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Differences in Heavy Metals Adsorption on Natural, Modified, and Synthetic Zeolites-A Review

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Abstract: This paper presents a comprehensive study of the differences in heavy metal adsorption on natural, modified, and synthetic zeolites. Heavy metal treatment and adsorption are critical issues in today's modern world, and despite advancements in technology, they remain a global challenge. Industrial effluents are a major source of heavy metal pollutants, which have a severe impact on human health and the environment. Therefore, removing heavy metals from contaminated water and wastewater is a necessity. Adsorption is the most commonly used method for removing heavy metals from the environment due to its cost-effectiveness, design, and performance. Among various adsorbents, zeolites are currently considered a suitable method due to their cost-effectiveness, simplicity, and the varying ion-exchange capacity of natural zeolites worldwide for cations such as ammonium and heavy metal ions. The findings of this research could provide useful information for developing efficient and cost-effective methods for the removal of heavy metals from water and wastewater, thus addressing a critical global issue. The outcomes of this research contribute to promoting a green and healthy environment.

Keywords: Zeolites, adsorption, toxic element, heavy metals, green environment.

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1. INTRODUCTION

Heavy metals are commonly defined according to their density; metals with a density higher than 5 g.cm^{-3} are classified as heavy metals (1). According to latest research, it shows that Fe, Pb, Cu, Ni, Cd, and Cr, etc. as heavy metals are the most common pollutants found in industrial wastewater (2) and heavy metals pollution is indicated as one of the most serious problems facing humans and other organisms due to its accumulation in the living organism's and non-biodegradability (3,4). For instance, research on primates has indicated that exposure to lead results in significant behavioral and cognitive deficits like learning ability, memory, adaptability, impairments in activity, and increased distraction, and Pb is known for its high carcinogenic and mutagenic dominance (2,5). Arsenic accumulation in living organisms, including humans, causes skin cancer, and black foot disease (6), and chronic exposure to Cr may produce several health issues (cancer, hepatic injury, and genetic defects) are reported (7). The recommended dietary intake of zinc, depending upon age and sex, is between 4 and 15 mg.day^{-1}. However, intake of excessively large doses of such elements by human, leads to severe damages to the health. Symptoms of zinc toxicity in humans include vomiting, dehydration, electrolyte imbalance, abdominal pain, dizziness, and lack of muscular coordination (8). Heavy metal contaminant exists in many industrial wastewaters, such as metal plating facilities, mining operations, nuclear powerhouse, fertilizer industries, paints and pigments, municipal and storm water run-off, battery and tannery industries (9). Heavy metal pollutants, especially metal ions such as (Fe^{3+}, Cr^{3+}, Cu^{2+}, and Pb^{2+}) are not disposable (10) and their stockpile in living organisms causing various infections that affect the brain nervous system, hematopoietic, and renal diseases. World Health Organization (WHO) recommends exceedingly low maximal suitable concentrations for the harmful heavy metal cations in daily use drinking water, this recommendation has been welcomed by governments around the world (11). In our ecosystem, there are huge sources of heavy metals that flow with the wastewater streams like batteries, agriculture activities, electroplating, smelting, mining operations, paint, and pigments (4). Technological and industrial promotion is known for their generation of toxic remaining chemicals with the potential to originate numerous infections in the animals and human body. Noteworthiness, the toxic metals are classified among the most concerning compounds in the environment (12), hence to meet increasingly stringent environmental quality and clean life standards, they must be removed from the polluted streams (13). There are various treatment processes available in the literature for metal-polluted waste streams, such as coagulation, chemical precipitation, oxidation of heavy metals, solvent extraction, membrane filtration, electrolytic processes (14), ion exchange (11), precipitation (4), reverse osmosis (15), clotting disambiguation (4), flotation, flocculation (16), electrochemical treatment technologies (12), adsorption and photocatalytic degradation of heavy metals, among these techniques and methods, adsorption as a cost-effective technology, offers flexibility and facile operation and design (14) are frequently in use due it's efficient in removing organic and inorganic contaminants from aqueous environments (17). On the other hand, activated carbon is widely acknowledged as the primary adsorbent for various adsorption processes due to its remarkable properties such as high surface area and superior adsorption capacity. However, its relatively high cost and the requirement for periodic regeneration pose certain challenges. This has prompted the quest for alternative adsorbents that are readily available and cost-effective. As a result, researchers have been actively seeking new adsorbents to replace activated carbon. (18). Zeolites are widely used as adsorbents in the removal of hazardous substances, and as advanced additives or catalysts in construction due to their low cost and high efficiency (19). However, zeolites are considered one of the most prominent types of inorganic cationic exchangers due to their exceptional properties such as high ion exchange capacity, remarkable selectivity, and ability to adapt to various natural environments (2). Ion exchange process is especially used to remove heavy metals and elements leading to hardness from water and wastewater (20).

This review presents a brief view of the mechanisms of heavy metal sorption on natural, modified, and synthetic zeolites. The major objectives were: Differences in heavy metals sorption on zeolites. Environmental implications of heavy metal removal. The studying of these objectives will provide valuable information about the use of zeolites to treat heavy metals in environmental pollution.

2. NATURAL, MODIFIED, AND SYNTHETIC ZEOLITES

Zeolites are crystalline aluminosilicates with a general formula of Ax/n (SiO_2) $(AlO_2)_x{\cdot}mH_2O$, where A represents a cation (21). These materials have attracted significant attention and have been extensively applied in the energy and environmental industries (22,23,20). As a result, fundamental research on their properties, such as ion exchange, adsorption, and catalysis, has become a key area of interest for the zeolite researchers in different application and synthesis research, such as green chemistry, materials science, green environmental science, and most commonly chemical engineering (24) to developed novel methods to overcome this issue. Highly dealuminated zeolites contain both mesopores and micropores (25), and the pores zeolites' dimensions provide size also suitable shape selectivity for the new guest molecules such as heavy metal ions. The micropores can restrict the diffusion rates of reactant and product molecules due to their configurational regime of diffusion of the zeolite molecules (26). Natural zeolites and synthetic zeolites, which are designated with specific letters that indicate Type A, X, Y, and ZSM, have been extensively studied (27).

The remarkable properties of natural zeolites and their modified forms have revolutionized environmental remediation processes, making them an indispensable tool in mitigating the harmful effects of pollution. These materials have been extensively studied by researchers for their remarkable adsorption capabilities, enabling them to capture a wide range of cations, anions, and molecular species. As a result, they have become highly versatile in various environmental remediation processes such as water and wastewater treatment, soil remediation, and aerial purification.

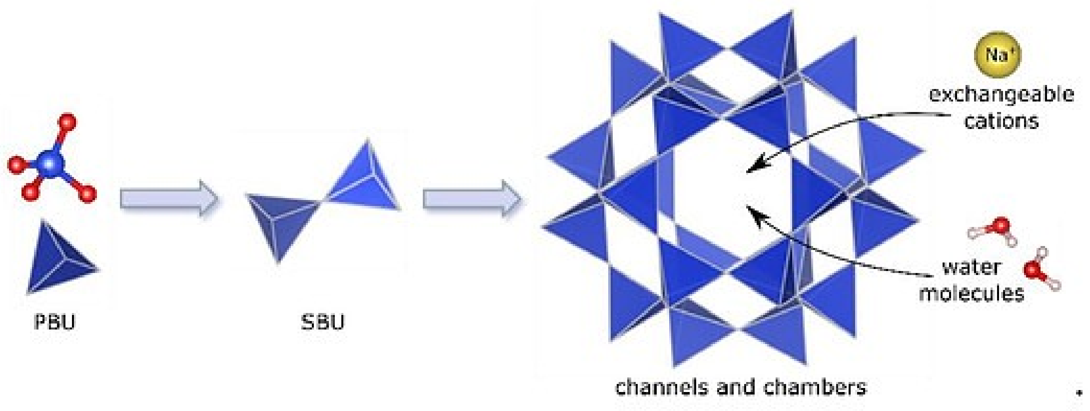

Figure 1: Schematic view of zeolite structure parched from ref (28).

Over the years, researchers have conducted numerous studies on the adsorption efficiencies of natural and synthetic zeolites, as well as their modified forms, in capturing various pollutants. These studies have mainly focused on removing heavy metal cations, including cadmium, lead, nickel, manganese, zinc, chromium, iron, and copper, as well as anionic species such as chromate and arsenate, and organic pollutants like volatile organic compounds (VOCs) such as benzene, toluene, ethyl benzene, and xylene. (24).

The modification of natural zeolites using heavy metals is a promising technique for enhancing their effectiveness in inorganic anion adsorption through surface precipitation. This approach involves the deposition of heavy metal ions onto the surface of natural zeolites to create an effective adsorbent material (29). The abundance of zeolite in nature, along with its low cost, stable structure even in acidic environments, and strong adsorption capacity, have made it an attractive option for industrial wastewater treatment (3, 30, 31). These desirable properties have led to an increase in interest in zeolites (3).

Natural crystalline aluminosilicate minerals include a class of materials named zeolites by the researcher, these natural zeolites materials like CP (clinoptilolite), phillipsite (32), and heulandite originating from alterations of glass-rich volcanic rocks structures that includes fresh or saline water in the molecules. There are also several synthetic and modified with different metal zeolites like ZSM-5, mordenite, and surfactant modified, also can be found alkaline-treated zeolites that can be designed and synthesized in the laboratory to obtain specific and acceptable properties in particular large surface areas with the different pore sizes to promote the application area and diversity (33). However, using natural zeolites, required an activation step to activate the metal side in the zeolite molecules. Natural zeolites show better properties than synthetic ones in commercial separation, it is maybe because synthetic zeolites will synthesize with special conditions and temperatures but natural zeolites form in natural conditions for long period (34).

Zeolite’s three-dimensional structure is mainly constructed by $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra (2,3). Zeolites are fascinating minerals that possess unique properties due to their microporous crystalline structure. Their framework is based on repeated units of silicon-oxygen and aluminum-oxygen tetrahedra, and they contain exchangeable alkaline and alkaline-earth metal cations that maintain charge neutrality within the crystal lattice. This characteristic allows zeolites to selectively exchange cations with certain other cations in solutions, such as Pb, Cd, Zi, and Mn. The ion-sieving properties of zeolites are used in various commercial applications, as they can selectively exchange ionic species with diameters small enough to fit through the entry ports of the internal zeolite framework while excluding larger species. This unique feature is particularly useful in industries such as water purification and chemical manufacturing (1). The extensive variation in chemical composition among zeolites necessitates a dependable classification system that is based solely on structural considerations. Framework zeolites, in particular, are constructed from primary building units (TO_4 tetrahedra) that are linked together to form a three-dimensional network, with each oxygen atom being shared by two tetrahedra. This sharing coefficient generally ranges from 2 to slightly less than 2. While this process generates numerous potential theoretical networks, only a small number of complex structural units, known as secondary building units (SBUs), have thus far been identified in silicate frameworks. These SBUs consist of a limited number of tetrahedra, typically no more than 16, and have been recognized in only such frameworks (30).

ZSM-5 is a unique and versatile synthetic zeolite that has revolutionized the petroleum industry since its first synthesis in 1975 by Mobil Oil Company. Unlike other naturally occurring zeolites, ZSM-5 has a high silica content and a distinctive pore structure with two different pore systems, which makes it an excellent heterogeneous catalyst for hydrocarbon isomerization reactions. Its chemical formula, $Na_nAl_nSi_{96}\text{-}nO_{192}\cdot 16H_2O$, highlights its composition, where the ratio of aluminum to silicon atoms can vary between 0 to 27. The pore system of ZSM-5 consists of zigzag and straight channels with a hydrophobic tendency, which makes it favorable for adsorbing non-polar molecules such as hydrocarbons. Furthermore, ZSM-5's hydrophobicity and pore size makes it an effective adsorbent for MTBE, a common gasoline additive. ZSM-5 in its raw or modified forms serves primarily as a catalyst and adsorbent, enabling it to find a wide range of applications in the chemical, petrochemical, and environmental industries (33).

CP is the most commonly occurring and abundant known natural zeolite, with significant reserves found in many sedimentary deposits worldwide (4, 33, 35). Its chemical composition is generally represented by the formula $Na_6[(AlO_2)_6(SiO_2)_{30}]\cdot 24H_2O$ (32,61), with a microporous crystal structure typical of alkali such as Na+K>Ca+Mg metals-rich HEU (heulandite) type zeolites with (Si/Al≥4) ratio. Clinoptilolite is also a member of heulandite zeolites that have many common orders, which consists of crystalline Al-silicates characterized by a cage-like microstructure contacted to the atoms by a tetrahedral geometry with three-dimensional type between SiO_4 and AlO_4 network, the order of the bonds is as follow: in this molecules, Si and Al's atoms are at the center of the molecules and oxygen atoms placed at the corners of the molecules of zeolite. The linkage between metals (Al and, Si) with oxygens has made basic tetrahedral geometry units linked through oxygen atoms to form a polyhedral network that constitutes secondary structures of the zeolites (35). Clinoptilolite possesses a two-dimensional channel system comprising three distinct channel types (33), as depicted in Figure 2.

Fe-modified zeolites have been found to exhibit a high capacity for adsorbing heavy metals in solution, effects by some factors: including pH, temperature, and metal concentrations (4). Clinoptilolite, due to its absorption capability for various pollutants, abundance, and relatively low cost, has emerged as an effective metal adsorbent for many water purification applications, especially in the field of removing heavy metals from industrial wastewater (14). Moreover, studies in the works of literature indicate that naturally availed zeolites, CP (clinoptilolite), possess lower adsorption capacities for toxic metals when compared to their synthetic counterparts (36).

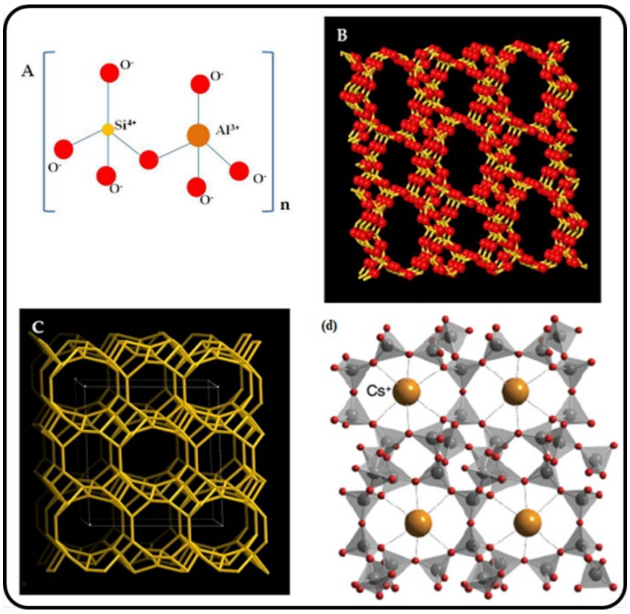

Figure 2: Simplified structure of the (a, b, and, c) (37), CP linked SiO4 tetrahedra and pores with metal cations (e.g., cesium, Cs+) available for ion-exchange (d) (38), that demonstrates the relationship between the trapped cesium ion and the framework.

Zeolites have a wide range of practical uses, including effective chemical sieves, water softeners, and adsorbents. Their unique structural characteristics and adsorbent properties make them particularly well-suited for these applications. The structural cavities and channels of zeolites are capable of hosting a variety of alkaline and alkaline earth cations and water molecules in different complexes. One of the most important applications of zeolites is the removal of heavy metals from drinking water and wastewater, which is typically achieved through a process called ion exchange. In this process, ions such as Na^+, K^+, and Ca^{2+} are utilized to replace the heavy metal ions in the water. Toxic metals from the solution such as drinking water replace the ion metals that are available in the pores of the zeolite. For the ion exchange process to be successful, several factors must be taken into consideration. These include the concentration and properties of both cations and anions, the temperature and pH of the system, as well as the crystal structure of the zeolite itself. By carefully controlling these variables, we can optimize the ion exchange process and achieve the best possible results (4). To obtain and create hierarchical zeolites, it is important to interconnect the inherent microspores with other pore systems that play complementary roles within the system. This can be achieved through various routes, such as post-synthesis modification, the use of soft templates in the starting gel, or the formation of composites with macro/mesoporous materials. By combining more than one strategy, it is possible to create macroporous monoliths with specific shapes and functional surfaces formed by the zeolite covering. This approach offers a powerful tool for tailoring the properties of zeolites to meet a wide range of industrial and scientific needs (12, 31).

Researchers have extensively studied the ability of naturally available and synthetic modified clays to conserve harmful chemicals and pathogenic bacteria at named clay surfaces. Zeolites differ from clays in that they typically occur in larger particle sizes, ranging in size from millimeters to greater. Additionally, unlike clays, zeolites do not exhibit shrink-swell behavior. This property makes them highly useful in a variety of applications, such as adsorbents, catalysts, and molecular sieves, where stability and consistency are critical factors in their effectiveness. (15). Both naturally occurring and synthetic zeolites are highly effective in adsorbing heavy metal cations from contaminated water streams. These metals include but are not limited to Cu^{2+}, Cd^{2+}, Cr^{6+}, Zn^{2+}, Pb^{2+}, and Hg^{2+}. Zeolites can selectively adsorb these metals due to their unique structural characteristics and surface chemistry, making them valuable tools in environmental remediation efforts. They measured the theoretical MAC (maximum adsorption capacities) of zeolite for Cu^{2+}, Cd^{2+}, Cr^{6+}, Zn^{2+}, and Pb^{2+} in seawater to be 3.05, 1.12, 0.32, 13.10, and 6.11 $mg.g^{-1}$, respectively. The addition of zeolite at varying dosages (0.5, 2.0, and 4.0 g L^{-1}) has been found to effectively reduce the bioaccumulation of cadmium. The reduction rate was found to increase with the dosage administered. This demonstrates the potential of zeolites as a cost-effective and efficient solution for reducing the harmful effects of heavy metal bioaccumulation in a variety of environments (24).

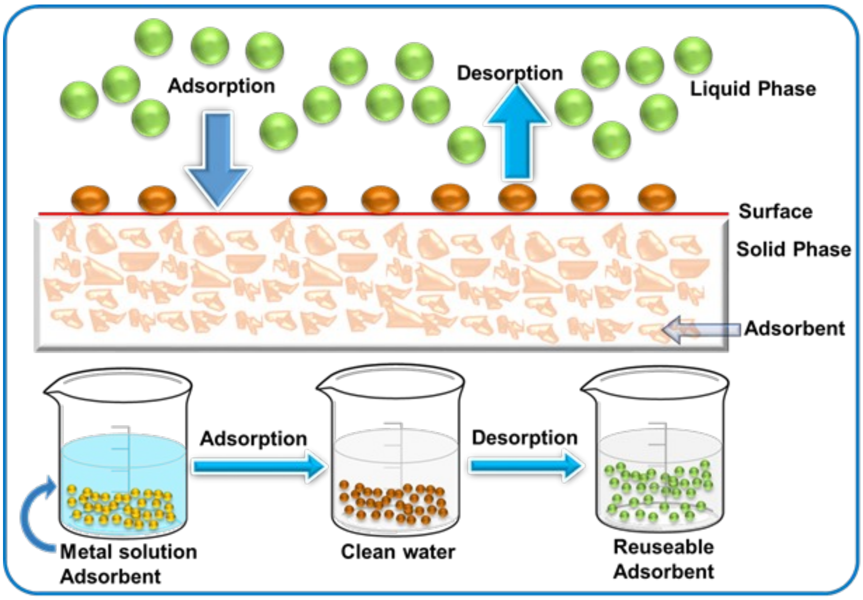

Figure 3: Schematic view of the mechanism of the metal ions adsorb–desorption process in wastewater.

Figure 4 demonstrates that the adsorption rate of NaCl-modified synthetic clinoptilolite for Pb^{2+} is minimally affected by pH, while the adsorption rates for Zn^{2+}, Cd^{2+}, and Cu^{2+} increase with increasing pH and adsorbent dosage. This is due to the high selectivity of clinoptilolite for Pb^{2+} over the other metal cations. At a pH of 2, NaCl-modified synthetic clinoptilolite has a low amount of adsorption for Zn^{2+}, Cd^{2+}, and Cu^{2+}, likely due to the low selectivity of clinoptilolite at low pH and the strong competition from H^+ ions. However, by decreasing the competition from H^+ at higher pH, the amount of adsorption significantly increases. In Figure 5, the removal efficiency of NaCl-modified synthetic clinoptilolite for Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} is shown. The data indicate that the removal efficiency and amount of adsorption are determined by various factors, such as theoretical adsorption capacity, selectivity, and solid-to-liquid ratio. A high solid-to-liquid ratio leads to higher removal efficiency but lower adsorption due to the increased amount of adsorbent. However, the solid-to-liquid ratio has a lesser effect on the adsorption behavior of clinoptilolite for Pb^{2+} due to its high selectivity. Overall, these results highlight the potential of NaCl-modified synthetic clinoptilolite as an effective adsorbent for removing heavy metals from contaminated water streams (11).

The ratio between Si and Al is the main and important parameter for the properties of zeolites, like hydrophilicity, and cation exchange capacity ph. Zeolites are a diverse group of materials that can be classified based on their Si/Al ratio. As the Si/Al ratio decreases, zeolites tend to have higher acidity and hydrophobicity, but lower ion exchange capacity. In aqueous solutions, cation exchange occurs through the substitution of Si^{4+} by Al^{3+}, leading to negative charges on the zeolite surface. When these negative charges are balanced by metal ions such as Ni^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, and Cd^{2+} in wastewater, zeolites become effective adsorbents with high cation exchange capacity. In addition, zeolites can become acidic when a proton (H^+) is used to balance the material charge, and the acidity of zeolites is proportional to the Al content and related to the Si/Al ratio. As the Si/Al ratio increases in zeolites, the number of cations that can interact favorably with water decreases. This leads to a reduction in hydrophilicity, making zeolites less water-friendly. However, the isomorphic substitution of Si^{4+} by Al^{3+} offers the opportunity to modify zeolites through the introduction of cations. Metal ions and surfactants can be added to zeolites to enhance their properties and tailor them to specific applications. This modification process can increase the selectivity and efficiency of zeolites for various adsorption and catalytic reactions. Modified zeolites can also exhibit improved stability and durability under harsh conditions. These modifications can expand the range of applications for zeolites and enhance their potential for industrial and environmental applications (33).

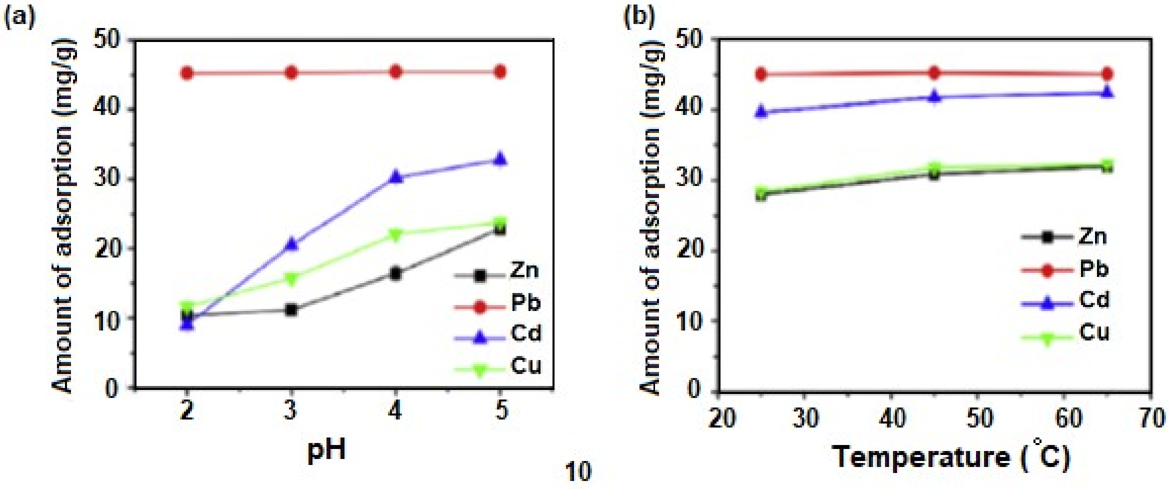

Figure 4: NaCl-modified synthetic-CP adsorption capacity for named metals ion as a function of pH(a) and temperature (b) (8).

Studies have been conducted on the adsorption behavior of four different metal ions, namely Pb^{2+}, Cu^{2+}, Cr^{6+}, and Cd^{2+}, on Fe_3O_4/mesoporous silica. The study showed that the pseudo-second-order model and Langmuir sorption isotherm were followed, with maximum adsorption capacities of 127.24, 125.80, 115.60, and 114.08 $mg.g^{-1}$ for Pb^{2+}, Cu^{2+}, Cr^{6+}, and Cd^{2+} metal ions, respectively. The results revealed that the binding capacity followed the order of $Pb^{2+} > Cu^{2+} > Cr^{6+} > Cd^{2+}$. In addition, the use of Fe_3O_4/SiO_2/Zr Metal-Organic Frameworks showed promising results for the removal of Pb^{2+}, methyl orange, and methylene blue, with adsorption abilities of 102.2, 128, and 219 $mg.g^{-1}$, respectively. The maximum adsorption capacity of 248 $mg.g^{-1}$ was achieved at pH 10 when utilizing Fe_3O_4/silica (0.14:1 mass ratio) for the removal of methylene blue at an equilibrium time of 100 minutes and a temperature of 25 °C. Furthermore, mesoporous γ-Fe_2O_3/silica NCs showed a maximum adsorption capacity of 476 $mg.g^{-1}$. These results suggest that these materials could be effective adsorbents for the removal of heavy metals and dyes from wastewater. The results highlight the potential of Fe_3O_4/mesoporous silica and Fe_3O_4/silica for the removal of heavy metals and dyes from contaminated water. The high adsorption capacity and efficiency of these materials make them attractive candidates for use in wastewater treatment applications. However, further research is needed to investigate the performance of these materials under different operating conditions and in real-world scenarios. (36).

Table 1 and Table 2 summarize the heavy metal (Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, $Ni^{2+,}$ and Cr^{3+}) maximum adsorption capacity in the natural, modified and synthetic zeolite. From the study of Tables 1 and 2, the reaction facilitated under acidic and neutral conditions that are obtained by using Nano Fe-Al zeolite the maximum adsorption capacity (MAC) of Cr (VI) metal ions collected the results show 44.74 $mg.g^{-1}$ at the pH of 3. On the other hand, Cr^{6+} ions removal efficiency at pH < 6 was extremely higher than Cr^{6+} ions removal efficiency at pH > 6, (5). Likewise, the maximum absorption capacity for Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, $Mn^{2+,}$ and Cr^{3+} by using natural zeolite is in the following order 159.00 $mg.g^{-1}$, 33.07 $mg.g^{-1}$, 25.76 $mg.g^{-1}$, 2.08 $mg.g^{-1}$, 0.44 $mg.g^{-1}$, 4.00 $mg.g^{-1}$, 5.81

mg.g^{-1}. In the next step by using modified and synthetic zeolite maximum absorption capacity for Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, $Co^{2+,}$ and Cr^{3+} are in the following results were obtained: 228.00 mg.g^{-1}, 129.30 mg.g^{-1}, 101.70 mg.g^{-1}, 132.10 mg.g^{-1}, 41.47 mg.g^{-1}, 83.2 mg.g^{-1}.

It is of utmost importance to perform an in-depth analysis of the isotherm data to formulate a precise equation that effectively represents the results, which can then be utilized for design purposes. The study of adsorption isotherm necessitates the exploration of equilibrium models such as (M-Lan), (M-Fre), (M-D.K. R), and (M-Fre-Iso). The results obtained from the sorption isotherm of natural and modified zeolites are presented in Table 3. The findings reported in Table 3 demonstrate that the removal of Cr^{3+} from metal solutions by Brazilian natural zeolite was accomplished with a high degree of efficiency, achieving removal rates of approximately 96-100%. Additionally, the adsorption isotherms are in alignment with the Freundlich models. Furthermore, an investigation was conducted on the adsorption behavior of natural-CP Greece and synthetic (NaP1) zeolites in the removal of Cr^{3+}. The result was 90% and the adsorption isotherm of these zeolites can be modeled by the Langmuir equation. In the same way, Cd^{2+} removal by modified zeolite (Zeolite A and X) from kaolin was studied and the result was about 99% of the adsorption isotherms of these zeolites were consistent with the (M-Lan), (M-Fre), (M-D.K.R), models. In another study, the Cd^{2+} removal from wastewater used for industrial application was investigated by applying Brazilian natural scolecite (84–59%), Kardjali natural zeolite (75–905), Greek-CP (90%), NaP1 from CFA (90%) and the above results were obtained. It should be noted that the adsorption isotherms of these zeolites can be modeled in the following order: Freundlich isotherm, Freundlich model, and Langmuir model.

Batch experimental data using zeolite A and X derived from kaolin as the adsorbent has been successfully explained by three adsorption isothermal models, namely (M-Lan), (M-Fre), and (M-D.K. R), for the removal of Cu^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+} metals. In contrast, the isothermal data obtained from synthetic zeolite derived from CFA is fully compatible with the Langmuir model. Furthermore, for Cu^{2+} adsorption isothermal data, the Langmuir model with natural clinoptilolite sourced from Turkey, Greece, and Bulgaria is the most effective. Similarly, the adsorption isotherm data for Pb^{2+}, Ni^{2+}, and Zn^{2+} can be best represented by the Langmuir model with natural clinoptilolite from Turkey, Greece, and Turkey, respectively. In recent times, clinoptilolite sourced from Turkey has been utilized to adsorb Co^{2+}, and the adsorption data are consistent with the (M-Lan), (M-Fre), and (M-D.K. R) models. Nonetheless, the adsorption isotherm data can be more precisely explained by the Langmuir model with synthetic NaA zeolite derived from CFA (10).

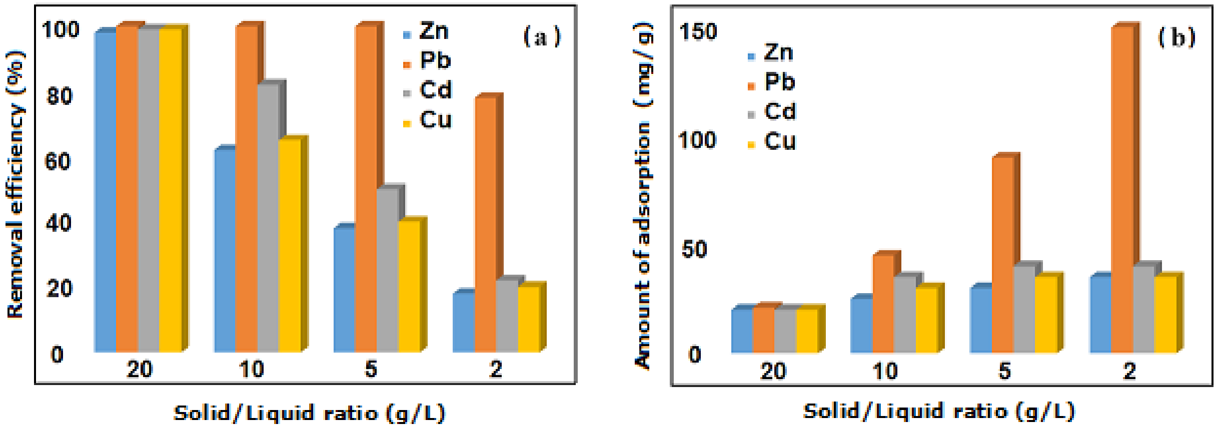

Figure 5: The removal efficiency of NaCl-modified synthetic-CP for Zn(II), Pb(II), Cd(II), and Cu(II) is demonstrated in Figure (a), along with the corresponding amount of adsorption (b), as a function of solid-to-liquid ratio (8).

Table 1. The (MAC) of reported N-Zeolite for Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, $Ni^{2+,}$ and Cr^{3+}.

Zeolite	*Metal*	*MAC (mg.g^{-1}, meq.g^{-1})*	*Ref*
China Na-CP	Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}	20.29, 159.00, 30.84, 20.28	(11)
America Na-CP	Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}	21.14, 158.70, 33.07, 22.82	
Ukraine Na-CP	Pb^{2+}, Cd^{2+}, Cu^{2+}	≈ 82, ≈ 19, ≈ 21	
Italy Na-CP	$Zn^{2+,}$ Pb^{2+}, Cd^{2+}, Cu^{2+}	8.17, 27.70, 4.22, 25.76	

Slovakia Na-CP	Pb^{2+}, Cd^{2+}, Cu^{2+}	≈ 85, ≈ 36, ≈ 28	
Turkish CP	Pb^{2+}, Zn^{2+}	0.29–0.73, 0.10–0.25	(29)
	Cu^{2+}, Ni^{2+}	0.02–0.22, 0.01–0.17	
Na-CP	Cr^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}	0.23, 0.06, 0.10, 0.18	
	Cd^{2+}	0.08	
Scolecite	Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}	0.05, 0.13, 0.06, 0.03	
	Co^{2+} Cd^{2+}	0.0078, 0.0032	
Bigadic CP	Pb^{2+}, Zn^{2+}, Cd^{2+}	0.22, 0.73, 0.0053	
Turkish CP	Co^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}	0.44, 0.28, 0.27, 0.15	
Brazilian scolecite	Cr^{3+}, Ni^{2+}, Cd^{2+}, Mn^{2+}	5.81, 2.08, 1.78, 4.00	
Sardinian CP	Cu^{2+}, Cd^{2+}, Pb^{2+}	0.34, 0.05–0.19, 0.27–1.20	(39)
	Zn^{2+}	0.10	
CP	Cd^{2+}	0.12–0.18	(40)
Mexican CP	Pb^{2+}	1.40	(41)
Ukraine CP	Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}	0.13, 0.40, 0.22, 0.037	(42)
Sardinian CP	Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}	0.34,0.05-0.19, 0.27-1.2, 0.1	(43)

1 Maximum adsorption capacity (MAC)

Table 2. The (MAC) of reported (M) and (S) Zeolite for Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Cr^{3+}.

Zeolite	***Metal***	***MAC (mg.g^{-1})***	***Reference***
Nano Fe-Al zeolite	Cr^{6+}	44.74	(7)
S-CP	Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}	31.74, 181.8, 44.64, 33.76	(11)
NaP1	Cr^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}	43.6, 50.8, 50.5, 32.6, 20.1	(10)
Blend of NaX and NaA	Cr^{3+}	71.1	
Blend of NaY and NaP	Cr^{3+}	83.2	
Zeolite X	Cd^{2+}, Zn^{2+}	92.00, 41.00	
NaX +- activated carbon	Cd^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}	129.30, 101.70, 2280, 132.10	
Zeolite 4A	Cu^{2+}	39.80-72.00	
Zeolite A	Zn^{2+}, Ni^{2+}	28.60, 24.65	
M-zeolite (NCP-GLU)	Co^{2+}	41.47	
M-zeolite (NCP)	Co^{2+}	19.05	
M-zeolite (MCP-GLU)	Co^{2+}	29.38	
Zeolite nanoparticles	Ni^{2+}	122	(44)

2 Synthetic-Clinoptilolite (S-CP)
3 Maximum adsorption capacity (MAC)
4 Modified (M) and Synthetic (S)

3. NATURAL, MODIFIED, AND SYNTHETIC ZEOLITES ENVIRONMENTAL IMPLICATIONS

In later years, the chemical industry rapidly evolved and significantly improved the conditions and quality of life in our society. Nevertheless, this industrial development has inevitably led to environmental pollution problems. For instance, the debasement of water resources is escalating at an alarming rate owing to the rapid proliferation of an assortment of pollutants emanating from sundry industrial sectors. This is primarily attributable to the commercialization of cutting-edge products and the implementation of innovative transformation technologies and processes (45). Human activities are the primary cause of heavy metal release into terrestrial and aquatic ecosystems. The extraction of mineral deposits containing considerable amounts of sulfide minerals and heavy metals represents a pivotal source of heavy metal contamination in the environment (46). The contamination of sites by both organic and inorganic pollutants is a complex and widespread environmental issue (17). The menace of environmental pollution is widely recognized as one of the paramount challenges of the contemporary world. It poses a severe threat to human health and ecosystems, with the potential to trigger environmental toxicity and other undesirable outcomes (47).

Toxic metals, such as heavy metals, are considered a high-priority class of pollutants due to their harmful nature. They frequently impede the beneficial use of wastewater for industrial applications and irrigation purposes. This underscores the significance of effective and efficient removal of these pollutants to mitigate their adverse effects on the environment and public health (48). Consequently, heavy metal pollution has attracted widespread concern (49). Land-based sources are a significant contributor to marine ecosystem pollution, with nutrients and pathogens from sewage treatment plants, pesticides from agriculture, metals from mining and smelting activities, traffic, and machinery manufacturing (50), and pharmaceutical industries (51). Protecting the environment and cleaning up water, air, and soil pollution is a matter of utmost importance worldwide, especially in developing countries. However, pollution remediation can be challenging due to four main factors: efficiency, recyclability, environmental safety, and cost-effectiveness. But it is possible to tackle these challenges to ensure a cleaner and healthier environment for ourselves and future generations. Working towards efficient, recyclable, safe, and affordable solutions, can effectively combat pollution and create a better world and environment. (52).

It is meaningful to note that there is no accurate description of what constitutes a heavy metal; however, the literary depiction characterizes it as an innate constituent possessing an elevated atomic mass and a density equivalent to or surpassing 5 $g.cm^{-3}$, which is minimum five times more elevated than that of aqueous substances. Some of the common heavy metals include Mn, V, Cr, Fe, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Pb, and Hg (29). The contamination of soil and water is a grave concern, particularly due to its ability to pervade the food chain and amass within the body. Human exposure to heavy metals can occur through the ingestion of contaminated food and water, as well as the inhalation of atmospheric particles laden with heavy metals. Despite the miniscule amounts, the accumulation of heavy metals within the body can trigger a host of medical ailments, such as neurological disorders, hormonal imbalances, cardiovascular failures, renal malfunctions, infertility, hair loss, endocrine disorders, respiratory and gastrointestinal problems, even cancer. A multitude of industrial processes discharges their wastewater into rivers, which eventually results in the deposition and enrichment of river sediments. This, in turn, leads to a heavy metal contamination crisis that necessitates stringent measures. River sediments are often employed to appraise the extent of heavy metal contamination through the utilization of a diverse set of defensive pollution indices. (53).

Table 3. The maximum heavy metals adsorption isotherms of natural, modified, and synthetic Zeolite (7).

Metal ion	***Zeolite***	***Zeolite origin***	***Metal removal rate (%)***	***Adsorption isotherms***
Cr^{3+}	Natural scolecite	Brazil	100.00–96.00	M-Fre-Iso
Cr^{3+}	CP	Greece	>90.00	M-Lan
Cr^{3+}	NaP1	CFA	>90.00	M-Lan
Cd^{2+}	Zeolite A	Kaolin	>99.00	M-Lan, M-Fre, M-D.K.R
Cd^{2+}	Zeolite X	Kaolin	>99.00	M-Lan, M-Fre, M-D.K.R
Cd^{2+}	Natural scolecite	Brazil	84.00–59.00	M-Fre-Iso
Cd^{2+}	Natural zeolite	Kardjali	75.00–90.00	M-Fre
Cd^{2+}	CP	Greece	>90.00	M-Lan
Cu^{2+}	Zeolite A	Zeolite A	>99.00	M-Lan, M-Fre, M-D.K.R
Cu^{2+}	CP	Turkey	77.96	M-Lan, M-Fre, M-D.K.R
Cu^{2+}	NaOH-M-CP	Bulgaria	95.00	M-Lan
Cu^{2+}	NaX +-activated carbon	CFA		M-Lan
Pb^{2+}	Zeolite X	Kaolin	>99.00	M-Lan, M-Fre, M-D.K.R

Pb^{2+}	Zeolite A	Kaolin	>99.00	M-Lan, M-Fre, M-D.K.R
Pb^{2+}	NaX +-activated carbon	CFA		M-Lan
Zn^{2+}	CP	Turkey	45.96	M-Lan, M-Fre, M-D.K.R
Zn^{2+}	Zeolite A	Kaolin	>99.00	M-Lan, M-Fre, M-D.K.R
Zn^{2+}	CP	Greece	>90.00	M-Lan
Zn^{2+}	NaP1	CFA	>90.00	M-Lan
Ni^{2+}	Zeolite A	Kaolin	>99.00	M-Lan, M-Fre, M-D.K.R
Ni^{2+}	Zeolite X	Kaolin	>99.00	M-Lan, M-Fre, M-D.K.R
Ni^{2+}	Natural scolecite	Brazil	96.00–40.00	M-Fre-Iso
Ni^{2+}	CP	Greece	>90.00	M-Lan
Ni^{2+}	NaP1	CFA	>90.00	M-Lan
Ni^{2+}	NaX +-activated carbon	CFA		M-Lan
Co^{2+}	NaA	CFA		M-Lan
Co^{2+}	CP	Turkey	66.10	M-Lan, M-Fre, M-D.K.R

1 Langmuir (M-Lan), Freundlich (M-Fre), Dubinin Kaganer Radushkevich (M-D.K.R), Freundlich isotherm (M-Fre-Iso)

2 Clinoptilolite (CP), M-CP (Modified- Clinoptilolite)

Marine surface sediments are known to pretense as a sink for harmful metal pollutants, but it's worth noting that these irregularities may not be fixed in sediments. When certain conditions arise due to natural or human-induced causes, such as changes in pH, dissolved oxygen, and redox potential, pollutants can be released back into the water. This can lead to secondary pollution sources, which can have detrimental effects on aquatic environments. It is vital to improving our understanding of heavy metal pollution in coastal regions, particularly in areas like the coastal regions of China that are grappling with significant challenges concerning this issue. Therefore, it is essential to monitor the pollution status of heavy metals in these areas to ensure effective mitigation measures. Removing undesirable metal ions from water systems is an essential task for environmental engineers, but it remains a challenging one. Lead, for example, is a heavy metal that can cause damage to biological systems and is released into the environment from various industrial sources. Removing lead from wastewater is a critical topic that has attracted considerable attention from researchers and policymakers alike.

When heavy metals in sediments or soils transform from stable fractions into susceptible, bioavailable, and mobile forms, they pose a threat to the health of animals and humans. For example, Cd exposure can increase the likelihood of osteoporosis and pulmonary cancer, while chronic dust exposure can lead to peripheral vascular disease. Excessive intake of Pb adversely affects the central nervous system, while Zn may result in infertility and renal disease. Cu can induce depression and Cr may cause tumors in respiratory organs (50). The presence of chromate Cr(VI) and arsenate (As(V)) anions in various sources of water is a prominent issue, as the toxicity of these species can result in death if they are taken over a long period or present in high concentrations (54). Heavy metals such as Cr, Cu, Zn, As, Cd, Pb, and Hg have been listed as priority control pollutants by the United States Environmental Protection Agency (USEPA) because of their potentially harmful, persistent, and irremediable behaviors, and have garnered increasing attention worldwide (50).

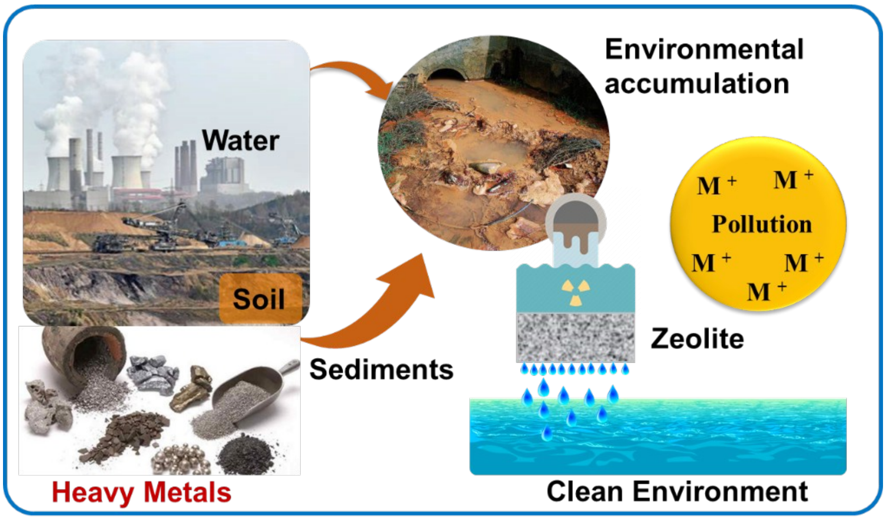

Figure 6: Heavy metal pollution from anthropogenic activities.

Green chemistry, defined as the design of products and processes to prevent or reduce the formation of hazardous chemicals (55), requires the use and development of synthetic reactions based on atomic economy (55). Green chemistry technology has come up as an effective strategy to alleviate venomous by exploiting natural resources for nanomaterial prevarication, lowering operating expenses, reducing environmental impacts, and providing superior biocompatibility, and chemical and thermal stability (56). Green routes are specifically designed to minimize the use and generation of substances that have harmful impacts on both human health and the environment. The goal of these routes is to prioritize the use of non-toxic or less-toxic alternatives and to reduce the overall environmental footprint of the processes involved. By adopting green routes, we can contribute to a more sustainable future for ourselves and the planet (36). As environmental awareness continues to grow, the aquaculture industry is taking proactive steps to mitigate the potential negative impacts of production on surrounding ecosystems. To this end, innovative solutions are being developed to reduce the presence of harmful contaminants in aquaculture waters, particularly in recycling systems and wastewater from aquaculture ponds. One such solution gaining traction is the use of eco-friendly adsorbents, such as natural zeolite minerals. This approach is seen as a promising way to effectively treat contaminated waters and wastewater while minimizing harm to the environment (24). Natural zeolites are aluminosilicate minerals as mentioned above also have porous structures that have high cation-exchange capacity, making them effective adsorbents for heavy metals. They have been used in various applications, including water treatment, gas separation, and catalysis. In the field of aquaculture, natural zeolites are effective in removing heavy metals from contaminated waters and wastewater.

In a study conducted by Hamed et al. (57), natural zeolite was used to remove heavy metals from the wastewater of a fish farm. The results showed that zeolite was able to effectively remove heavy metals, including Cu, Zn, and Pb, from the wastewater. Another study by Zorpas et al. (58) investigated the use of natural zeolites for the removal of heavy metals from a recirculating aquaculture system. The results showed that the zeolites were able to remove a significant amount of heavy metals from the system, resulting in a reduction of the total dissolved solids and chemical oxygen demand. Overall, the use of natural zeolites as eco-friendly adsorbents is a promising approach for treating contaminated waters and wastewater in aquaculture. It is an effective and sustainable solution that can help mitigate the negative impacts of aquaculture production on the environment.

4. DISCUSSION

There exists a range of methods for purifying heavy metals from contaminated areas, including chemical precipitation, solvent extraction, oxidation, membrane filtration, photocatalytic degradation, and adsorption. The use of these techniques must adhere to the principles of green chemistry, particularly those about economic and environmental considerations. Due to high tax costs, post-treatment issues, and environmental concerns, many of the aforementioned methods are not extensively employed for removing heavy metals.

Zeolites have been identified as potentially valuable adsorbents for heavy metal removal due to their high efficiency, low cost, and eco-friendliness. As the primary inorganic cation exchangers, zeolites offer exceptional ion exchange stowage, selectivity, and compatibility with the natural environment, making them ideal for use in a variety of environmental remediation processes, wastewater treatment, and air purification.

Studies on the adsorption capacity of different zeolite types - including natural, modified, and synthetic - have indicated that natural zeolites can achieve maximum adsorption capacity between 40-100%, while synthetic and modified zeolites can reach up to

90-99%. Adsorption isotherms for metal ions are modeled using Freundlich, Langmuir, or DKR equations, with the maximum adsorption capacity of isotherms reaching about 40-100%. In summary, zeolites are highly effective adsorbents for removing harmful heavy metals from industrial-produced wastewater.

5. CONCLUSION

Heavy metals pose a severe threat to the environment, jeopardizing the health of humans, animals, and plants. Removing these metals from the environment is vital to reduce diseases and creating a green and healthy ecosystem. It also plays an important role in maintaining the balance of the ecosystem and recycling metals that are facing a gradual reduction of mineral resources.

Fortunately, the removal of harmful heavy metals from industrial wastewater provides a valuable and essential solution to environmental pollution challenges. Recent research has found that zeolites are a promising material for heavy metal removal from polluted environments and industrial wastewater. Here are the main points:

1 Among various refining processes, adsorption is a cheap and flexible technology method for the generous removal of organic also inorganic materials. Using zeolite is a suitable method for heavy metal removal as it is cost-effective and straightforward compared to other methods.

2 The adsorption isotherms of several metal ions can best be modeled by M-Fre, M-Lang, or DKR equations. Synthetic and naturally occurring zeolites have successfully adsorbed a wide range of heavy metal Cu, Zn, As, Mo, Ag, Cd, Pb, and Hg from various contaminated water streams.

Zeolites possess a highly desirable microporous crystalline structure that enables them to selectively exchange ionic species based on their size. Due to the size of the entry ports in the internal zeolite framework, only species with diameters that fit through these ports can be exchanged, while larger species are eliminated. This unique property of zeolites, known as ion-sieving, finds widespread application in various commercial fields.

3 The maximum absorption capacity of Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cr$^{3+,}$ and Cr^{6+} by natural, modified, and synthetic zeolite is in the following order: 228 mg.g^{-1}, 129.3 mg.g^{-1}, 101.7 mg.g^{-1}, 132.1 mg.g^{-1}, 41.47 mg.g^{-1}, 83.2 mg.g^{-1} and 44.74 mg.g^{-1}, respectively.

4 Among the types of zeolites, including natural scolecite, Zeolite A and X, NaX +- activated carbon, modified zeolite (NCP-GLU), and a blend of NaY and NaP, the best type for removing heavy metals with the highest adsorbent capacity is identified.

5 The adsorption isotherms' capacity for removing heavy metals using different types of zeolites ranges from 40-100%. This result indicates that zeolites are excellent adsorbents for removing heavy metals from industrial wastewater.

6. CONFLICT OF INTEREST

There are no conflicts that need to be reported.

7. REFERENCES

1. Türksoy. R., T. G., Yalçın., E. İ., Türksoy. Ö., Demir. G.Y.,. Removal of heavy metals from textile industry wastewater. *Frontiers in Life Sciences and Related Technologies.* 2021, *2* (2), 44-50. Available from: <DOI>.

2. Motsa, M. M.; Thwala, J. M.; Msagati, T. A. M.; Mamba, B. B. The potential of melt-mixed polypropylene–zeolite blends in the removal of heavy metals from aqueous media. *Physics and Chemistry of the Earth, Parts A/B/C.* 2011, *36* (14), 1178-1188. Available from: <DOI>.

3. El-Azim, H.; Mourad, F. Removal of Heavy Metals Cd (II), Fe (III) and Ni (II), from Aqueous Solutions by Natural (Clinoptilolite) Zeolites and Application to Industrial Wastewater. *Asian Journal of Environment & Ecology* 2018, *7*, 1-13. Available from: <DOI>.

4. Aghazadeh, S.; Safarzadeh, E.; Gharabaghi, M.; Irannajad, M. Modification of natural zeolite for Cu removal from waste waters. *Desalination and Water Treatment* 2016, *57*, 1-8. Available from: <DOI>.

5. World Health, O. *Lead in drinking-water: background document for development of WHO guidelines for drinking-water quality*; WHO/SDE/WSH/03.04/09; World Health Organization., Geneva, 2003. Available from: <URL>.

6. Krauklis, A.; Ozola, R.; Burlakovs, J.; Rugele, K.; Kirillov, K.; Trubaca-Boginska, A.; Rubenis, K.; Stepanova, V.; Klavins, M. FeOOH and Mn$_8$O10Cl$_3$ modified zeolites for As(V) removal in aqueous medium. *Journal of Chemical Technology & Biotechnology.* 2017, *92* (8), 1948-1960. Available from: <DOI>.

7. Kong, F.; Zhang, Y.; Wang, H.; Tang, J.; Li, Y.; Wang, S. Removal of Cr(VI) from wastewater by artificial zeolite spheres loaded with nano Fe–Al bimetallic oxide in constructed wetland. *Chemosphere.* 2020, *257*, 127224. Available from: <DOI>.

8. Türkmen, M. Removal of Heavy Metals From Wastewaters by Use of Natural Zeolites. In *Fresenius Environmental Bulletin.* , 2002; Department of Environmental Engineering, Dokuz Eylül University.: Vol. 13, pp 574-580.

9. Dursun, S.; Pala, A. I. Lead pollution removal from water using a natural zeolite. *Journal of International Environmental Application and Science.* 2007, *2*, 11-19.

10. Yuna, Z. Review of the Natural, Modified, and Synthetic Zeolites for Heavy Metals Removal from Wastewater. *Environmental Engineering Science.* 2016, *33* (7), 443-454. Available from: <DOI>.

11. Li, Y.; Bai, P.; Yan, Y.; Yan, W.; Shi, W.; Xu, R. Removal of Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu2+ from aqueous solution by synthetic clinoptilolite. *Microporous and Mesoporous Materials.* 2019, *273*, 203-211. Available from: <DOI>.

12. Bessa, R. A.; França, A. M. M.; Pereira, A. L. S.; Alexandre, N. P.; Pérez-Page, M.; Holmes, S. M.; Nascimento, R. F.; Rosa, M. F.; Anderson, M. W.; Loiola, A. R. Hierarchical

zeolite based on multiporous zeolite A and bacterial cellulose: An efficient adsorbent of Pb^{2+}. *Microporous and Mesoporous Materials.* 2021, *312*, 110752. Available from: <DOI>.

13. Mirjana Golomeova, A. Z., Krsto Blazev, Boris Krstev, Blagoj Golomeov. Removal of Heavy Metals from Aqueous Solution using Clinoptilolite and Stilbite. *INTERNATIONAL JOURNAL OF ENGINEERING RESEARCH & TECHNOLOGY (IJERT) .* 2014, *03* (11), 1029-1035. Available from: <DOI>.

14. Habeebullah, T.; Munir, S.; Awad, A.; Morsy, E.; Seroji, A.; Mohammed, A. The Interaction between Air Quality and Meteorological Factors in an Arid Environment of Makkah, Saudi Arabia. *International Journal of Environmental Science and Development.* 2014, *6*, 576-580. Available from: <DOI>.

15. Taamneh, Y.; Sharadqah, S. The removal of heavy metals from aqueous solution using natural Jordanian zeolite. *Applied Water Science.* 2017, *7* (4), 2021-2028. Available from: <DOI>.

16. TEKİN, B. a. A., ÜNSAL. Intake of divalent copper and nickel onto natural zeolite from aqueous solutions: a study in mono- and dicomponent systems. *Turkish Journal of Chemistry.* 2022, *46* (4), 1042-1054. Available from:<DOI>.

17. Zhang, Y.; Alessi, D. S.; Chen, N.; Luo, M.; Hao, W.; Alam, M. S.; Flynn, S. L.; Kenney, J. P. L.; Konhauser, K. O.; Ok, Y. S.; et al. Lead (Pb) sorption to hydrophobic and hydrophilic zeolites in the presence and absence of MTBE. *Journal of Hazardous Materials.* 2021, *420*, 126528. Available from: <DOI>.

18. Apreutesei, R.; Catrinescu, C.; Teodosiu, C. Surfactant-Modified Natural Zeolites for Environmental Applications in Water Purification. *Environmental engineering and management journal.* 2008, *7*, 149-161. Available from: <DOI>.

19. Bandura, L.; Panek, R.; Madej, J.; Franus, W. Synthesis of zeolite-carbon composites using high-carbon fly ash and their adsorption abilities towards petroleum substances. *Fuel.* 2021, *283*, 119173. Available from: <DOI>.

20. Zorbay, F.; Arslan, S. Zeolitler ve Kullanım Alanları. *Karaelmas Science and Engineering Journal.* 2012, *2*, 63-68. Available from: <DOI>.

21. Li, Y.; Liang, G.; Chang, L.; Zi, C.; Zhang, Y.; Peng, Z.; Zhao, W. Conversion of biomass ash to different types of zeolites: a review. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects.* 2019, *43*, 1-14. DOI: 10.1080/15567036.2019.1640316. Polatoglu, I. Chemical behaviour of clinoptilolite rich natural zeolite in aqueous medium. the Graduate School of Engineering and Sciences of
izmir Institute of Technology., Izmir, 2005. Available from: <URL>.

22. Zeng, S.; Wang, R.; Zhang, Z.; Qiu, S. Solventless green synthesis of sodalite zeolite using diatomite as silica source by a microwave heating technique. *Inorganic Chemistry Communications.* 2016, *70*, 168-171. Available from: <DOI>.

23. Wu, Q.; Meng, X.; Gao, X.; Xiao, F.-S. Solvent-Free Synthesis of Zeolites: Mechanism and Utility. *Accounts of chemical research.* 2018, *51* (6), 1396-1403. Available from: <DOI>.
24. Ghasemi, Z.; Sourinejad, I.; Kazemian, H.; Rohani, S. Application of zeolites in aquaculture industry: a review. *Reviews in Aquaculture.* 2018, *10* (1), 75-95. Available from: <DOI>.

25. Davis, M. E. Zeolites from a Materials Chemistry Perspective. *Chemistry of Materials* 2014, *26* (1), 239-245. Available from: <DOI>.

26. Tao, Y.; Kanoh, H.; Abrams, L.; Kaneko, K. Mesopore-Modified Zeolites: Preparation, Characterization, and Applications. *Chemical Reviews.* 2006, *106* (3), 896-910. Available from: <DOI>.

27. Ramos-Guivar, J. A.; Taipe, K.; Schettino, M. A., Jr.; Silva, E.; Morales Torres, M. A.; Passamani, E. C.; Litterst, F. J. Improved Removal Capacity and Equilibrium Time of Maghemite Nanoparticles Growth in Zeolite Type 5A for Pb(II) Adsorption. *Nanomaterials (Basel).* 2020, *10* (9). DOI: 10.3390/nano10091668 From NLM. Ülkü, S. CHEMICAL BEHAVIOUR OF CLINOPTILOLITE RICH NATURAL ZEOLITE IN AQUEOUS MEDIUM. In *Izmir Institute of Technology administrators.*, 2005.

28. Krol, M. M. Natural vs. Synthetic Zeolites. 2020.

29. Wang, S.; Peng, Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal.* 2010, *156* (1), 11-24. Available from: <DOI>.

30. Passaglia, E.; Sheppard, R. A. The Crystal Chemistry of Zeolites. *Reviews in Mineralogy and Geochemistry.* 2001, *45* (1), 69-116. Available from: <DOI>. (acccessed 6/14/2023).

31. Batur, J.; Duan, Z.; Jiang, M.; Li, R.; Xie, Y.; Yu, X.-F.; Li, J.-R. Molecular Modification of Zeolites with Cold Atmospheric-Pressure Plasma Jet: A Green and Facile Strategy. *Chemistry of Materials.* 2023, *35* (10), 3867-3879. Available from: <DOI>.

32. Nguyen, M. L., Tanner, C. C. Ammonium Removal From Wastewaters Using Natural New Zealand Zeolites. *New Zealand Journal of Agricultural Research.* 1998, *3* ((41)), 427-446. Available from: <DOI>.

33. Zhang, Y. Characteristics and Mechanisms of Heavy Metal and MTBE Adsorption on Zeolites and Applications in Permeable Reactive Barriers. University of Cambridge, Robinson College 2019.

34. Ozekmekci, M.; Salkic, G.; Fellah, M. F. Use of zeolites for the removal of H2S: A mini-review. *Fuel Processing Technology.* 2015, *139*, 49-60. Available from: <DOI>.

35. Montes Luna, A. d. J.; Castruita de León, G.; García Rodríguez, S. P.; Fuentes López, N. C.; Pérez Camacho, O.; Perera Mercado, Y. A. Na+/Ca^{2+} aqueous ion exchange in natural clinoptilolite zeolite for polymer-zeolite composite membranes production and their $CH_4/CO_2/N_2$ separation performance. *Journal of Natural Gas Science and Engineering.* 2018, *54*, 47-53. Available from: <DOI>.

36. Abdullah, N. H.; Shameli, K.; Abdullah, E. C.; Abdullah, L. C. Solid matrices for fabrication of magnetic iron oxide nanocomposites: Synthesis, properties, and application for the adsorption of heavy metal ions and dyes. *Composites Part B: Engineering* 2019, *162*, 538-568. Available from: <DOI>.

37. Mastinu, A.; Kumar, A.; Maccarinelli, G.; Bonini, S. A.; Premoli, M.; Aria, F.; Gianoncelli, A.; Memo, M. Zeolite Clinoptilolite: Therapeutic Virtues of an Ancient Mineral. *Molecules.* 2019, *24* (8). Available from: <DOI>. From NLM.

38. Kraljević Pavelić, S.; Simović Medica, J.; Gumbarević, D.; Filošević, A.; Pržulj, N.; Pavelić, K. Critical Review on Zeolite Clinoptilolite Safety and Medical Applications in vivo. *Front Pharmacol.* 2018, *9*, 1350. Available from: <DOI>. From NLM.

39. Cincotti, A.; Mameli, A.; Locci, A. M.; Orrú, R.; Cao, G. Heavy Metals Uptake by Sardinian Natural Zeolites: Experiment and Modeling. *Industrial & Engineering Chemistry Research.* 2006, *45*, 1074-1084.

40. Gedik, K.; Imamoglu, I. Affinity of Clinoptilolite-based Zeolites towards Removal of Cd from Aqueous Solutions. *Separation Science and Technology - SEPAR SCI TECHNOL* 2008, *43*, 1191-1207. Available from: <DOI>.

41. Llanes-Monter, M.; Olguín, M.; Solache, M. Lead sorption by a Mexican, clinoptilolite-rich tuff. *Environmental science and pollution research international.* 2007, *14*, 397-403. Available from: <DOI>.

42. Sprynskyy, M.; Buszewski, B.; Terzyk, A. P.; Namieśnik, J. Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite. *Journal of Colloid and Interface Science.* 2006, *304* (1), 21-28. Available from: <DOI>.

43. MUDABER, S. N. B., BATUR. Jenaidullah., . Zeolites as effective adsorbents for heavy metal removal in wastewater treatment of Kabul city-A review. *IAR Journal of Engineering and Technology.* 2023, *4* (2), 20-31. Available from: <DOI>.

44. Yurekli, Y. Removal of heavy metals in wastewater by using zeolite nano-particles impregnated polysulfone membranes. *Journal of Hazardous Materials.* 2016, *309*, 53-64. DOI: https://doi.org/10.1016/j.jhazmat.2016.01.064.

45. Dhaouadi, F.; Sellaoui, L.; Reynel-Ávila, H. E.; Landín-Sandoval, V.; Mendoza-Castillo, D. I.; Jaime-Leal, J. E.; Lima, E. C.; Bonilla-Petriciolet, A.; Lamine, A. B. Adsorption mechanism of Zn^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} ions by carbon-based adsorbents: interpretation of the adsorption isotherms via physical modelling. *Environmental Science and Pollution Research.* 2021, *28* (24), 30943-30954. Available from: <DOI>.

46. Wingenfelder, U.; Hansen, C.; Furrer, G.; Schulin, R. Removal of Heavy Metals from Mine Waters by Natural Zeolites. *Environmental Science & Technology.* 2005, *39* (12), 4606-4613. Available from: <DOI>.

47. Chen, Y.; Liu, Q.; Xu, M.; Wang, Z. Inter-annual variability of heavy metals pollution in surface sediments of Jiangsu coastal region, China: Case study of the Dafeng Port. *Marine Pollution Bulletin.* 2020, *150*, 110720. Available from: <DOI>.

48. Kocaoba, S.; Orhan, Y.; Akyüz, T. Kinetics and equilibrium studies of heavy metal ions removalby use of natural zeolite. *Desalination.* 2007, *214* (1), 1-10. Available from: <DOI>.

49. Javanbakht, V.; Ghoreishi, S. M.; Habibi, N.; Javanbakht, M. A novel magnetic chitosan/clinoptilolite/magnetite nanocomposite for highly efficient removal of Pb(II) ions from aqueous solution. *Powder Technology.* 2016, *302*, 372-383. Available from: <DOI>.

50. Qiao, D.; Wang, G.; Li, X.; Wang, S.; Zhao, Y. Pollution, sources and environmental risk assessment of heavy metals in the surface AMD water, sediments and surface soils around unexploited Rona Cu deposit, Tibet, China. *Chemosphere.* 2020, *248*, 125988. Available from: <DOI>.

51. Nour, H. E.; El-Sorogy, A. S.; Abd El-Wahab, M.; Nouh, E. S.; Mohamaden, M.; Al-Kahtany, K. Contamination and ecological risk assessment of heavy metals pollution from the Shalateen coastal sediments, Red Sea, Egypt. *Marine Pollution Bulletin.* 2019, *144*, 167-172. Available from: <DOI>.

52. Lu, F.; Astruc, D. Nanomaterials for removal of toxic elements from water. *Coordination Chemistry Reviews.* 2018, *356*, 147-164. Available from: <DOI>.

53. Shirani, M.; Afzali, K.; Jahan, S.; Strezov, V.; Soleimani-Sardo, M. Pollution and contamination assessment of heavy metals in the sediments of Jazmurian playa in southeast Iran. *Scientific Reports.* 2020, *10*. Available from: <DOI>.

54. Yıldırım, A.; Mudaber, S.; Öztürk, S. Improved Sustainable Ionic Liquid Catalyzed Production of Symmetrical and Non-Symmetrical Biological Wax Monoesters. *European Journal of Lipid Science and Technology.* 2019, *121* (2), 1800303. Available from: <DOI>.

55. Mudaber, S. Biyolojik vaks mono esterlerin etkin ve yeşil sentezi. Yayınlanmamış yüksek lisans tezi. Bursa Uludağ Üniversitesi, Bursa Turkiye, 2018.

56. Li, R.; Batur, J.; Bian, H.; Wang, Y.-J.; Duan, Z.; Xie, Y.; Li, J.-R. Green and Facile Fabrication of Metal Oxide/Red Phosphorus Composite Catalysts for CO_2 Photoreduction. *ACS Sustainable Chemistry & Engineering* 2022, *10* (26), 8658-8668. Available from: <DOI>.

57. Hamed, M.; Hussein, S.; Salama, A.; Mamoon, A. Use the natural zeolite (clinoptiolite) in removal of ammonia and heavy metals and improving water quality in fish ponds. *Al-Azhar Journal of Agricultural Research* 2022, *47*, 79-88. Available from: <DOI>.

58. Zorpas, A. A.; Pedreño, J. N.; Candel, M. B. A. Heavy metal treatment and removal using natural zeolites from sewage sludge, compost, and agricultural soils: a review. *Arabian Journal of Geosciences.* 2021, *14* (12), 1098. Available from: <DOI>.