Original Research Article

Application of a Novel Surfactant-Modified Natural Nano-Zeolite for Removal of Heavy Metals from Drinking Water

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ABSTRACT

This work, the application of a surfactant-modified natural nano-clinoptilolite for the removal of several two valances heavy metal cations (*i.e.,* Cu^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+} and Zn^{2+}) from aqueous media was discussed. Triton X-100 was used as modifier and to achieve maximum efficiency of adsorption; variables such as the concentration of surfactant, contact time, the working temperature and pH of sample solution were optimized. The results revealed that, the maximum adsorption was achieved at a solution with the pH of 6, containing 2 mL of triton X-100 and 2 g/L of clinoptilolite at 45 °C. The obtained selectivity series for the adsorption of cations were $Pb^{2+}>Cu^{2+}>Cd^{2+}>Ni^{2+}>Zn^{2+}>Fe^{2+}$. The maximum adsorption capacity of the modified zeolite for Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+} was 91.34, 85.71, 78.27, 76.18, 67.41 and 63.45 mg/g, respectively. The adsorption data were acceptably fitted to the both Freundlich and Langmuir isotherms.

GRAPHICAL ABSTRACT
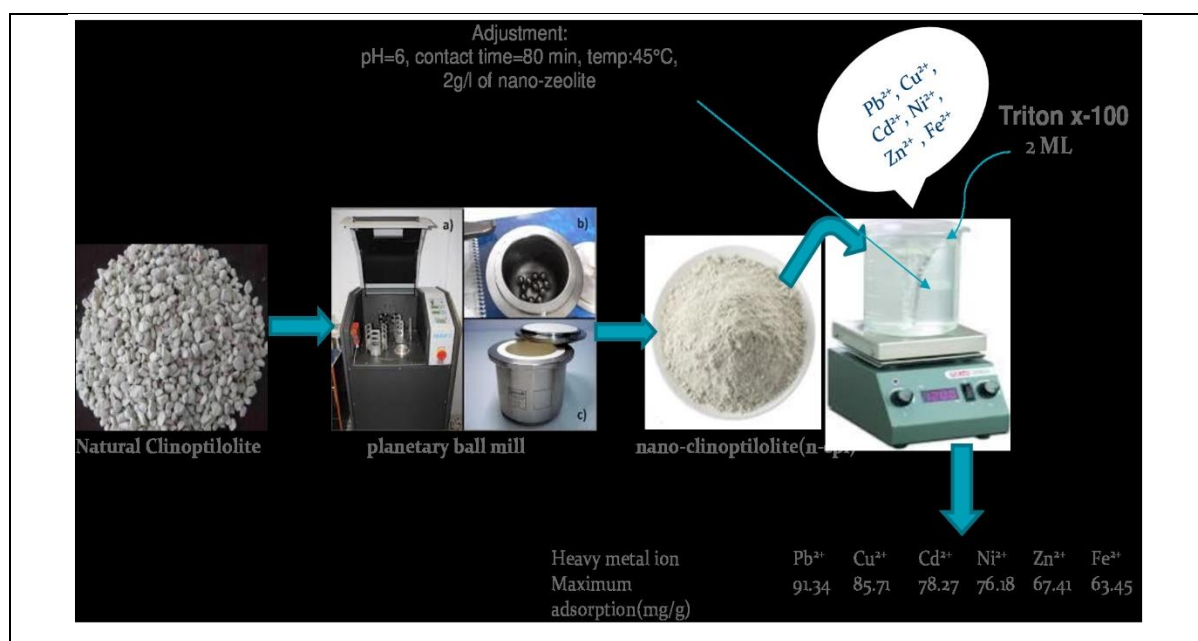
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Introduction

The presence of the heavy metals in drinking water is one of the most pressing environmental problems that we encounter today. Sustainability of these pollutants in the environment has made hard their removal from water resources. Some of these ions (micronutrients) in very small amounts may play a role in the biological systems but they are toxic in high concentrations. Some other heavy metal ions, even at very low concentrations, are toxic and they are harmful to human health. Today, the risk of heavy metal pollution is one of the main concerns in all societies. In recent years, domestic and industrial sewage treatment methods have progressed, thanks to the advancement of technology. Some methods, such as the use of specific catalysts, nano-materials and cheap adsorbents (bio or mineral), the use of ion exchange materials, the application of filtration methods, electro coagulation, ion exchange and emulsion liquid membrane removal have been developed and presented as useful methods for removing the toxic heavy metal ions from the water and wastewater resources [1]. The growing population in many countries, as well as the industries; high demand for water and on the other hand, the shortage of non-contaminated water resources, have encouraged scientists to find out cost-effective solutions to treat the polluted water [2]. Among the various methods used for removing the heavy metals from the contaminated water resources, zeolites, as the inexpensive adsorbents with high abilities to absorb metal ions and a porous structure, appears to be a good choice for this purpose. In addition, the researchers have shown that by adding some surface active agents (surfactants) to zeolites, the ability of them to absorb heavy metal ions is being increased dramatically [3]. Zeolites are hydrated aluminum silicates with small pores containing alkaline and alkaline earth metals that can be exchanged with other cations.

These compounds are harmless and have the ability to absorb and exchange heavy metal cations [4]. Because of the presence of electrical charge on the surface of zeolites and their porous structure, along with the specific crystalline structure of these materials, the adsorption phenomenon on zeolite surface is complicated [5].

There are many natural zeolites around the world which most of them were investigated by the researchers. The most abundant zeolites are clinoptilolite, chabazite, erionite, heulandite, mordenite stilbite and phillipsite. While barerite and paulingite have low abundance. The common formula of a zeolite is $M_{x/n}[Al_xSi_yO_2(x+y)]\cdot pH_2O$, where M represents either an alkaline metal or an alkaline earth metal cation, with a capacity of n; p is the amount of water crystallization per unit cell of the zeoliteand $y/x=1–6$, $p/x=1–4$ [4]. Clinoptilolite is one of the most abundant zeolite that is widely used in many parts of the world. Many researchers are interested in various properties of Clinoptilolite, such as its surface properties, as well as ionic exchange properties [6-9]. For instance, in one of researches [10], the ability of Na-Clinoptilolite for the adsorption of some heavy metal ions including: Ni^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Cs^+, Zn^{2+} and Hg^{2+} as well as Cr^{3+} has been determined. Some of these natural porous materials have not a good affinity for metal adsorption. In many cases, there is a need to treat the natural zeolite in a way to improve its adsorption capacity.

In the past few years, a group of chemical substances (mainly surfactants) has been used to enhance the adsorption capacity of natural zeolites for heavy metal ion adsorption [2]. Surfactants are usually organic compounds that have hydrophobic groups in the tail and hydrophilic groups that play the role of the head. Therefore, they are usually slightly soluble in water and organic solvents. They can be classified as ionic and nonionic according to their hydrophilic moiety [11]. Surfactants

affect some useful processes which are led to enhancement of pollutant removal. For example, they may increase the solubility, decrease the surface tension or enhance the foam formation [12]. Some studies showed that the addition of complexing agents and surfactants to the zeolites will increase their removal capacity for some heavy metal ions. Ionic and non-ionic surfactants in combination with complexing agents were studied and results showed that these combinations resulted in a better elimination for heavy metal ions from soil contaminated samples [13].

In this research, a natural modified clinoptilolite was used as an absorbent for the elimination of some heavy metal cations from aqueous solutions. The effects of some affecting factors such as pH of the solution, contact time, the working temperature and concentration of surfactant were investigated and optimized. Freundlich and Langmuir adsorption equation isotherms were applied to the data to get information about the interaction between target cations and the modified clinoptilolite.

Experimental

Adsorbent

A natural zeolite (clinoptililite) was used in this study for the removal of heavy metals. The clinoptilolite was taken from the most famous Iranian zeolite deposit (Semnan zeolite), located in East-north of Iran. This natural clinoptilolite was used as an adsorbent for removal of before mentioned heavy metal ions. According to the supplier's claim, the initial particle size range of natural zeolite was between 2 μm and 20 μm.

X-ray diffraction technique was used to determine the mineralogical structure of it Which revealed that the zeolite sample contained clinoptilolite as the major fraction of it (Table 1) with mainly calcium and potassium exchangeable cations (Table 2).

To achieve maximum efficiency of zeolite for adsorption of heavy metal ions, it was grounded using a planetary ball mill whereby the particles with a diameter between 87 nm and 200 nm were obtained (Figure 1).

The Brunauer-emmett-Teller (BET) technique revealed that the surface area of the sample particles was increased to 135.932 m^2/g and the total pore volume was 0.382 cm^3/g. The original specific surface area of the particles was 56.515 m^2/g. To modify the Zeolite, some affecting parameters including; pH, temperature, contact time, surfactant concentration and initial metal ion concentration were optimized.

Table 1. XRD analysis of natural zeolite

Phase	Chemical composition	Percent in sample
Clinoptilolite	$KNa_2Ca_2(Si_{29}Al_7)O_{72}.24H_2O$	66
Cristobalite	SiO_2	14
Anorthite	$(Ca,Na)(Si,Al)_4O_8$	7
Orthoclase	$KAlSi_3O_8$	5
Mordenite	$(Ca,Na_2,K_2)Al_2Si_{10}O_{24},7H_2O$	4
Dolomite	$CaMg(CO_3)_2$	2

Table 2. XRF analysis of natural zeolite

Element	Percent in sample	Element	Percent in sample
Si	70.72	Fe	3.10
Al	10.14	Na	Na
Ca	9.39	Ti	Ti
K	3.54	Mg	Mg
Total	100		

Figure 1. grinned clinoptilolite particles diameter
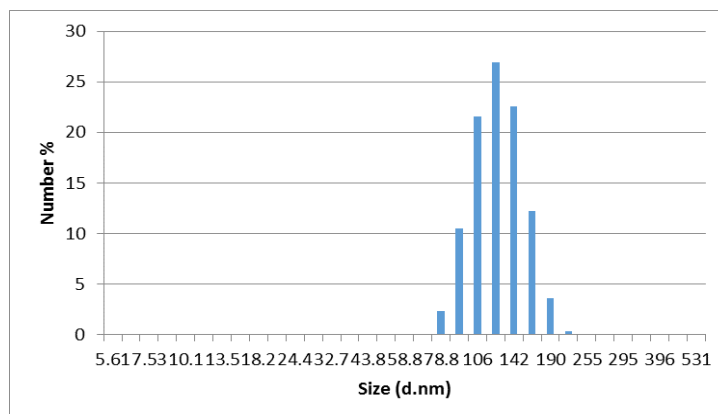
Chemicals

All the heavy metal cations solutions, Triton X-100, and NaCl (analytical grade) were purchased from Merck KGaA Company (Darmstadt, Germany), while the NaOH and HCl (analytical grade) were obtained from the Sigma Aldrich.

Adsorbate

Six heavy metal ions including, Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+} were selected as adsorbate ions. The analytical concentrations for each ion prepared directly from 1000 mg/L standard analytical grade solution (Merck). Triton X-100 also used as surfactant (Merck).

Experimental

The grinded clinoptilolite samples were washed 5 times with double distilled water (18.2 MΩ). After each washing process, the sample solution was centrifuged for 2 min at 1500 rpm and subsequently the water was depleted. Then the sample was dried in an oven (Memmert UN55, Germany) for 24 h at 105 °C. 50 gr of washed zeolite which was dried at the previous section, was transferred to a 1000 mL Erlenmeyer flask and 500 mL of double distilled water was added to 20 g (188.67 mmol) of analytical grade NaCl (1 M). The mixture was then stirred by a Heidolph (Germany) magnetic stirrer for 24 h at 180 rpm at laboratory temperature (23-25 °C). The washing and centrifuging processes were repeated until no Cl^- remained in the solution (Mohr titration). The sample was dried again at 105 °C for 24 h in an oven. After that, the zeolite was put in a desiccator for the rest of study.

To study the effectiveness of the adsorption power of the zeolite, a solution containing 1 g of nano-clinoptilolite was added to 500 mL of double distilled water and stirred at 180 rpm, then the effect of various parameters such as the temperature, the concentration of surfactant, the initial concentration of adsorbate, the contact time and the pH of the sample solution on the adsorption efficiency were evaluated and optimized for all tests. The initial and final concentrations of heavy metal ions in the sample were determined by a graphite furnace atomic absorption spectrometer (Shimadzu AA-6300, Kyoto, Japan). The adsorption capacity was calculated by using the following Equation 1.

$$q_e = V(C_0 - C_f)/m \tag{1}$$

Where q_e is the mass of adsorbed cations per unit mass of adsorbent (mg/g), C_0 and C_f are the initial and final metal ion concentrations, (mg/l), respectively. V is the volume of the aqueous phase (l) and m is the mass of adsorbent used (g).

Langmuir and Freundlich adsorption isotherms have been adopted for interpreting data.

Langmuir: $q = a.bC/1+b.c$ or $q/c = 1/a.b + c/a$

Where c (mg/l) is the amount of a metal adsorbed per mass unit of sorbent at equilibrium, q (mg/g) is the amount of adsorbate at complete monolayer and b (mg/g) is the slope and a (mg/g) of adsorption capacity.

Freundlich: $q = k.C^{1/n}$ or $\log q = \log k + 1/n.\log C$

Where c and q are as defined for Langmuir, k and n are adsorption constants.

Results and discussion

The influence of some effective parameters on the adsorption phenomena such as solution pH, temperature, contact time, concentration of the surfactant, and initial concentration of the heavy metal cations were investigated.

Effect of contact time

The 20, 40, 60, 80, 100 and 120 min were selected and a 100 ppm single sample of aimed cations added to zeolite container. The pH of the solution was adjusted at pH=7.0.

Figure 2 demonstrates the obtained results. As can be seen, for all ions up to 80 min the adsorption has an increasing trend and then smoothly decreased or stayed constant. The results showed that, a high sorption rate occurred in the initial contact time and equilibrium was achieved in around 80 min, which was due to the high concentration gradient between the heavy metal ions and clinoptilolite surface. At the first minutes, the adsorption rate was very high. Then the rate was decreased as most of the adsorption sites were occupied by the adsorbate ions [14,15].
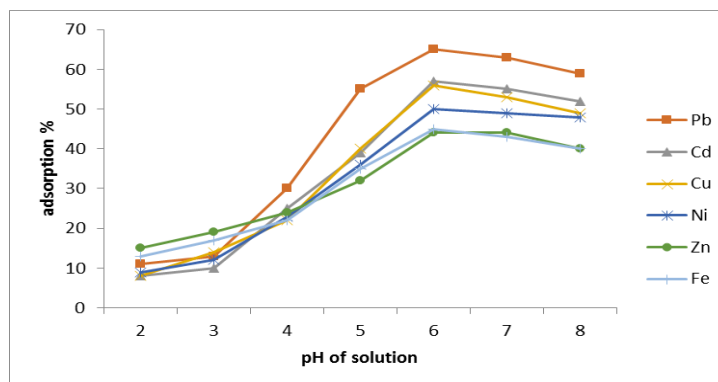
Effect of pH

The pH of the solution has a strong effect on zeta potential of the adsorbents and chemistry of the solution. To determine the pH effect on adsorption process, several solutions with pHs ranged from 2 to 8 was prepared for each ion. HCl (0.5 M) and NaOH (0.5 M) were used to adjust the pH of the solutions. Figure 3 shows the effect of pH on adsorption phenomenon. As it is obvious, the maximum adsorption has seen in pH=6. This result was attributed to augmentation of the negative zeta potential of the clinoptilolite with high solution pH [13]. At pHs less than 3, it seems that H^+ ions compete with heavy metal ions to adsorption on available active sites of zeolite surface. In higher pHs, due to decreasing of H^+ ions concentration, the aimed heavy metal ions, adsorbed on zeolite surface more easily [16].
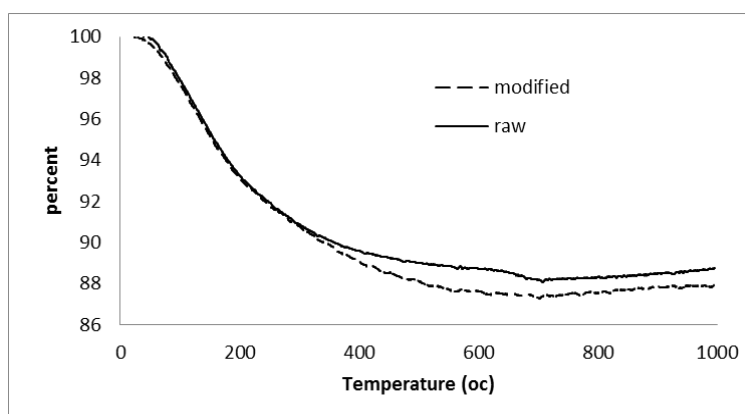
Figure 2. Effect of contact time on adsorption of heavy metals on clinoptilolite surface
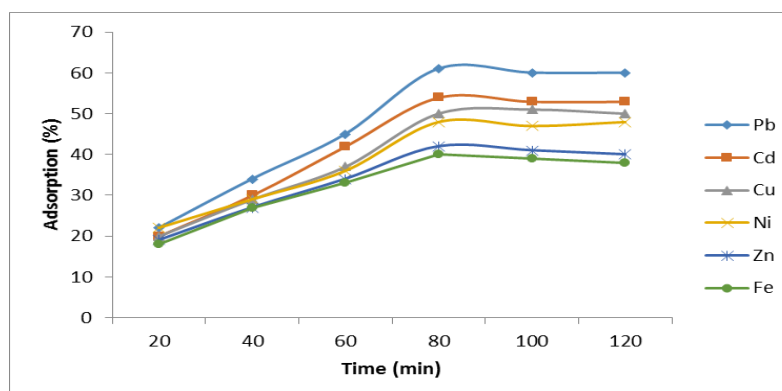
Figure 3. Effect of the solution pH on adsorption of heavy metals on clinoptilolite surface

Figure 4. Mass reduction trend for the raw and the modified zeolite

Effect of surfactant concentration

In this study, the nonionic surfactant (Triton X-100) was used to improve the zeolite efficiency on heavy metal ions adsorption. To determine the possibility of surfactant adsorption on zeolite surface, 10 mL of surfactant were added to a 500 mL flask containing 5 g nano-zeolite and stirred for 72 h at 50 °C and 100 rpm. After this time, the contents of the flask were centrifuged at 1500 rmp for 2 min and washed (5 times) to eliminate the non-absorbed surfactant. The process was continued by drying at 95 °C for 24 h in an oven. The Thermal Gravimetric Analysis (TGA) showed about two percent decrease in mass of the sample. This mass reduction proves that surfactant has been adsorbed on the nano-zeolite surface (Figure 4).

To prepare samples for the surfactant concentration effect studies, six containers containing 0.5 to 3 mL (0.773 to 4.66 mmol) of Triton X-100 and 1 g of nano-zeolite were selected. Figure 5, shows the effect of triton X-100 concentration on adsorption efficiency. It is clear that, in 2 mL/L of triton X-100 addition, we have the maximum adsorption.

Effect of initial metal ion concentration

The results of the increasing of the heavy metal ions concentrations from 50 to 200 ppm revealed that there is an increase in the adsorption capacity of the adsorbent upon increasing the initial metal ion concentration (Figure 6). The high concentration of heavy metal ions increases their absorption rate on the adsorbent surface. The high initial concentration of the adsorbed ions resulted in greater driving force that may overcome the resistance of the mass transfer between the liquid and solid phases [17,18]. In addition, at the starting of the adsorption process, the adsorption capacity is very high because there are many free sites in clinoptilolite surface that heavy metal ions can adsorbed by them [19].

Figure 5. The effect of the surfactant concentration on adsorption of heavy metals on the clinoptilolite surface
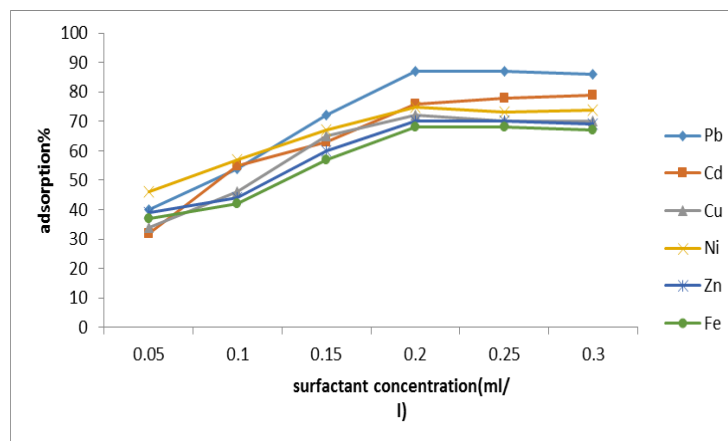
Figure 6. The initial concentration effect on the adsorption capacity
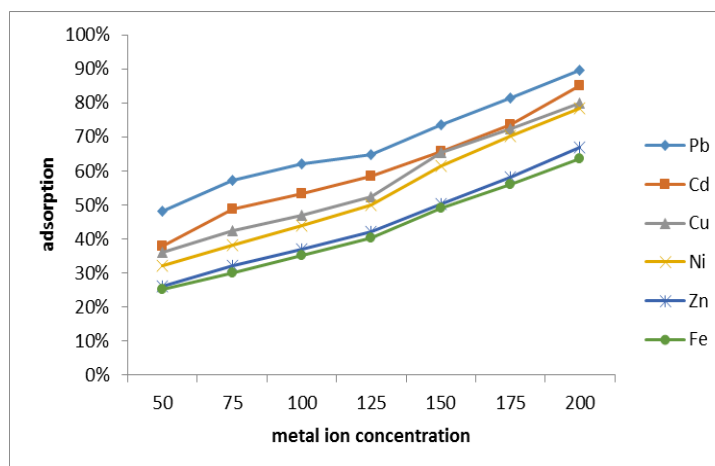

Effect of temperature

The results showed that, the heavy metal adsorption on zeolite was increased when the solution temperature was increased from 20 °C to 60 °C. As the temperature rises, the zeolite absorption capacity increases for all target cations. As increasing of the temperature, the viscosity of solution getting higher. On the other hand, ion's diffusion coefficient will also increase in zeolite's boundary layer. These phenomenas will resulted a higher level of heavy metal ion adsorption on clinoptilolite surface (Figure 7)[13].

Adsorption isotherms

The experimental adsorption equilibrium data of heavy metal ions on modified clinoptilolite were fitted *via* applying the Langmuir and Freunlich isotherm models, which are usual models on the aqueous phase adsorption. These adsorption models give a representation of the adsorption equilibrium between the adsorbate in solution and the surface active sites of the adsorbent. The Langmuir equation relates the coverage of molecules on the solid surface to the concentration of a medium above the solid surface at a fixed temperature and adsorption is the monolayer. The Freundlich model supports this idea that the adsorption surface is heterogeneous, that interaction among adsorbed molecules can occur and multilayer adsorption is possible [20]. Table 3 shows the fitting of the parameters of the experimental results to the Langmuir and Freundlich equation parameters.

Figure 7. Effect of temperature on heavy metal adsorption
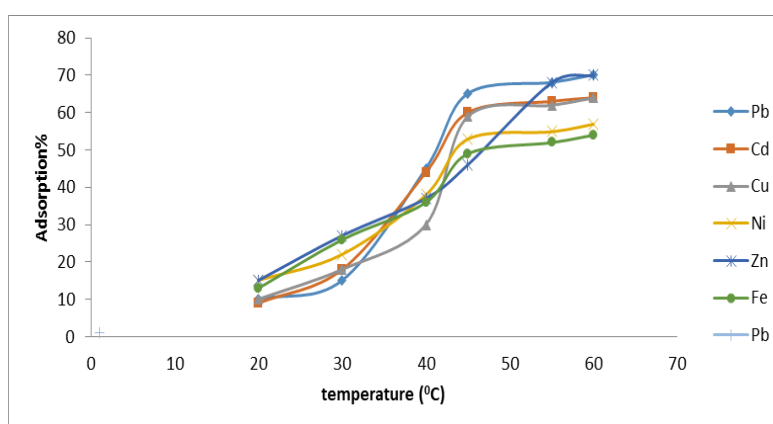
Table 3. Langmuir and Freundlich parameters calculated from Cu^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+} and Zn^{2+} isotherms using modified clinoptilolite

Heavy metal	Langmuir			Freundlich		
ion	a	B	R^2	k	n	R^2
Pb	1.987	68	0.9845	1.387216	0.733837	0.9864
Cd	6.94	20.58	0.998	1.316953	0.752106	0.9905
Cu	10.46	16.78	0.968	1.109579	0.85955	0.988
Ni	10.76	15.75	0.9869	1.19382	0.865351	0.9938
Zn	21.2	13.1	0.9896	1.197911	0.927472	0.9981
Fe	277.63	1.242	0.991	1.18572	0.949668	0.9932

Conclusion

In this study, the adsorption capacity of a surfactant-modified nano-clinoptilolite for some heavy metal ions such as Cu^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+} and Zn^{2+} was investigated. The results demonstrated that, several parameters such as pH, adsorption time, the initial concentration of aimed ions, surfactant concentration, and temperature affected the adsorption phenomenon. The adsorption of the aimed heavy metal ions from the aqueous solution using Triton X-100 as the surfactant to modify nano-Clinoptilolite was found to be effective as approximately 60-90% of the metal ions removed at equilibrium. The Pb and Cd cations were removed in the higher percentages; however, the Zn and Fe ions had the minimum adsorption between the studied cations. Therefore, it was concluded that this modified zeolite can provide a better efficiency for heavy metal ions. The maximum adsorption capacity was observed at a solution with the pH of 6, the high concentration of the heavy metal ions which contains 2 mL of surfactant and high temperature. Adsorption data of the highly significant heavy metal ions were fitted to Freundlich isotherm. Metal adsorption data were also fitted to the Langmuir adsorption isotherm.

Disclosure statement

No potential conflict of interest was reported by the authors.

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