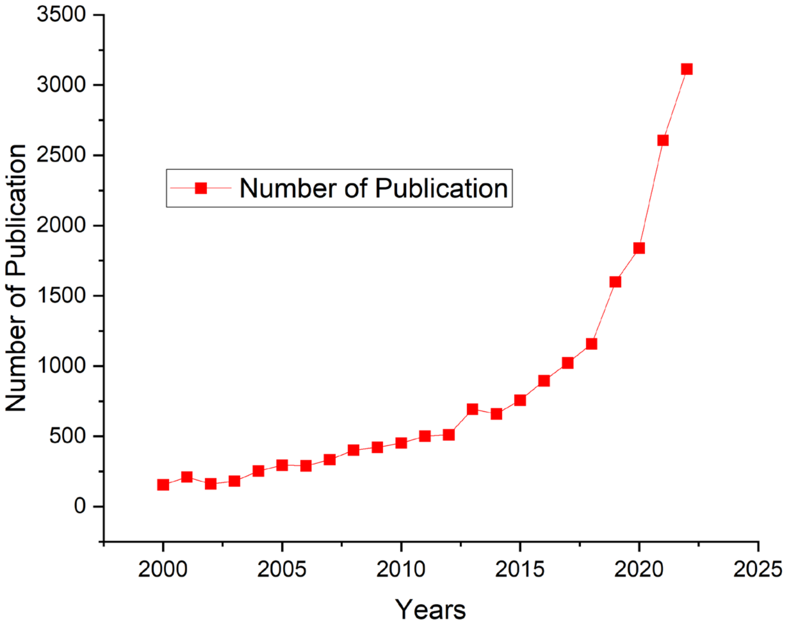

Figure 2. Number of articles indexed by Scopus with the keywords "zeolite for heavy metal removal"

ZEOLITE

Zeolites are composed of the tetrahedral (TO_4), with T being the central atom, mostly Si and Al [19]. In forming a 3-dimensional zeolite structure, each tetrahedral is connected by one oxygen atom and forms a secondary structure in simple polyhedrons such as hexagonal cubes and prisms. These secondary structures will combine and create a more complex 3-dimensional tertiary structure [20]. One type of zeolite is zeolite Y, which has a Faujasite structure composed of sodalite and ß-cage, illustrated in Figure 3.

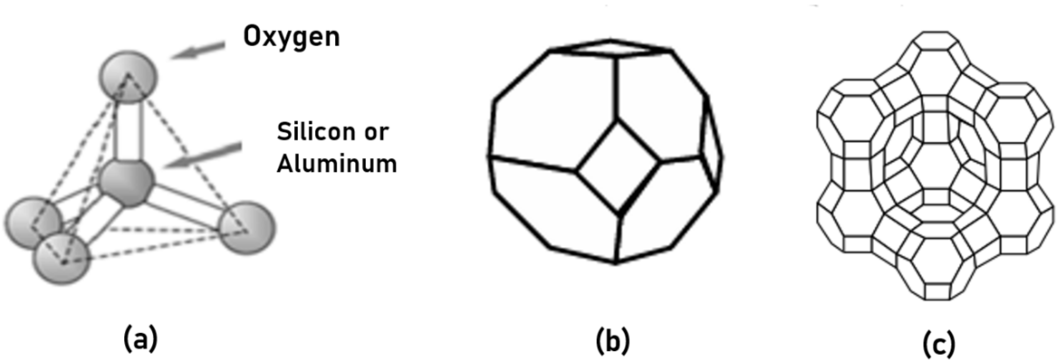

Figure 3. (a) Primary structural unit of zeolite [21], (b Sodalite, ß-cage Zeolite Y, and (c) Faujasite, structure of tertiary zeolite [22]

Zeolites are crystalline aluminosilicates with an open 3D framework structure consisting of interconnected silicate (SiO_4) and aluminate (AlO_{4+}) tetrahedra, sharing all oxygen atoms to form regular intra-crystalline cavities and molecularly sized channels. A defining characteristic of zeolites is their structure, which consists of 4-coordinate atoms forming tetrahedra (Figure 4). These tetrahedra are connected to each other by their corners and form many complex structures. The framework structure may contain connected cages, cavities, or channels large enough to allow entry of small molecules. The large void system explains the constant low specific density of these compounds. In zeolites used for various applications, the voids are interconnected and form long and wide channels that vary in size depending on the compound. These channels allow resident ions and molecules to move easily in and out of the structure. The aluminosilicate framework carries a negative charge and attracts positive cations residing in the cage to compensate for the negative charge of the framework.

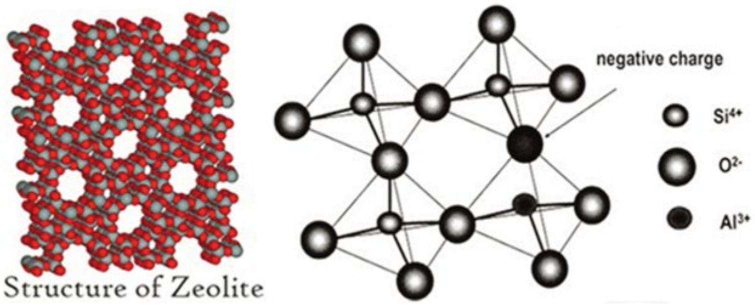

Figure 4. Structure of zeolite [23]

NATURAL ZEOLITE

Natural zeolite is formed due to natural processes found in crevices of igneous or metamorphic rocks. In addition, natural zeolite is also found in sedimentary rocks. About 40 types of natural zeolite have been identified in the last 200 years with the types of zeolites that are found in nature, including erionite, analcime, chabazite heulandite, clinoplite, and mordenite [24]. Natural zeolites are applied in various fields, such as catalysts in esterification reactions, heavy metal adsorbents such as Cu(II), and fertilizers in agriculture [25]–[27]. However, natural zeolite has weaknesses in the industrial sector, and the main weakness is that the channel diameter of natural zeolite is very small; one example is clinoptilolite, which has a channel diameter of 0.30–0.40 nm. This causes its application as an adsorbent to be limited and cannot be applied to gases and organic compounds that have larger molecular sizes [28].

Properties

Ion exchange, adsorption, dehydration, and rehydration of zeolite, which are related to its structure, framework, and composition, are important in determining the properties of zeolite. First, the large system of channels and cavities in the zeolite structure and the existence of extra-framework cations make cation exchange possible. The cation exchange capacity of natural zeolite is twice that of bentonite clay, ranging from 2–4 milliequivalents per gram [29]. Substitution of Al^{3+} with Si^{4+} in the zeolite structure creates an insufficient positive charge in the framework. The net negative charge is neutralized by cations such as Na^+ and K^+ located in cavities within the structure [30]. When zeolite comes into contact with solutions containing high concentrations of cations, ion exchange can occur between Na^+ and ions [29].

Chemical Composition

The common chemical composition of zeolite is $Ma/b[(AlO_2)a(SiO_2)y].cH_2O$, where M represents the alkali metal or alkaline earth metal cation, b represents the valence cation of the earth metal, c is the amount of water of crystallization per unit cell, and a and y represent the total number of silicate $[SiO_4]^{4-}$ and aluminate $[AlO_4]^{5-}$ tetrahedral cells in a unit cell of zeolite [31]. The main components of natural zeolite are silicon oxide (SiO_2) and aluminum oxide (Al_2O_3). Clinoptilolite ($[Na, K, Ca]_6[Si, Al]_{36}O_{72}\cdot 20H_2O$) and modernite ($[Ca, Na_2, K_2]Al_2Si_{10}O_{24}\cdot 7H_2O$) have a high component of silica (approximately 70%) and have been used for industrial purposes [32]. They are generally used as heavy metal adsorbents, control agents, water filtration, and molecular sieves [33]–[36].

SYNTHETIC ZEOLITE

As explained earlier, zeolite is an aluminosilicate crystal that can form naturally. However, natural zeolite has characteristics of low purity and non-uniform sizes [37]. In addition, the formation of natural zeolite takes several days to decades to form, and researchers are trying to synthesize zeolite in the laboratory. The advantage of synthetic zeolite compared to natural zeolite lies in its structure and properties, such as porosity, crystallinity, surface area, and acidity, which can be adjusted based on variations in synthesis parameters [38], [39]. Based on the data reported by the International Zeolite Association (IZA), 21 zeolite types were reported with different structures and properties. It indicated that zeolite was a versatile material that could be synthesized depending on various parameters, i.e., the ratio of Al/Si, types of templates, temperature, duration, synthesis methods, and other parameters.

Nowadays, synthetic zeolites are used commercially more often than natural zeolites due to the purity of the crystallized product and uniformity of particle size. The source of the first synthetic zeolites was standard chemical reagents. Much of the research in basic zeolite science has been performed on natural zeolites. The main advantage of synthetic zeolites over natural zeolites is that they can be engineered with a wider range of chemical properties and pore sizes and have higher thermal stability. However, natural zeolites do not have suitable ion affinities, for example, Cu [40], Cs and Co [41], and Ur [42] ions.

Currently, the main problem in zeolite research is the availability and cost of raw materials, especially silica sources. On the other hand, commercial silica (including sand) is available as a gel, sol, fume, or amorphous solid of varying reactivity and selectivity. The preparation of synthetic zeolites from silicon and alumina chemical sources is expensive. However, cheaper raw materials such as clay minerals, natural zeolites, coal ash, municipal solid waste incineration ash, and industrial slag are used as raw materials for zeolite synthesis. The use of waste in the synthesis of zeolites contributes to minimizing environmental problems, often in water filtration, by removing heavy metals or ammonium and converting them into attractive and useful.

METHODS OF ZEOLITE SYNTHESIS

Synthetic zeolite can be synthesized from various silica and aluminum sources by reacting silica and aluminum compounds in an alkaline solution at pH= 8-13 and calcined to obtain the desired crystal form and zeolite properties [43]. Various methods related to zeolite synthesis in the laboratory include hydrothermal, solvothermal, and sol-gel methods, alkali fusion, and alkali leaching. One of these methods, hydrothermal, requires lower temperatures and uses water as a solvent, so this method is cheaper and more environmentally friendly than other methods [44]. The advantages of each method are represented in Table 1.

Table 1. The advantages of different zeolite synthesis method

Synthesis method	Reaction Condition	Type of Zeolite	Advantages	Ref.
Hydrothermal	90°C for 2 h	Zeolite sodium aluminosilicate (NaA)	High reactivity, low pollution and energy consumption, good crystal quality	[45]
	150°C for 48 h	ZSM-5 Zeolite		[46]
Solvothermal	180°C for 12 h	ZSM-22	Easy control over the size, shape distribution, and crystalline product	[47]
Sol-gel method	90°C for 24 h	Zeolite sodium faujasite (NaY)	A versatile method with less energy consumption and no need for special and expensive equipment.	[48]
Alkali fusion	600°C for 6 h	Zeolite X	Use of low-grade raw materials and production of high-quality anhydrous zeolite	[49]
Alkali leaching	100–300°C for 2 h	Sodalite	Allows impure raw materials and offers very efficient products	[50]

The hydrothermal method is a single-crystal synthesis method that relies on the solubility of minerals in hot water under high pressure. Compared to other methods, the advantage of the hydrothermal method is its ability to create a crystalline phase that is unstable at the melting point. Several factors influence the zeolite synthesis process using the hydrothermal method, such as temperature and pressure, the ratio of silica and aluminum, precursors, alkalinity, curing time, and templates [31]. The hydrothermal method has advantages such as a simple process, a wide source of raw materials, and high product crystallinity. However, there are disadvantages to using the hydrothermal method, such as the long crystallization time, the large amount of raw material, and the high pressure required [51].

The synthesis of zeolite by the hydrothermal method can be carried out from various sources of commercial silica and aluminum, natural materials, and waste. However, many researchers use waste and natural materials such as zeolite raw materials to reduce production costs. One of them has been reported by Jin et al. [52] to synthesize zeolite NaA by hydrothermal method with alkaline activation. Zeolite NaA is synthesized from coal precursor with low alkaline concentration. Nevertheless, the synthesized zeolite NaA has a crystallinity of 87.56% and has high purity. Research by Aragaw and Ayalew [53] also synthesized zeolite from natural materials, namely kaolin from Ethiopia. Zeolite-X was successfully synthesized by the hydrothermal method, as indicated by the appearance of three main peaks on the XRD diffractogram at 2θ: 19.04°, 32.12°, and 33.84°.

ZEOLITE MODIFICATION

Modification is an approach taken to change or improve the properties of natural and synthetic zeolite to increase adsorption, catalytic, and other applications. In general, zeolite modification can be carried out using two methods, namely the physical method and chemical modification (Figure 5) [54]. Physics modification includes modification using thermal modification and ultrasonic modification. Thermal modification can be done using a furnace or microwave. Wahono et al. [55] reported using modified natural zeolite by calcination at high temperatures. Calcination is carried out over a temperature range of 400–800°C. Calcination of natural zeolite shows changes in crystal structure with the appearance of anorthite peaks when calcined at 400–800°C. At this temperature, the surface area of natural zeolite decreases when the calcination temperature is higher. Before calcination, natural zeolite that had undergone dealumination had a surface area of 146.91 m^2/g, but after the 800°C calcination process, there was a significant decrease in surface area, namely 35.72 m^2/g [55]. Ultrasonic modification utilizes ultrasound to improve geothermal properties by promoting the dissolution of Al-Si, strengthening the bonding at the interface between solid particles or gel phases, accelerating the polycondensation process, and improving the formation of semi-crystalline to crystalline phases, also increasing compressive strength and thermal stability of polymers [56].

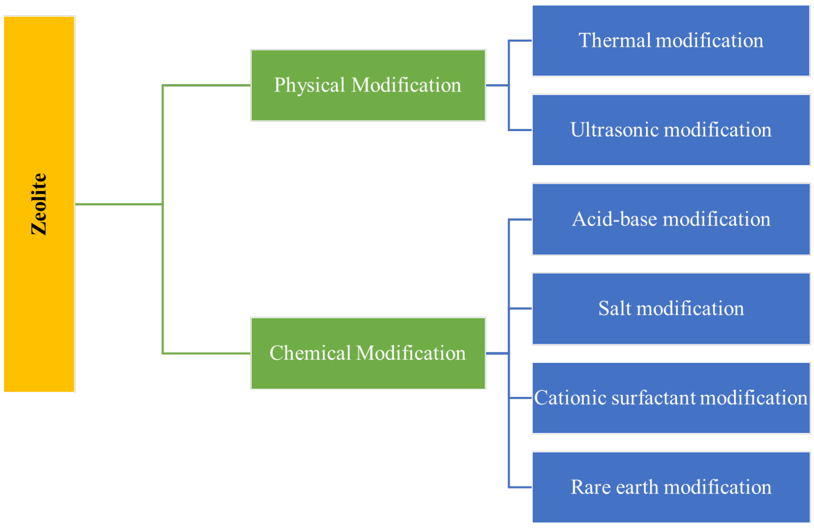

Figure 5. Classification of zeolite modification

Chemical modification includes using acids-bases, salts, cationic surfactants, and rare earth modification. Several studies have been carried out regarding the modification of zeolite by chemical methods. For example, Baskan et al. [57] modified the natural zeolite clinoptilolite using sodium chloride (NaCl) and iron (III) chloride ($FeCl_3$) to increase the adsorption capacity of the arsenic solution. Research conducted by Ngapa et al. [58] used the hydrothermal method to increase the adsorption capacity, cation exchange capacity (CEC), and adsorption capacity of organic substances. Yuan et al. [59] modified natural zeolite with the addition of magnetite particles (Fe_3O_4), and the results obtained increased the adsorption capacity as the pH of the solution decreased. On the other hand, Aboelfetoh et al. [60] modified the zeolite using tin ferrite ($SnFe_2O_4$) to increase the ability and capacity of zeolite adsorption on heavy organic compounds. Overall, zeolite modification is a promising approach to improve the performance of natural zeolites as adsorbents or catalysts in various environmental and industrial applications.

ZEOLITE AS HEAVY METAL ADSORBENT

Zeolites are frequently used as heavy metal adsorbents because of their special characteristics. Their porous design and large surface area are efficient at adsorbing heavy metal ions from aqueous solutions. The following are the main applications for zeolites as heavy metal adsorbents: ion exchange is one of the main methods used to adsorb heavy metals. They have a strong ion-exchange capacity and can substitute heavy metal ions for exchangeable cations in their structure (Figure 6). Zeolites can efficiently capture and immobilize heavy metals to the ion-exchange process. In addition, zeolites can selectively adsorb heavy metal ions according to their size, charge, and chemical characteristics. They are useful in removing heavy metals from contaminated water because of their selectivity. Zeolites also have a large surface area because of their porous structure, which offers plenty of active sites for heavy metal adsorption. Zeolites are also cost-effective for long-term use since they can be regenerated and reused after heavy metal adsorption by desorbing the captured metals under controlled circumstances [61]. Therefore, by removing heavy metals that may harm ecosystems and human health, zeolites play a significant role in environmental remediation, cleaning up contaminated water sources, industrial wastewater, and soil.

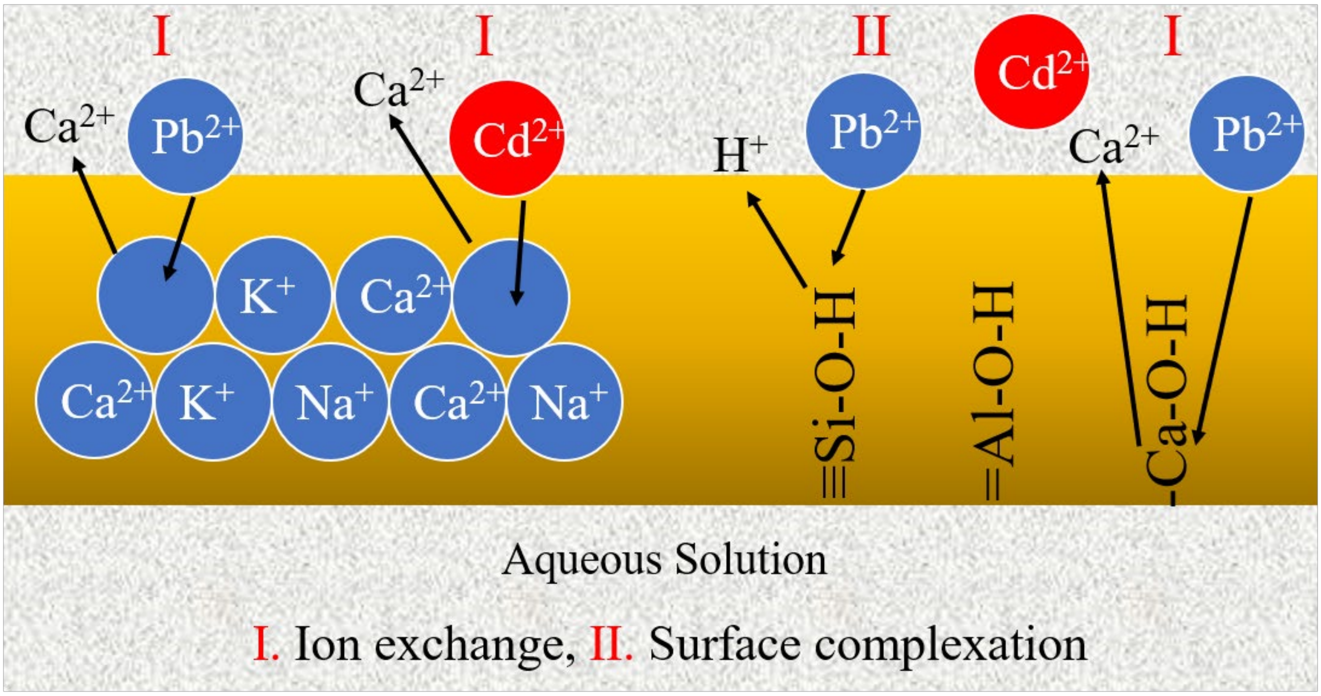

Figure 6. Schematic diagram for removal of heavy metals ion (Cd, Pb) with zeolite [62]

ARSENIC (As) ADSORPTION

Arsenic is the first element of the Agency for Toxic Substances and Disease Registry (ATSDR) lists that threatens human health. The prevalent forms of arsenic in water are inorganic, namely Arsenite (III)) and Arsenate (V). Besides its inorganic form, arsenic is also found in its organic forms, such as monomethylarsonate (MMA) and dimethylarsinate (DMA). Inorganic arsenic has a higher level of toxicity than organic form, with As(III) being more toxic than As(V) [63]. Exposure to Arsenic can interfere with human health, such as the nervous system, kidney, cardiovascular, respiratory, gastrointestinal, skin, and hematology, as well as diabetes and mutagenic and carcinogenic effects. Therefore, the adsorption of metal arsenic is of particular concern to researchers. Therefore, overcoming arsenic pollution is very important for human health and the sustainability of environmental and living creatures [64].

Natural zeolite, as a potential adsorbent of arsenic, has a negative charge on the surface. Therefore, natural zeolite cannot adsorb arsenic. Hence, it is vital to modify zeolite to have a positive surface. Several modifications have been reported to increase zeolite's adsorption capacity of arsenic in inorganic forms. One modification that has been carried out is the modification of the zeolite surface by surfactants. The process of modifying zeolites with surfactants is illustrated in Figure 7. Initially, ion exchange occurs between the cations in the zeolite and the cationic surfactants, forming a monolayer on the surface. Subsequently, a double layer is created as an outcome of ion exchange and tail-tail interactions of the surfactant. This process changes charge from negative to positive on the zeolite's surface, enhancing its adsorption capacity [65].

Barron et al. [64] conducted a study that involved modifying a natural zeolite, clinoptilolite, with hexadecyltrimethyl-ammonium (HDTMA) bromide. According to the research findings, the HDTMA-modified natural zeolite has 12.5 times greater arsenic adsorption capacity than the unmodified natural zeolite. The study of Gennaro et al. [63] also showed the same results as that of Barron et al. Gennaro et al. observed the ability of natural zeolite modified with HDTMA-Br and HDTMA-Cl surfactants. The findings indicate that modifying the zeolite surface with a cationic surface enhances its adsorption capability. Both types of modified zeolite can adsorb up to 80% of arsenic within an hour and 100% within two hours. Additionally, it was observed that pH significantly influences arsenic uptake with an adsorption of 0.19 mg/g at pH 7, increasing the adsorption capacity of zeolite. Surface modification can also be achieved by metal deposition on the surface of zeolite. Abdellaoui et al. [66] synthesized zeolite W from Fly Ash and modified the surface with Zr (5.04% wt) and Fe (6.9% wt) metals. The research findings demonstrate the effective removal of up to 99.87% As(V) by the adsorbent over a broad pH range from 2 to 10. The adsorption capacity is significantly high, with a value of 42.31 mg/g, compared to natural fly ash and unmodified zeolite. Both metals play a crucial role in adsorption because they form active sites on the zeolite surface, allowing them to capture As(V) with forms Ze-O-As and Fe-O-A bridge.

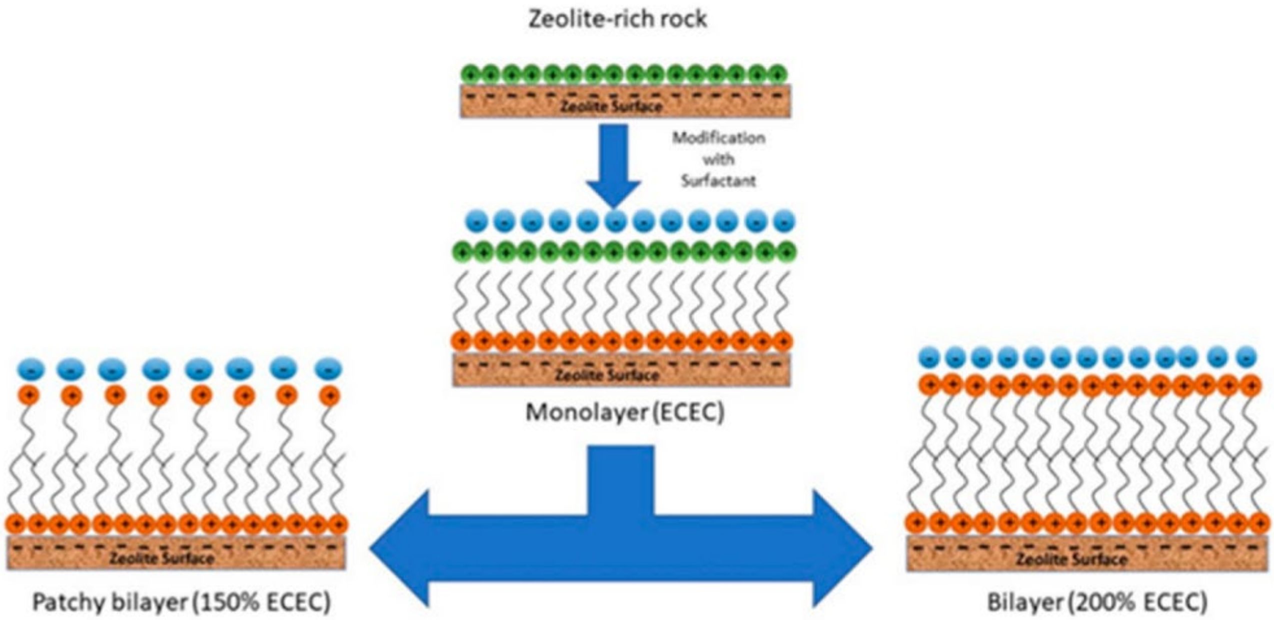

Figure 7. Schematic of zeolite surface modification using cationic surfactant [63]

The combination of zeolite with other materials is also reported to increase the adsorption capacity of zeolite. Zou et al. [67] synthesized a composite of iron oxide (nZVI)@ZSM-5, in which the surface of zeolite was modified with sulfur. The research showed that adding sulfur to the iron oxide (nZVI)-ZSM-5 composite increased the removal percentage from 89.1% to 94.5%. On the other hand, surface modification composite also reduces iron leaching. When using this composite, the Langmuir As(V) adsorption capacity shows a high adsorption capacity, namely 204.36 mg g–1. In addition, the high structural stability of S-nZVI-ZSM-5 shows that this adsorbent is effective and environmentally friendly. The synthesis of zeolite composites was also reported by Soni et al. [68], who synthesized zeolite composites derived from fly ash with reduced graphene oxide (rGO). The research results show that zeolite-rGO compost has a higher adsorption capacity than zeolite or rGO. The adsorption capacity of Zeolite-rGO reaches 49.23-145 µg/g [67].

CHROMIUM (Cr) ADSORPTION

Chromium is one of the toxic and carcinogenic metals that can damage renal and respiratory organs and affect the immune system of humans. This metal is produced by industrial waste and contaminates the groundwater and soil. Chromium can be found on Earth in different oxidation states, namely -2, -1,0, +1, +2, +3, +4, +5, and +6. Cr(III) and Cr(VI) are the most stable forms of chromium, with Cr(VI) metal ions being the most dangerous than other forms, and Cr (IV) is 500 times more toxic than Cr(II) [68].

Campos et al. [69] investigated the impact of surface modification on natural zeolite (mordenite) using cationic surfactants and their ability to remove Cr(VI). The findings revealed that surface modification with sulfuric acid-hexadecyltrymethylammonium (H_2SO_4-HDTMA) led to a 93% increase in its ability to remove As(VI). This is due to the negative charge most zeolites have due to isomorphic cation substitution in the crystal lattice, which causes natural zeolites to have little or no affinity for anionic species. In a study by Angaru et al. [70] using zeolite-based bimetallic composites supported by zero-valent iron (nZVI) and nickel (Ni) (nZVI/Ni@Faujasite Zeolite-A or FZA) from fly ash waste at low cost. This modification aims to adsorb heavy metal anions Cr(VI)) and cations (Cu(II)) from industrial waste at pH 3 and 5, respectively. The average surface area of nZVI/Ni@FZA (154.11 m^2/g) is much larger than FZA (46.6 m^2/g) and nZVI (4.76 m^2/g) based on N_2-adsorption instrument measurements. Based on the research results, the factors that affect the adsorption of Cr(VI) and Cu(II) by nZVI/Ni@FZA, namely pH, initial concentration, time, temperature, co-existing metals, ionic strength, and cumulative loading ability. The maximum adsorption capacities of nZVI/Ni@FZA were 48.31 mg/g and 147.06 mg/g for Cr(VI) and Cu(II). This capacity is higher than nZVI@FZA and FZA. This suggests that Ni has an important role in increasing the reduction ability of nZVI. In addition, the isothermal and kinetic results reveal that both heavy metal adsorption processes are Langmuir-monolayer adsorption. The thermodynamic results show that removing metal ions by adsorption is endothermic and tends to be spontaneous. The application of nZVI/Ni@FZA as adsorbents in industrial wastewater treatment shows that heavy metal concentrations have been successfully reduced to a predetermined standard limit. In addition, the adsorption capacity of nZVI/Ni@FZA was higher than that of nZVI@FZA and FZA. The overall results show that nZVI/Ni@FZA is a promising, efficient, and economically viable adsorbent for wastewater treatment.

LEAD (Pb) ADSORPTION

While natural sources can contribute to Pb(II) metal pollution, the primary factor is industrial activity, including waste from battery production, disposal of used batteries, and mineral mining processes [71]. If water is contaminated with Pb, there is potential for accumulating this substance through the food chain in humans. Pb can negatively impact the nervous system, reproduction, respiration, and human body tissues. To prevent this, US Environmental Protection Agency (USEPA) recommends that a maximum limit of below 0.02 mg/L is set for Pb in water [72].

Zeolite has commonly been employed as an adsorbent for Pb, with both natural and synthetic types being utilized. Praipipat et al. [73] conducted a study whereby a composite of iron(III) oxide-hydroxide-zeolite A, derived from sugarcane bagasse fly ash, was synthesized using various techniques to adsorb Pb. The study's findings suggest that incorporating iron(III) oxide-hydroxide can enhance the adsorption capacity of zeolite A, up to 416.67 mg/g for zeolite A and 666.67 mg/g for the composite. Figure 8 presents the mechanism of lead (II) adsorption on the iron(III) oxide-hydroxide-zeolite A composite. There are three mechanisms involved in Pb adsorption. Firstly, the positively charged Pb ion (Pb^{2+}) is adsorbed by the O^{2-} on the zeolite, forming a strong coordination bond between Pb^{2+} and O^{2-}. Secondly, the hydroxyl groups on zeolite A combine with iron(III) oxide-hydroxide to form complex molecules with shared electrons, subsequently adsorbing the lead ions. The last adsorption mechanism involves the absorption of lead ions by carboxylate groups of sodium alginate formed on the surface of zeolite A by deprotonating hydrogen from carboxylate groups to obtain a negative charge. Adding iron(III) oxide-hydroxide results in a boosted adsorption capacity, owing to the amplified negative charge on the zeolite's surface [74].

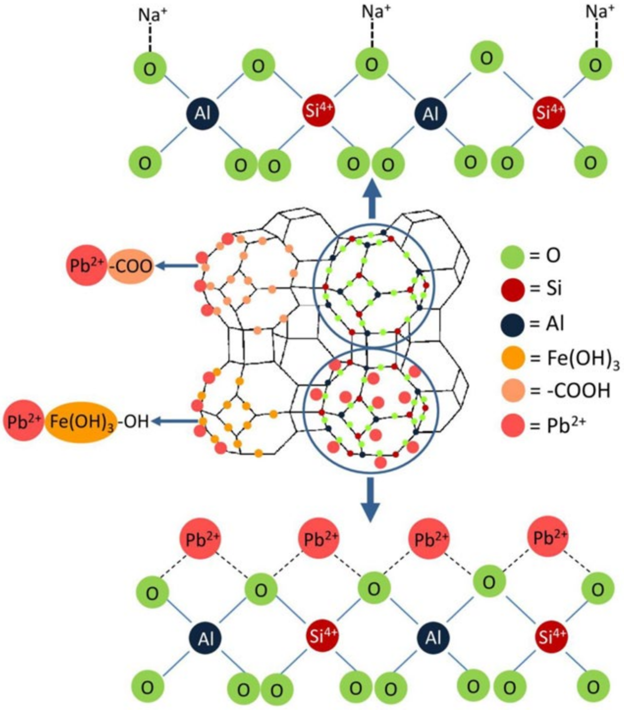

Figure 8. Mechanism adsorption of Pb with iron(III) oxide-hydroxide-zeolite A [73]

Table 2. Adsorption capacity of several zeolites for Pb(II) removal

Adsorbent	Adsorption Capacity (mg/g)	References
Zeolite from industrial fly ash	196.24	[76]
Zeolite from low-calcium fly ash	186.22	[77]
Zeolite X from Kaolin Egypt	213.416	[78]
Zeolite A from Egyptian Kaolin	182.336	[78]
Zeolite from South Lampung	72	[79]
Synthetic Zeolite with Al and silica gel	9.33	[80]

The use of zeolite as a lead adsorbent has also been reported by Bu et al. [75] which had been synthesized by the hydrothermal method. The synthesized NaY zeolite has a surface area, pore volume, and average of 759.008 m^2/g, 0.318 cm^3/g, and 6.450 nm. The synthesized NaY zeolite showed a high adsorption capacity for removing Pb^{2+} metal ions [73]. The amount of Pb(II) adsorption increased with the increase in the number of NaY. However, the adsorption capacity will reach maximum when the NaY dose exceeds 0.5 g/L. This shows that a greater amount of NaY is needed to remove Pb^{2+} at a higher concentration of Pb^{2+} [75]. The several types of zeolites used for Pb(II) adsorption are listed in Table 2.

CADMIUM (Cd) ADSORPTION

Cadmium (Cd) is a heavy metal that is non-degradable in living organisms and is toxic even in small concentrations [81]. Cadmium can come from various industrial waste processes, such as battery waste, mineral mining, and industrial paint companies [82]. Cadmium contamination in waters can lead to bioaccumulation with a biological half-life of >30 years and cause various human health problems. In light of this, the maximum cadmium concentration allowed in drinking water, according to the recommendations of the World Health Organization (WHO) and The European Public Health Alliance (EPHA), is 0.003 mg/L [83].

The utilization of zeolites for cadmium adsorption has been extensively developed. However, further research is necessary, particularly regarding exploiting cheap and widely available raw materials. Lv et al. synthesized zeolite A from residuals of lithium leaching [74]. The observations indicate that synthesized zeolite A has a substantial adsorption capacity of 193,798 mg/g. The findings also reveal that pH and temperature affect adsorption speed. The synthesized zeolite A showed better Cd(II) adsorption at higher pH levels. Low pH levels resulted in competition between H^+ and Cd, compromising the adsorption process and the integrity of the zeolite framework. As the pH increases, the deprotonation process in the hydroxyl groups of the zeolite is encouraged, consequently increasing its adsorption capacity. Lv Siamati's research has revealed the adsorption mechanism, demonstrating that it results from the ion exchange between Na^+ and Cd^{2+} and the interfacial reaction between Cd^{2+} and the hydroxyl groups in the zeolite structure [74].

Nguyen et al. have also reported similar research regarding using zeolite as a cadmium (II) adsorbent [84]. Based on the research results of Nguyen et al., there was an increase in Cd(II) metal adsorption using iron-modified zeolite (ICZ). ICZ has a higher adsorption Cd(II), 0.93 mg/g, and the zeolite only adsorbs Cd(II) as big as 0.52 mg/g. The results carried out by Tasic et al. [85] showed that natural zeolite from certain natural sources showed high adsorption efficiency for cadmium. Another study reported by Peng et al. [86] strengthens the contribution of natural zeolite in overcoming cadmium pollution in wastewater. Research on zeolite modification has also been carried out to improve the performance of natural zeolite as an adsorbent. For example, Vasylechko et al. [87] modified natural zeolite with hydrochloric acid (HCl) for 24 hours and found that this modification increased the adsorption efficiency of cadmium by 88–92%. Another study by Zhang et al. [88] explored modified zeolite with Zn-layered double hydroxides (Zn-LDHs) coating with an efficiency above 67%.

NICKEL (Ni) ADSORPTION

Nickel metal pollution can come from various sources, such as cell phone and medical equipment waste, and the largest contributor comes from the mineral mining industry [89]. Nickel is a hazardous and cancer-causing substance that can dissolve easily in waste streams. The World Health Organization (WHO) mandates a limit of 0.01 mg/L of nickel in drinking water and 2 mg/L of nickel discharge in wastewater. High levels of exposure to this metal can result in kidney and lung damage, in addition to causing shortness of breath, vomiting, and skin and nose dermatitis [90]. Therefore, the adsorption of nickel metal from water and waste solutions is a significant research focus in controlling environmental pollution.

Natural and modified zeolite have become promising adsorbents for reducing nickel content in water systems. Research related to the use of zeolite as a nickel adsorbent has been reported by Shaheen et al. [91], who reported that natural zeolite (clinoptilolite) can adsorb up to 28% of Ni(II) in water. In addition, Pahlavanzadeh and Motamedi [92] also revealed the ability of zeolite to reduce nickel content from solution. Pahlavanzadeh and Motamedi [90] used 3A zeolite and 3A modified zeolite with $Mg(OH)_2$. The modified 3A zeolite showed a 20% increase in Ni adsorption compared to zeolite 3A without modification. Zeolite 3A can adsorb up to 95% Ni(II) within 2 hours. A study reported by Mehdi et al. [93] explored the use of natural zeolite (mordenite) modified with sodium chloride (NaCl) to enhance the adsorption ability of nickel from wastewater. Mehdi's research results show that Na-mordenite zeolite has a high area of 124.95 m^2/g with a total pore volume of 0.45 cm3/g and can remove up to 95.13% Ni(II) concentration [93]. In addition, Iznaga et al. [94] used a modified natural zeolite with ammonia for nickel adsorption and found that the adsorption capacity increased with increasing temperature. In addition, Rohmah et al. [95] modified the zeolite with dithizone-immobilized coal fly ash (IFA) and reported the results of increasing nickel adsorption faster than activated coal fly ash (AFA).

MANGAN (Mn) ADSORPTION

Manganese is a pollutant in the environment, particularly in waters, due to the activities of the iron and steel industry. Manganese forms many alloys as it is used in steel alloys to improve forging qualities in strength and hardness with industrial alloys, especially in stainless steel. Mn metal ion speciation is highly dependent on the pH of the solution, and manganese (Mn) exists as Mn(II) from pH 2 to pH 8 [96]. In a study by Putra et al. [97], Mn(II) adsorption characteristics on zeolite adsorbents synthesized from bottom ash under alkaline hydrothermal conditions modified with dithizone showed increased adsorption capacity. The adsorption equilibrium results of Mn(II) metal ions followed the Langmuir isotherm model with maximum adsorption capacities of synthetic zeolite and dithizone-modified zeolite of 14.493 mg/g and 15.873 mg/g, respectively. Meanwhile, the thermodynamic model of Mn(II) metal ion adsorption produces a negative enthalpy energy (ΔH^o) (exothermic process). In addition, the adsorption results of dithizone-modified zeolite towards Mn(II) metal ions are not better and tend to be weak because Mn(II) ions are considered strong acids, while the –NH and –SH active groups in dithizone are soft bases. Other studies on zeolite synthesis from fly ash and its application as an Mn(II) metal adsorbent also showed high efficiency. For example, Belviso et al. [98] compared the absorption behavior of manganese from fly ash and synthesized zeolite. The batch method with different masses of the two adsorbents (10–60 g) was added to a solution containing a total metal Mn concentration of 10 mg/L. The results indicated that the two adsorbents are effective for removing Mn from aqueous solutions by precipitation due to the high pH of the solid/liquid mixture. Moreover, both adsorbents can remove almost all Mn contaminants (~99%) in just a few minutes. After 5 minutes, the amount of Mn removed was very high and remained constant until t = 60 minutes. This batch method revealed that the short contact time was sufficient to reduce the amount of Mn in the contaminated solution. Thus, synthetic zeolite is a more suitable adsorbent for removing Mn from polluted water than fly ash.

CONCLUSIONS

Zeolite is an excellent adsorbent for heavy metals. It has properties such as ion exchange, adsorption, dehydration, and rehydration, which are environmentally friendly, low cost, regenerative, easily accessible, and readily available, making zeolite an excellent adsorbent. These properties can help reduce costs and pollution from many environmental pollutants. In addition, to obtain a greater adsorption capacity of heavy metals, the properties of zeolites can be improved by various modifications with acids, bases, salts, surfactants, or metals. Modification by surfactants and metals is widely used to increase the adsorption capacity of heavy metals such as chromium and Arsenic. The batch adsorption system used is another important factor in heavy metal removal. In addition, the adsorption behavior of heavy metals in zeolite can be determined in relation to the mathematical model. According to the literature review, the Langmuir model is the most suitable mathematical model for adsorption isotherms and pseudo-first and pseudo-second order for adsorption kinetics. However, the main factor for achieving higher adsorption of heavy metals in zeolite depends on the contaminated pollutant water source and the zeolite's nature. Although some research results have been presented indicating that zeolites can adsorb metals in pollutant water samples, no detailed studies have been presented that analyze the mechanism or behavior of zeolites in the presence of other elements which may contain different organic and inorganic constituents, depending on their origin. Future research should analyze the performance of zeolite in actual waters from different sources to study its behavior under various conditions.

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