

HEAVY METAL ADSORPTION BY CLINOPTILOLITE FROM AQUEOUS SOLUTIONS

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ABSTRACT

The chromium, cobalt and cadmium removal from wastewaters by natural and modified zeolites was examined by using a batch-type method. A clinoptilolite-type Turkey natural zeolite was 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 and modified zeolites were determined. The kinetics of adsorption indicates the process to be diffusion controlled.

Keywords: heavy metals, natural zeolite, adsorption, kinetics, wastewater.

INTRODUCTION

Heavy metals are common pollutant found in various industrial effluents. The stricter environment regulation on the discharge of heavy metals make it necessary to develop various technologies for the removal. Waste streams containing low-to-medium level of heavy metals are often encountered in metal plating facilities, electroplating, mining operations, 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 precipitation, 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 solution. 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 (1,2)

Clinoptilolite is a mineral zeolite of the Heulandite group. The structures of zeolites consist of a three-dimensional framework of SiO_4 and AlO_4 tetrahedral (3). The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Al^{3+} for Si^{4+} 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 solutions 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 radio-isotopes. Clinoptilolite for heavy metal and radionuclide ions adsorption has been investigated by many authors (3-8).

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 costs for these effluents, recent investigations have focused on the use of low cost adsorbents. Clinoptilolite was shown to have high selectivity for certain heavy metal ions such as Pb^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} . A significant number of researchers have done experiments, which have determined different selectivity sequences of natural zeolites for a 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 (9-13). The reaction- and diffusion controlled models have been proposed to describe the adsorption kinetics, which are based on the relative importance of the chemical reactions to diffusion transfer. The results of the kinetic studies by Eligwe et al. (14) 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, pH, and initial concentration. The uptake kinetics of cobalt and selenite was studied by Papelis et al. (15). The rate data were interpreted with a diffusion model, in which a linear isotherm was employed to express the local equilibrium relationship. The above models may be satisfactory under the particular experimental conditions; however, these models and their parameters normally are system specific (pH-dependent) and cannot be applied to other conditions (16).

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

MATERIALS AND METHODS

Natural zeolite 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 de-ionised 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 hours 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 zeolite, Sample 2; natural zeolite was treated with 2 M HCl solution over a period of 24 h., after washing, modified zeolites were dried at 105°C for 1h. Sample 3; the zeolite was prepared with 2M HNO₃ solution over a period of 24h.

The chemical composition of the natural sample was determined by XRF analysis. The analysis was performed on natural zeolites, in an attempt to determine their effect on the zeolite crystal structure. The natural Clinoptilolite obtained from Biga-Çanakkale region, was stated to be 40-50% pure. The impurities include ilite, montmorinolite, feldspar, calcite, quartz and halite.

Stock solutions of cobalt, lead and chromium were prepared in deionized 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 g was mixed in 100 ml 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 a period of 24h. The blank experiments were simultaneously carried out without the adsorbent. After the agitation for an equilibrium period, the supernatant solution was filtered through 0.45µm microporous membrane filter.

These first experiments were conducted at room temperature. In the second set of experiments is investigated the influence change of initial concentration on the uptake of lead, chromium

and cobalt ions. An accurate weight (4.00 g) zeolite sample 1, 2, and 3 was mixed and stirred with 100 ml solutions of lead, chromium and cobalt, respectively. The investigated initial concentrations were 1, 5, 10, 25, 50, 75 and 100 mg/l. After shaking in a thermostatic system, the solid phase was separated by filtration through a 0.45 μ m microporous membrane filter. The final pH of solutions was recorded by pH meter and concentrations of lead, chromium and cobalt ions at equilibrium were determined by the atomic adsorption spectrophotometry ($20\pm 0.5^{\circ}\text{C}$) (17).

RESULTS AND DISCUSSION

Chemical analysis of the zeolite is presented in Table 1.

Table 1. Chemical composition of zeolite samples tested (%).

Components	Sample 1	Sample 2	Sample 3
SiO ₂	55.80	55.80	55.80
Al ₂ O ₃	13.32	13.35	13.36
CaO	5.75	5.42	5.01
Na ₂ O	3.90	4.82	5.92
K ₂	2.35	1.48	0.92
Fe ₂ O ₃	1.30	1.28	1.29
MgO	0.70	0.66	0.67
Loss of ignition	17.00	16.60	16.80

The lead, chromium and cobalt metal ions removal efficiencies for tested zeolite samples are shown in Figs. 1, 2, and 3. Respectively, 16.8, 19.73, 18.71 mg/g Co^{+2} , 17.86, 19.99, 19.74 mg/g Cr^{+4} and 10.31, 21.51, 23.53 mg/g Pb^{+2} were taken up by 4.00 g zeolite

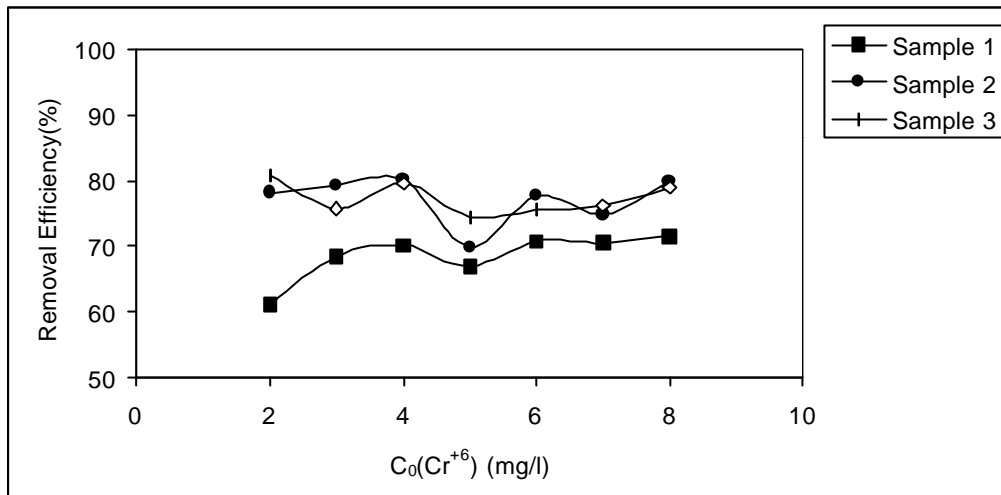


Fig.1. Cr^{+6} ion removal efficiency by zeolite samples as a function of initial concentration; m(zeolite): 0.40 g; V (solution): 100 ml.

sample 1, 2 and 3. It was clear that, for treated zeolite samples, lead and chromium was more selectively removed than cobalt. The pH value of chromium, lead and cobalt solutions was increased from 4.5. This significantly increased pH value during the experiments was due to the simultaneous uptake of hydrogen ions by zeolite samples and hydrolysis of zeolites.

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

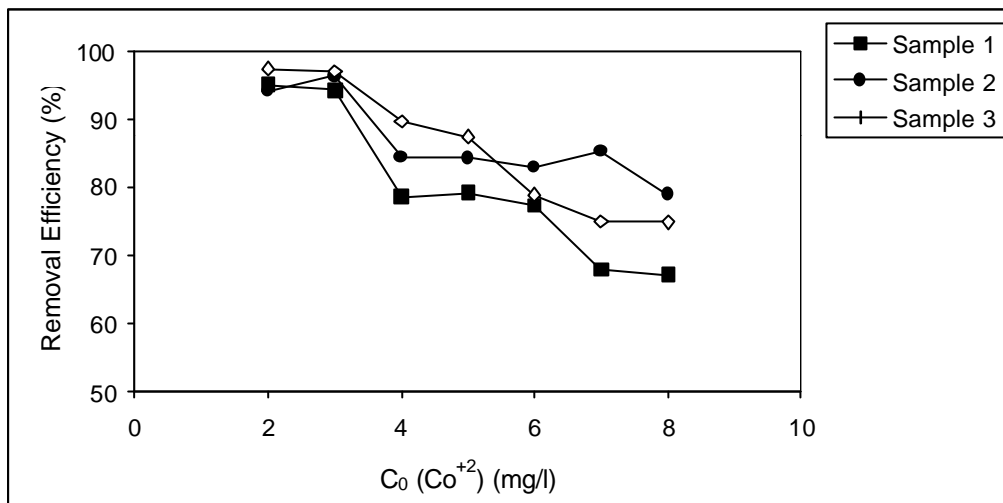


Fig.2. Co²⁺ ion removal efficiency by zeolite samples as a function of initial concentration; m(zeolite): 0.40 g; V (solution): 100 ml.

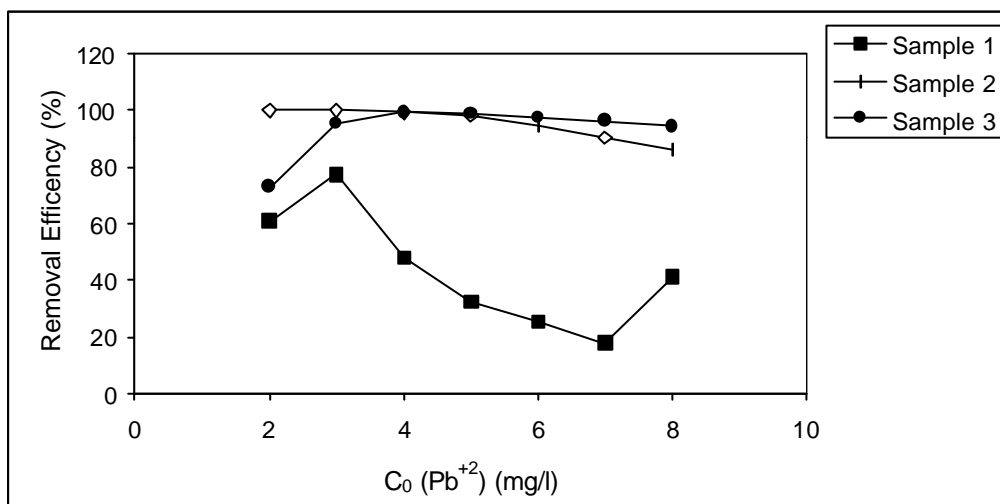


Fig.3. Pb²⁺ ion removal efficiency by zeolite samples as a function of initial concentration; m(zeolite): 0.40 g; V(solution): 100 ml.

These results indicate 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 of between 67,13 and 90% for all zeolite samples1, 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 ions were determined using equation of Lagergren and Weber and Morris (18), respectively which are as follows.

For rate constant of adsorption;

$$\log(q_e - q) = \log q_e - \frac{K}{2.3}t$$

For rate constant of pore diffusion;

$$\frac{C_t}{C_0} = K' t^{0.5} \quad \text{where } t; \text{ time(min), } q; \text{ amount of metal ion adsorbed at time, t(mgg}^{-1}\text{), } q_e;$$

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 (Figs. 4, 5 and 6) suggests the applicability of Lagergren equation, however, the plot of C_t / C₀ vs t^{0.5} (Figs. 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 (18).

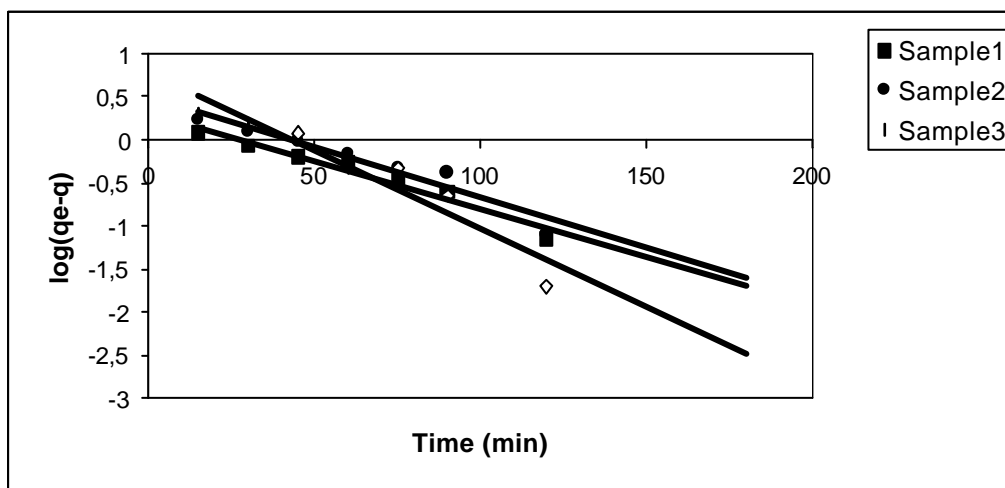


Fig. 4 Kinetics of Co(II) adsorption using by Lagergren plot.

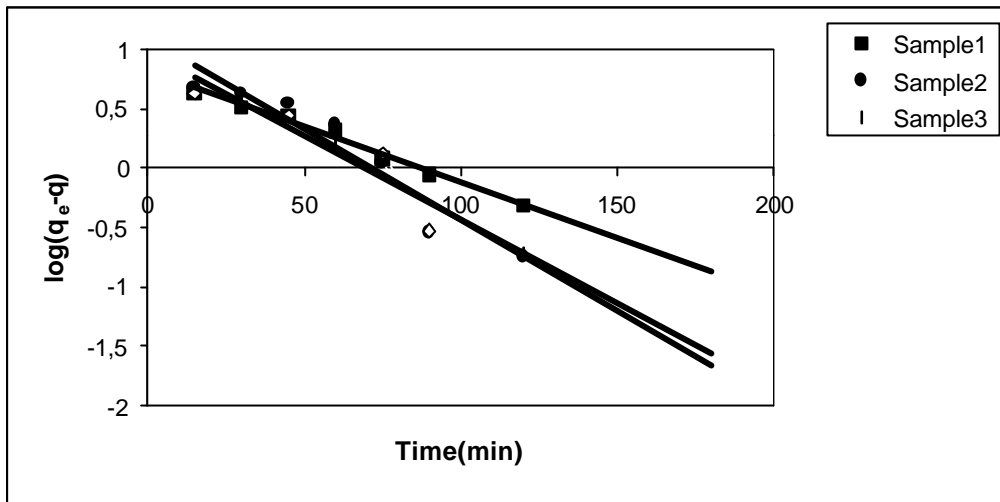


Fig. 5. Kinetics of Pb(II) adsorption using by Lagergren plot.

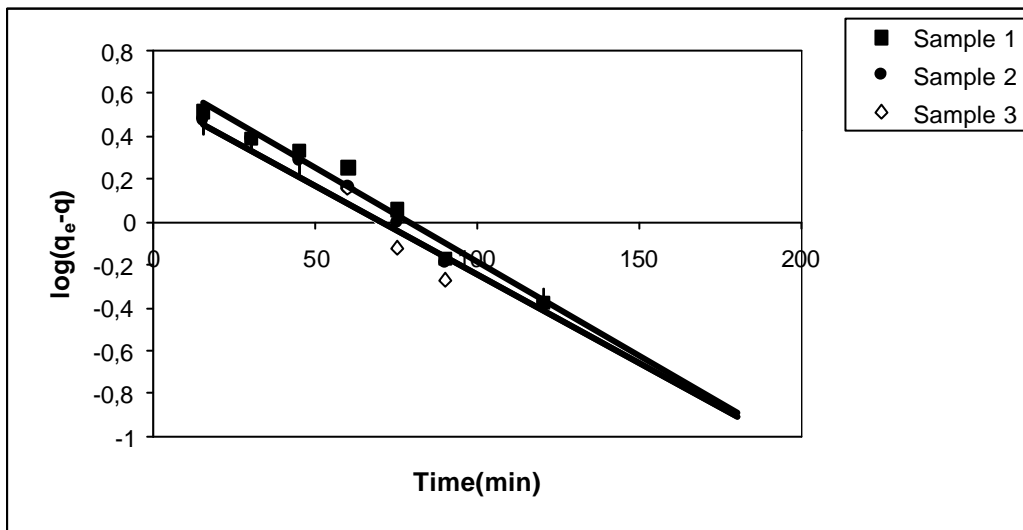


Fig. 6. Kinetics of Cr(VI) adsorption using by Lagergren plot.

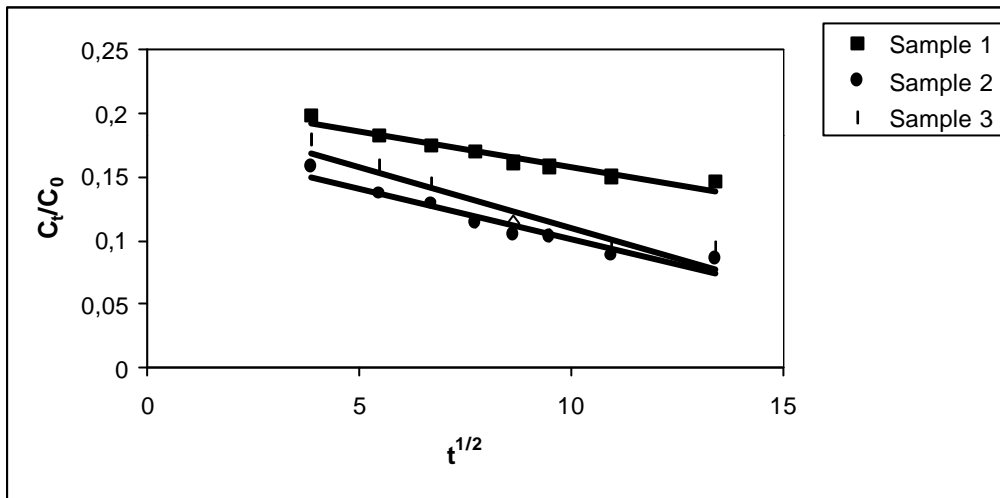


Fig. 7. Kinetics of Co(II) adsorption using by Weber et al.

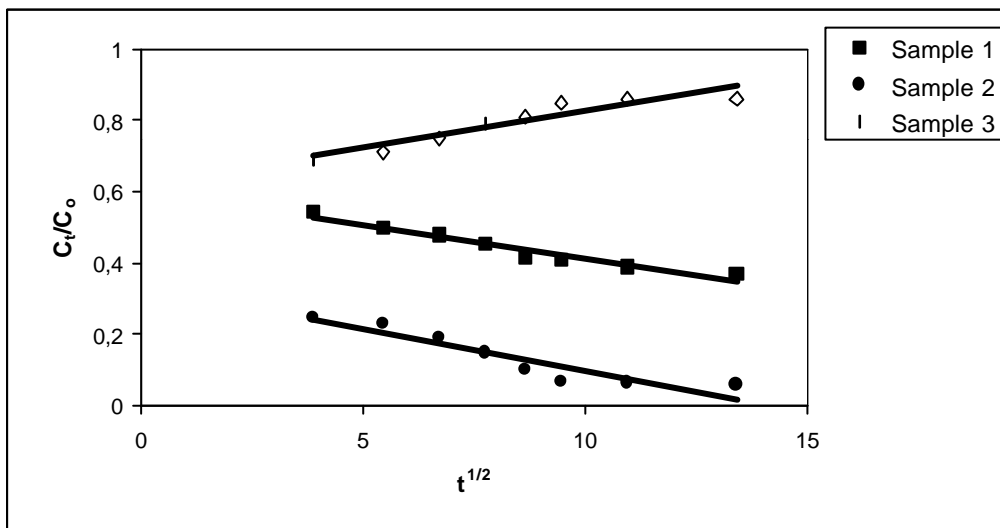


Fig. 8. Kinetics of Pb(II) adsorption using by Weber et al.

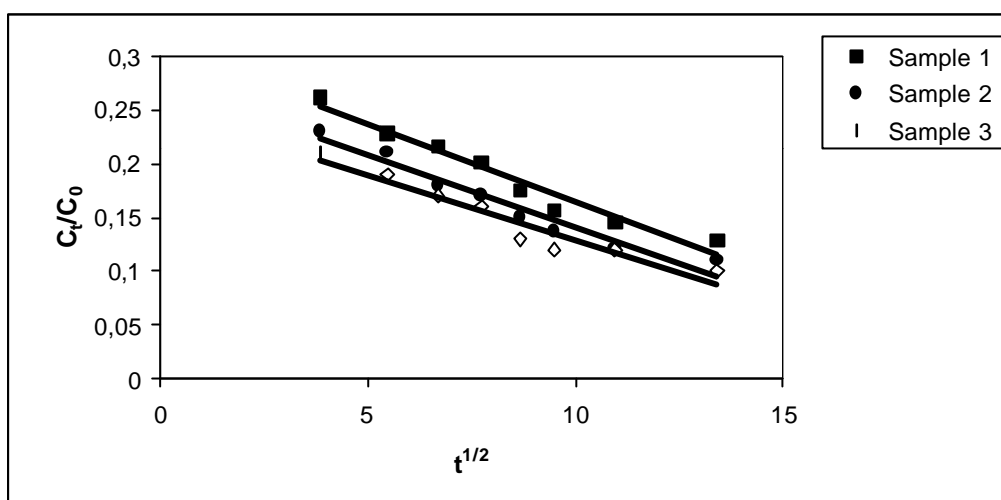


Fig. 9. Kinetics of Cr(VI) adsorption using by Weber et al.

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

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

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

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 above 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 concentration in solution by using the treated zeolite. The initial rate of removal increases with increases in the initial cadmium concentration level. However, the ultimate removal rate remains more or less the same. At lower concentrations, i.e., concentrations equal to 2.0 mg/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 dependent. It may be noted from the figure that the equilibrium is established in 60 min and the period of equilibration 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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