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Review

Sorbents Based on Natural Zeolites for Carbon Dioxide Capture and Removal of Heavy Metals from Wastewater: Current Progress and Future Opportunities

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Abstract: This review is dedicated to the potential use of natural zeolites for wastewater treatment and carbon dioxide capture. Zeolites, due to their microporous structure and high surface activity, are used as sorbents. One effective application of zeolites is in wastewater treatment, which leads to the removal of pollutants and improvement in water quality. Zeolites can also be used for carbon dioxide capture, which helps reduce its concentration in the atmosphere and addresses climate change issues. This review examines recent research on the use of natural zeolites for the removal of heavy metals from water and CO_2 capture. It explores the broad applications of natural zeolites by understanding their adsorption capabilities and the mechanisms affecting their performance in water purification from heavy metals and CO_2 capture.

Keywords: natural zeolites; clinoptilolite; adsorption; carbon dioxide; heavy metals; capture

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1. Introduction

In the modern world, the problem of climate change and global warming caused by greenhouse gas (GHG) emissions and water pollution with heavy metals as a result of anthropogenic activities is becoming increasingly urgent [1,2]. It is known that carbon dioxide, methane, nitrous oxide, and fluorinated gases are greenhouse gases, among which carbon dioxide, formed during the combustion of fossil fuels, makes the greatest contribution to climate change and is the main cause of the greenhouse effect. The concentration of carbon dioxide (CO_2) in the atmosphere is monitored annually and is ~401 ppm and is expected to increase to ~550 ppm by 2050 [3]. The European Union (EU) has set a target to reduce CO_2 emissions by 40% by 2030 to keep global warming below 2 degrees [4]. Over the past decade, carbon capture and storage (CCS) and carbon capture utilization (CCU) technologies have been developed to reduce the amount of CO_2 in the atmosphere [5–7]. In general, there are four main methods of carbon dioxide capture: cryogenic distillation, membrane separation, absorption in liquids, and adsorption on solids [8–10]. Of these, absorption based on liquid amines is the most common method used in industry. However, significant disadvantages, such as high energy consumption of the regeneration process and corrosion of equipment, low absorption capacity, and loss of solvent, make this method ineffective [11]. The existing shortcomings can be overcome by the CO_2 adsorption method based on solid adsorbents, where the adsorption efficiency can be improved by changing the structure of the adsorbent material [12,13]. Many adsorbents have been investigated for CO_2 capture, including natural zeolites, activated carbons, mesoporous silica, organometallic compounds, and others [14,15]. Among these porous materials, natural zeolites are considered preferable in CO_2 capture due to their low cost and wide availability in many regions of the world [16,17].

In addition to climate change, the world is facing an ever-growing water crisis due to the need for clean drinking water. Wastewater and water resources are polluted with heavy metals, oil, organic matter, etc., due to the rapid growth of industrial development [18]. Among the water pollutants, heavy metals are a major concern due to the increasing number of industries discharging them into wastewater. Several treatment processes, such as ion exchange, sedimentation, phytoextraction, ultrafiltration, adsorption, reverse osmosis, and electrodialysis, are used to remove heavy metals from water. At present, adsorption is preferred for the removal of these pollutants due to its ease of handling and removal efficiency [19,20]. On the other hand, the efficiency of the adsorption process and its cost-effectiveness are limited by the physicochemical characteristics and cost of the adsorbent [21,22]. One of the effective ways to solve these problems is the use of natural zeolites as sorbents [19,20]. Natural zeolites, due to their low cost and availability, have a wide application. The properties of zeolites make them attractive candidates for use in many types of industrial applications such as catalysis, as ion exchangers for the removal of heavy metal ions, radioactive elements, air separation, natural gas purification, water purification processes, and as an adsorbent in the adsorption process [23–26]. Thus, natural zeolites are effective sorbents that can be used to purify contaminated water from heavy metals and adsorb carbon dioxide, which makes them valuable materials in solving environmental problems. Despite the promising potential, there are still gaps in understanding the adsorption mechanisms and optimization of capture processes.

The purpose of this review article is to summarize the current knowledge on the dual application of natural zeolites for both heavy metal and carbon dioxide capture, identify gaps in knowledge, and suggest areas for future research. Unlike previous reviews that have treated CO_2 capture and heavy metal removal as separate topics, our review integrates these processes into a cohesive analysis. We examine the efficiency of natural zeolites in capturing CO_2 and removing heavy metals from contaminated water within a single framework. This holistic approach not only highlights the advantages of natural zeolites over other materials but also provides a comprehensive overview of their potential to address interconnected environmental issues. By combining these aspects, we offer new insights and identify opportunities for future research that leverage the combined benefits of natural zeolites.

2. Natural Zeolites

Natural zeolites are crystalline microporous aluminosilicate materials with a specific framework structure. They are widely used in the petrochemical and chemical industries, as well as in water purification, due to their excellent ion-exchange capacity, abundance in nature, and low cost [2,27].

Most natural zeolites are formed by exposing volcanic ash to various physical and chemical influences at high temperatures and pressures [28]. Swedish mineralogist Alex F. Cronstedt introduced the term zeolite into science in 1756.

Zeolite is derived from the Greek words (zein), “to boil,” and (lithos) “stone,” and literally means “boiling stone” [29]. Zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earth metal cations, characterized by notable properties such as a highly regular and open microporous structure [30,31]. The two primary components of zeolites are SiO_2 and Al_2O_3, which are interconnected by shared oxygen atoms. The arrangement of these components in the tetrahedral configurations of SiO_4 and AlO_4 results in various types of zeolites. Four oxygen atoms are covalently bonded to a central Al or Si atom [32]. The general chemical formula of natural zeolites is ($M_2/nO{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}yH_2O$), where x equals two or more depending on the connection of tetrahedral AlO_4 units only to SiO_4 units, and n is the cation valence (mainly potassium, sodium, calcium, and magnesium) [33] (Figure 1). Table 1 shows the types of natural zeolites.

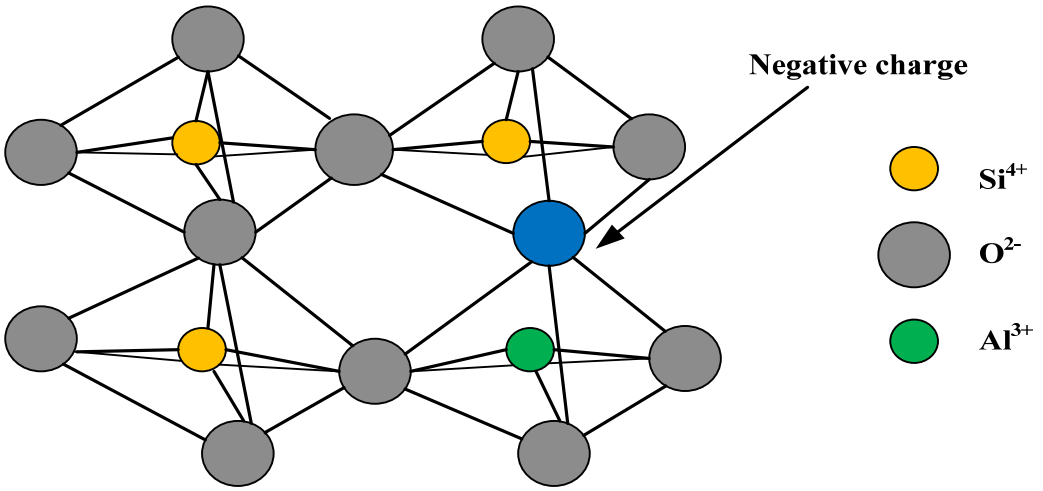

Figure 1. Structure of the zeolite framework [33].

Table 1. Types of natural zeolites.

Zeolite Type	Structure Type	Chemical Formula	Symmetry
Clinoptilolite	HEU	$(Na,K,Ca)_6[Al_6Si_{10}O_{24}]\cdot 12H_2O$	Monoclinic
Mordenite	MOR	$(Na, K)_8[Al_{12}Si_{24}O_8]\cdot 24H_2O$	Orthorhombic
Chabazite	CHA	$(Ca,Na)_2[Al_6Si_{12}O_{24}]\cdot 6H_2O$	Phombohedral
Philipsite	PHI	$(K_2,Na_2,Ca)Al_4Si_{12}O_{24}\cdot 12H_2O$	Monoclinic
Analcime	ANA	$Na[AlSi_2O_6]\cdot H_2O$	Cubic
Erionite	ERI	$(Na,K,Ca)_{1-x}[Al_{12}Si_{24}O_8]\cdot 6H_2O$	Hexagonal
Stilbite	STI	$(Na,Ca)_4Al_9Si_{20}O_{18}\cdot 7H_2O$	Monoclinic
Laumontite	LAU	$(Ca_2Al_{10}Si_{12}O_{20})\cdot 4H_2O$	Monoclinic
Ferrierite	FER	$(K,Ca)_{1-x}[Al_{12}Si_{24}O_{18}]\cdot 6H_2O$	Orthorhombic

According to the International Zeolite Association, around 250 zeolites have been identified, including more than 70 natural zeolites [34]. Among them, the most common are clinoptilolite, analcime, laumontite, mordenite, chabazite, and phillipsite [35]. The International Zeolite Association classifies zeolites into three types: low-silica zeolites (Si/Al = 1–2), medium-silica zeolites (Si/Al = 3–10), and high-silica zeolites (Si/Al > 10) [33]. Due to their unique physicochemical properties, natural zeolites can replace other expensive materials in a wide range of applications. Several varieties of natural zeolites are particularly promising for carbon dioxide capture, including clinoptilolite CLI), chabazite (CHA), mordenite (MOR), ferrierite (FER), faujasite (FAU), and phillipsite (PHI) [36].

Clinoptilolite. Clinoptilolite is the most widespread natural zeolite in the world, belonging to the heulandite group of zeolites with the general formula $(Na,K,Ca)_6[Al_6Si_{10}O_{24}]\cdot 12H_2O$) [37]. Clinoptilolite exhibits regular porosity with a complex pore structure. The framework of clinoptilolite consists of two parallel channels (channels A and B), with ten-membered (10 MR, channel A with an aperture of 3.0 × 7.6 Å) and eight-membered rings (8 MR, channel B with an aperture of 3.3 × 4.6 Å). These channels are interconnected by eight-membered rings oriented along the A-axis (C-channel with 8 MR, aperture of 2.6 × 4.7 Å) [38]. The Si/Al ratio in clinoptilolite, characteristic of natural clinoptilolite, ranges from 4 to 5.2. This results in an unbalanced negative framework where charge-balancing cations occupy positions within the pore channels of the clinoptilolite structure. Na^+ and Ca^{2+} cations are located in the 10-membered ring channels (4.4 × 0.72 nm), Na^+ and Ca^{2+} cations in the 8-membered ring channels (0.41 × 0.47 nm diameter), the K^+ cation is positioned in the vertical 8-membered ring channels (0.40 × 0.55 nm diameter), and the Mg^{2+} cation is located in the center of the 10-membered ring channel [39]. The most common cations balancing the charge are Na^+, K^+, Ca^{2+}, and Mg^{2+}. There are also various forms of minerals depending on high and low silicon content. Na^+ and K^+ are the main cations in the ion exchange

complex of the high-silica type. Their chemical composition and crystalline phases also vary depending on the geological soil layer. The characteristics and composition of natural zeolites vary according to their geographical distribution [40]. Next, we will consider the data on natural zeolite reserves worldwide (Table 2).

Table 2. Chemical composition of various natural zeolites around the world.

Natural Zeolite, Country	Major Oxides Content (%)										Ref
	CaO	SiO_2	K_2O	Na_2O	Fe_2O_3	Al_2O_3	FeO	MgO	TiO_2	SiO_2/Al_2O_3	
Natural Zeolite, China	3.17	66.34	1.37	0.73	0.99	12.23	-	0.98	0.16	5.4	[41]
Transcarpathian clinoptilolite, Ukraine	3.01	67.29	2.76	0.66	1.26	12.32	0.25	0.99	0.26	5.5	[42]
Clinoptilolite, Australia	2.09	68.26	4.11	0.64	1.37	12.99	-	0.83	0.23	5.2	[43]
Clinoptilolite, Kazakhstan	3.2	65.5	2.83	2.04	0.87	14.27	0.53	0.8	0.2	4.6	[44]
Clinoptilolite, Russia	2.95	72.3	3.08	0.23	3.73	9.68	0.23	1.47	0.44	7.5	[45]
Clinoptilolite, Spain	3.95	68.15	2.80	0.75	1.30	12.30	-	0.90	-	5.5	[46]
Clinoptilolite, Romania	3.77	65.80	1.44	1.35	2.07	12.30	-	0.63	-	5.3	[47]
Clinoptilolite, Greece	0.76	68.25	1.66	4.12	1.41	13.19	-	1.14	0.17	5.2	[39]
Natural Zeolite, Egypt	0.55	49.0	0.58	0.29	3.48	32.6	-	0.23	1.32	1.5	[48]

Global Reserves of Natural Zeolites

Most zeolites are found in nature as minerals in deposits around the world. The interest of scientists in zeolite materials has increased due to their widespread occurrence on the Earth's surface, resistance to acidic environments, high selective adsorption and ion-exchange capacity, as well as high thermal stability and tunable microporous crystalline structure. Due to these unique properties, zeolites are promising materials for a wide range of industrial applications as sorbents, catalysts, and molecular sieves [49–53]. Currently, over 70 types of zeolites are known in more than 40 countries around the world, and the world's reserves of zeolites amount to several tens of billions of tons [34]. Depending on the volume of reserves, deposits are classified into large, medium, and small. A large zeolite deposit exceeds 100 million tons, a medium deposit ranges from 10 to 100 million tons, and a small deposit is up to 10 million tons. The major explored reserves of natural zeolites are concentrated in Europe, Russia, Japan, and the USA. Of these, 10–20 billion tons are found in the USA, Japan, and post-Soviet countries, while 1–10 billion tons are located in Italy, Yugoslavia, Bulgaria, and other countries [54]. Some of the large and well-known natural zeolite deposits are located in the following countries: USA (California, Oregon, Arizona, Nevada), India (Maharashtra); China (Hebei province), Russia (Kamchatka, Sakhalin, Primorsky Krai), Cuba (Pinar del Río province), Italy (Sardinia), Japan (Hokkaido), and Kazakhstan (East Kazakhstan and Almaty regions). Each natural zeolite deposit has its own characteristics in terms of composition, structure, and use.

In Kazakhstan, two major zeolite deposits are known: the Tayzhuzgen deposit, located in the Tarbagatay district of the East Kazakhstan region (with confirmed reserves of 7.1 million tons and projected reserves of 215 million tons), and the Chankhanay deposit, located in the Kerbulak district of the Almaty region (with confirmed reserves of 5.5 million tons and projected reserves of 120 million tons). The Tayzhuzgen deposit is larger compared to the Chankhanay reserves [55,56]. They are also classified as medium-porous zeolites. The zeolite from the Chankhanay deposit mainly consists of the mineral clinoptilolite and is characterized by a high iron oxide content. There are also significant zeolite reserves in the regions of Central and Northern Kazakhstan, where mining and processing of these minerals are actively conducted. The mineral composition of natural zeolites in Kazakhstan often includes clinoptilolite, mordenite, and faujasite. The availability of natural zeolite in Kazakhstan also makes it an economically efficient and sustainable option for use as a sorbent in various chemical processes.

3. Mechanism of CO_2 Adsorption on Natural Zeolites

The study of the mechanism of CO_2 adsorption on the surface and in the pores of natural zeolites is an important area of research in chemistry and materials science. Natural zeolites are microporous minerals with a three-dimensional structure consisting of triangular and hexagonal lattices of silicon and aluminum, which have high surface activity. This feature of zeolites provides the presence of many small pores and channels that serve as active centers for CO_2 adsorption [57]. The process of CO_2 capture on natural zeolite involves a number of physical and chemical interactions that occur on the surface and in the pores of the material. The main mechanism of the CO_2 adsorption process is shown in Figure 2. The mechanism of CO_2 adsorption on natural zeolites is a complex process that occurs due to a combination of various factors. Gas molecule adsorption on the surface of a solid is divided into physical and chemical adsorption [58,59]. The main stages and principles determining the mechanism of CO_2 adsorption on natural zeolites include structural features, ion exchange, and physical and chemical adsorption.

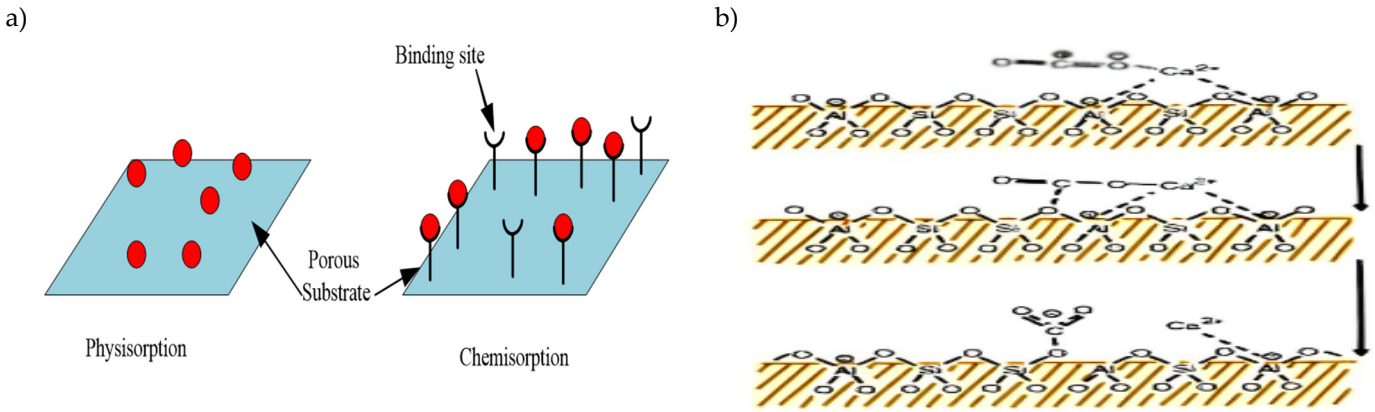

Figure 2. (**a**) Physical and (**b**) chemical adsorption [60].

Zeolites have the ability to perform ion exchange, i.e., the exchange of ions between their surface and the external environment. A significant part of the CO_2 adsorbed on the zeolite occurs due to ion exchange. The surface of the zeolite contains ions of sodium, potassium, calcium, and other metals, which can be exchanged for CO_2 ions. Besides ion exchange, physical adsorption is an important mechanism for CO_2 adsorption on zeolites. The accumulation of the adsorbate on the surface of the solid due to weak intermolecular Van der Waals forces is called physical adsorption. The surface area and microporous structure of zeolites provide a large available surface for interaction with CO_2 molecules. CO_2 molecules physically penetrate the micropores of the zeolite, where they are held due to weak Van der Waals attractive forces. Given the significant quadrupole moment of CO_2, these interactions are particularly strong, allowing CO_2 to be efficiently captured by the zeolite framework. This process is characterized by the release of heat and a negative enthalpy change (ΔH), and it is generally reversible, meaning that the adsorbed CO_2 can be desorbed by reducing pressure or increasing temperature. Chemical adsorption results in the accumulation of gas molecules on the surface of the adsorbent due to the formation of chemical bonds [61]. In chemical adsorption, the activation energy is significantly higher than in physical adsorption since it involves the formation and breaking of chemical bonds. Chemical adsorption, on the other hand, involves a stronger interaction where CO_2 molecules form chemical bonds with the zeolite, typically through acid-base reactions with surface cations. This type of adsorption is more stable at higher temperatures and generally requires more energy for desorption, making it less reversible compared to physical adsorption. The formation of these chemical bonds results in a positive ΔH, indicating an endothermic process.

The desorption of CO_2 from zeolites primarily follows the reversal of the adsorption mechanisms. Physical adsorption can be reversed by reducing pressure or raising the tem-

perature, which weakens the Van der Waals forces holding the CO_2 molecules. In contrast, chemically adsorbed CO_2 requires breaking the stronger chemical bonds, which typically involves higher temperatures. Ion exchange also plays a crucial role in both adsorption and desorption, where cations such as Na^+, K^+, and Ca^{2+} on the zeolite surface can exchange with CO_2, thereby enhancing the material's adsorption capacity. The ion exchange process can be reversed by altering the ionic environment or introducing competing gases. In the flow of flue gases, the method of physical adsorption is less selective than chemical adsorption as the primary means of interaction between molecules and surfaces are Van der Waals interactions [62]. Each type of adsorption corresponds to a certain type of material physical or chemical adsorbent [63–65].

3.1. Natural Zeolites as Sorbents for Carbon Dioxide Capture

Flue gas is a mixture of gaseous combustion products released during the operation of industrial enterprises and power plants, as well as in the process of burning fossil fuels [66,67]. The main components of flue gas include nitrogen (N_2), carbon dioxide (CO_2), water vapor (H_2O), oxygen (O_2), as well as various sulfur oxides (SO_x) and nitrogen oxides (NO_x). The concentration of CO_2 in flue gas typically ranges from 5 to 15% by volume, making it a significant source of greenhouse gas emissions into the atmosphere. The temperature of flue gases from which CO_2 needs to be captured can vary depending on the combustion process, but it generally falls within the range of 100 to 200 °C [68]. For effective CO_2 capture using natural zeolites, it is important to adjust the temperature of the gas stream, as CO_2 adsorption on zeolites occurs most efficiently at lower temperatures (typically around 30–50 °C) [69,70]. The process of CO_2 adsorption using zeolites involves several key stages: adsorption of carbon dioxide on the surface of the zeolite at elevated pressure, subsequent pressure reduction, and desorption of the captured CO_2 for further utilization or disposal.

Among the most promising adsorbents are natural zeolites such as clinoptilolite, chabazite, mordenite, and philipsite, which have demonstrated high efficiency in CO_2 capture. Due to their porous structure and ion-exchange properties, natural zeolites are considered promising sorbents for CO_2 capture [71]. However, natural zeolites possess several limitations that must be considered when using them for CO_2 capture. The main limitations include adsorption capacity, sensitivity to moisture, heterogeneity of composition, insufficient mechanical strength, limited process selectivity, and thermal stability [72].

Various activation methods are employed to enhance the physicochemical characteristics of natural zeolites, such as surface modification, ion exchange, composite material creation, and optimization of regeneration processes [60] (Table 3). Mechanochemical activation, which involves high-energy milling, is an effective method for creating specific defects in solid materials, thereby improving the physicochemical properties of natural zeolites [73]. Specifically, mechanochemical activation of clinoptilolite is aimed at producing nanoscale powders, although this is limited by its porous structure and other physical characteristics [74,75]. Additionally, it is important to study the adsorption properties of natural zeolites, taking into account their porous structure in both raw and modified forms. The study conducted by Kowalczyk and colleagues [76] highlighted key aspects of the pore structure of natural and modified mesoporous zeolites, particularly clinoptilolites. The authors demonstrated how thermal treatment and modification using HCl affects the porosity of these materials. By comparing experimentally obtained pore diameters with those calculated from SEM data, the researchers concluded that both natural and modified clinoptilolites are mesoporous materials with pore sizes ranging from 2 to 50 nm.

To enhance the sorption properties of untreated natural zeolites, modifications such as acid and alkali treatment, ion exchange, and metal loading are utilized [77]. Natural clinoptilolites are characterized by relatively low specific surface area, which can be significantly increased after modification [78,79]. For instance, the study by Wahono and colleagues [52] demonstrated that natural zeolite from an Indonesian deposit, containing a mixture of mordenite and clinoptilolite, exhibits increased CO_2 adsorption capacity after chemical and

physical treatment, including calcination and dealumination. The zeolite treated with 12 M HCl solution and calcined at 400 °C showed the highest specific surface area (179.4 m^2/g), while the dealumination process led to an increase in the Si/Al ratio to 11–12. These data indicate that physicochemical modification contributes to the increased porosity of the material and, consequently, to the enhancement of its adsorption properties. The maximum CO_2 adsorption capacity, recorded at 0 °C and 30 bar pressure, was 5.218 mmol/g, confirming the effectiveness of the modifications carried out.

Alkaline treatment of natural zeolites leads to desilication, which facilitates the formation of additional mesopores due to the removal of silicon atoms [80,81].

Specifically, in the study in [82], the authors investigated the effect of NaOH concentration on the treatment of clinoptilolite followed by calcination. The results indicated that increasing NaOH concentrations from 0.5 to 1 M led to a significant increase in CO_2 adsorption volume from 5.2308 to 20.2700 cm^3/g, significantly influencing the composition, structure, and adsorption characteristics of the samples. At the same time, the SiO_2/Al_2O_3 ratio in the treated samples decreased to 4.96. Figure 3 illustrates the morphological differences between natural clinoptilolites and those subjected to NaOH treatment.

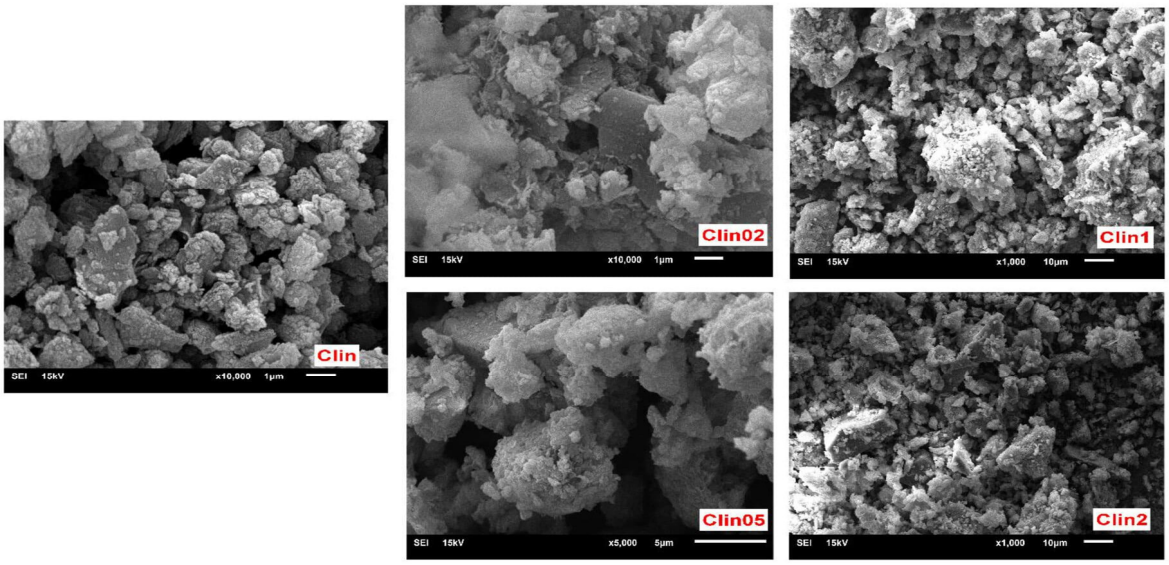

Figure 3. SEM images illustrating the morphological differences between natural clinoptilolites and those subjected to NaOH treatment [82].

NaOH treatment of clinoptilolite causes significant structural changes, including changes in the crystal structure as indicated by the sharpening of the XRD peaks in the (020), (100), and (101) lattice planes, especially in the concentration range of 0.5–1 M. This structural change directly correlates with the increased surface area and pore volume, which are critical for the improved adsorption properties. Furthermore, SEM analysis showed a transformation of the morphology from rod-shaped to more spherical particles, further demonstrating the structural impact of NaOH treatment at higher concentrations.

The ion-exchange properties of zeolites play a critical role in their application, affecting adsorption characteristics, selectivity in separation processes, catalytic efficiency, and various other physical properties, making zeolites indispensable in a wide range of technological applications [83]. For instance, in a study by Cavallo et al. [84], CO_2 capture on synthetic LTA-type zeolite and natural clinoptilolite was shown to be effective at different temperatures (from 25 to 150 °C). The use of ion exchange with Na^+ and Ca^{2+} ions contributed to an increase in CO_2 adsorption capacity. Notably, natural zeolite Clino was found to be most effective at 150 °C, while synthetic LTA performed better at temperatures of 25–60 °C. IR spectroscopy revealed that the presence of Fe^{2+} ions in the Clino structure enhances its interaction with CO_2. The untreated Clino exhibited better results than its

modified analogs, NaClino and CaClino. At 25 °C, the NaClino sample demonstrated a high CO_2 adsorption capacity (2.4 μmol/g), whereas the adsorption capacity of Clino at 150 °C was 0.7 mmol/g, which was 66% lower compared to the lower temperature.

In a study by Davarpanah et al. [69], CO_2 capture using clinoptilolite and its ion-exchanged forms was investigated in the temperature range of 25 to 65 °C. The breakthrough data obtained were compared with the results for commercial zeolite Z13X. Na^+ and Ca^{2+} cations were used in the experiment. At 25 °C, the adsorption capacity of the samples was ranked as follows: Z13X > Na-Clino > Clino > Ca-Clino. However, at 65 °C, the untreated clinoptilolite exhibited the highest CO_2 adsorption, reaching 0.6 mmol/g, which was 20% higher than that of zeolite 13X. The authors attributed this result to the lower isosteric heat of adsorption of CO_2 on clinoptilolite. Additionally, FTIR spectroscopy revealed that unmodified clinoptilolite forms linear CO_2 adducts on K^+ and Mg^{2+} cations, as well as carbonate-like compounds at active sites. Meanwhile, in Na-exchanged clinoptilolite, Na^+ ions reduce the surface basicity, leading to the formation of single cationic centers that facilitate the formation of linear CO_2 adducts.

In another study [38], the CO_2 adsorption capacity of clinoptilolite was evaluated using alkali and alkaline earth ion-exchanged forms. The results demonstrated the following order of CO_2 adsorption capacity: $Li^+ \approx Na^+ > K^+ > Rb^+ > Cs^+$. This is attributed to the fact that smaller cations have a higher charge density, which increases the surface potential. Additionally, the smaller size of these cations allows them to occupy less space in the zeolite pores, thereby freeing up more space for CO_2 molecule adsorption.

In the study in [85], the authors explored the modification of clinoptilolite using alkali metals (Li^+, Mg^{2+}, and Ca^{2+}), amines (MEA, TEA, hexylamine), and ionic liquids ([bmim]PF6, [bmim]NO_3, [bmim]Br, and [bmim]Cl). It was found that strong interactions between the applied substrate-modifiers and CO_2 molecules are key factors in increasing the adsorption capacity of clinoptilolite. Experimental data showed that CO_2 adsorption increased by 4.18, 3.58, and 4.35 times under 4 bar pressure for clinoptilolite/Li^+, clinoptilolite/2% MEA, and clinoptilolite/5% [bmim] PF6 samples, respectively.

Prior to the use of natural zeolites, after their chemical and physical treatment, preliminary thermal treatment is necessary. This step includes calcination, which, as is known, does not lead to structural changes in zeolites at temperatures up to 300 °C. However, at temperatures ranging from 350 °C to 550 °C, the destruction of the zeolite structure may occur, which should be taken into account when selecting thermal treatment regimes [86].

In the study [87], attention was focused on the adsorption properties of clinoptilolite for the separation of CO_2 from a CO_2/CH_4 mixture. Clinoptilolite, a natural zeolite, demonstrated an adsorption capacity for CO_2 of 2.8 mmol/g at 277 K and 10 bar pressure, showing promising selectivity for CO_2 adsorption. The heat of adsorption for CO_2 on clinoptilolite was measured at 21.03 kJ/mol, indicating moderate interaction between CO_2 molecules and the surface of clinoptilolite. However, the adsorption properties of clinoptilolite can be further enhanced through various modification methods, such as ion exchange, making it a viable material for CO_2 capture in industrial processes. In dynamic adsorption experiments, clinoptilolite exhibited a CO_2 breakthrough time of approximately 417 s, demonstrating its potential as an efficient and natural adsorbent for CO_2 capture. This material presents a cost-effective and accessible solution for industrial applications aimed at reducing CO_2 emissions.

The Preparation Methods of Natural Zeolites

Natural zeolites possess significant potential in various fields, including water and air purification, catalysis, and energy storage. However, to achieve optimal efficiency of these materials, it is crucial to carefully select and apply appropriate preparation methods. Zeolite preparation involves various techniques, such as thermal activation, chemical modification, and mechanical treatment, each of which has a substantial impact on the properties of the final product. Research on zeolite preparation methods demonstrates that properly selected techniques can greatly enhance their characteristics, such as porosity, adsorption capacity,

and catalytic properties. Thermal activation is one of the primary methods of zeolite preparation, involving the heating of the material to high temperatures to remove organic contaminants and partially regenerate the zeolite structure. For instance, in the study in [88], the authors show that thermal activation significantly increases the porosity of zeolites and improves their adsorption properties. Additionally, in the study in [89], the stages of zeolite preparation from the Tayzhuzgen and Shankanay deposits for CO_2 sorption are described. The zeolites from these deposits were prepared for CO_2 sorption through three stages: mechanical grinding, granule formation with the addition of water, and thermal activation at 600 °C. Specifically, the zeolites from the Tayzhuzgen deposit exhibited high CO_2 sorption capacity, increasing CO_2 uptake from 22% to 27.4% at 300 °C. The zeolites from the Shankanay deposit also showed improved sorption properties but with lower efficiency, with CO_2 sorption capacity increasing from 12.4% to 18.3%. This improvement is attributed to the increase in specific surface area after thermal activation and the homogeneity of particles after mechanical processing. Another important direction is chemical modification, which enhances the adsorption and catalytic properties of zeolites. In the study conducted by Jiang et al. [90], the modification of natural clinoptilolite for CO_2 capture was thoroughly investigated. The authors applied several preparation methods, including roasting, acid pickling, a combination of acid pickling and roasting, and ion exchange, to enhance the adsorption capacity of clinoptilolite. In this study, natural clinoptilolite with particle sizes ranging from 0.300 to 0.391 mm was modified through several techniques. For roasting, the clinoptilolite was washed, dried at 100 °C, and then roasted in a muffle furnace at various temperatures (200 °C, 300 °C, 400 °C, 500 °C, and 600 °C) to determine the optimal roasting temperature. Acid pickling modification was performed by immersing the clinoptilolite in HCl solutions of varying concentrations (1 to 6 mol/L) for 40 h, followed by washing and drying at 100 °C. A combined acid pickling–roasting method was also applied, where samples were ground into different particle sizes, immersed in HCl, washed, dried, and roasted. Further modification was achieved through ion exchange by treating the acid pickled–roasted clinoptilolite with nitrate solutions of Na^+, Cu^{2+}, Mg^{2+}, and Ca^{2+} at 85 °C for 24 h, followed by drying and air cooling. The best conditions for each modification method were identified through experimentation. They found that acid pickling–roasting and ion exchange modification resulted in the highest CO_2 adsorption capacities, reaching 730 mL/g and 876.7 mL/g, respectively. Additionally, ion exchange modification with Na^+ significantly improved the CO_2 removal efficiency, achieving 92.5% in a simulated coking exhaust environment. The study highlights that the modification techniques, particularly the combination of acid pickling and roasting, as well as ion exchange with specific cations, enhance the porosity and ion exchange capacity of clinoptilolite, which in turn improves its CO_2 adsorption performance. Moreover, the regeneration of clinoptilolite through vacuum desorption and heating retained up to 89% of its initial adsorption capacity, proving the material's reusability and effectiveness in CO_2 capture applications.

Current research shows that approaches to thermal activation, chemical modification, and mechanical activation can significantly enhance the properties of zeolites. Further studies in this area are necessary to provide a deeper understanding of the effects of various methods on the properties of zeolites and their applications.

In summary, Section 3 of this article provides an in-depth analysis of the mechanisms and applications of natural zeolites in CO_2 capture, with particular attention to their role in wastewater treatment and flue gas cleaning. This study highlights the effectiveness of natural zeolites, such as clinoptilolite, chabazite, and mordenite, in CO_2 adsorption, which is attributed to their microporous structure, high cation exchange capacity, and a combination of physical and chemical adsorption processes. Additionally, it is demonstrated that the efficiency of these materials can be significantly improved through various surface modifications, including chemical treatments and activation methods, which enhance their surface area and ion exchange properties. Despite the advantages of natural zeolites, they face challenges such as limited adsorption capacity, sensitivity to moisture, and thermal instability. Further research is needed to optimize zeolite structures, particularly through the

development of composite materials and combined purification methods. A critical focus of future studies should be improving regeneration methods to maintain long-term efficiency in CO_2 capture and heavy metal removal from wastewater. Efficient regeneration will reduce operational costs and make zeolites more viable for industrial applications. Developing composite materials based on natural zeolites offers the potential to overcome current limitations, especially under high temperature and moisture conditions. Additionally, it is crucial to conduct research in real-world conditions to assess long-term performance and economic feasibility. Various adsorbents based on natural zeolites for CO_2 capture are summarized in Table 3.

Table 3. Adsorbents based on natural zeolites for CO_2 capture.

Year	Zeolite Type	Preparation Method	Adsorption Capacity CO_2	Process Conditions	Ref.
2001	Natural Mordenite	ion exchange	1.8 mmol/g	T = 17 °C and 0.26 bar	[91]
2017	ZnCHA	ion exchange	2.7 mmol/g	T = 25 °C and 95 kPa	[92]
2017	Tuff natural zeolite Campania	acid treatment	0.102 mmol/g	T = 25 °C and 1.01325 bar	[93]
2017	13X-K (from kaolin), 13X-B (from bentonite) and 13X-F (from feldspath)	hydrothermal treatment	6.9 mmol/g	T = 25–55 °C	[94]
2019	K-Chabazite	hydrothermal method	2.42 mmol/g	T = 30 °C and 1 bar	[95]
2020	Natural calcite-rich mordenite-clinoptilolite zeolite (Indonesia)	magnetic suspension balance	5.218 mmol/g	T = 0 °C and 30 bar	[52]
2019	Natural clinoptilolite (USA)	ion exchange	1.2–1.7 mmol/g	T = 30–70 °C and 1 bar	[96]
2020	Na-Clino NZ clinoptilolite	ion exchange	0.6 mmol/g	T = 65 °C	[69]
2022	Clinoptilolite	N/A	3.064 mmol/g	T = 25 °C and 10 bar	[5]
2023	NaClino	ion exchange	2.2 mmol/g	T = 25 °C and 1000 mbar	[84]
2024	Natural Clinoptilolite	acid pickling–roasting and by ion exchange	730 mL/g and 876.7 mL/g (92.5%)	T = 300 °C, 0.4 MPa	[90]

4. Removal of Heavy Metal Ions from Wastewater Using Natural Zeolites

One effective application of natural zeolites is their use in wastewater treatment, leading to the removal of pollutants and improvement of water quality [97–99]. Heavy metals represent a group of chemical elements with high atomic mass and density, exhibiting toxic properties at high concentrations [100]. These include lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), nickel (Ni), copper (Cu), and zinc (Zn), among others [100]. Heavy metals are present in water in the form of cations (e.g., $Pb^{2+,}$ $Cu^{2+)}$ and anions (e.g., $Cr_2O_7{}^{2-}$, $CrO_4{}^{2-}$, and other compounds). Removing heavy metals from drinking water to safe concentrations is essential to ensure public health and well-being [101]. Table 4 shows the data reflecting the harm, dose, and amount of heavy metals in wastewater.

Table 4. Harm, maximum permissible concentration, and amount of heavy metals in wastewater [102].

Heavy Metal, mg/L	Harmful to Health	Maximum Permissible Concentration (MPC)	Quantity in Wastewater, mg/L
Lead (Pb)	Accumulation in bones and tissues, damage to the nervous system, kidneys, cardiovascular system, anemia	0.03	0.1–2.0
Cadmium (Cd)	Damage to kidneys, bones, lungs, carcinogenic effect	0.005	0.01–0.1
Copper (Cu)	Gastrointestinal irritation, liver and kidney damage, anemia	1.0	0.1–1.5
Zinc (Zn)	Toxicity at high concentrations causes nausea, vomiting, diarrhea, organ damage	5.0	0.5–10.0
Chrome (Cr)	Skin damage, irritation of mucous membranes, carcinogenic effect (especially Cr VI)	0.05 (Cr VI), 2.0 (Cr III)	0.1–1.0 (Cr VI), 1.0–5.0 (Cr III)
Nickel (Ni)	Allergic reactions, lung damage, carcinogenic effect	0.1	0.1–2.0

Table 4. *Cont.*

Heavy Metal, mg/L	Harmful to Health	Maximum Permissible Concentration (MPC)	Quantity in Wastewater, mg/L
Mercury (Hg)	Toxic effects on the central nervous system, kidneys, liver, immune system, teratogenic effect	0.001	0.001–0.1
Arsenic (As)	Carcinogenic effect, damage to skin, respiratory system, cardiovascular system	0.01	0.01–0.1

The key process of heavy metal adsorption from wastewater using natural zeolites involves several stages: initially, natural zeolites undergo pretreatment to enhance their adsorption properties [103]. Zeolites are typically treated with acids or bases to remove impurities and increase the availability of active sites. The process begins with the preparation of wastewater containing heavy metals by filtration or other methods to remove large particles and impurities. Subsequently, natural zeolites are added to the wastewater and thoroughly mixed to ensure uniform distribution of the adsorbent. After mixing, the zeolites are left in the wastewater for a specific period to adsorb the heavy metals. Once the adsorption process is complete, the zeolites with adsorbed metals are separated from the wastewater by filtration or sedimentation. Saturated zeolites are regenerated for reuse, involving treatment with various reagents to remove the adsorbed metals and restore their activity. Numerous studies have investigated the use of natural zeolites from various deposits for the removal of heavy metal ions from wastewater. In many countries, local natural zeolites such as clinoptilolite, phyllosilicate, mesolite, and chabazite are used as cost-effective sorbents for heavy metal removal from wastewater [104].

4.1. Mechanism of Adsorption of Heavy Metals from Wastewater

Heavy metal pollution of wastewater is a significant problem for developing countries as these elements are widely present in waste from various industrial sectors [105]. Zeolites possess high surface activity and the ability to retain metals due to their molecular structure. The mechanism of heavy metal adsorption from wastewater by natural zeolites occurs through ion exchange [106]. In this process, heavy metal ions in the wastewater are attracted to the negatively charged surface of the zeolite particles. These heavy metal ions then replace the exchangeable ions on the zeolite surface, effectively trapping the heavy metals and removing them from the water. Additionally, the porous structure of natural zeolites facilitates the physical adsorption of heavy metal ions on the surface and within the pores of the zeolite particles. This provides additional adsorption sites for heavy metal ions, enhancing removal efficiency. Overall, the adsorption of heavy metals by natural zeolites is an effective and environmentally friendly method for treating wastewater contaminated with heavy metals. The mechanism of adsorption of heavy metal ions using natural zeolites is illustrated in Figure 4.

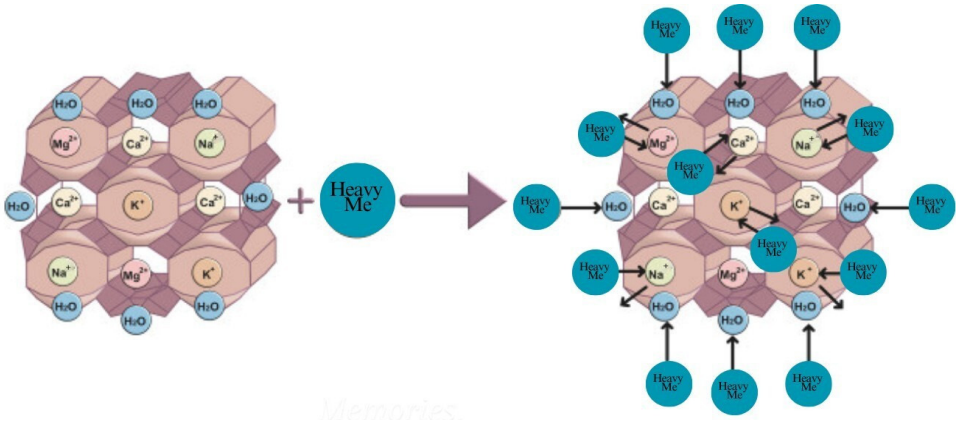

Figure 4. Mechanism of adsorption of heavy metal ions with natural zeolites [107].

4.2. Adsorbents for Wastewater Treatment Based on Natural Zeolites

In recent decades, extensive research has been conducted on the use of natural zeolites as adsorbents for wastewater treatment, particularly for the removal of heavy metals. For example, clinoptilolite, one of the most prevalent types of natural zeolites, has demonstrated high effectiveness in removing contaminants such as ammonium and heavy metals due to its high capacity and selectivity [108]. However, the efficiency of adsorption depends on several factors, including the type of zeolite, its structure, and operational conditions, often necessitating the optimization of parameters to achieve the best results [109].

Despite their potential, the adsorption of heavy metals using natural zeolites faces several limitations. Primarily, the efficiency of the process can be constrained by the choice of zeolite and its physicochemical characteristics, such as pore size and surface activity. For instance, some zeolites may be less effective in adsorbing certain heavy metals due to their structure and chemical properties. Additionally, competition with other ions in the solution can significantly reduce adsorption efficiency, which is particularly relevant in real wastewater conditions where various types of contaminants are present [110].

To overcome these limitations and enhance process efficiency, various methods are being developed and investigated. The literature discusses approaches such as the development of new zeolite types with improved adsorption properties, optimization of process conditions (e.g., pH and temperature), and the application of additional treatment methods, such as pre-treatment of wastewater or combined purification systems.

Comparing natural zeolites with metal oxides has shown that unmodified zeolites generally possess relatively low adsorption capacities for heavy metal removal [111,112]. However, modification of zeolites can significantly enhance their effectiveness. For example, Gaikwad et al. [113] demonstrated that zeolite derivatives, such as apophyllite and thomsonite, are capable of efficiently removing zinc (Zn) from solutions, achieving maximum removal efficiencies of 86.2% and 81.6%, respectively.

The study in [114] investigated the removal of copper, nickel, cobalt, and iron ions by natural zeolite from water resources in the concentration range of 0.5–3.5 mg-eq/L. The maximum quantities of adsorbed Cu^{2+}, Fe^{2+}, Ni^{2+}, and Co^{2+} ions were 0.023, 0.021, 0.020, and 0.011 mg-eq/L, respectively. The ions are ordered by decreasing adsorption capacity: $Cu^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+}$. The authors highlight that the adsorption capacity of zeolite increases with the concentration of metal ions. X-ray fluorescence (XRF) analysis using the Rietveld method revealed that the zeolitic tuff from the Yagodninskoye deposit contains clinoptilolite-Na (23.0%), clinoptilolite-Ca (52.1%), and mordenite (12.9%). Crystal lattice analysis of mordenite shows that the unit cell sizes of the treated zeolite decrease along the a and b axes, and their volume reduces compared to the original zeolite. This effect is observed in the order of Cu > Ni > Co > Fe.

Methods for enhancing the properties of natural zeolites include thermal and chemical treatment, as well as chemical modification [115]. Specifically, treatment of natural clinoptilolite with NaOH solutions led to changes in the SiO_2/Al_2O_3 ratio, indicating alterations in the zeolite structure and improved adsorption properties.

Researchers are also actively employing various modification methods to enhance the adsorption properties of zeolites. For instance, Velarde et al. [107] investigated the effectiveness of natural Bolivian zeolite and its modified NaCl form for cadmium removal from aqueous solutions. It was found that natural BZ adsorbed 20.2 mg/g of cadmium, whereas the modified NaBZ exhibited an adsorption capacity of 25.6 mg/g. The modified zeolite demonstrated increased adsorption capacity, attributed to improvements in the material's physicochemical properties.

The study in [116] investigated the adsorption of heavy metal ions, such as lead (Pb^{2+}), copper (Cu^{2+}), zinc (Zn^{2+}), and nickel (Ni^{2+}), using sodium-enriched zeolite (Na-Z). The results demonstrated high adsorption efficiencies: 89% for Pb^{2+}, 72% for Cu^{2+}, 61% for Zn^{2+}, and 58% for Ni^{2+}. The following graphs present the adsorption kinetics data for these ions, modeled using pseudo-first-order (PFO), pseudo-second-order (PSO), and mixed-order (MO) kinetic models (Figure 5).

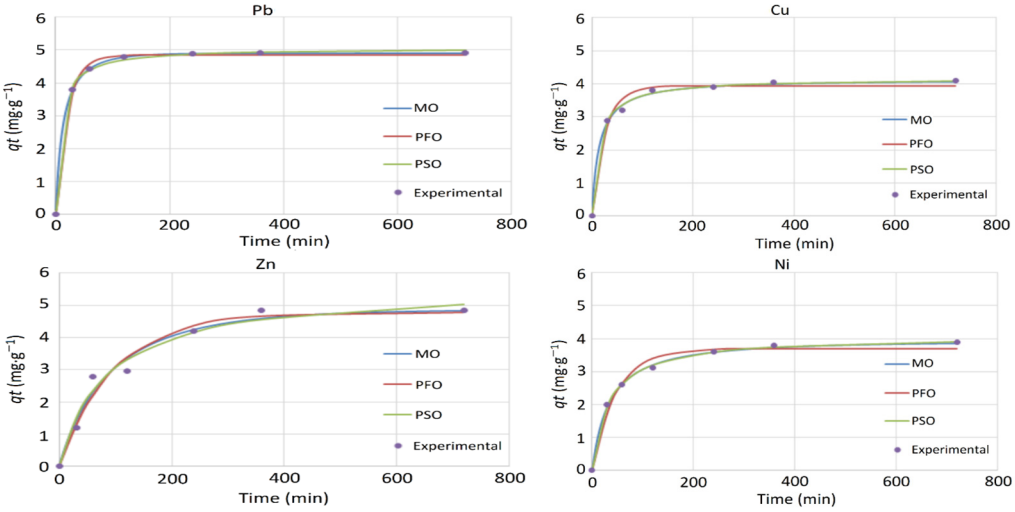

Figure 5. Adsorption kinetics data for Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} ions on Na-enriched natural zeolite, fitted by pseudo-first-order (PFO), pseudo-second-order (PSO), and mixed-order (MO) kinetic models [116].

As can be seen from Figure 5, the kinetic models exhibit varying degrees of alignment with the experimental data. The mixed-order model (MO) demonstrated the highest accuracy in describing the adsorption processes for Cu^{2+} and Ni^{2+} ions. In contrast, the adsorption of Pb^{2+} and Zn^{2+} ions was better described by the pseudo-second-order (PSO) and pseudo-first-order (PFO) models, suggesting differences in the adsorption mechanisms for these metals.

Additionally, the study showed that the presence of inorganic and organic compounds with ion exchange or complex-forming functional groups on the zeolite surface significantly enhances its adsorption activity towards heavy metals. Specifically, the research presented in [117] investigated the removal of Cu(II), Co(II), and Ni(II) ions from aqueous solutions using natural zeolites from the Kholinskoye deposit. The heulandite (ZH) used as the carrier was modified with 4-(3-triethoxysilylpropyl)thiosemicarbazide (TSC), which significantly improved the zeolite's selectivity and adsorption capacity. The adsorption capacities of the modified zeolite (ZH-TSC) were 0.46 mmol/g (29.5 mg/g) for Cu(II), 0.42 mmol/g (24.9 mg/g) for Co(II), and 0.28 mmol/g (16.6 mg/g) for Ni(II). The authors suggest that the adsorption of metal ions on the modified zeolite is due to the formation of chelating complexes through donor–acceptor interactions between nitrogen and sulfur atoms with metal ions.

Another study [118] examined the removal of cadmium and lead from wastewater of an oil refinery in Kermanshah using Iranian clinoptilolite. The zeolite was modified with 5 M of HCl. BET analysis results showed that the specific surface area of the adsorbent increased more than six-fold after modification. Fourier-transform infrared spectroscopy (FTIR) results demonstrated an enhancement of Si-O-Si groups post-modification. X-ray diffraction and X-ray fluorescence analyses confirmed that the modified adsorbent has improved properties for heavy metal adsorption. Experiments were conducted in a continuous adsorbent layer with a volume of 330 mL at room temperature. The impact of operational parameters, such as initial heavy metal concentration, wastewater flow rate, and adsorbent dose, on the adsorption rate was evaluated. The results showed that maximum removal of cadmium and lead was achieved at the highest concentrations of heavy metals and adsorbent dose, with the lowest flow rate. The modified adsorbent exhibited higher efficiency in removing heavy metals. Under optimal operating conditions and using the modified adsorbent, cadmium and lead removal from wastewater reached 85.9% and 98.9%, respectively.

The article in [119] presents a study on the adsorption properties of natural (ZPCli), sodium-exchanged (ZPCliNa), and acid-modified (ZPCliH) zeolites concerning Cd^{2+}, Ni^{2+},

and Zn^{2+} ions. The analysis revealed that the adsorption capacity for Cd^{2+} was highest, while it was lower for Zn^{2+} and Ni^{2+}. Significant structural changes in zeolites after H_2SO_4 modification were confirmed by a six-fold increase in sodium content in ZPCli after NaCl treatment and a reduction in levels of K^+, Ca^{2+}, and Fe^{2+}. Acidic treatment led to the removal of sodium and a decrease in other cations, which was attributed to the incorporation of H^+ ions into the zeolite structure. Additionally, a reduction in aluminum content and an increase in the Si/Al ratio were noted, which may affect the cation exchange properties of the material.

Alkaline treatment is one of the most widely used methods that significantly impacts the structure and cation exchange properties of zeolites [80]. In particular, acid and alkaline treatments can substantially alter the structure of zeolites, enhancing their effectiveness in heavy metal removal. The study presented in [111] involved treating natural clinoptilolite with sodium hydroxide (NaOH) solutions with concentrations ranging from 0.1 to 4 M for the removal of heavy metals such as cadmium (Cd^{2+}), copper (Cu^{2+}), and chromium (Cr^{3+}) ions. Results showed that treatment with NaOH solutions up to 0.5 M led to a slight decrease in the SiO_2/Al_2O_3 ratio, whereas concentrations of 1.0 M and above resulted in a significant reduction of this ratio. This indicates substantial changes in the zeolite structure, which may affect its adsorption properties and heavy metal removal efficiency.

The study in [120] reviewed the use of natural zeolites for the adsorption of heavy metal ions such as Cu^{2+}, Pb^{2+}, and Cd^{2+} from industrial wastewater. The research focused on parameters affecting the adsorption rate, including adsorbent mass, initial solution concentration, pH level, adsorbent particle size, and mixing intensity. It was found that increasing the initial solution concentration from 100 to 400 mg/L enhances the driving force of the process, improving heavy metal removal efficiency. However, after reaching equilibrium, the initial solution concentration remains nearly constant due to the reduction in active sites on the adsorbent surface. Moreover, the study of adsorbent particle size (100 and 200 μm) showed that adsorbents with smaller particle sizes adsorb Cu^{2+}, Pb^{2+}, and Cd^{2+} ions more effectively, as smaller particles create more active sites and contacts for metal adsorption. Increasing the mixing speed to 100, 200, and 300 rpm also enhances heavy metal removal efficiency by significantly improving the external mass transfer, which controls the adsorption rate.

Furthermore, the effectiveness of natural Jordanian zeolite (JNZ) for removing nickel (Ni^{2+}) ions from aqueous solutions was investigated by the authors of [121]. The study evaluated the effects of various factors, such as interaction time, initial metal concentration, adsorbent concentration, and temperature, on the adsorption process. The experiments showed that optimal adsorption of Ni^{2+} ions was achieved at pH 4, with a removal efficiency of 65.01%. Increasing the initial concentration of Ni^{2+} ions from 2 to 50 mg/L improved the zeolite's ability to remove these ions, with nickel adsorption efficiency reaching 153.846 mg/g. These results were corroborated by Langmuir and Freundlich isotherm models.

In the study in [122], it was demonstrated that the treated Philippine natural zeolite (PNZ) modified with NaCl (MPNZ) exhibited maximum adsorption capacity for heavy metal ions, particularly copper, zinc, and nickel. MPNZ showed adsorption efficiencies for copper at 99.96%, zinc at 88.49%, and nickel at 86.67% in multi-ion solutions, which are significantly higher compared to untreated zeolite. The surface functionalization of PNZ resulted in a notable increase in pore size, from 10.11 nm for PNZ to 13.36 nm for NaCl-modified PNZ (MPNZ) and 15.59 nm for NaOH-modified PNZ, enhancing the adsorption capacity by removing impurities and creating new micropores.

The SEM micrographs in Figure 6 provide clear evidence of the surface morphology changes after modification. The untreated PNZ (Figure 6a) shows a less developed porous structure, while the NaCl-modified MPNZ (Figure 6b) exhibits a much more developed surface with larger and more defined pores. This change in morphology aligns with the observed improvements in adsorption performance, as the larger pore size allows for better accessibility and interaction with heavy metal ions. Furthermore, the decrease

in the Si/Al ratio from 4.02 to 3.76 suggests an increase in the negative charge within the zeolite framework, which enhances the cation exchange capacity and improves the efficiency of metal ion adsorption. The maximum adsorption efficiency was achieved at pH 9 and with an initial solution concentration of 100 ppm. Adsorption equilibrium data were best fitted by the Langmuir isotherm model, confirming monolayer adsorption on a homogenous surface.

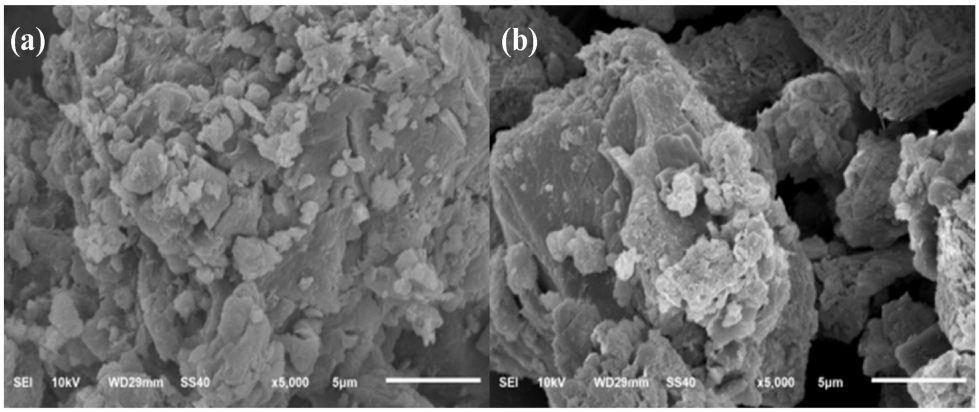

Figure 6. SEM micrographs illustrating the surface structure of (**a**) untreated PNZ and (**b**) NaCl-modified MPNZ [122].

The authors of [123] investigated the removal of heavy metals, such as cadmium and copper, from aqueous solutions using natural Jordanian zeolite. The authors investigated the influence of parameters such as initial concentration (Co), contact time (t), and varying adsorbent mass (m) on the efficiency of heavy metal removal. The concentration of heavy metals in the solution ranged from 80 to 600 mg/L. The ability of the zeolite to remove cadmium and copper was evaluated using the Langmuir isotherm, with capacities of 25.9 mg/g for cadmium and 14.3 mg/g for copper. Kinetic analysis showed that the adsorption of cadmium and copper is best described by the pseudo-second-order model, indicating a chemisorption process. The results demonstrate that as the initial concentration of metals increases (from 80 to 600 mg/L), removal efficiency decreases as the available active sites on the surface of the adsorbent fill up more quickly, leading to a reduction in adsorption capacity. Increasing the mass of zeolite improved the adsorption of cadmium and copper, which is attributed to the increased available surface area of the adsorbent. Additionally, the maximum removal efficiency of heavy metals was achieved within the first 20 min of the process, with cadmium adsorbing faster than copper.

In the study in [124], the authors investigated the influence of key parameters such as adsorbent mass, initial solution concentration, pH, particle size, and agitation speed on the efficiency of heavy metal removal (Cu^{2+}, Pb^{2+}, and Cd^{2+}) using natural zeolite. The experiments demonstrated that increasing the adsorbent mass from 1 g to 10 g resulted in an increase in Cu^{2+} removal efficiency from 60% to 99%. Similarly, raising the initial pH from 1 to 7 improved removal from 62% to 94%. Agitation speed played a crucial role, with efficiency rising from 90% to 94% as the speed increased from 100 to 300 rpm. A higher initial solution concentration (from 100 to 400 mg/L) led to an increase in adsorption from 0.5 mg/g to 2.1%. Similar trends were observed for Pb^{2+} and Cd^{2+} ions. The highest adsorption rate was observed in the initial hours of the experiment, followed by a slower rate, indicating saturation of the zeolite's active sites. These findings highlight the importance of optimizing parameters for maximizing heavy metal adsorption efficiency.

Regeneration and Desorption of Natural Zeolites for Heavy Metal Removal

The regeneration of natural zeolites plays a crucial role in maintaining their long-term efficacy in removing heavy metals from industrial wastewater, reducing operational costs, and enhancing the sustainability of treatment systems. Natural zeolites exhibit high physi-

cal and chemical stability, allowing them to withstand a variety of operational conditions and chemical exposures [125]. However, the impact of frequent adsorption-desorption cycles on the structural and sorptive properties of zeolites requires further analysis, particularly in terms of their stability and regeneration potential under real-world conditions.

Zeolite regeneration methods significantly influence their economic viability and environmental efficiency. The primary methods include thermal treatment, chemical regeneration, and rinsing, each with distinct advantages and limitations depending on the type of contaminants and operational conditions [126]. For example, thermal regeneration removes accumulated ions through high temperatures, while chemical regeneration utilizes acids, bases, or specialized reagents such as ethylenediaminetetraacetic acid (EDTA) to restore the sorption capacity of zeolites [127].

The effectiveness of zeolite regeneration and durability can also be significantly improved through structural modification and pretreatment. Studies have shown that modified zeolites exhibit enhanced regenerative properties and greater stability compared to untreated samples [128]. Specific modifications, such as structural alterations or the addition of functional groups, significantly enhance their ability to be reused and extend their operational lifespan.

An example of regeneration using sodium chloride is provided in the study by Hana Salman et al. [129], where natural zeolites were regenerated using a NaCl solution (20 g/L). The study demonstrated that after several adsorption-desorption cycles, the zeolites' ability to remove heavy metals such as Ni^{2+}, Zn^{2+}, Pb^{2+}, and V^{5+} remained high, with minimal loss of sorptive capacity. After regeneration, the highest efficiency was observed for Ni^{2+}, followed by Zn^{2+}, Pb^{2+}, and V^{5+}, reflecting the zeolite's varying affinity for these metals. The regeneration process showed that, despite the more challenging desorption of V^{5+} and Pb^{2+}, the zeolites maintained their adsorption capacity and, in some cases, such as for Ni^{2+} and Zn^{2+}, even demonstrated slight improvements.

The regeneration of alkali-treated zeolites [130] revealed that after three adsorption and regeneration cycles, the reduction in Pb^{2+} removal efficiency was only 17.6%. This result underscores the high potential of these zeolites for repeated use, which offers significant economic benefits for industrial wastewater treatment systems.

In another study [131], the regeneration process of zeolites saturated with lead and zinc was examined. The use of 3 M KCl for lead and 1 M KCl for zinc allowed for desorption efficiencies of more than 99.5% and 98.5%, respectively. However, the regeneration efficiency decreased with each cycle, especially for zinc, indicating a reduction in the sorptive capacity of the zeolite after multiple uses. This decrease in efficiency is attributed to the formation of difficult-to-remove compounds within the zeolite structure, complicating further metal removal.

Thus, despite the high initial efficiency of natural zeolites in adsorption–desorption processes, their repeated use is limited by the reduction in regeneration capability after several cycles. This must be considered when designing industrial wastewater treatment systems, where not only high purification efficiency but also long-term economic feasibility of adsorbent use is crucial.

Desorption of Heavy Metals: Research on the desorption of heavy metals from natural zeolites is significantly less extensive compared to adsorption studies. The authors of the works in [132,133] note that the desorption process can be reversible relative to adsorption, especially when using modified zeolites in various environments. For instance, if adsorption occurs in an acidic medium, an alkaline environment is necessary for effective desorption, and vice versa. It is important to highlight that the desorption process often proceeds more slowly than adsorption because metals that are easily adsorbed by the zeolite may be more resistant to desorption [131]. Furthermore, desorption studies can enhance our understanding of adsorption mechanisms by revealing the reversibility of the process. For example, the study in [134] observed that the adsorption of arsenate (As(V)) on modified zeolite was not reversible at various pH values, indicating the complexity of desorbing certain heavy metals. Additionally, the research by Salman et al. [129] inves-

tigated the desorption of natural zeolites. The results showed that desorption efficiency varied depending on the type of metal: Ni^{2+} was desorbed most easily, while Pb^{2+} and V^{5+} were less susceptible to desorption. The desorption sequence, according to the results, was as follows: $Ni^{2+} > Zn^{2+} > Pb^{2+} > V^{5+}$. These data confirm that natural zeolite exhibits high selectivity for heavy metals such as vanadium and lead, which complicates their desorption and necessitates additional measures for regeneration. Nevertheless, the regeneration efficiency remains sufficient for the repeated use of zeolites without significant loss of their sorption properties.

In conclusion, Section 4 offers a comprehensive evaluation of the potential of natural zeolites as effective sorbents for heavy metal removal from wastewater. The findings show that natural zeolites, particularly clinoptilolite, have a strong capacity to adsorb heavy metals, making them highly suitable for wastewater treatment due to their porous structure and high cation exchange capacity. Furthermore, the research underscores the importance of modifying zeolites through methods such as acid or alkaline treatments to boost their adsorption efficiency. These modifications increase surface area and ion exchange capacity, leading to higher removal rates of heavy metals. However, the challenge of regenerating and reusing zeolites remains, as the process is often costly and technically demanding. Optimizing regeneration techniques is crucial for the sustainable and large-scale application of natural zeolites in industrial processes.

Future directions for research include several key areas that will help enhance the practical use of natural zeolites for heavy metal removal. First, improving regeneration methods is crucial to making zeolites more cost-effective and sustainable for long-term use in water treatment. This will help reduce operational costs and make the process more economically viable. Second, there is a need for additional studies under real-world conditions to evaluate how modified zeolites perform in industrial wastewater systems, which will provide valuable insights for scaling up their application. Third, developing composite materials that combine zeolites with other adsorbents may significantly improve their adsorption capacity and selectivity, making them more versatile for various industrial uses. Although natural zeolites show great potential for addressing heavy metal contamination in wastewater, further research and development are essential to overcome the current challenges and fully utilize their capabilities. Adsorbents based on natural zeolites for the removal of heavy metals from wastewater are summarized in Table 5.

Table 5. Adsorbents based on natural zeolites for the removal of heavy metals from wastewater.

Year	Adsorbent	Heavy Metal	Concentration of M(II)	Dose (g/L)	Adsorption Capacity	Equilibrium Temperature	Isotherm Model	Ref.
2019	NZ (Russia)	Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+}	0.5–3.5 mg-eq/L	S:L = 1:5	0.023; 0.020; 0.011 and 0.021 mg-eq/L	T = 20 ± 2 °C	Langmuir and Freundlich	[114]
2020	NZ (Iran)	Pb^{2+}	25–250 mg/L	20–50 g/L	99.96–99.4%	T = 25 °C, pH = 4.5	Langmuir and Freundlich	[135]
2020	NZ and modified clinoptilolite	Ni^{2+} and Co^{2+}	423.57–721.29 mg/L	4.1–9.8 g	92.80 and 33.67%	T = 40.2–53.1 °C, pH = 5.1–6.9	RSM-CCD and ANN	[136]
2020	NZ	Cu^{2+}, Pb^{2+} and Cd^{2+}	100–400 mg/L	400 mg/L	94, 99, 70%	T = 25 °C, pH = 5–7	-	[20]
2021	NZ (Greece)	Zn^{2+} and Cd^{2+}	10–200 mg/L	10–60 g/L	35 and 50%	T = 25 °C, pH = 4.5	-	[137]
2022	NZ (Indonesia)	Pb^{2+}	50–400 mg/L	0.5–5.0 g/L	60.75%	T = 27 °C, pH = 2–10	Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich	[130]
2022	NZ (Algerian)	Ni^{2+}	10 mg/L	0.32 g/L	95.13%	T = 25 °C, pH = 5.27	Avrami kinetic model and Redlich-Peterson isotherm	[120]
2023	NZ Shankanay (Kazakhstan)	Cu^{2+}, Cd^{2+}, Pb^{2+} and Ni^{2+}	Cu = 10.52 mcg/mL, Cd = 10.35 mcg/mL) and Pb = 11.02 mcg/mL	1 g/L	Cu-Cd 99%, Pb—100% and Ni—85%	T = 25 °C, pH = 6	-	[138]

Table 5. *Cont.*

Year	Adsorbent	Heavy Metal	Concentration of M(II)	Dose (g/L)	Adsorption Capacity	Equilibrium Temperature	Isotherm Model	Ref.
2023	NZ Clinoptilolite (Georgia)	As^{3+}	10 mg/L	20–25 mg/L	99.6%	T = 25 °C, pH = 4–9	Langmuir and Henry	[139]
2024	BZ and NaBZ (Bolivia)	Cd^{2+}	10–500 mg/L	1 g/L	78.6 and 96.9%	T = 25 °C, pH = 6	Langmuir and Freundlich	[107]
2024	NZ Apophyllite and Thomsonite (India)	Zn^{2+}	50–250 mg/L	25–700 mg/L	81.6 and 86.2%	T = 25 °C, pH = 2–6	Freundlich, Langmuir, Redlich-Peterson, Dubinin-Radushkevich and Temkin isotherms	[113]
2021	NZ (Jordan)	Ni^{2+}	20 mg/L	1000 mg/L	153.846 mg/g	T = 30 °C, pH = 4	Langmuir and Freundlich.	[121]
2020	NZ (Kazakhstan)	Pb^{2+}	0.5–5.0 g/L	5–500 mg/L	14 mg/g	T = 25 °C, pH = 6	Langmuir and Freundlich	[140]
2021	ZH-TSC (Russia)	Cu^{2+}, Co^{2+} and Ni^{2+}	100 mg/L	5–90 mg/L	29.5, 24.9 and 16.6 mg/g	T = 25 °C, pH = 5	-	[117]

5. Prospects and Conclusions

Natural zeolites are attractive materials for use as sorbents for carbon dioxide (CO_2) capture and the removal of heavy metals from water due to their low cost and widespread availability in many regions of the world. In addition, they offer an economically viable alternative to synthetic materials.

The high cation exchange capacity of zeolites enables their use in the removal of heavy metal cations from industrial wastewater. However, one of the main challenges associated with the reuse of zeolites after cation removal from solutions is their separation, which typically requires costly technologies. Therefore, further research should focus on developing more efficient regeneration methods for zeolites to remove heavy metal cations, allowing their repeated use without significant expenses for processing and cleaning.

There is a limited amount of research in the literature addressing the suitability of natural zeolites for CO_2 capture. Key criteria to consider when evaluating the use and effectiveness of adsorbents in the CO_2 capture process include capacity, selectivity, adsorption and desorption rates, the required temperatures for adsorption and desorption, thermal and mechanical stability, regeneration capability, and the cost of regeneration. For the practical application of natural zeolites in the future, it is necessary to conduct studies under real-world conditions to assess their effectiveness in wastewater treatment systems and CO_2 capture.

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