



Research article

Modification of natural zeolites and their applications for heavy metal removal from polluted environments: Challenges, recent advances, and perspectives

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ABSTRACT

In recent decades, environmental pollution has become a significant problem for human health and environmental impact. The high accumulation of heavy metals in waters and soils from different sources was conducted by finding efficient and environmentally friendly treatment methods and materials for their removal. Natural zeolites have found wide-ranging applications in environmental remediation and protection, considering various treatment and modification methods designed to enhance the natural zeolites' adsorptive or ion-exchange capabilities for increased efficiency. This paper briefly consolidates the recent scientific literature related to the main characteristics of natural and modified zeolites, the advantages and limitations of their environmental remediation application, and summarizes the methodologies applied to natural zeolites in order to improve their properties. Their application for removing heavy metals from water systems and soils is also comprehensively discussed. This review highlights the excellent potential of natural zeolites to be used after specific treatment or modification as a sustainable and green material to solve numerous environmental pollution issues.

1. Introduction

Environmental pollution is one of the critical problems worldwide, which has increased demands for environmental protection and sustainable use of natural and non-toxic materials for decontamination at industrial scale [1]. In recent years, natural zeolites received considerable attention due to their natural abundance, unique properties, low cost, non-toxicity, attractive physicochemical properties and efficiency in the adsorption of common pollutants [2] such as heavy metals, other inorganic compounds (ammonium, nitrites, nitrates, etc.) [3–9] and organic pollutants (pesticides, dyes, total petroleum hydrocarbons, etc.) [10–14]. Due to their structure and chemical composition, in their unmodified form, natural zeolites display an affinity mainly for cations, especially for monovalent cations, thus their applications are related to cationic pollutants [15,16]. However, the removal efficiency of zeolites depends both on the pollutant and zeolite characteristics [17–19].

Heavy metals are elements with either high atomic weight or high density, greater than 5 g/cm³ [20]. In current practice, the term 'heavy metal' includes metallic elements and metalloids which are toxic to the biota. Increased concentrations of heavy metals in environments can be from natural or anthropogenic sources. The natural sources of heavy metals comprise the weathering of rocks and volcanic eruptions, whereas primary anthropogenic sources consist of industrial activities such as mining, smelting, use of fertilizers

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and pesticides, or combustion of fossil fuels [21]. Heavy metals are well-known to cause diseases such as cancer of the skin, liver, lungs, and bladder, damage to the brain and reproductive organs, kidney dysfunctions, and affect the immune system [22–25], thus they are critically concerning because of the numerous contaminated sites [26,27]. Moreover, heavy metals are practically nonbiodegradable due to their long half-time of hundreds of years and have bioaccumulation capacity in the human body. Thus, technologies to reduce or eliminate heavy metals in wastewater, drinking and surface waters to permissible levels are extremely important [28,29].

Natural zeolite deposits found across all continents display various mineral content and types, but there are no accurate statistics on the world reserves [30,31]. About 70 types of natural zeolite occur worldwide, and more than 250 zeolites similar to the natural ones have been synthesized. The main natural zeolite sources are in Slovakia, Bulgaria, Greece, Italy and United States of America [32,33]. Natural zeolites were produced by conversion of volcanic glass under various geochemical settings [34], their chemical formula being $(M^+{}_x, M^{2+}_y)[Al]_{(x+2y)}Si_{n-(x+2y)}O_{2n} \times mH_2O$, where $M^+{}_x$ and M^{2+}_y are monovalent or divalent metal ions, $[Al]_{(x+2y)}Si_{n-(x+2y)}O_{2n}$ is basic structure, and m is the number of molecules of water [35–37]. The natural zeolite framework is an infinite lattice of three-dimensional tetrahedra comprising Si and Al connected by O atoms [30,38]. The presence of Al in this structure induces a negative charge to the overall lattice [39], the ratio Si/Al playing an important role in the zeolite properties [40]. Their internal framework contains channels and cages which enclose H_2O molecules and cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} , which neutralize the negative charge of the three-dimensional lattice. These cations can be involved in ion-exchange processes and replaced in the zeolite structure by other cations [41,42]. Natural zeolites are commonly used in many areas, including industry, medicine, cosmetics, agriculture, animal husbandry, biotechnology, waste management and pollution control [33,43–46]. Due to the presence of impurities, the specific area of natural zeolites is smaller than that of synthetic zeolites, which is unfavorable for environmental remediation. However, the efficiency of various strategies for removing the impurities and increasing the specific surface area and porosity of natural zeolites are noticeably limited to the stability of zeolite structure [47].

In recent decades, many studies have been conducted on modifying natural zeolites to increase their specific surface area or determine their selectivity to a particular substance or group of substances. The commonly used techniques to activate the natural zeolites are single or combined thermal, chemical (acids, bases, or inorganic salts), modification with surfactant and modification by metal oxides. In choosing modification techniques, both the intended use and the economic cost-effectiveness should be considered [48].

Several previous papers independently reviewed the use of natural or synthetic zeolites for removing heavy metals from waters [2, 3,29,30,49] or for soil conditioning [50]. In this context, this review was conducted to systematically present the latest progress in treating and modifying natural zeolites for their use in the remediation of water and soil polluted by heavy metals. This work also calls for greater involvement of scientists in future research on using natural zeolites for heavy metals removal from polluted environments for the future development of natural zeolites and their applications. Overall, this review will lead to a deep understanding of the treatment and modification of natural zeolites and a comprehensive background and knowledge of applications for removing heavy metals from polluted environments.

2. Methodology

The following academic databases: Scopus, Google Scholar, ScienceDirect, Springer, Taylor & Francis, and Wiley, were used to find linked publications in the last 30 years that present the modification of natural zeolites for use in the remediation of waters and soils contaminated with heavy metals. The search keywords 'Natural Zeolite' AND 'Heavy metals' AND 'Treated' OR 'Modified' were used in the first step. In the Scopus database $n = 232$ documents were found, of which 170 articles, 20 conference papers, 22 reviews, 12 book chapters, 2 conference reviews, 1 erratum, 1 short survey. Through these, 38 other documents from other databases were added, and the abstracts of all these selected documents were read. Only those dealing with the modification of natural zeolites for their subsequent use in the remediation of water and soil polluted with heavy metals were considered appropriate to be included in this

Table 1
Chemical composition and cation exchange capacity of various natural zeolites around the world.

Zeolite type, country	Major oxides content (%)							References
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	
CLI, Romania	65.80	12.30	2.07	3.77	0.63	1.35	1.44	[53]
CLI, Ecuador	48.74	12.09	7.64	8.12	2.74	2.43	0.83	[54]
CLI, Croatia	64.93	13.39	2.07	2.00	1.08	2.40	1.30	[55]
CLI, Serbia	65.63	12.97	1.48	3.21	1.41	1.20	1.33	[56]
CLI, Serbia	66.57	13.13	2.30	3.85	0.56	1.27	1.17	[57]
CLI, Ukraine	68.64	11.50	1.57	2.38	0.89	0.29	3.12	[58]
CLI, Ukraine	70.39	12.68	8.05	0.31	0.27	2.28	1.36	[59]
CLI, Italy	65.26	12.11	0.50	0.35	0.51	5.85	0.43	[60]
CLI, Australia	68.26	12.99	1.37	2.09	0.83	0.64	4.11	[61]
CLI, China	65.72	13.50	1.30	3.10	0.63	1.16	3.14	[62]
CLI, Turkey	64.28	12.07	0.84	2.47	2.07	5.62	0.83	[63]
CLI, Spain	68.15	12.30	1.30	3.95	0.90	0.75	2.80	[64]
CLI, Iran	66.50	11.81	–	3.11	0.72	2.01	3.12	[65]
CLI, Brazil	68.79	11.71	5.25	3.34	1.31	2.75	0.62	[66]
CLI, Mexico	70.17	11.07	1.12	1.73	0.35	0.83	4.90	[67]

literature review.

3. Structural and physicochemical characterization of natural and modified zeolites

The notion of zeolites was primarily described by the Swedish mineralogist Axel Fredrick Cronstedt in 1756, who gave them the name derivative from the Greek words (zeo – ‘to boil’ and lithos – ‘stone’) [45,51]. Naturally, the most common zeolites, *i.e.* analcime, chabazite, clinoptilolite, erionite, ferrierite, laumontite, mordenite, and phillipsite, occur widespread in crustal layers dating from the Cenozoic and the Mesozoic [52].

Natural zeolites are crystalline hydrated aluminosilicates containing alkaline or alkaline earth cations in a 3D framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra connected through oxygen bridges. They belong to the group of cation exchangers owing to the excess negative charge on the zeolite surface results in the isomorphic replacement of Si by Al in the primary structural unit [35,48]. Natural zeolites received significant attention due to their unique physicochemical properties, such as high ion exchange capacity without any structural modification, large void volume, reversible dehydration, adsorption of molecules, catalytic activity, etc. [30,33,50]. Since the cation exchange ability is expressed as the cation exchange capacity (CEC), depending on the substitution of Si by Al, the natural zeolites display a CEC value in the range 1–4 mmol M^+/g zeolite [50]. The physicochemical properties are tightly connected to the geological deposits. Table 1 provides the basic chemical composition of natural zeolites expressed as the mass fraction of major oxide components in various deposits worldwide.

The zeolite structure influences the outstanding CEC and the internal surface area, which are implied in the exchanges with charged species and chemically adsorb species and make these natural minerals suitable for soil and water environmental remediation [50,68]. However, the natural zeolites themselves still encounter several limitations, *i.e.* (i) their availability in the surrounding areas of mining operations, (ii) impurities, and (iii) the CEC in the typical range of 2–4 meq/g, and hydrophilicity of natural zeolites (*e.g.* clinoptilolite) are restricted by their limited hydroxyl groups and higher Si/Al ratio (3–6) resulting in low ion adsorption performance [69]. The adsorption characteristics of any natural zeolite depend upon its composition, type, number and location of cations and Si/Al ratio, as well as on the physicochemical and structural properties of the adsorbent. In order to improve the properties of raw zeolites, single or combined thermal treatment and chemical modification, *i.e.* acid and alkaline treatment or surfactant impregnation, are among the commonly employed methods [70].

Adsorption, kinetic, isotherm and thermodynamics models.

Many efforts have been done to express the sorption of metal ions on zeolite surfaces from aqueous solutions. Metal ions adsorption can be calculated by Eq. (1) [71].

$$q_t = (C_o - C_t) \frac{V}{m} \quad (1)$$

where C_o (mg L^{-1}) is the initial concentration of metal ion, C_t (mg L^{-1}) is the metal ion concentration after contact with the zeolite

Table 2
Adsorption isotherm, kinetic and thermodynamic equations and their parameters.

Model	Equations	Description	References
<i>Isotherms adsorption models</i>			
Langmuir	$\frac{1}{q_e} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} \quad (2) \quad q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (3)$	q_e is metal concentration on the zeolite at equilibrium (mg g^{-1}); q_{max} is the maximum adsorption capacity (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}); a_L (L mg^{-1}) is linked to the energy of adsorption; and K_L/a_L is the monolayer adsorbent capacity	[71]
Freundlich	$\log q_e = b_f \log C_e + \log K_f \quad (4)$ $q_e = K_f C_e^{(1/n)} \quad (5)$	K_f is related to adsorption capacity and $1/n$ is the adsorption intensity.	[71,72]
Dubinin Radushkevich	$\ln q_e = \ln q_{\text{max}} - \beta \epsilon^2 \quad (6)$ $\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$ $E_L = \frac{1}{\sqrt{2\beta}} \quad (8)$	β is the Dubinin Radushkevich constant (mol^2/kJ^2), T is the absolute temperature (K); R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), E_L is the mean free energy (kJ mol^{-1})	[73]
<i>Kinetic models</i>			
Pseudo first order (PFO)	$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$ $q_t = q_e (1 - e^{-k_1 t}) \quad (10)$	q_e and q_t are the amount of metal ion adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the PFO rate constant	[71,72]
Pseudo second order (PSO)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$ $q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (12)$	q_e and q_t represent the quantity of metal ion adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) represent the PSO rate constant	[71,72]
Mixed order model	$q_t = q_e \frac{1 - e^{-k_1 t}}{1 - f_2 e^{-k_1 t}} \quad (13)$	q_t is the adsorption capacity at time t (mg g^{-1}) f_2 is the mixed order coefficient	[74]
Intraparticle diffusion	$q_t = k_{ip} \sqrt{t} + c_{ip} \quad (14)$	k_{ip} is the diffusion coefficient ($\text{mg g}^{-1} \text{ min}^{-1/2}$), c_{ip} is the intraparticle diffusion constant (mg g^{-1})	[74]
<i>Thermodynamic parameters</i>			
Adsorption thermodynamic parameters	$\Delta G = -RT \ln K_c \quad (15)$ $\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (16)$	ΔG is Gibbs free energy change; ΔS is standard entropy change; ΔH is enthalpy change, R is the gas constant, T is the absolute temperature and K_c is the distribution coefficient	[74]

during time t , V (L) is the volume of solution, and m (g) is the zeolite weight.

The adsorption isotherm describes the phenomenon of retaining of a substance from a gaseous or liquid or media to a solid substrate at a constant temperature and pH [48]. The Langmuir, Freundlich and Dubinin–Radushkevich models are the most widely used in the experimental sorption data for metals ions. The Langmuir isotherm implies a monolayer sorption onto the adsorbent surface, the Freundlich isotherm suggests that the adsorption happens onto a heterogeneous surface [72], while the Dubinin-Radushkevich model can be applied to describe if the adsorption process onto zeolite is of physical or chemical nature [73]. The Langmuir (linear – Eq. 2, nonlinear – Eq. 3), Freundlich (linear – Eq. 4, nonlinear – Eq. 5), and Dubinin-Radushkevich (Eqs. 6, 7 and 8) isotherm model equations are presented in Table 2.

Kinetics have an essential role as it presents crucial information about the reaction pathway and the rate-controlling mechanism of reactions in the adsorption process [72]. The pseudo-first order (PFO, Table 2, Eqs. 9 and 10) and pseudo-second order (PSO, Table 2, Eqs. 11 and 12) models were the most used to study adsorption kinetics. The PFO kinetic model, first proposed by Lagergren 1898 [75], states the removal process as adsorption preceded by diffusion through a boundary. The PSO kinetic model, first suggested by Blanchard et al. [76], is founded on the hypothesis that adsorption develops a second-rate kinetic process. This model depicts the sorption mechanism as controlled by chemisorption, which implies a sharing or exchange of electrons between the solute and the sorbent. The equation of the mixed order model is shown in Eq. 13, while the kinetic intraparticle diffusion model based on the use of an intraparticle diffusion constant is also used to describe the adsorption kinetic (Table 2, Eq. 14).

The equilibrium data at different temperatures are used to evaluate the adsorption thermodynamic parameters such as enthalpy (ΔH), Gibbs free energy (ΔG) (Eq. 15), and entropy (ΔS) (Eq 16) listed in Table 2.

4. Fundamental aspects of environmental remediation using natural zeolites

High ion-exchange capacity, excellent selectivity for different cations at normal temperature, relatively high specific surface area and low prices make natural zeolites attractive treatment materials for removing heavy metals from the environment [15,77,78]. These adsorbents can remove heavy metals from polluted waters by ion exchange, chemisorption or mechanical removal [79]. Also, they were successfully applied for the remediation of the polluted soils by diminishing the mobility of the metals in soil, thus decreasing the heavy metals transfer to the plants, by the so-called “stabilization” process, without significantly altering the natural function of soils [33,43,80]. Efficiency in the environmental remediation is contingent on the type, quantity and porosity of used natural zeolites, particle size and initial concentration of contaminants, pH and ionic strength of the solution, contact time between zeolite and solution, pressure, temperature, and presence of other organic and inorganic contaminants [35,48].

Natural zeolites are often physically or chemically modified because of their relatively low ion exchange capacity in natural form [78,81]. It was observed that, compared to other major cations (K^+ , Mg^{2+} , Ca^{2+}), Na^+ has a better efficiency in the ion-exchange process; consequently, zeolites modification to Na form is used to improve their efficiency for pollutant removal [82]. Moreover, their negatively charged lattices that allow the adsorption of cations in the surrounding environment are an important feature in their use to remove pollutants from aqueous media and soil [83]. Also, the Si/Al ratio, specific surface area and pore volume significantly influence their adsorption performance [84]. The large specific surface of zeolites allows for the adsorption of molecules smaller than the pore size [85]. Besides, natural zeolites exhibit a higher resistance towards acidic solutions than synthetic zeolites [86]. Amongst more than 40 known natural zeolite minerals, clinoptilolite is one of the most abundant and most studied natural zeolites due to its extraordinary properties, low density, and open reticular structure, which permits the access of small particles in the adjacent environment into the internal structure. Due to its selectivity for NH_4^+ , Sr^{2+} and Cs^+ and specific heavy metals, clinoptilolite is widely used to treat wastewater and polluted soils [87].

Zeolites are occurring in nature mainly in sedimentary rocks and require at least a minimum mechanical processing to be activated. In zeolites cavities and channels exist active centers that play an essential role in the adsorption of different substances, including heavy metals. Zeolites have an excellent thermal stability which grows with increasing Si/Al ratio. Usually, the natural zeolite has no structural change at temperatures up to 300 °C, while the destruction of its structure arises at temperatures ranging between 350 °C and 550 °C. The modification of active centers provides them with new characteristics, which largely expands their applicability [48]. The improvement of natural zeolites' adsorptive properties is based on the modification on their physico-chemical characteristics. The modification of zeolites with an inorganic salt solution or acid solution implies that the exchangeable cations from the zeolite structure are replaced by other cations (H^+ or Na^+) from the contact solution. The modification with a solution of inorganic salts such as $FeCl_3$ can lead to the formation of oxi-hydroxides on the zeolite surface, with an affinity for anions in solution [35,46].

5. Advantages and limitations of using natural zeolites for environmental remediation

Considering the importance of heavy metals removal from contaminated waters, many attempts have been made over time to find efficient treatment strategies to achieve this. Next to the adsorption methods, techniques based on chemical and electrochemical deposition, ion exchange, filtration, extraction, electrocoagulation, flotation, osmosis, etc. are used to remove heavy metals from water [48]. Among the existing adsorbent materials (bentonite, zeolite, titanium dioxide, zinc oxide, calcium carbonate, chitin, chitosan, activated carbon), zeolite and bentonite are, by far, the most inexpensive materials [88].

Various literature data have documented the extensive use of natural and synthetic zeolites for water remediation, while the research on zeolite application to stabilize pollutants in the soil is still limited [89]. Modified natural zeolites can be adjusted to the soil pH and not cause extra pollution in the designed environment. However, since they are natural materials, not in pure form, they can include several compensating ions that can compromise their properties and limit their use. They contain pores in negatively charged

channels and cavities, making them suitable to interact for the retention of other substances from the surroundings by ion exchange (physical process) or by sorption (chemical process). They generally have a high degree of crystallinity, an extensive internal surface area, and volumes with well-defined cavities. An essential feature of zeolites is the reversible hydration and rehydration and reversible interaction with the ions and molecules from the surroundings [90,91]. Regarding their mechanical properties, zeolites have a low hardness, being easily extracted, crushed, and micronized [92]. The main advantage of using natural zeolites is that they are inexpensive natural and ecological resources spread in many areas worldwide. The ability of natural zeolites to be regenerated and other relevant properties, such as their selectivity to eliminate heavy metal toxicity from aqueous media and soils, must also be considered.

Due to their natural provenience, natural zeolites have several limitations compared to synthetic zeolites. The first limitation is that zeolitic tuffs contain a mixture of minerals, *i.e.*, one mineral as the primary phase, over 50 % zeolite (mainly clinoptilolite or mor-denite) [91], accompanied by many other minerals. Moreover, trace impurities, such as heavy metals, may make them unsuitable for some applications; however, the desorption of heavy metals from natural zeolites was deficiently investigated [22]. Moreover, the cation content in natural zeolites is highly variable. Natural zeolites may have Ca^{2+} , Na^+ , or K^+ as the dominant exchangeable cations, which implies that they have different characteristics [90]. They have a wide range of Si/Al ratios, which control the ion exchange capacity and retention of cations inside the pores and channels and thus induce variable properties. Natural zeolites have significantly smaller pore sizes, making them less useful for applications where the adsorption of large molecules is necessary. The framework structure of natural zeolites is not always perfect, and the pore openings are not identical for all rings [91]. Natural zeolites may have low adsorption capacity for some substances or cannot retain some neutral or negatively charged molecules; thus, modifying their surface or Si/Al ratio could be necessary.

The main advantages and limitations [93] of using natural zeolites for environmental remediation are briefly presented in Table 3.

Besides the numerous studies presenting the advantages of using natural zeolites as amendments in polluted soils, there is limited literature on the potential disadvantages of the long-term application of natural zeolites [94]. The main concerns refer to (1) the long-term effects of natural zeolites on the pH of soil or the likelihood of releasing large amounts of elements (*i.e.*, Na, K, Ca, Mg, Fe, Al) via the exchange process, (2) the heavy metals binding with natural zeolite is not well understood, and, consequently, the persistence of heavy metal immobilization, (3) the general stability of added zeolites in soils, (4) the role of climatic and environmental conditions, and mineral-type and size play in the natural zeolite persistence in soil requiring specific tests and long-term evaluation [50,94,95].

It is known that the contact between zeolite and the aqueous solution containing metal ions leads to several physicochemical processes involving the interactions of both the aqueous media and the metal ion with the zeolite. These interactions consist mainly of protonization-deprotonization of the surface of zeolite, formation of complexes with surface functional groups of zeolites, ion exchange, and dissolution-precipitation [48]. Metal ions are retained by zeolite by diverse types of bonds of different strengths. Strong chemical bonds involving the creation of inner-sphere complexes may be formed, or weak physical bonds and the creation of electrostatic outer-sphere complexes may appear. Chemical bonds imply mechanisms of ligand modification, the establishment of a covalent bond, a hydrogen bond, and steric or orientation effects. Cations with a small hydrated radius enter more straightforwardly into the cavities of zeolites that contain exchangeable cations. Thus, they are more easily exchanged. The higher electric charge of metal ions favours the ion exchange. Progressively, the metal ions retained firstly by ion exchange are also fixed to the inner sites of the zeolite, forming more stable chemical bonds [48]. However, the soil characteristics and the fractionation and speciation of heavy metals in soil may influence the binding of heavy metals with natural zeolite. Several recent studies investigated soil characteristics and contact time's effect on the heavy metal's mobility change over time [89,94,96]. Generally, the main finding of these studies was that the mobile fraction of heavy metals decreases during the contact period between added zeolite and soil, which proves the binding of metals on the zeolite.

Additionally, the contradictory results displayed by literature data underline a significant variation in the CEC value of natural zeolites owing to differing structural defects, the nature of cage structures, and ion-absorption ability [94]. Even though natural zeolites have been widely used for the remediation of heavy metal-polluted soils, the correlated information, particularly and general comments and specific reviews, is very limited.

Natural zeolites have great potential as low-cost, capable adsorbent materials for removing heavy metals from different sources contaminating the water [97]. The main challenges toward achieving the effective remediation of waters are the efficiency of used

Table 3
Main advantages and limitations of using natural zeolites for environmental remediation.

Advantages	Limitations
<ul style="list-style-type: none"> • Simultaneous interaction with contaminants by ion exchange and sorption of molecules and ions • High degree of crystallinity • Low density material • Large internal surface area and volume • Reversible hydration and dehydration • Shape selectivity • Low-cost material and widespread worldwide • Rock with low hardness which makes them easy to process • "Ready-to-use" for many applications after a minimum processing (crushing and heating) • May be used for multicomponent purposes 	<ul style="list-style-type: none"> • Natural zeolitic tuffs contains a mixture of minerals • Exchangeable cations in natural zeolites are highly variable • Degree of crystallinity varies • Internal surface area, internal volume and pore radius are variable • Low adsorption capacity for some substances, modification can be necessary • Their affinity is mainly for cations, modification is required for other substances • Variable properties even in same quarry • May contains impurities, including traces of heavy metals, requiring thus purification, or restricted uses for some purposes

natural zeolites, their regeneration and the safe disposal of the wasted adsorbents [70,74,98]. The pH of the aqueous media strongly influences the CEC of used natural zeolite for heavy metals removal [98]. It should be also noted that the sorption of divalent metal ions from multicomponent systems is generally lower than that of single-component systems, a possible explanation being the competition between ions [48].

6. Methodologies applied to natural zeolites to improve their properties

The efficiency of natural zeolites in various applications, including environmental remediation, depends directly on their physicochemical, structural, and morphological properties. However, like other natural materials, they can incorporate several compensating ions that can bargain their properties and limit their use. The natural zeolites contain impurities such as Fe^{2+} , SO_4^{2-} , quartz, other zeolites, clay minerals, feldspars and amorphous glass, which diminishes the content of valuable components in mineral materials and restrict their commercial applications where purity and uniformity are critical [99,100]. Therefore, single or combined thermal, chemical, modification with surfactant and other modification treatments of natural zeolites (Fig. 1) can be applied to remove these impurities, enhance their structural properties, improve their affinity towards cation and allow the use of these natural materials in a wide range of applications [70,101–103]. Thermal and chemical treatments may provoke cation migration from the zeolite framework and cation replacement by the newly introduced cation species, thus disturbing the cation location and pore opening [104]. So, the ions are replaced by more removable ions under the exchange conditions, resulting in a higher presence of one cation and the conversion of zeolite into a near homoionic form with improved effective exchange capacity [104,105].

Each methodology has its advantages and drawbacks, their choice for a specific application being a challenge. Thus, the acid, alkaline and salt treatments of natural zeolites enhance the structural properties, *i.e.* surface area, pore size and microporosity, while the modification with metallic reagents and cationic surfactants adjust the zeolite' surface in order to enhance the affinity towards different anionic contaminants [10,33,104,106,107].

Natural zeolites treated with acids, bases or salts display higher cation adsorption and heavy metal removal efficiency; additionally, the process is simple, fast, and accessible. However, since an excess quantity of reagent can strongly disturb crystallinity and decrease the adsorption capacity, this amount must be strictly controlled [35]. In alkaline media, the Si–O–Si bond is quickly attacked by OH^- ions and Si can be removed from the zeolite framework, while the Si–O–Al bond is relatively stable owing to the negative charge of AlO_4^- which defends Al from the attack of OH^- ions. Oppositely, in acid media, the Si–O–Al bond is unstable, and Al can be easily extracted from zeolite framework due to the opposing charged AlO_4^- and H^+ . Accordingly, a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio conveys a higher amount of Si–O–Si bond, while a lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio involves a higher amount of Si–O–Al bond [108].

The acid treatment produces more accessible adsorption sites in the zeolites and increases the surface area and microporosity. The specific pore volume, pore size distribution, surface area, acidity and distribution of the acidic sites are important textural characteristics in the adsorption of heavy metals [102]. Additionally, the Si/Al ratio rises due to the dealumination process, while the growth in surface area and adsorption capacity was more effective than other treatment methods [2,108]. Dissolution of some amorphous material that obstructs the pores of natural zeolites is another advantage of acid modification. Therefore, the effectiveness of acid treatment is contingent on the mineral purity, chemical composition, structure, and working conditions [35].

The alkaline treatment can dissolve the Si from natural zeolites or even eliminate the crystal structure of zeolite, enhancing the textural properties, while preserving the structural Al. The increase in the number of acid and adsorptive sites occurs concomitantly with the Si removal and the decrease in the Si/Al ratio [2]. Besides, the alkaline treatment adjusts the textural properties (pore size and specific surface area), enhances the adsorption capacity, selectivity and accessibility, produces mesoporosity and enriches the Al content, thus improving the acidic properties of the natural zeolites [102,103].

The salt treatment was demonstrated to eliminate the water and inorganic impurities from the zeolite channels via exchanging metal ions within the zeolite structure, but the main limitation is the high cost of reagents [2]. Cationic surfactants raise the pore volume and pore diameter, and reduction the surface area of the natural zeolites owing to the clogging of the pore channels with surfactant [109].

An important challenge associated with using natural zeolites as adsorbents is their regeneration capacity in order to recover the adsorbed heavy metals, followed by their reuse in many cycles without any significant loss of the initial performances [30,98]. Generally, inorganic (HCl, HNO_3 , H_2SO_4) and organic (HCOOH , CH_3COOH) acids, alkalis (NaOH, KOH) and salts (NaCl, KCl, NH_4Cl , Na_2CO_3 , K_2CO_3 , $\text{Ca}(\text{NO}_3)_2$) were used to recover the natural zeolites used to remove heavy metals by ion exchange processes [48,83,109–114]. Generally, the acid solutions are preferred for natural zeolite regeneration, although the occurrence of the dealumination process can decrease their stability and lead to significant damage to the zeolite structure [115]. When using inorganic acids, a regeneration efficiency of nearly 96 % was obtained for Ni using 0.1 M HCl, but the clinoptilolite surface was entirely covered by H^+

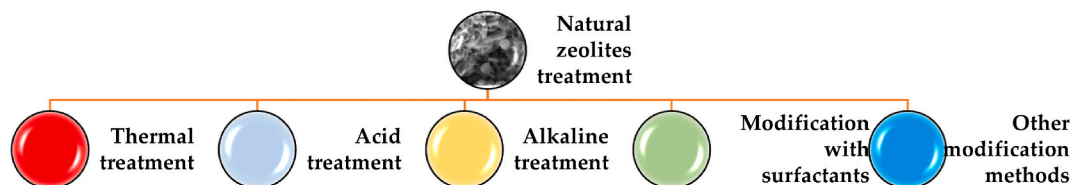


Fig. 1. Methodologies applied to natural zeolites to improve their physicochemical properties.

ions and the coordination spheres of chelated Ni were interrupted [116]. The regeneration and reusability experiments revealed the ability of the NaOH-treated natural zeolite to be used for up to three cycles of the Pb adsorption process with a 17.6 % reduction in adsorption performance [102]. When using salts, high regeneration efficiencies for natural clinoptilolite were reported for Cd (72–97 %) using 1 M NaCl by about seven cycles [112], Pb (95 %) using 30 g/L NaCl at pH = 11.5 in a fixed bed column [117], Pb (99.5 %) using 3 M KCl for many cycles [118], Ni (84.0 %) using 20 g/L NaCl after three cycles for 3h [119], and Cd (88–92 %) using 1 M KNO₃ [120]. However, the number of regeneration cycles of natural zeolites strongly depends on the zeolite type and the composition of wastewater [30,118]. Margeta et al. [35] reported a desorption efficiency of over 92 % for the release of individual Cd, Ni and Pb for the regeneration of natural zeolite-clinoptilolite using 3 M KCl, 0.5 M NaCl, 1 M KNO₃, 0.1 M HCl, depending on the metal desorbed from the zeolite. All studies on zeolite regeneration have been carried out at a laboratory scale, which limits their conversion to larger systems working under environmental conditions.

6.1. Thermal treatment of natural zeolites

The thermal treatment of natural zeolites permits the removal of impurities and improve physicochemical, structural, and morphological properties. The thermal treatment is a simple and green method to desorb water and organic molecules from the internal channels of zeolites, thus increasing their pore volume and specific surface area [121]. The water molecules from natural zeolites are removed at 100–110 °C, without any obvious structural modification. The bonded water molecules start to be removed at 150 °C, the complete removal occurring at 350–380 °C [98].

Table 4

A summary of the thermal treatment of natural zeolites for heavy metals removal from environment.

Pollutant(s)	Environment	Zeolite/Treatment	Main results	References
Ni, Cu, Cd, Pb	Water	<ul style="list-style-type: none"> natural zeolites with size fraction of 0.2–3.0 mm treatment with HNO₃ followed by thermally treatment at 450–600 °C, in argon 	<ul style="list-style-type: none"> the adsorption capacity for metals improved significantly by thermal activation the optimal thermal treatment temperature was 550 °C for 2h, in inert atmosphere 	[98]
Mn, Cd, Cr, Zn, Fe, Ni, Co, Cu, Ba, Pb, Sr	Wastewater	<ul style="list-style-type: none"> clinoptilolite - natural zeolite thermal treatment at 200 °C 	<ul style="list-style-type: none"> removal efficiency of metals varied as follows: Mn > Cd > Cr > Zn > Fe > Ni > Co > Cu > Ba > Pb > Sr natural zeolite was support for microbial community formation during wastewater treatment 	[125]
Fe and Mn	Water	<ul style="list-style-type: none"> clinoptilolite - natural zeolite with particle size <0.5 mm, 0.5–1.25 mm and 2–3 mm thermal treatment at 250 and 550 °C 	<ul style="list-style-type: none"> the highest removal efficiency for Fe was reached using 0.5–1.25 mm particle size and thermal treatment at 550 °C the higher removal efficiencies for Mn were found using 2–3 mm particle size and thermal treatment at 250 °C 	[73]
Cu, Cd, Cr, Ni, Zn and Pb	Aqueous solutions	<ul style="list-style-type: none"> clinoptilolite - natural zeolite thermal treatment at 200 °C 	<ul style="list-style-type: none"> selectivity pattern of Pb > Cr > Cu > Zn > Cd > Ni no important changes were observed in metals removal efficiency for the treatment temperatures of 200 and 350 °C at 550 °C, a reduction in the removal efficiencies was remarked 	[126]
As, Cu, Ni, Pb and Zn	Aqueous solution	<ul style="list-style-type: none"> natural zeolite with particle size of 35–180 μm drying at 110 °C for 5 h 	<ul style="list-style-type: none"> particle size strongly influenced the removal efficiency maximum adsorption capacities of 125.2, 20.31, 14.65, 13.54 and 11.68 mg/g were obtained for Pb, As, Cu, Zn, and Ni a selectivity pattern of Pb > As > Cu ~ Ni ~ Zn was observed 	[127]
Zn	Soil	<ul style="list-style-type: none"> clinoptilolite rich natural zeolite air drying at room temperature 	<ul style="list-style-type: none"> the adsorbed amount and strength of Zn binding decreased in the following order: synthetic > perlite by-product > natural zeolite 	[4]
Cd, Cr, Cu, Pb, Zn	Soil	<ul style="list-style-type: none"> clinoptilolite - natural zeolite thermal treatment at 200 °C for 2 h natural zeolite amendment (3 and 6 wt%) to soil for heavy metal immobilization for 3 months 	<ul style="list-style-type: none"> the concentrations of metals in the soil solution of soil mixed with natural zeolite decreased, excepting Zn 	[128]
Hg	Soil	<ul style="list-style-type: none"> clinoptilolite - natural zeolite of two particle sizes (<0.04 mm and 0.6–0.8 mm) drying at 60 °C 	<ul style="list-style-type: none"> leaching of Hg from soil decreased from 12.8 to 42.2 μg/L (in untreated soil) to 1.9–20.3 μg/L in the soil treated with natural zeolite immobilization of Hg species with removal efficiencies up to 90.5 % 	[129]
Cu, Pb, Zn, Cd, Co, Cr, Ni	Soil	<ul style="list-style-type: none"> clinoptilolite - natural zeolite with particle size <100 mm thermal treatment at 200 °C for 2 h, in air 	<ul style="list-style-type: none"> thermal treatment at 200 °C does not produce noticeable changes in zeolite structure stabilization of Cu, Pb, Zn, Cd, Co, Cr, Ni in a contaminated soil using 5 and 10 % zeolite amendment and equilibrated for 3 months 	[130]

The framework structure of natural zeolites is very responsive to variations in water-vapor pressure and temperature [47,122]. These imply changes in unit-cell size and geometry, and removal of cations from the framework channels, while high temperatures may lead to rupture of the Al–Si framework. Thus, the thermal treatment of zeolites may strongly influence their characteristics [123]. The heating treatment of zeolites can occur as (1) reversible dehydration attended by the reorganization of extra-framework cations and remaining water molecules with minimal changes of the framework or unit-cell volume; (2) reversible dehydration conveyed by a strong distortion of the framework and a considerable diminishing of unit-cell volume and (3) reversible dehydration at low temperature accompanied by significant alterations in the framework, followed by irreversible modifications due to the breaking of Al–O–Si bonds prior to whole dehydration [68].

The thermal treatment carried out at too high temperatures may cause damage to the zeolite framework and reduce crystallinity and, thus, the specific surface area [124]. Oppositely, untreated zeolites may contain water and other impurities in internal pores, providing a small specific surface area. Thus, the treatment temperature of zeolites is highly important for intended uses. In this regard, Kukobat et al. [122] reported that water evaporation from natural zeolite up to 200 °C leads to a growth in the specific surface areas, while extra growth in temperature leads to lower porosity. Medfai et al. [99] presented a methodology for purifying natural zeolites by combining heat treatment at 350 °C and acid treatment.

Table 4 presents several examples of the thermal treatment of natural zeolites intended to be subsequently used to remove heavy metals from various environmental compartments. The main remarks provided by the authors of the studies are also concisely presented.

Generally, an activation temperature of 200–350 °C and small particle size (<1 mm) were reported as sufficient to improve the adsorption capacity of zeolite for heavy metals, while, higher temperatures, which means higher energy consumption, do not significantly improve it [126]. On the contrary, at high temperatures (>550 °C) under ambient conditions, the natural zeolites lose their adsorptive capacity [94,95]. However, Kuldeyev et al. [98] reported high adsorption capacities (94–98 %) for Cd, Ni and Pb from heavily polluted waters, using natural zeolites with a particle size of 3 mm, thermally treated at 500 °C in an inert atmosphere. A higher immobilization effect for heavy metals was reported using 10 % thermally treated natural zeolite at 200 °C for 2 h as soil amendment [130] compared with air-dried zeolitic material [94].

6.2. Acid treatment of natural zeolites

The acid treatment of natural zeolites is among the most common and straightforward methods for natural zeolite modification and purposes to leach the exchangeable cations from the surface of the zeolites, substituting them with H⁺ ions. Furthermore, acid treatment would raise mesoporosity and microporosity by removing impurities even in the deepest cavities [131], thus improving the adsorption capacity of natural zeolites. The effectiveness of acid treatment is contingent on the zeolite type, mineral purity, chemical composition, structure and working conditions, *i.e.* zeolite/solution contact time, thermal treatment before and after modification, pre-treatment with water or other solutions, etc. [35,132]. Also, acid treatment is an effective method to modify the SiO₂/Al₂O₃ ratio of natural zeolites and increase their specific surface area. Acid concentration, time and temperature quantitatively influence the dealumination of zeolite and the SiO₂/Al₂O₃ ratio of natural zeolite [108]. The low Si zeolites are unstable in the acid environment and their decationization is conducted by other chemical methods, such as treatment with salts (usually NH₄Cl) followed by heating to remove ammonia and hydrogen.

A summary of the acid treatment of zeolites for heavy metals removal from water is presented in Table 5.

Table 5

A summary of acid treatment of natural zeolites for heavy metals removal from environment.

Pollutant (s)	Environment	Zeolite/Treatment	Main results	References
Pb	Water	<ul style="list-style-type: none"> natural zeolites (chabazite and clinoptilolite) treatment with 12.1 M HCl solution and heating at 85 °C 	<ul style="list-style-type: none"> treatment with HCl eliminated Ca, Mg, Na, K, Al, Fe from the framework Si framework remained intact 	[132]
Cr	Aqueous solution	<ul style="list-style-type: none"> natural zeolite treatment with 0.5 M HCl solution using a 1:3 acid ratio for 1 h at 70 °C and drying at 105 °C and calcination at 350 °C 	<ul style="list-style-type: none"> increase in SiO₂ and decrease in Al₂O₃ content decreased cation exchange capacity due to Al reduction reduction in exchangeable cations due to the removal of Na⁺, K⁺, Mg²⁺ and Ca²⁺ cations the removal percentage of Cr(VI) using NaOH-activated natural zeolite (16 %) was higher compared to HCl-activated zeolite (10 %). 	[133]
Cd, Cu, Ni, Pb	Synthetic aqueous solution	<ul style="list-style-type: none"> clinoptilolite - natural zeolite of 0.71–1.0 mm 2 M HCl, 24 h static conditions 	<ul style="list-style-type: none"> efficiency of metals removal was inversely proportional to the metal concentration the adsorption efficiency was Pb²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺ the maximum sorption capacity was 4.22 mg/g for Cd²⁺ at an initial concentration of 80 mg/L and 27.7, 25.76, and 13.03 mg/g for Pb²⁺, Cu²⁺ and Ni²⁺ at an initial concentration of 800 mg/L 	[134]
Pb, Co, Cr and Zn	Aqueous solution	<ul style="list-style-type: none"> washed zeolite mixed with acetic for 1 h and drying at 170 °C for 24 h 	<ul style="list-style-type: none"> a removal efficiency of 89.51 % (Cr), 81.07 % (Cr) and 78.24 % (Zn) 	[135]

Huntley et al. [100] modified naturally occurring zeolites (chabazite and clinoptilolite) with concentrated HCl (12.1 M) for Pb removal from water, but unexpectedly, the increase in pore size/number of pores after the acid treatment decreased the ability of the zeolite to remove the Pb^{2+} ions. A more significant removal of Pb^{2+} ions from synthetic solution was reported by activation of natural zeolite with 1 N NaOH (81.43 %) compared to 0.5 M HCl (13.57 %) activation under similar conditions [101]. Similar results were reported by Ren et al. [110], when the adsorption capacity of Cr(VI) reached a maximum at pH = 4. A possible explanation is that at acidic pH, the negative charge Cr(VI) species are adsorbed by the high protonation degree of zeolite surface the zeolite; at higher pH, the protonation degree of the surface decreases and the surface becomes more negative, resulting in lower adsorption [101]. Conversely, the adsorption capacity of Pb(II) from wastewater increased with the pH due to the different metal ions forming exist at different pH values [110]. Moreover, since no significant difference in the binding capacity of heavy metals from a solution using HCl-treated clinoptilolite was remarked, Sprynskyy et al. [134] concluded that there are specific centers on the zeolite structure for each cation.

6.3. Alkaline treatment of natural zeolites

The alkaline treatment of zeolites intends to disrupt the covalent bonds amongst O and H of the OH groups in the tectosilicate structure and to replace H^+ with Na^+ , producing an electronegative bond between O and Na [131]. A brief illustration of alkaline treatment of zeolites is presented in Table 6.

The adsorption capacity of alkali-treated zeolites for heavy metals from water/aqueous solutions was significantly (10–20 %) higher than those of untreated samples, probably due to the improvement in the mesoporosity of the natural zeolite [136,137]. Moreover, the alkali-treated natural zeolite with a low SiO_2/Al_2O_3 ratio and high hydroxyl group content displayed excellent ion exchange properties and hydrophilicity compared to the natural zeolite with a higher SiO_2/Al_2O_3 ratio and lower hydroxyl group content [138]. The same group of researchers reported that the adsorption capacity for Cd, Cu, and Cr of the same alkali-treated zeolite progressively improved under medium NaOH concentrations (0.1–3 M) and slightly decreased under higher NaOH concentrations (2.0–4.0 M) [137].

The specific surface area, average pore size, and total porous volume were significantly improved using a 2 N NaOH solution, allowing the entrance of heavy metals into the clinoptilolite structure and, consequently, a better stabilization of Cd and Zn in contaminated sediments [86].

6.4. Modification with surfactants of natural zeolites

Recently, surfactant modification has been extensively explored in order to improve the properties of natural zeolites to remove the organic compounds mainly [69,143]. A brief illustration of the modification of zeolites with surfactants is presented in Table 7. These chemical species are amphiphilic molecules containing a polar head (ionic or neutral) and a non-polar tail (one or more hydrocarbon chains). The large surfactant molecules cannot pass in the natural zeolite' cavities and channels and the modification process occurs on

Table 6

A summary of alkaline treatment of natural zeolites for heavy metals removal from environment.

Pollutant(s)	Environment	Zeolite/Treatment	Main results	References
Cu	Aqueous solution	<ul style="list-style-type: none"> natural zeolite treatment with 1 M and 2 M NaOH solution, 200 rpm, for 4 h 	<ul style="list-style-type: none"> natural zeolite modified using alkaline treatment displayed higher Cu uptake compared to that modified using a 1 M acetic acid solution, under the same experimental conditions 	[104]
Cr ⁶⁺	Aqueous solution	<ul style="list-style-type: none"> natural zeolite mixed with a 1 N NaOH solution in a 1:3 ratio for 1 h at 70 °C, followed by drying at 105 °C 	<ul style="list-style-type: none"> the amount of Al increased slightly cation exchange capacity increases due to higher amount of Na^+ improved the removal efficiency of Cr⁶⁺ 	[133]
Pb ²⁺	Aqueous solution	<ul style="list-style-type: none"> natural zeolite mixed with a solution of NaOH (0.5–5.0 g/L) at 90 °C and dried at 120 °C 	<ul style="list-style-type: none"> NaOH 1 g/L offered by the highest Pb²⁺ a removal efficiency of 60.75 %, and adsorption capacity of 136.26 mg/g 	[136]
Cd ²⁺ , Cu ²⁺ , and Cr ³⁺	Aqueous solution	<ul style="list-style-type: none"> natural clinoptilolite zeolite pre-dried at 60 °C, 24 h and mixed with 0.1–4 M NaOH solutions 	<ul style="list-style-type: none"> the crystal structure of clinoptilolite not affected under low NaOH concentration (≤ 0.5 M); partially transformed into zeolite Na–P under a 1 M NaOH concentration, and entirely transformed into zeolite Na–P under 2–4 M NaOH concentration the adsorption capacity of the NaOH-treated zeolite for Cd²⁺, Cu²⁺, and Cr³⁺ progressively improved (0.1–3 M NaOH) and then slightly reduced (4 M NaOH) 	[137]
Cr and Mn	Aqueous solution	<ul style="list-style-type: none"> natural clinoptilolite zeolite pre-dried at 60 °C for 24 h and mixed with 2 M NaOH solution 	<ul style="list-style-type: none"> low SiO_2/Al_2O_3 ratio, and high hydroxyl group content showed outstanding hydrophilicity and ion exchange properties high adsorption capacity, i.e. 86.5 % of Cr and 67.4 % of Mn 	[138]
Cd and Zn	Sediment	<ul style="list-style-type: none"> natural clinoptilolite treatment with a 2 N NaOH solution followed by calcination at 200, 300, 400, 500 and 600 °C, for 2 h 	<ul style="list-style-type: none"> NaOH modified clinoptilolite of 2–4 mm and 600 °C had the best effect on the removal of Cd and Zn in the aqueous solution, comparing to NaCl, LaCl₃, ZrOCl₂, and Ce(NO₃)₃ under the same experimental conditions 	[86]

Table 7A summary of **modification** with surfactants of natural zeolites for heavy metals removal from environment.

Pollutant (s)	Environment	Zeolite/Treatment	Main results	References
As	Aqueous solution	<ul style="list-style-type: none"> natural mordenite and natural clinoptilolite treatment with HDTMA = hexadecyltrimethylammonium bromide 	<ul style="list-style-type: none"> both modified natural zeolites required about 20 and 10 h, respectively to reach a state of equilibrium both modified natural zeolites reduced As(V) concentration below the WHO guideline values of 50 ppb As in drinking water 	[110]
Cr	Aqueous solution	<ul style="list-style-type: none"> natural zeolite with particle size of 0.12–0.18 mm treatment with hexadecyltrimethyl ammonium bromide (HDTMA) and cetylpyridinium chloride (CPC) stirred at 60 °C for 5 h under water-cooled reflux condenser 	<ul style="list-style-type: none"> natural zeolite has little or no affinity to Cr(VI), while modification by HDTMA and CPC significantly enhanced the adsorption capacity 	[139]
As	Wastewater	<ul style="list-style-type: none"> natural zeolite pretreated with NaCl was treated with hexamethyl-1, 9-nonanediammonium dibromide at 150 rpm for 24 h 	<ul style="list-style-type: none"> As removal increased by increasing dosage of adsorbent and contact time As removal efficiency from wastewaters was higher than 99 % after stirring for 180 min at pH = 6.9 	[140]
Cr, Pb	Wastewater	<ul style="list-style-type: none"> natural zeolite was placed in cetyltrimethylammonium bromide (CTMAB) and cetylpyridinium bromide (CPB), separately, and shaken at 35 °C for 48 h 	<ul style="list-style-type: none"> adsorption capacity of Cr(VI) by the modified zeolites was increased by 2–4 times relative to that by unmodified zeolite the adsorption capacity of Pb followed the order: unmodified zeolite > CTMAB-modified zeolite > CPB-modified zeolite, which is opposite to that of Cr(VI) adsorption 	[141]
As, Cd	Soil	<ul style="list-style-type: none"> natural zeolite pretreated with NaOH was shaken with HDTMA-Br at 25 °C for 24 h 	<ul style="list-style-type: none"> sequential extraction results showed that the addition of HDTMA-modified zeolite not only increased the residual fraction of As (by 2.7–5.9 %), but also reduced the toxicity-related fraction (by 2.3–2.7 %) comparing to the unmodified zeolite and blank treatments acid exchangeable Cd, the most mobile fraction of Cd, was significantly decreased from 10.06 mg kg⁻¹ to below 4.60 mg kg⁻¹ 	[142]

the outer surface [144].

The progress in exploiting surfactants to modify the surface of zeolite has aided in holding excellent adsorbability for anionic metals. The surfactant surface coverage played significantly increased the As(V) sorption capacity considering that the hexadecyltrimethylammonium (HDTMA) loading level on zeolite exceeded the monolayer coverage [110]. The presence of impurities (i.e., CaCO₃ and MgCO₃) blocked the surface area and, consequently, impeded the formation of surfactant bilayers by co-precipitation [139]. Wen et al. [142] also used HDTMA-modified zeolite to stabilize As and Cd in soils, simultaneously. Sequential extraction of As and Cd from soil treated with HDTMA-modified zeolite showed an increase in the residual fraction of As and a reduction of the toxicity-related fraction. The oxidizable and exchangeable fractions of Cd in the soil treated with HDTMA-modified zeolite were substantially higher than those in the blank soil. Moreover, the enzyme activity assays disclose that the microbial environment was deeply improved in the soil treated with HDTMA-modified zeolite [142]. Modified nanoscale zeolite with N,N,N,N',N',N'-hexamethyl-1,9-nonanediammonium dibromide was successfully applied for the effective removal of As(V) from wastewaters at pH = 6.9, after stirring for 180 min [140]. Other studies reported that higher adsorption capacity for As and Cr from wastewater by natural zeolites modified with cationic surfactants increased [141]. In all cases, the heavy metal removal efficiencies of surfactant-modified zeolites depended on the heavy metal concentration, pH, co-occurring solutes and speciation in the case of As [110].

6.5. Other modifications methods of natural zeolites

When used in wastewater treatment, the microporous structure of natural zeolites, besides the negative charge which requests to be compensated by cations in their crystal structure, guarantees the removal of cationic species. Thus, modifying natural zeolites increases the removal efficiency of cationic species, concomitantly enabling the removal of anionic species and organic compounds [70]. The chemical modification of natural zeolites using a highly concentrated solution of inorganic salts (NaCl, Na₂CO₃, CaCl₂, BaCl₂, FeCl₃, and NH₄Cl) provides the uniform compensation of cations within the crystal structure and, thus, the optimization of CEC value. By interacting zeolite and an inorganic salt (i.e., NaCl), the cations H⁺ and Na⁺ from the solution exchange the exchangeable cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) from the zeolite network [48]. Generally, higher adsorption capacities of natural zeolites for heavy metals from water/aqueous solutions were reported when using various salts compared to other chemicals [103,112]. In this regard, higher Cd adsorption capacity on natural clinoptilolite treated using 1 M NaCl than 1 M KCl, CaCl₂ or HCl, at 25 °C, for 24 h, 150 rpm [112]. The high Cd removal capacity was explained regarding the clinoptilolite transformation in a homoionic Na-form, as well as the occurrence of other removal mechanisms associated with the ion exchange [112]. Ricardo-García et al. [145] also treated natural zeolites with

Table 8

A summary of other treatment methods of zeolites for heavy metals removal from environment.

Pollutant(s)	Environment	Zeolite/Treatment	Main results	References
Ni	Aqueous solution	<ul style="list-style-type: none"> natural zeolite with particle size of 0.3–0.5 mm treated separately with 1 M NH₃, 1 M NaOH and 1 M NaCl solutions at pH = 5, sorbent dosage 4 g/L, contact time 30 min, room temperature 	<ul style="list-style-type: none"> sorption capacity increased in the following order: NH₃-treated zeolite (9.9 ± 0.6) < natural zeolite (19.7 ± 0.3) < NaOH-treated zeolite (24.0 ± 0.9) < NaCl-treated zeolite (28 ± 2) mg·g⁻¹ 	[145]
Pb ²⁺ , Zn ²⁺ , Ni ²⁺ , Cr ³⁺	Solution	<ul style="list-style-type: none"> zeolite X, sodalite, and zeolite A obtained from natural sources: bauxite, and obsidian 	<ul style="list-style-type: none"> removal >96 % for Pb²⁺, Zn²⁺, and Cr³⁺ and around 70 % of Ni²⁺ for all the investigated zeolites 	[148]
Hg	Water	<ul style="list-style-type: none"> Na-zeolite prepared by mixing 100 g natural zeolite with to 1 M NaCl at 60 °C, 7 days the Ag exchanged zeolite was obtained by mixing Na-form of the zeolite with 0.1 M AgNO₃ solution at room temperature, for 24h, under dark conditions 	<ul style="list-style-type: none"> natural zeolite was effective in removing Hg from Hg(NO₃)₂ solutions, but was not effective in removing Hg from HgCl₂ solutions natural Ag-zeolite was also efficient for Hg removal from HgCl₂ solutions 	[149]
Ni	Aqueous solution	<ul style="list-style-type: none"> mordenite-type natural zeolite modified (fraction <125 µm) in Na form zeolite treated with 1 M HNO₃ to remove impurities, then immersed in a 5 M NaCl solution, for 8 days 	<ul style="list-style-type: none"> a material with high specific surface area (S_{BET} = 124.95 m²/g) and total pore volume of 0.45 cm³/g a maximum adsorption capacity of 36.79 mg/g at 60 °C for Ni, obtained by the Langmuir isotherm 	[150]
Cr(VI)	Solution	<ul style="list-style-type: none"> natural zeolite heated at 110 °C for 3h, activated by 2 M of HCl for 24 h activated zeolite was modified with FeCl₃ solution in different ratios 	<ul style="list-style-type: none"> modified zeolite reduced Cr(VI) concentration from artificial solution from 70 mg/L to 0.24 mg/L, achieving an 87 % removal rate a removal efficiency of 93.33 % after 4 h contact time 	[151]
Cd	Aqueous solution	<ul style="list-style-type: none"> natural zeolite treated with a 2 M NaCl solution for 24 h 	<ul style="list-style-type: none"> Cd adsorption on zeolite increased with increase in initial Cd concentration 	[152]
Ca/Mg (hardness)	Groundwater	<ul style="list-style-type: none"> natural zeolite mechanically activated at different periods of time (2 h, 4 h, 6 h, 8 h) at 600 rpm 	<ul style="list-style-type: none"> natural zeolite significantly improved adsorption capacity with enhancing the activation time by 2 h (296 mg/g), 4 h (367 mg/g), 6 h (392 mg/g), and 8 h (450 mg/g) 	[153]
Hg	Aqueous solution	<ul style="list-style-type: none"> clinoptilolite-natural zeolite, fraction 0.6–0.8 mm, modified with Fe on 3 stages: mixed with a 1 M Fe(NO₃)₃·9H₂O, 1 M NaOH and 4 % NaNO₃ solution and dried at 40 °C 	<ul style="list-style-type: none"> sorption of Hg(II) was highly sensitive to the effect of pH the removed amount of Hg by modified zeolite (0.54 mmol Hg/g) was twice higher than onto unmodified natural zeolite (0.28 mmol Hg/g) 	[147]
Cd	Aqueous solution	<ul style="list-style-type: none"> philipsite rich natural zeolite with grain size of 0.595–1.41 nm shaken with 2 N NaCl or CaCl₂ for 24 h 	<ul style="list-style-type: none"> Na treated zeolitic tuff has the maximum exchange capacity than other types of calcium and acid treated zeolites zeolite structure is damaged at pH = 1–2 as removal efficiency becomes unremarkable 	[154]
Pb, Cu, Zn and Cd	Sediment	<ul style="list-style-type: none"> natural zeolite of different grain size was immersed in a solution of 2 M NaCl at 75 °C for 3 h centrifugation and drying at 105 °C for 3h 	<ul style="list-style-type: none"> NaCl-modified zeolite displayed the highest CEC and metal sorption compared with acid (2 N HCl) and alkaline (2 N NaOH)-modified zeolite, under the same experimental conditions 	[80]

different chemicals (NH_3 , NaCl and NaOH) under the same experimental conditions in order to remove Ni from aqueous solutions and the highest sorption capacity was achieved using a 1 M NaCl solution [145].

Natural zeolite and modified natural zeolite with silver in Ag^+ , Ag_2O and Ag^0 forms were used to remove mercury from $\text{Hg}(\text{NO}_3)_2$ and HgCl_2 aqueous synthetic solutions [146]. Unmodified natural zeolite was found to be effective in removing Hg from $\text{Hg}(\text{NO}_3)_2$ solutions, but removal of Hg from HgCl_2 solutions by unmodified zeolite was low. Modification with silver converted the natural zeolite into an active nanocomposite sorbent for Hg removal from HgCl_2 solutions. In contrast, Ag modification does not influence the effectiveness of the Hg removal from $\text{Hg}(\text{NO}_3)_2$ solutions. The study showed a strong relationship between ion exchange, surface Ag–Hg reactions and the aqueous phase Hg speciation. It was demonstrated that natural zeolite and its Ag^0 form were more efficient in Hg removal than commercial ion exchangers and had similar performances to activated carbon. These results are of high importance because it was demonstrated that a widespread, inexpensive, environmentally friendly natural material has similar or even superior absorptive capabilities compared to other synthetic materials. This makes natural zeolite and its silver-modified forms attractive materials to be applied on an industrial scale in real-world scenarios to solve a critical environmental issue [59].

Inorganic substances like Fe or Mn oxides and oxyhydroxides display a high affinity for heavy metal ions due to their oxygen-containing functional groups interacting with heavy metals [147]. Thus, the improved sorption capacity of modified zeolites with Fe^{3+} increases their affinity towards heavy metals. Ugrina et al. [147] used Fe^{3+} -modified clinoptilolite to remove Hg from aqueous solutions. It was found that the quantity of removed Hg by Fe-modified zeolite (clinoptilolite) was twice higher than natural zeolite (0.54 mmol Hg/g and 0.28 mmol Hg/g, respectively). Also, modifying natural zeolites with transition metals such as Cu or Co improves zeolite's adsorption capacity [146]. A short presentation of other possibilities to modify zeolites for heavy metals' adsorption is shown in Table 8.

7. Perspectives

In recent years, numerous studies have been published about the modification methods of natural zeolites to improve their adsorption capacity for heavy metals. It is well known that zeolites can easily regenerate and recover their adsorption properties. However, less attention was paid to the regeneration of spent zeolites after the adsorption experiments, even though this is an attractive feature for their future practical use. The regeneration cycles make adsorbent more efficient and, subsequently, provide lower costs. Therefore, the management of adsorbent materials after they adsorbed potentially toxic elements should be more intensely considered for upcoming studies. Another topic for future studies is the comparison of the methodologies for natural treatment, considering their costs to produce low-priced adsorbent materials. Indeed, natural zeolite is a low-cost material, but the technologies employed for its transformation into an efficient adsorbent material should also be inexpensive. The thermal treatment using microwave heating applied for natural zeolites could improve their adsorption capacity since excessive power and prolonged heating destroy the structure. Future research should be oriented on obtaining adsorbing materials with a wide range of contaminants in water, considering the large spectra of existing contaminants in the environment and the need to eliminate all of these. The development of materials based on their adsorptive capacity combined with other technologies for removing pollutants can be necessary to obtain this. Upcoming studies should analyze the performances of natural zeolites in real waters and soils from different sources and pollution levels in order to investigate their behavior and action mechanism under diverse environmental conditions. Not least, transferring the modification technologies from the laboratory experiments to the industrial scale is still limited and needs future work.

8. Conclusions

Natural zeolites occupy a significant place among the most commonly and affordable adsorbents for heavy metals, due to their accessibility, low cost, high specific surface area and adsorption efficiency. This review summarized the research and progress on modifying zeolites' surface and framework structure to improve their adsorption capacity, as published in papers mainly from recent years. Natural zeolites have unique properties based on their porous structure containing channels and cavities and their overall negative charge, which permits them to interact with the substances from the surroundings by ion exchange or sorption. The attractive ion exchange, adsorption, dehydration-rehydration, and rehydration properties, as well as being cheap, environmentally friendly, regenerative, easily accessible and available, make them exceptional adsorbents for cations, mainly heavy metals. In addition, the characteristics of natural zeolites can be improved by their modification using thermal treatment or by chemical modifications with bases, acids, surfactants, salts, or other reagents. In summary, using natural zeolite resources instead of applying other toxic or synthetic adsorbents that generate various pollutants will support diminishing costs and pollution. However, the contaminated water/soil source and the properties of the natural zeolite used considerably affect the efficiency of adsorption/immobilization. Future research should focus on an in-depth analysis of using natural, modified zeolites for heavy metal removal from polluted environments and to transfer the results obtained in laboratory conditions to industrial applications.

Etic statement

An ethics statement is not applicable because this study is based exclusively on published literature.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Marin Senila: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Conceptualization. **Oana Cadar:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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