

Heavy metal adsorption by clinoptilolite from aqueous solutions

P.P. WANI and S.R. THORAT

School of Environmental and Earth Sciences North Maharashtra University, Jalgaon (India)

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ABSTRACT

The present investigation has been carried out to assess a chromium, cobalt, and cadmium from wastewaters by natural and modified zeolites were examined by using batch type method. A clinoptilolite type synthetic / natural zeolite were pretreated with HCl and HNO₃ to improve the adsorption capacity for heavy metals. The removal efficiencies and kinetics of heavy metals such as chromium, cobalt and cadmium on natural modified zeolites were determined. The kinetics of adsorption indicates the process to be diffusion controlled. This process is very well work in industrial treatment plant of various industries using heavy metals for their production.

Key words: Heavy metal, natural zeolites, adsorption, kinetics, wastewater treatment

INTRODUCTION

Heavy metals are common pollutants found in various industrial effluents. The stricter environment regulation on the discharge of heavy metal it is necessary to develop various technologies for removal. Waste streams containing low to medium level of heavy metals are often encountered in metal plating facilities, electroplating, mining operation, fertilizer, battery, manufacture, dyestuffs, chemical pharmaceutical, electronic device manufactures and many others. Most of heavy metals are highly toxic and are not biodegradable; therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards. Many methods including chemical precipitations, electro deposition, ion exchange, membrane separation and adsorption have been used to treat such streams of these methods, traditional chemical precipitation is the most economic but is inefficient for dilute solutions. Ion exchange and reverse osmosis are generally effective, but have rather high maintenance and operation costs and

subject to fouling. Adsorption is one of the few promising alternatives for this purpose, especially using low cost natural sorbents such as agricultural wastes, clay materials, zeolite, biomass and seafood processing wastes (Kesraoui-Ouki S *et.al.* 1994, Orhan Y. *et.al.*1993).

Clinoptilolite is a mineral zeolite of the Heulandite group. The structures of zeolites consists of a three dimensional framework of SiO₄ and AlO₄ tetrahedral (Curkovic L. *et.al.* 1997). The aluminum ion is small enough to occupy the position in the center of tetrahedron of four oxygen atoms, and isomorphous replacement of Al³⁺ for Si⁴⁺ raises a negative charge in the lattice. The net negative is balanced by the exchangeable cation (sodium, potassium and calcium). These cations are exchangeable with certain cations in solution such as lead, cobalt, zinc and manganese. The fact that zeolite exchangeable ions are relatively innocuous (sodium calcium and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. One of the earliest applications of a natural zeolite was in removal and purification of cesium and strontium

radioisotopes. Heavy metal for Clinoptilolite and radionuclide ions adsorption has investigated by many investigators (Curkovic L. *et.al.* 1997, Akyuz T. *et.al.* 2000, Wani *et.al.*, 2007).

The removal of heavy metal ions from industrial wastewaters using different adsorbents is currently of great interest. Activated carbon has been tested for the removal of inorganic ions from aqueous solution. However, in order to minimize processing cost for these effluents, recent investigations have been focused on the use of low cost adsorbents. Clinoptilolite was shown to have high selectivity for certain heavy metal ions such as Pb²⁺, Cd²⁺, Zn⁺ and Cu⁺. A significant number of researchers have done experiments, which have determined different selectivity sequences of natural zeolites for range of various metals, but they have

all agreed that Clinoptilolite shows a strong affinity for lead and cobalt. Most of them have suggested that pretreatment of natural zeolites enhances their ion-exchange ability (Malliou E. *et.al.* 1994, Kim K.S., Choi H.C. 1998 and Wani and Thorat, 2007). The reaction and diffusion control models have been proposed to describe the adsorption kinetics, which are based on the relative importance of the chemical reaction to diffusion transfer. The results of the kinetic studies by Eligwe *et. al.* showed that the adsorption reaction is first order with respect to the metal cation solution concentration. It was found that the rate constant was a function of metal ion concentration, P^H, and initial concentration. The uptake kinetics of cobalt and selenite was studied by Papelis *et.al.* The rate data were interpreted with a diffusion model, in which a linear isotherm was employed to express the local

Table 1: Chemical composition of zeolite sample tested (%)

Component	Sample 1	Sample 2	Sample 3
SiO ₂	55.80	55.80	55.80
Al ₂ O ₃	13.32	13.36	13.36
CaO	5.75	5.01	5.01
Na ₂ O	3.90	5.92	5.92
K ₂ O	2.35	0.92	0.92
Fe ₂ O ₃	1.30	1.29	1.29
MgO	0.70	0.67	0.67
Loss of ignition	17.00	16.80	16.80

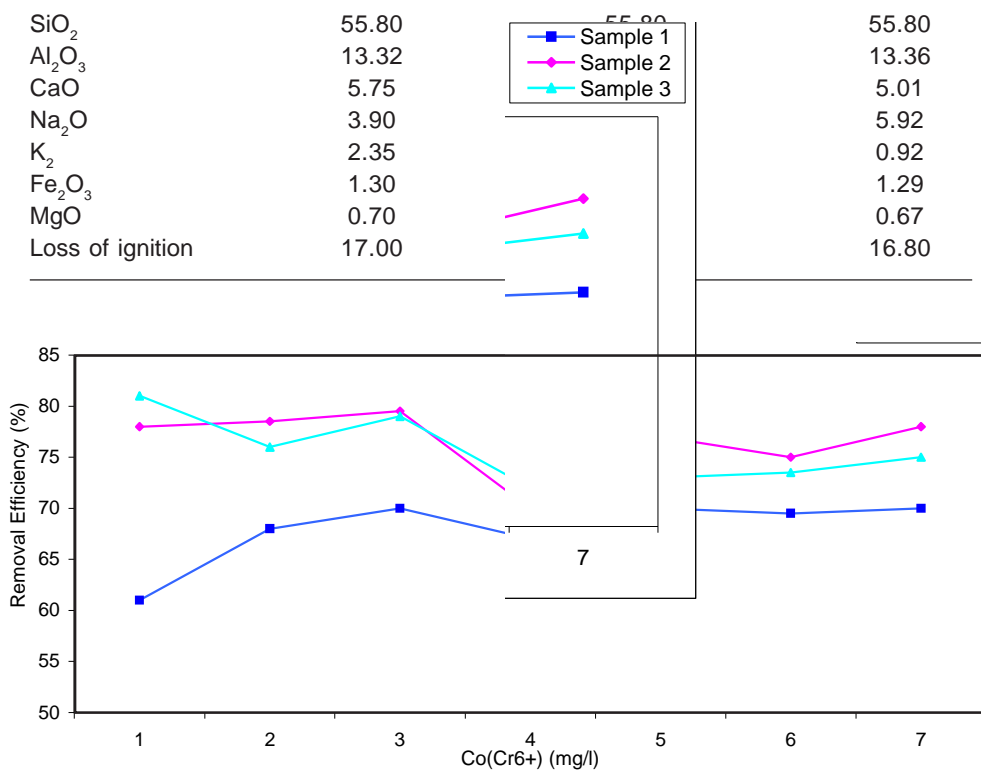


Fig. 1: Showing Cr6+ ion removal efficiency by zeolite samples as a function of initial concentration; m (zeolite) 0.40g; V (Solution): 100ml

equilibrium relationship. The above models may be satisfactory under the particular experimental conditions; however, these models and their parameters normally are system specific (P^H -dependent) and cannot be applied to other conditions (Yiacoumi S. and Tien C. 1995, Wani and Thorat, 2007).

The aim of the investigation is to study the adsorption mechanism of Co (II), Pb (II) and Cr (VI) ions onto natural and modified zeolites from wastewater.

MATERIAL AND METHODS

Natural zeolites sample was obtained from Biga-Canakkale region of Turkey. It was ground

to approximately 200-mesh size powder. A given amount of the material was washed with deionised water three-four times to remove any dust and other water-soluble impurities. The sample was then dried in an electric oven at 150-200°C for 2-3 hrs before using for adsorption purpose.

Metal removal studies were carried out using Clinoptilolite in three different forms; one untreated and two treated samples. Sample 1; natural zeolites, Sample 2; natural zeolite was treated with 2M HCl solution over period of 24 hrs, after washing, modified zeolites were dried at 105°C for 1 hr. sample 3; the zeolite was prepared with 2M HNO_3 solution over a period of 24 hr.

The chemical composition of the natural

Fig. 2: Showing Co^{+2} ion removal efficiency as a function of initial concentration; n

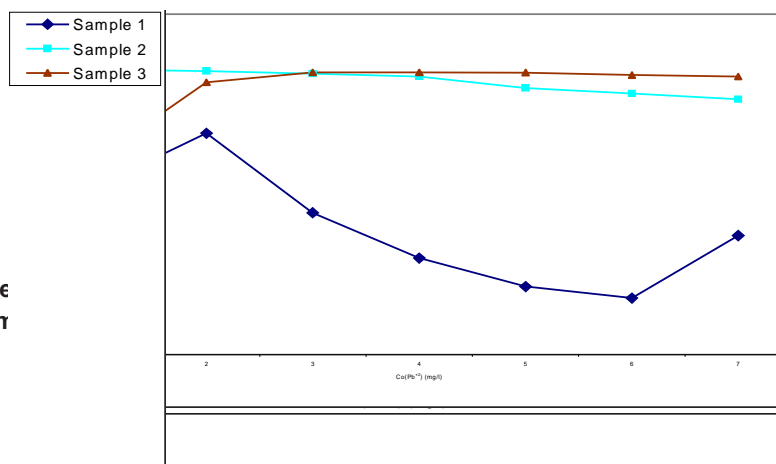


Fig. 3: Pb^{+2} ion removal efficiency by zeolite samples as a function of initial concentration; m(zeolite):0.40g; V(solution):100ml

sample was determined by XRF analysis. The analysis was performed on natural zeolites, in an attempt to determine their effect on the zeolites crystal structure. The natural Clinoptilolite obtained from Biga-Canakkale region, was stated to be 40-50% pure. The impurities include ilite, montmorillonite, feldspar, calcite, quartz and halite. Stock solutions of cobalt, lead and chromium were

prepared in deionised water using the analytical reagent grade cobalt chloride, lead chloride and potassium chromate. The exact concentration of metal ions was verified by AAS.

Adsorption tests were conducted in 250 ml. glass tubes. A zeolite sample of 4.0 gm. was

Fig. 4: Shows that kinetics of Co(II) adsorption using Lagergren plot

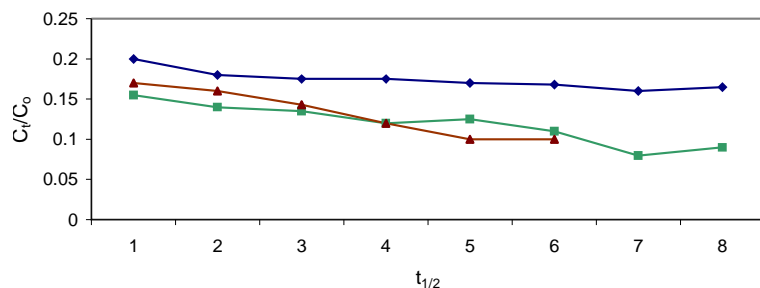


Fig. 5: shows kinetics of Cr(VI) adsorption using langergren plot

Fig. 6: Showing kinetics of Co(II) adsorption using by Weber et.al

mixed in 100ml. lead, cobalt, and chromium solutions of concentrate ranging from 1 to 100 mg/l by mechanical shaking at a speed of 250 rpm/min for period of 24hr. The blank experiments were simultaneously carried out without the adsorbent. After the agitation for an equilibrium period, the

supernatant solution was filtered through 0.5um micro porous membrane filter.

These first experiments were conducted at room temperature. In the second set of experiments is investigated the influence change

Table 2: The rate constants of adsorption and pore diffusion of heavy metals.

	Co (II)			S1	Pb (II)			Cr (VI)		
	S1	S2	S3		S2	S3	S1	S2	S3	
K (min ⁻¹)	0,01114	0,01170	0,01809	0,0093	0,01524	0,01408	0,008766	0,01000	0,008282	
K (min ^{-1/2})	0,0054871	0,007860	0,009519	0,01890	0,02361	0,02057	0,01453	0,01347	0,012588	

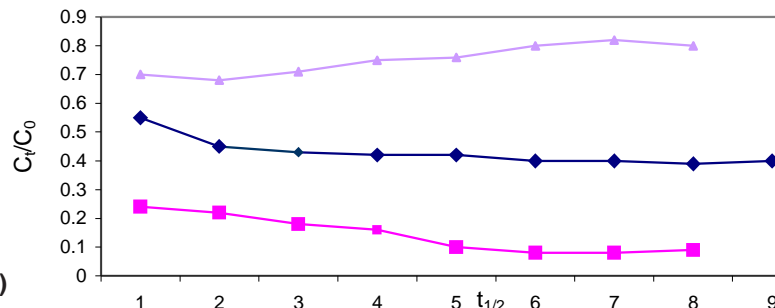


Fig. 9: Showing kinetics of Cr(VI)

Fig. 8: Showing kinetics of Pb(II) adsorption using by Weber et.al.

of initial concentration on the uptake of lead,

chromium and cobalt ions. A accurate weight (4.0 gm.) zeolites sample 1,2 and 3 was mixed and stirred with 100ml. solutions of lead, chromium and cobalt respectively. The investigated initial concentrations were 1,5,10,25,50,75 and 100mg/l. After shaking in a thermostatic system, the solid phase was separated by filtration through a 0.45um micro porous membrane filter. The final P^H of solutions was recorded by P^H+ meter and concentration of lead, chromium and cobalt ions at equilibrium were determined by the atomic adsorption spectrophotometry 20± 0.5°C) (17)

RESULT AND DISCUSSION

Chemical analysis of the zeolite is presented I table 1

The lead chromium and cobalt metal ions removal efficiencies for tested zeolite samples are shown in Fig. 1,2 and 3 respectively, 16.80, 19.73, 18.71 mg/g Co²⁺, 17.86, 19.99, 19.74 mg/g Cr⁴⁺ and 10.31, 21.51,23,53 mg/g Pb²⁺ were taken up by 4.00 g zeolite.

Sample 1,2 and 3. It was clear that, for treated zeolite samples, lead and chromium was more selectively removed than cobalt. The P^H value during the experiments was due to the simultaneous uptake of hydrogen ions by zeolite sample and hydrolysis of zeolites.

The removal efficiencies of Pb (II) by the untreated zeolite (S1) are lower than that of the treated zeolite.

These results indicates that the order of efficiency is as follows: S2>S3>S1 for Co (II) and Pb (II) and S3>S2>S1 for Cr (VI). At cobalt concentration less than 10 mg/l, removal efficiencies of about 94.8% were achieved by all zeolite samples. At higher cobalt concentrations, the removal efficiency decreased to a value between 67,13 and 90% for all zeolite samples 1, 2 and 3 (Fig. 3). In contrast, at higher concentration for Cr (VI) and Pb (II), the removal efficiencies by all samples were increased. However, it was also clear that for all the zeolite

samples tested lead was more selectively removed than cobalt.

The rate constant of adsorption pore diffusion and mass transfer coefficient of metal ion were determined using equation of Lagergren and Weber and Morris (Panday K.K., *et.al.* 1985) respectively which are as follows.

For rate constant of adsorption;

$$\text{Log } (q_e - q) = \text{log} q_e - K/2.3$$

For rate constant of pore diffusion;

$C_t/C_0 = Kt^{0.5}$ Where t; time (min), q; amount of metal ion adsorbed at time t (mgg⁻¹), q_e; amount of metal ion adsorbed at equilibrium (mgg⁻¹), C₀; initial concentration of metal ion (mg l⁻¹), C_t; concentration of metal ion a time t (mgg⁻¹), K; rate constant of adsorption (min⁻¹).

A straight line plot of log (q_e-q) Vs t (Fig. 4,5 and 6) suggests the applicability of Lagergren equation, however, the plot of C_t/C₀ Vs t^{0.5} (Fig. 7,8,9), although linear for a wide range of contact period, do not pass through the origin, indicating that the pore diffusion is not the only rate controlling step (Panday K.K., *et.al.* 1985).

The rate constant of adsorption and pore diffusion were calculated from the slopes of the respective plots and given in table 2

CONCLUSION

At lead and cobalt concentrations less than 4 mg l⁻¹ removal efficiency was between 80-100% using the untreated zeolites. At the same time concentration of chromium, removal efficiency was about of 70%. It was clear that the lead and cobalt ions were more selectively removed than chromium with the untreated zeolite. But the removal of lead ion is very fast and that finally 92% upon the initial cadmium concentration level. However, the ultimate removal rate remains more or less the same. At lower concentration i.e. concentrations equal to 2.0mg/l or less, rate is lower than the initial concentration except of the S2 zeolite. This shows that the removal of metal ion is highly

concentration dependant. It may be noted from the figure that the equilibrium is established in 60 min. and the period of equilibrium is concentration independent. The removal of Pb

(II) and Co (II) by the treated zeolites increases from 70 to 100%. The rate is not affected by the treatment of zeolite for Cr (VI).

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