

Application of natural and modified Zeolites in removing heavy metal Cations from aqueous media: an overview of including parameters affecting the process

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Abstract: *Natural, modified and synthesized minerals have been extensively employed for the removal of heavy metals and hazardous Ions from water and wastewater. As one of the most widely distributed earth materials, natural zeolite has been subjected to many studies for its removal of heavy metals from water. Zeolite minerals can be effectively employed for the treatment of metal-contaminated wastewater streams and aqueous solutions due to their wide availability, low-cost and high effectiveness advantages. This work reviews the existing knowledge and research on the removal of heavy minerals by different types of natural and modified zeolite. We compiled and critically reviewed more than 100 scientific articles and papers. This review article focuses on the examination of different parameters affecting the removal process and their individual impact on adsorption and ion exchange as the main mechanisms of the process.*

Keywords: Zeolite, heavy metals, adsorption, ion exchange, removal efficiency.

1. Introduction

Rapid industrialization has led to increase disposal of heavy metal into the environment. The metals are of special concern because of their persistency. Intense industrial and anthropogenic activities results in the contamination of environment with several contaminants, including heavy metals. Removal of heavy metals from wastewater has become a major concern nowadays because of its ability to contaminate water bodies. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. These heavy toxic metals entered into the water bodies through waste water from several sources such as vehicle exhaust, metal plating industries and industries of Cd- Ni batteries, mining, pigments, stabilizers alloys, laundry detergents, surfactants, pesticides, dyes, paints, etc. [1]-[3]. When the concentration of these pollutants exceeds certain limits, their presence seriously endangers the environment and the human health and remediation actions are necessary. Inefficient ways in managing heavy metal ions in water and wastewater may cause long-term risk to the ecosystem and humans. Several processes exist for removing dissolved heavy metals, including, but not limited to, ion exchange, precipitation, ultrafiltration, reverse osmosis, electro dialysis and adsorption [50]. Many of these approaches demand high energy & cost or advanced operational requirements. The need of safe and economical methods for the elimination of heavy metals from contaminated waters has developed interest towards the production of low cost alternatives to

commercially available adsorbent [4], [5]. Adsorption by zeolite minerals is one of the easiest, safest and most cost-effective methods for the removal of these metals from aqueous solutions [4]-[6]. The use of natural zeolites and their modified forms as metal sorbents offers the advantages of the low-cost, the availability in big quantities in many parts of the world, and the combination of high sorption capacity with the ability to modestly adjust the pH of the aqueous system. In addition, the natural zeolites, do not introduce additional pollution in the environment [3]-[9]. Several researchers have studied the removal performance of heavy metal ions by natural & modified zeolites which will be discussed in following pages.

Zeolites are crystalline aluminosilicates enclosing pores occupied by cations and water molecules, permitting reversible ion exchange and reversible dehydration. The cationic makeup of the aluminosilicate consists of aluminum ions (Al^{3+}) in a predominantly Si framework (an aluminosilicate). The charge imbalance resulting from the substitution of aluminum atoms for silicon atoms requires a nearby cation to preserve electrical neutrality, so the cation content is directly related to the Al content. In nature, these cations are typically alkaline earth elements such as Na^{+1} , Ca^{+2} , Mg^{+2} and metal ions.

Zeolites can provide adsorption sites with exchangeable cations for heavy metal ions and porosity for free metals, with ion exchange and molecular adsorption being the main mechanisms, respectively. The process of adsorption is now widely accepted, very effective and economically viable to be used to remove heavy metal ions in industrial waste as well as in drinking water. Besides ion exchange and adsorption, the other mechanisms indirectly involved during

heavy metal removal from aqueous solutions via zeolites are surface precipitation [44], [10] and destruction of clinoptilolite structure (i.e. dissolution of the clinoptilolite framework cations) [44], [52]. A wide variety of heavy metals can be removed from the liquid phase at significant quantities and kinetics is usually fast.

2. Methodology

This study has done on the base of a review of over 100 scientific articles and books mostly published in the last 10-15 years and available through the international scientific databases. The goal of this study is to compile the existed knowledge to explore the efficiency of natural and modified zeolite in removal of heavy metal from water with special focus on the inclusive factors affecting the process. In order to keep the volume of the article in reasonable limits and to prevent overlapping of the content of the present paper with the source papers which already have been published, reproduction of details of some of the reference articles was cautiously avoided. Instead, an attempt was made to summarize and compare the most important properties of different types of natural and modified zeolites (which are discussed in separate studies) as well as the reported results by universal researchers.

The first part of the manuscript gives a brief description of zeolite minerals and their occurrences as well as some physical properties are presented. Later, the most important experimental results carried out by researchers in different literature concerning the removal capacity and efficiency of zeolites in heavy metal adsorption based on different environmental variables & factors are compiled, compared and summarized to define a proper and applicable relation. Based on aforementioned approach, function of each parameter and their effect on heavy metals removal categorized and studied separately.

3. Result and discussion

3.1. Zeolite characterization, origin and basic properties

Zeolites are natural, hydrated aluminosilicate minerals with crystalline microporous structure and belong to the mineral type of 'tectosilicates'. In contrast to other tecto-silicates such as feldspar and quartz, the zeolite framework is remarkably open. Zeolite has cages and tunnels that can loosely hold water molecules. These channels and cages are adequate for adsorbing molecules smaller than these channels and/or tunnels, so in this regard, zeolites are known as "molecular sieves" [48]. The zeolite structure causes zeolite to have negatively charged surface. Negatively charged surface of zeolites can be used for adsorption of alkali earth metals. This structure consists of three-dimensional frameworks of SiO_4 and AlO_4 that are linked to each other by sharing oxygen atoms. The replacement of tetravalent silicon by trivalent aluminium in the mineral's structure creates a net negative charge that is counterbalanced by the presence of cations (usually Ca^{2+} , Na^+ and K^+) which are situated in cavities [11], [12]. These cations are exchangeable with other cations including heavy metals. The zeolite's framework structure encloses cavities occupied by large ions and water molecules which are able to

move, allowing ion exchange. The removal of the heavy metal ions with zeolite is a result of ion exchange and/or adsorption property of zeolite. Both processes are parallel but one of them is prevailing depending on the solid to the liquid ratio [10], [18]. Ion exchange properties of zeolites are due to the weakly bonded extra-framework cations which are mobile and easily exchanged with solution cations [51]. Adsorption of positively charged cations and complex formation are enabled because of the different shape of surface crystal faces, surface imperfections, broken bonds and edge sites, as well as the amphoteric nature of hydroxyl groups $[(\text{Al/Si})\text{-OH}]$ [44]. Zeolites can be classified by considering the topology of the framework. Zeolites having the same topology constitute a zeolite framework type. Currently there are 206 known framework types recognized by the Structure Commission of the International Zeolite Association [12]. An important feature is the effective width of the channels which determines the accessibility of the channels to incoming cations. Zeolite channels are formed by different combinations of linked rings of tetrahedra. The channels that are wider at their narrowest parts can receive larger cations into their structure [11]. As it has been stated, removal of heavy metals from aqueous solution by means of zeolite mainly is based on adsorption and ion exchange process and a lot of researches have been done over the past decade.

Natural zeolites occur in different geological settings as rock-forming minerals in many locations in the world. Natural zeolites are common in (1) saline alkaline lake deposits formed through essentially closed-system alteration of volcanic ash; (2) vertical sedimentary sequences formed through open-system alteration and/or burial diagenesis of volcanic ash; (3) hydrothermally altered volcanic or sedimentary rocks; and (4) deep-sea sediments [13]. Most of the zeolite ore deposits are derived from tuffs, and the hydration of volcanic glass is often considered the preliminary stage of zeolitization. Natural zeolites, generally, are mined in the form of brittle, solid rocks.

3.2. Factors affecting the removal process

The mineral's removal capacity from the liquid phase depends on several physicochemical factors related to both of sorbent and the liquid phase characteristics including initial metal concentration in the solution, temperature, solution pH, presence of other competitive ions, agitation speed, mineral grain size and its concentration, plus mineral specification itself. The early five factors are solution dependent and latest three factors are mineral dependent parameters. The mechanism of each parameter on removal process has been categorized separately and explored as follow.

3.2.1. Effect of heavy metal concentration

The initial metal concentration in the liquid phase significantly affects the adsorption process. Several studies have documented the effect of initial metal concentration on metal uptake by minerals. In most cases the increase of initial concentration resulted in an increase of the adsorption capacity and a decrease of the overall removal efficiency [14], [15], [18], [19], [20], [36], [58].

Erdem et al. [20] examined the adsorption of Zn^{2+} on natural zeolite for varying initial metal concentration and found that the adsorption efficiency decreased with increasing metal concentration. A similar trend was observed by Oren and Kaya [36] for zinc uptake by Gordes and Bigadic zeolite. Coruh and Ergun [14] found that the highest adsorption capacity of natural and modified clinoptilolite for Ni ions obtains at initial metal concentration of 200 mg/L while the highest removal happens at the concentration of 12.5 mg/L. Perić et al. [19] reported that the increase of initial zinc concentration resulted in a decrease of metal adsorption on natural zeolite. Increased removal efficiencies at low initial metal concentrations have also been reported by Erdem et al. [20], Cabrera et al. [18] and Wu et al. [15]. The determination of the maximum metal concentration where total saturation of the adsorbent occurs is important for practical applications. High initial concentration means that more metals are available and thus, more metal ions are adsorbed for constant adsorbent mass. At higher initial metal concentrations the driving force to overcome the mass transfer resistance for the migration of the metals from the bulk solution to the mineral surface increases [16]. However, each unit mass of adsorbent is subjected to a larger number of metal cations, which gradually fill up the sites until saturation is reached. In such a case, further increase of metal concentrations is not accompanied with an increase in the amount of metal adsorbed per unit mass of adsorbent. Furthermore, the level of surface precipitation strongly depends on the initial metal concentration.

At low metal concentrations, the adsorbent surface coverage is low and the formation of surface complexes is the main mechanism. The increase of metal concentration favors the concentration of compounds and aggregates on mineral surface. A further increase in metal concentration results in saturation of adsorption sites and surface precipitation is the main uptake mechanism [17]. The saturation of active sites is usually faster in the cases where minerals exhibit low selectivity for a metal. However, this is not always the fact, since the metal complexes formed or entrapped in the mineral's surface may accelerate the surface saturation even at low concentrations of metals that present high affinity for the specific mineral.

3.2.2. Effect of temperature

Most studies of heavy metal adsorption show that an increase in temperature enhances the adsorption process [14], [21]-[25]. Usually, at elevated temperatures the metal uptake is higher due to higher affinity of the mineral for the metal and/or an increase in the active sites of the solid. At higher temperature the energy of the system facilitates the attachment of metals on the mineral's surface [16]. Also, at higher temperatures ions become smaller due to their reduced hydration and their movement becomes faster [10], resulting in higher removal efficiencies.

Temperature increase results in changes related to both kinetics and equilibrium attributed to: (i) increase in the kinetic energy which facilitates the access of the metal ions to the active adsorption sites, (ii) increase in the surface activity of the mineral resulting in higher affinity or increase in the active adsorption sites, (iii) decrease in the mass transfer resistance. The increase in temperature is accompanied with a decrease in the thickness of the

boundary layer surrounding the mineral, so that the mass transfer resistance of the adsorbate in the boundary layer decreases, facilitating the diffusion of metals in the adsorbent. Thus, the effective diffusion coefficient of ions in solid phase usually increases and an increase in external mass transport is observed [14] [16], [23]. As temperature is increased, the retarding specific or electrostatic interactions become weaker and the ions become smaller because solvation is reduced [10]. However, at very high temperatures physical damage to the mineral can occur, reducing its adsorption capacity [23]. In most cases it is desirable to evaluate the adsorption capacity of minerals at room temperature, since at higher temperature the operational cost of the process increases. Rajic et al. [26] studied the removal of nickel using natural zeolitic tuff and found that the increase in temperature from 25 to 65 °C resulted in a threefold increase of adsorption, showing that the process was endothermic and spontaneous. Enhanced removal of nickel at elevated temperatures has been documented in several studies involving heavy metal uptake by natural minerals [21], [27]-[29]. El-Kamash et al. [29] reported that the increase of temperature resulted in an increase of the adsorption capacity on synthetic zeolite A towards zinc. The authors suggested that this occurred due to the increase of active sites and due to the change in pore size and the enhanced rate of intraparticle diffusion.

3.2.3. Effect of pH

It is well recognized that the pH is an important parameter impacting the adsorption process. solution pH has a significant impact on heavy metal removal by zeolites since it can influence metal speciation, integrity of zeolite (mineral's surface properties) and also H^+ ions are considered as competitive in ion exchange [3], [8], [30], [44], [48]; it impacts on the extent of metal precipitation and the type of complexes formed between the ligands and metals. . pH is one of the most important parameters influencing not only site dissociation, but also the solution chemistry of the heavy metals since hydrolysis, complexation by organic and/or inorganic ligands, precipitation and availability of heavy metals are all influenced by it [31]. The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption. The different metal species dominating in the solution at various pH differ in their charge and ability to adsorb on the mineral. The activity of the adsorbent's functional groups is strongly affected by solution pH. The point of zero charge pH (pH_{pzc}) is the pH of the solution at which the overall observed charge on the surface of the mineral is zero. At $pH < pH_{pzc}$, the functional groups are protonated and the positively charged surfaces dominate. In this case, the attraction of negatively charged ions is possible to occur. In highly acidic environment, several functional groups become protonated and act as positively charged species, resulting in reduced attraction between the metals and the minerals. Deprotonation of functional groups occurs at increasing pH and these behave as negatively charged moieties, attracting heavy metals [8], [32]. However, at alkaline environment, the solubility of metals decreases allowing precipitation, which may complicate the sorption

process [30]. Precipitation occurring at alkaline environment masks the true extent of metal sorption on minerals; this is why it is important when the mineral behavior is examined at high pH values to determine the soluble metal concentration prior to the addition of the mineral. In addition, at low pH values the concentration of external H^+ increased (due to lowered pH). since H^+ ions are considered as competitive in ion exchange, heavy metal uptake is reduced correspondingly [8], [44], [58].

Camacho et al. [47] examined the removal efficiency of MnO_2 modified clinoptilolite for As^{5+} and found that the minimal and maximal adsorption happens at pH of 2-3 and 6 respectively. They also stated that Arsenic adsorption decreased as pH increased from 6 to 9.

Coruh and Ergun [14] found that the highest adoption capacity of natural and modified clinoptilolite occurred at the pH range of 7–8, while the adsorption was also high and stable at the pH range of 4–6. Oren and Kaya [36] found that minimum uptake of Zn^{2+} occurred at the pH 3 and removal capacity increase with the increase in pH of solution. They stated that at high pH condition, Zn ions form complexes with OH^- . Hence, zinc hydroxyl species may participate in the adsorption and precipitate onto the zeolite structure and contribute as a parallel mechanism in removal as well as ion exchange. Katsou et al. [27] found that at the pH range of 4–7 the removal of nickel due to adsorption on zeolite was stable, while the highest nickel removal obtained at $pH \geq 8$ was mainly attributed to precipitation.

Argun [23] found that the optimal solution pH for adsorption of Ni^{2+} on natural zeolite was 6, while at an acidic environment the performance of clinoptilolite reduced due to the presence of protons that competed with nickel ions for the available adsorption sites. Precipitation was observed at pH higher than 8. Kocaoba et al. [33] obtained the maximum adsorption for nickel on zeolite at $pH \geq 6$, however the authors mentioned that at the alkaline region the true adsorption capacity was lower since precipitation also occurred.

3.2.4. Effect of competitive ions

The initial concentration of competing ions in the solution influences the adsorption of heavy metals on minerals. The presence of other cations apart from the one that must be removed from wastewater has a negative influence on the adsorption process [40]. The adsorbent's performance depends on the type and concentration of other ions that co-exist in the liquid phase and more importantly with the selectivity of the adsorbent for ions compared to its selectivity towards the heavy metal under investigation.

Presence of anions together with heavy metal ions leads to formation of metal-anion complexes, which may adsorb weakly or not at all to zeolite surface, thus, resulting in reduced heavy metal uptake [46]. As the concentration of anion increases, participation of cation in complexes gets higher. Heavy metal-anion complexes may possess negative charge, which, in turn, results in reduced heavy metal removal [8]. Mier et al. [48] observed that when anions are present, efficiency of Pb^{2+} and Cd^{2+} removal was significantly diminished. In some cases, as Doula and Ioannou [46] reported, anionic species may interact with surface sites of zeolites leading to increase in surface negative charge and enhance heavy metal removal by

zeolites. They stated that Cu^{2+} uptake was enhanced in the presence of Cl^- and NO_3^- due to possible increase in surface negative charge, which further results in a surface complexation mechanism.

The presence of other cations in the solution can reduce the adsorption capacity compared to that obtained for the uptake of each metal individually in single metal systems, particularly when the mineral is more selective for the competing cations rather than the heavy metal. The reduction in the adsorbent's performance depends on its selectivity and affinity for the respective ion in comparison with the competing ions, as well as the ionic properties and the concentration of each ion. The parameters that impact on the performance of an adsorbent are related to the adsorbent characteristics, the properties of the cations and the liquid medium characteristics [8], [10].

Zeolite selectivity for the various cations is a function of their free hydration energy and of the electrostatic interactions among the free ions and those located in the zeolite structure according to the Eisenmann–Sherry model, [43]. The results of Erdem et al. [49] study indicate that energetically less favorable sites become involved with increasing metal concentration in the aqueous solution. Also they found that metal selectivity of natural clinoptilolite with Si/Al ratio of 4.66 in their solution was in the order of $Co^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$. The selectivity order of metal cations in clinoptilolite with Si/Al ratio of 4.2 is given by Caputo and Pepe [40] as:

$Cs^+ > NH_4^+ > Pb^{2+} > Na^+ > Sr^{2+} > Cd^{2+} > Zn^{2+} \approx Cu^{2+}$. This order confirms the high selectivity of clinoptilolite for monovalent cations with low charge density. Furthermore, the high mineral selectivity for Pb^{2+} is attributed to the low hydration energy of the cation. Langella et al. [22] have found similar results as the clinoptilolite selectivity order is: $NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} \approx Zn^{2+}$. Consequently, clinoptilolite selectivity is mainly determined by the free energy of hydration of the cations. According to Blanchard et al. [41], the selectivity of Na-clinoptilolite follows the order of $Pb^{2+} > NH_4^+ > Cu^{2+}$, $Cd^{2+} > Zn^{2+}$, $Co^{2+} > Ni^{2+} > Hg^{2+}$.

From the above discussion, it can be concluded that the hydration energy, the charge density (ratio of charge/ionic radius) and the dimensions of the hydrated ions provide an indication of the mineral's preference for the different metals during competitive adsorption. However, the mineral's selectivity also depends on other parameters such as the geometry and/or the orientation of the ion. For example, clinoptilolite is very selective for the ammonium ion, despite its high hydration energy. This happens because NH_4^+ can easily penetrate through the clinoptilolite's channels by suitably transforming its orientation [8]. Wingenfelder et al. [38] attribute the higher hindrance of Zn and Cd adsorption on zeolite and the low hindrance of Pb adsorption that occurs with the increase of Ca^{2+} concentration in the solution to the low Si/Al ratio and the low charge density of zeolite. Lead is characterized by the lowest hydration energy and as a result its adsorption on zeolite is favoured. At the same time its presence in the solution reduces the adsorption of Cd and Zn, while the presence of other cations (i.e. Ca^{2+}) has a small impact on lead adsorption. In the study of Panayotova and Velikov [42] the presence of Mg^{2+} in wastewater slightly decreased the uptake of Ni and Zn by NaCl-zeolite from

multi-metal solutions (Pb, Cd, Cu, Zn, Ni), while a significant decrease in the adsorption of both metals by the modified zeolite was observed due to the presence of Ca^{2+} that is characterized by lower hydration energy compared to the two heavy metals.

3.2.5. Effect of environmental agitation

The rate of the adsorption process may be controlled by external mass transfer or/and intraparticle diffusion. External mass transfer is usually important at the initial stages of the process. The application of appropriate agitation increases ion mobility in the solution and thus, the mass transfer resistance reduces [36]. At high agitation rates, the boundary layer becomes thinner, which usually enhances the rate of solute diffusion through the boundary layer. Under high agitation speed, the external diffusion coefficient increases [44]. In most cases the increase in stirring speed is associated with an increase in the rate of adsorption, particularly during the early stages of the process. However its total effect is negligible in removal process. Shawabkeh et al. [45] found that the rate of adsorption zinc from wastewater increased with increasing agitation speed. Similar result has been observed by Wang and Peng [59] for Pb^{2+} uptake using modified natural zeolite. Kocaoba et al. [33] investigated the effect of agitation speed (5–250 rpm) on adsorption of nickel on natural zeolite and found that the uptake increased up to 150 rpm and thereafter remained constant. Breaking up of particles at higher agitation speeds may also occur. Trgo and Perić [44] stated that the potential breaking up of mineral particles due to high agitation rate enhanced the adsorption performance since freshly broken adsorption sites were revealed; thus greater stirring speeds increased the number of available adsorption sites.

3.2.6. Effect of mineral grain size

The effect of Zeolite particle size on heavy metal removal has been investigated by several researchers [10], [16], [21], [24], [34]–[38], [57]. Since adsorption is a surface phenomenon, the extent of adsorption is proportional to the specific surface area which is defined as that portion of the total surface area that is available for adsorption [24]. Thus more finely divided and more porous is the solid greater is the amount of adsorption accomplished per unit weight of a solid adsorbent. The specific area of the mineral depends on particle size, pore size distribution and surface roughness. Particles with smaller diameter are characterized by larger specific surface area, and thus adsorption is enhanced and shorter time is required to reach equilibrium. Each adsorption site is characterized by its availability and accessibility with respect to the incoming ion. Since the concentration of the available sites is constant, the availability of active sites remains almost constant between larger and smaller particles. However, the accessibility of metal ions to available sites would be facilitated when the adsorbent consists of smaller particles, since the diffusion paths of ions become shorter [10]. Thus, the reduction in particle size is expected to favour the process. Although the grain size can affect the adsorption capacity, usually the differences are not critical. Most studies showed that the smaller grain size favoured the adsorption capacity due to the mineral's larger specific surface area [21], [34], [35], [38]. Some studies reported that the grain size did not impact, or had a small impact on the adsorption capacity [21], [36]. In

porous materials, the internal surface area is much more critical than the external one. Therefore, changes in the external surface imposed by the grain size will have a limited effect on the mineral's adsorption capacity [36], [57]. In terms of kinetics, it has been reported that the impact of grain size is more important during the early stages of adsorption [38]; this can be related to the fact that external diffusion is usually critical at the initial stages of adsorption. In the adsorption processes in which film diffusion is dominant, the grain size seems to influence more the adsorption process, while in the cases where intraparticle diffusion is dominant the impact of the mineral grain size attenuates. Inglezakis [10] reported that the conduction of experiments with adsorbents of different diameter reveals the control stage of adsorption. The rate is proportional to the particle radius when film diffusion is the control stage and inversely proportional to the square root of the particle radius, when intraparticle diffusion controls the process.

3.2.7. Effect of adsorbent concentration

The mineral mass in the solution affects the adsorption process, since it determines the availability of active sites. Most studies report that higher mineral concentrations resulted in increased metal removal [14], [15], [18], [39], [47] and reduced amount of metal adsorbed per unit mass of adsorbent [35], [36]. Two reasons can explain this decrease in the adsorption capacity: the first is associated with the unsaturated adsorption sites and the second one with particle aggregation resulting in a decrease of the total surface area and an increase of the diffusion path length. These interactions between mineral particles become important when the adsorbent mass in the solution is high and may physically block some adsorption sites from the incoming metal ions [35], [36]. Oren and Kaya [36] found that the increase in mineral concentration resulted in a decrease of zinc uptake. The authors mentioned that lower mineral concentrations resulted in enhanced adsorption due to the increase in the solid/liquid interface area, resulting from the dilution of the suspension. At low mineral concentrations high amount of metals is readily available to be captured by few available sites. An increase in the solid concentration increases the surface area of the adsorbent, which in turn increases the number of binding sites for the same liquid volume and thus the total amount of metal that is removed increases [36].

3.2.8. Effect of mineral (adsorbent) specification

Specific chemical composition of zeolites (amount of exchangeable ions, Si/Al ratio), purity of natural material, channel dimensions are among the factors that affect heavy metal removal. According to Godelitsas and Armbruster [53], the rather low Si/Al ratio and the consequently increased theoretical cation exchange capacity (TCEC) are advantageous for removing dissolved cations from aqueous solutions. In this sense, Ouki and Kavannagh [54] demonstrated that chabazite is more efficient than clinoptilolite for metals removal owing to its larger window size that controls access to the pore system and higher Al^{3+} substitution of Si^{4+} providing a negative framework favorable to superior ion exchange capability [54]. In addition, the cation exchange capacity of clinoptilolite is markedly dependent on its original chemical composition and sample purity. For instance, Cincotti et al. [55] studied clinoptilolite

samples originated from the same source but having different purities (20% and 50%) and observed lower capacities with sample having low clinoptilolite content. Also, Gedik and mamoglu [56] studied two different clinoptilolite sources having different purities and chemical compositions and compared them for their Cd²⁺ removal from aqueous solutions. They observed that higher capacity was attained for the sample having high clinoptilolite and Na⁺ ion content, even though it's TCEC was lower.

4. Conclusion

It has been recognized that natural and modified minerals is effective for the removal of heavy metal ions from water and wastewater. Extensive studies have been conducted in order to evaluate the impact of several parameters on zeolite removal efficiency. The investigation has shown that the heavy metal concentration, solution pH and temperature, presence of competitive ions, environmental agitation as well as the adsorbent type, size and concentration are usually the most influential parameters.

Heavy metal Removal capacity increases with higher pH, elevated temperature, higher environmental agitation, high concentration and smaller grain size of adsorbent while high concentration of metals and presence of competitive ions decreases heavy metal Removal capacity. However, for applied purposes in big scale, the actual impact of factors would be much more intricate since they act simultaneously in solution and obviously impose effect on each other.

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