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Removal of Heavy Metal Ions in Wastewater by Semnan Natural Zeolite

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Many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution. Industrial wastewater contain a variety of heavy metals such as Pb, Cd, Hg, Cu, Ni, Zn and Cr and have a high potential of contaminating the receiving water bodies. These metals that tend to accumulate in organisms, causing numerous diseases and disorders. They are also common groundwater contaminants at industrial and military installations. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, extraction, ultra filtration, reverse osmosis and solid phase extraction. The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently. In this study, the potential of Semnan natural zeolites has been investigated for removal of heavy metal cations from industrial waste waters.

Key Words: Natural zeolites, Heavy metals, Adsorption, Wastewater.

INTRODUCTION

Several industrial wastewater streams may contain heavy metals including the waste liquids generated by metal finishing or the mineral processing industries[1,2]. The toxic metals, probably existing in high concentrations (even up to 500 mg L^{-1}), must be effectively treated/removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment[3].

In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely studied. Their presence in streams and lakes has been responsible for several types of health problems in animals, plants and human beings[4,5]. Among the many methods available to reduce heavy metal concentration from wastewater, the most common ones are chemical precipitation, ion-exchange adsorption and reverse osmosis. Most of these methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Ion exchange is feasible when an exchanger has a high selectively for the metal to be removed and the concentrations of competing ions are low. The metal may then be recovered by incinerating the metal-saturated resin

and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view. This has encouraged research for use of low-cost adsorbent materials to purify water contaminated with metals[6,7].

The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently. Among the available techniques, sorption has been used as one of the most practical methods. A sorbent must be eco-friendly, cost-effective, industrially viable and efficient for a wide range of concentration of different pollutant metals. Though activated carbon[8], silica gel[9] and activated alumina[10] are popular and effective adsorbents, their use is restricted for being not cost-effective.

Zeolites represent an attractive native material for removing heavy metal ions from industrial and processing effluent water[11-17]. Their advantages are the following: low cost, stability and abrasion resistance, low swelling capacity, their exchangeable ions are relatively harmless zeolites are pre-treated with aqueous solutions containing sodium cations (activation stage) which improve materials reactivity. As seen from the literature review, zeolites can be used for the removal of some heavy metals from wastewaters. The zeolite samples from different regions show different behaviour in ion-exchange processes. In this study, the adsorption properties of natural zeolite (North-East Iran) to some heavy metals cations in solution were investigated.

EXPERIMENTAL

Natural zeolite samples used in this study were obtained from the Semnan Province north-east region, Iran. The samples were crushed in a jaw and rotary crushers up to 10 mm. The crushed samples were homogenized and passed through 0.8-2.0 mm sieves. Representative samples were dried in an oven at 100 ± 5 ºC for 24 h before characterization and experimentation. All used chemicals were of analytical laboratory grade (AR), produced by Merck (Germany).

All reagents used were of analytical (Merck) grade. Test solutions of heavy metal ions for both cases of single and multiple species adsorption were prepared from their nitrate salts by serial dilution of stock lead, copper, cadmium and zinc ion solution (1000 mg L^{-1} each) using deionized distilled water. Blank solution of deionized distilled water was analyzed by AAS to ensure that it did not contain lead, copper, cadmium and zinc ions.

For preparing multiple species (Pb + Cu + Zn + Cd) stock solution, the amounts of nitrate salts of all the 3 metal ions required for a particular concentration were calculated and the appropriate amounts of each salts were taken to a standard flask (1 L) in the molar ratio of 1:1:1:1 and made up the solution up to the mark. Analytical pure hydrochloric acid (HCl) and nitric acid were used. All solutions were prepared with deionized water.

A Shimadzu (Tokyo, Japan) flame atomic absorption spectrometer model AA680 with an air-acetylene flame was used for heavy metals ions analysis. A Metrohm E-632 pH meter was used for pH measurement of the solutions.

Properties of natural zeolites: A chemical analysis of the treated zeolite is presented in Table-1. This study showed that natural zeolite contained a complement of exchangeable sodium, potassium and calcium ions.

TABLE-1
CHEMICAL COMPOSITION OF NATURAL ZEOLITE SAMPLE

Chemical composition	Per cent (wt %)	Chemical composition	Per cent (wt %)
SiO_2	69.21	Na_2O	1.20
Al_2O_3	12.10	K_2O	1.40
FeO	1.20	SO_3	0.10
CaO	2.02	H_2O	11.20
MgO	1.60	–	–

RESULTS AND DISCUSSION

The adsorption of copper, lead, zinc and cadmium ions from synthetic aqueous solutions onto zeolite was studied in laboratory batch mode. The batch adsorption experiments were carried out in a glass reactor with a useful volume of 500 mL under mechanical stirring and constant temperature of 25 ºC. At the end of the predetermined time interval, the adsorbent was removed by the filtration, while the equilibrated metal concentration was determined in the filtrate by means of the atomic absorption spectrophotometer using the air-acetylene flame. Four experimental series were performed.

Heavy metal removal: The performance of the zeolite in reducing the heavy metal levels in both synthetic solutions and wastewaters was assessed by calculating the percentage of metal removed after the 1 h mixing period. The following equation was used for each metal tested:

$$\% \text{ Metal Removal} = \frac{C_i - C_x}{C_i} \times 100$$

where C_i is the initial metal concentration and C_x is the metal concentration after contact with the zeolites.

Effect of contact time: The effect of time on the adsorption of metal ions by zeolite was studied by taking 1 g sorbent with 100 mL of 100 mg L^{-1} metal ions solution in different flasks. Fig. 1 shows the effect of contact time on adsorption of metal ions using zeolite. The results show that the percentage of metal ion adsorption by zeolite increased with increasing time of equilibration and it reached the plateau value at about 1 h for the metal ions. Therefore 1 h was selected for further experiments.

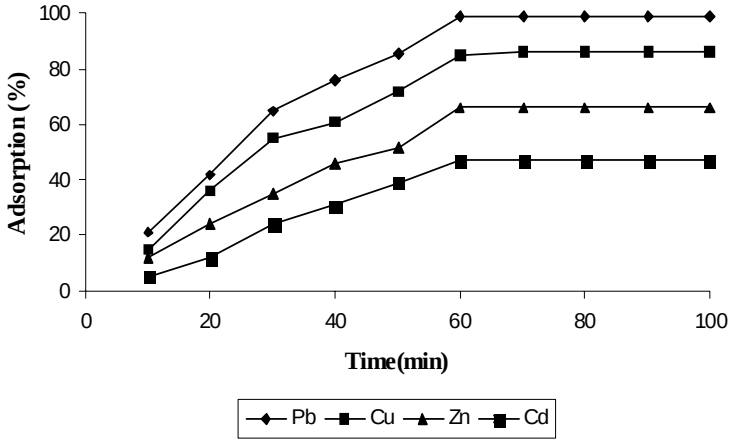

Fig. 1. Effect of contact time on the removal of heavy metal ions (C_0: 50 mg L^{-1}), m: 1 g, V: 100 mL

Effect of the zeolite amount: The sorption of metal ions on the zeolite amount was studied on variable amounts of sorbents (from 0.2 to 2 g) in constant solution volume (100 mL) with 1 h stirring time. The results indicated that the adsorption percentage increased with the increasing amount of the sorbent. Therefore the number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal removal at a high dose. This is due to the greater availability of the exchangeable adsorption sites at the available larger sorbent surface area. The optimum metals adsorption percentages were 99.2, 85.8, 66 and 47 % for Pb(II), Cu(II), Zn(II) and Cd(II), respectively. The optimum zeolite amount was selected as 1g per 100 mL solution containing heavy metal ions.

Influence of agitation speed: In order to estimate the effect of stirring rate on the metal removal efficiency, experiments took place under various stirring rates ranging from 50 to 250 rpm. As shown in Fig. 2, the percentage of adsorption values was slowly increased with agitation speed. 200 rpm stirring rate was selected as the optimum agitation speed for all metals.

Influence of solution pH: Fig. 3 illustrates the effect of pH on the removal of different initial heavy metals concentrations on zeolite. The pH value of the investigated solution was adjusted in a range from 1 to 10 by hydrochloric acid or ammonia. The adsorption percentages were increased after pH 4 for all metals. At higher pH the adsorption percentage was relatively slow and gradually attained 99.9 % adsorption at pH 10. The pH 6 was chosen as the optimum studying pH for all metals for avoiding precipitation of metals.

Determination of adsorption capacity: The adsorption capacity of zeolite in lead, copper, zinc and cadmium was estimated experimentally for each metal under the optimum conditions. The equilibration time was 1 h and the stirring rate was kept constant at 200 rpm. The initial concentrations of metal ions in solutions were varied in the region 10-100 mg L^{-1}.

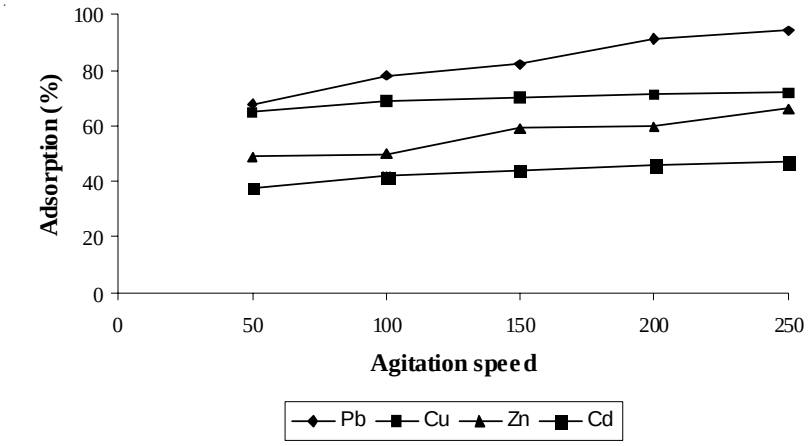

Fig. 2. Effect of agitation speed for heavy metal ions removal capacities of zeolite (C_0: 100 mg L^{-1}), m: 1 g, V: 100 mL

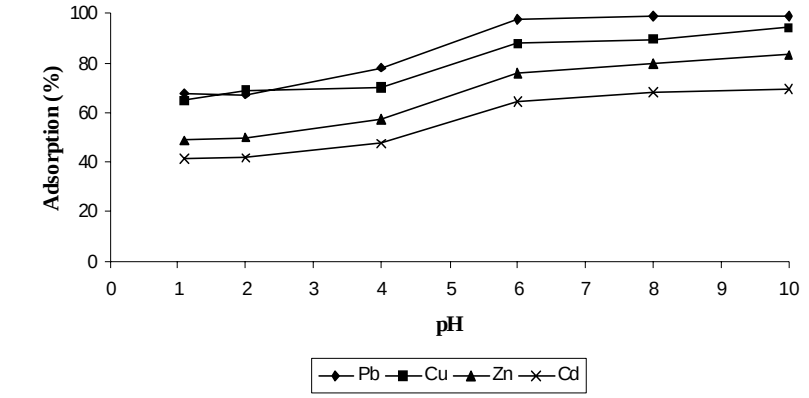

Fig. 3. Effect of pH on the removal of heavy metal ions (C_0: 100 mg L^{-1}), m: 1 g of zeolite, V: 100 mL

Once adsorbent capacity was established, we set out to determine how complete the extent of adsorption was. For this purpose, we used industrial wastewater samples containing between 10 and 100 mg L^{-1} of heavy metals and contacted them with 1 g of adsorbent to bring heavy metal concentrations down to below prescribed minimum tolerable limits. In all cases metal concentrations were brought to below detectable and legal limits.

Conclusion

The results shows that zeolite can be used as adsorbent for removal of some heavy metals ion from wastewater. Adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) by zeolite has been shown to depend significantly on the pH, adsorbent amount and agitation speed. Studies on the rate of uptake of heavy metal ions by the zeolite

indicated that the process was quite rapid and maximum adsorption occurred within the first one hour of contact. Within 1 h, 1 g of residue is able to adsorb between 10 and 100 mg of heavy metal according to the following sequence of affinity: Pb > Cu > Zn > Cd and with complete adsorption of pollutants if heavy metal concentrations are lower than adsorption capacity. Zeolite adsorbent may be an alternative to more costly adsorbents such as activated carbon and commercial adsorbents for the treatment of aqueous wastes containing mixed metal ions.

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