

Uptake of lead and cadmium by clinoptilolite

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Abstract

The ion exchange systems of lead and cadmium, using the zeolite clinoptilolite, were examined. The metal uptake is increased with increasing temperature. At low temperatures the exchange of lead is mainly with the sodium ions but at higher temperatures potassium present in the zeolite lattice can be replaced, increasing the metal uptake. In the case of cadmium, the exchange occurs only with sodium ions, irrespective of the temperature of the solution. The zeolite particle size influences significantly the metal uptake. An increase is observed with decreasing particle size. From the experimental results the diffusion coefficients and activation energies of the ion exchange systems are calculated.

Key words: Metal removal; Metal uptake; Ion exchange; Zeolites; Lead; Cadmium

1. Introduction

Zeolites are used in various technological areas, but very recently they have found extensive use in the field of waste water treatment. Clinoptilolite is one of the most important zeolites and its ion exchange characteristics have been studied more, compared with other natural zeolites. This is because clinoptilolite is found in extensive deposits worldwide, it has a stable structure and shows high selectivity for various cations. Its preference for certain ions, such as ammonia, has led to its use in several plants for wastewater treatment (Chelishev

et al., 1974; Renaud et al., 1980; Blanchard et al., 1984; Loizidou and Townsend, 1987a, 1987b; Loizidou, 1989).

The optimization of the mechanical design and operation of water purification plants requires a basic knowledge of the factors influencing the ion exchange processes. The ion exchange equilibria and the kinetics of the exchange processes are two of the most important factors that can influence the performance of these water purification systems.

This study concentrates on the ion exchange behaviour of Greek clinoptilolite for lead and cadmium ions. The influence of the particle size and the temperature at which the ion exchange takes place are examined in detail.

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2. Materials and methods

The zeolite was crushed and sieved to obtain particle size fractions of 160–600 μm , 0–600 μm , 600–1000 μm and 1000–2000 μm . The zeolite was converted to its sodium form by successive washings with sodium nitrate solution. The kinetic experiments were performed on a bench scale by equilibrating clinoptilolite with $\text{Pb}(\text{NO}_3)_2$ or $\text{Cd}(\text{NO}_3)_2$ solutions, the total external concentration being 0.01 N.

The same experimental procedures were repeated at two different temperatures, 25°C and 50°C, using the above mentioned particle sizes of clinoptilolite. Samples were removed at several time intervals and analyses were performed on the solution phase for Pb and Cd as well as for Na^+ , K^+ , Ca^{2+} and Mg^{2+} , in order to check the behaviour of the ion exchange systems. Also, in order to evaluate the equivalent radius of the zeolite fractions used, sieving was repeated using an appropriate apparatus with a narrower aperture. Details of the experimental procedures have been reported elsewhere (Malliou et al., 1992).

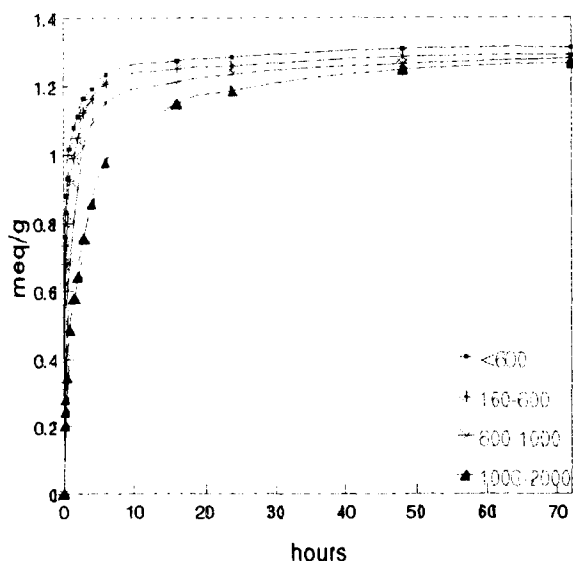


Fig. 1. Kinetic behaviour of lead with particle size of clinoptilolite at 25°C.

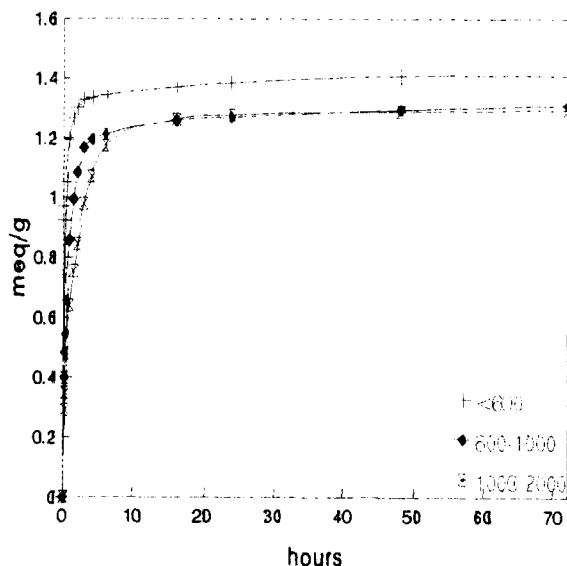


Fig. 2. Kinetic behaviour of lead with particle size of clinoptilolite at 50°C.

3. Results and discussion

3.1. Kinetics of ion exchange

The kinetic behaviour of sodium clinoptilolite with lead (Na-CLI/Pb) is given in Fig. 1 and Fig. 2. Equilibrium is reached within 24 h for all parti-

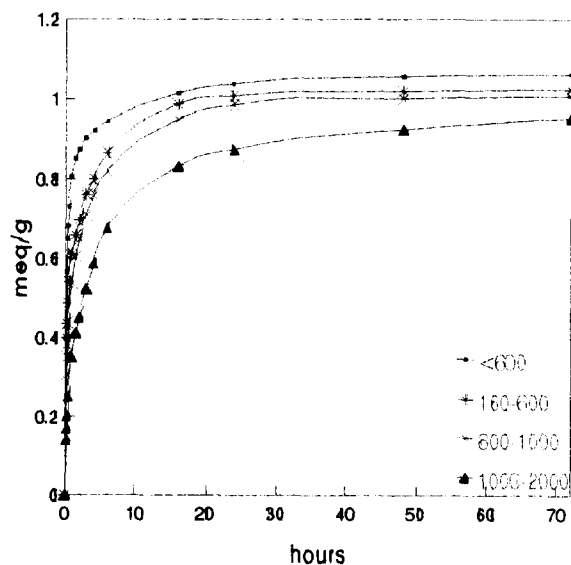


Fig. 3. Kinetics of cadmium with clinoptilolite of various particle sizes at 25°C.

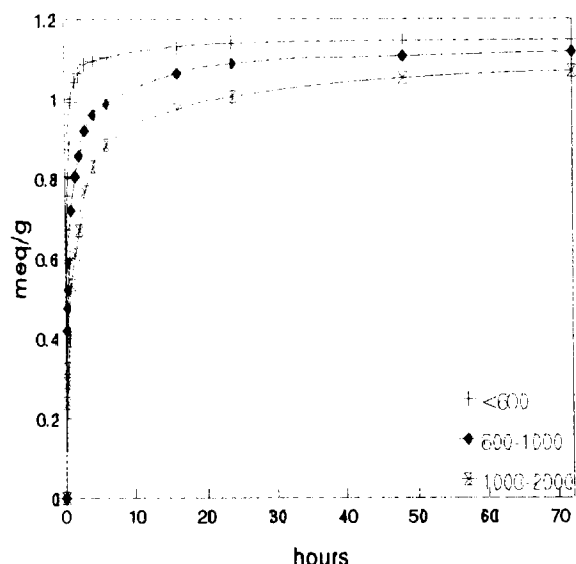


Fig. 4. Kinetics of cadmium with clinoptilolite of various particle sizes at 50°C.

cle sizes of clinoptilolite. Lead uptake is increased by decreasing the particle size, but at equilibrium the difference is minimized. A significant increase of lead exchange is observed by increasing the temperature of the system. Also, during the exchange process, apart from sodium ions, potassium ions are released into the solution, indicating the preference of the zeolite for lead ions. Calcium and magnesium are detected in trace amounts. It is observed that the amount of potassium released increases with time and this phenomenon is observed for all particle sizes. It is possible that the lead ions initially substitute for the sodium ions and eventually can exchange with potassium. This

is well explained since potassium ions are firmly bound to the zeolite structure and they are not as mobile as sodium ions (Galabova, 1979). By increasing the temperature to 50°C (Fig. 2), the potassium release is much higher compared with lower temperatures, i.e. it is nearly double.

For the Na/Cd exchange system, cadmium uptake is illustrated in Fig. 3 and Fig. 4, for the two temperatures of exchange and the various particle sizes of clinoptilolite. The metal uptake is increased by increasing the temperature and significant differentiation is observed for the various particle sizes. Potassium exchange with cadmium is very limited since only traces of potassium are detected in the solution after the exchange. Table 1 shows lead and cadmium uptake at equilibrium for the two temperatures and the four different particle sizes of clinoptilolite. As it can be seen for clinoptilolite, even at equilibrium, a partial exchange is observed since its theoretical exchange capacity is calculated to be 1.70 mEq/g. Also, the metal uptake is decreased by increasing particle size and the exchange is higher at elevated temperatures.

By examining the kinetics of exchange for the first 6 h, through the fractional attainment of equilibrium, as shown in Figs. 5–8, the following comments can be reported.

The exchange rate for both lead and cadmium is higher for the smaller particle diameter and the rate is decreased significantly with time. During the ion exchange process ions have to move through the pores of the zeolite mass, but also through the channels of the lattice. Diffusion is faster through the pores and is retarded when ions move through the smaller diameter channels.

It is generally seen that when the exchange is

Table 1
Metal uptake at equilibrium

Particle size (μm)	Pb and Cd taken at equilibrium (mEq/g)			
	Pb ²⁺		Cd ²⁺	
	25°C	50°C	25°C	50°C
< 600	1.312	1.408	1.062	1.150
160–600	1.294	—	1.025	—
600–1000	1.286	1.311	1.009	1.123
1000–2000	1.270	1.292	0.980	1.081

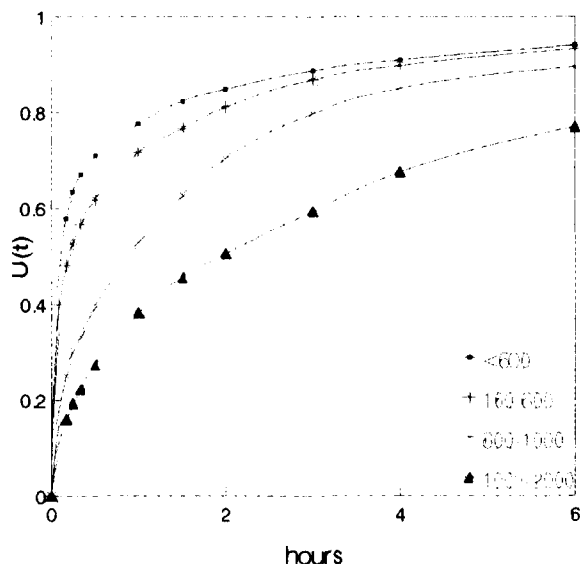


Fig. 5. Fractional attainment of equilibrium for Pb/Na-CLI at 25°C.

~90%, approximately after 6 h of equilibration, the exchange rate is very low. Initially the exchange is between the sodium ions which occupy positions in the crystal which are readily accessible to lead or cadmium ions and the process is very rapid.

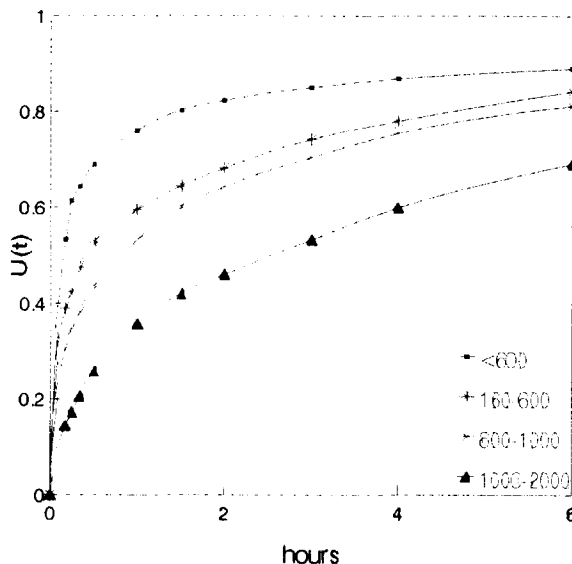


Fig. 7. Fractional attainment of equilibrium for Cd/Na-CLI at 25°C.

In order to understand the behaviour of the ion exchange system, the diffusion coefficients are calculated using appropriate equations, as explained elsewhere (Malliou et al., 1993). The calculated diffusion coefficients are shown in Table 2. The diffusion coefficients decrease when particle size is

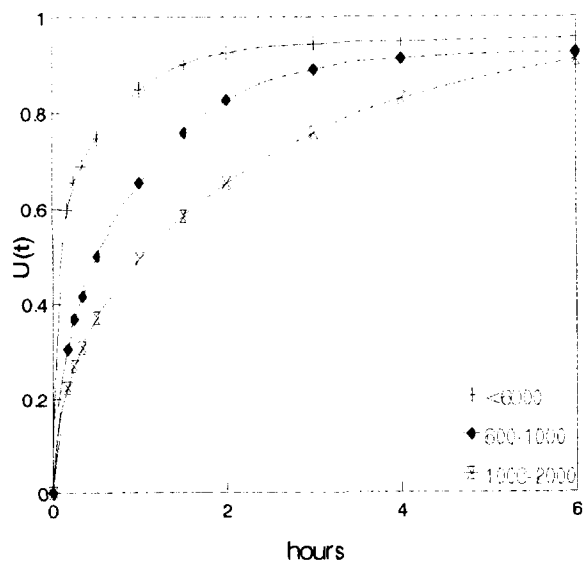


Fig. 6. Fractional attainment of equilibrium for Pb/Na-CLI at 50°C.

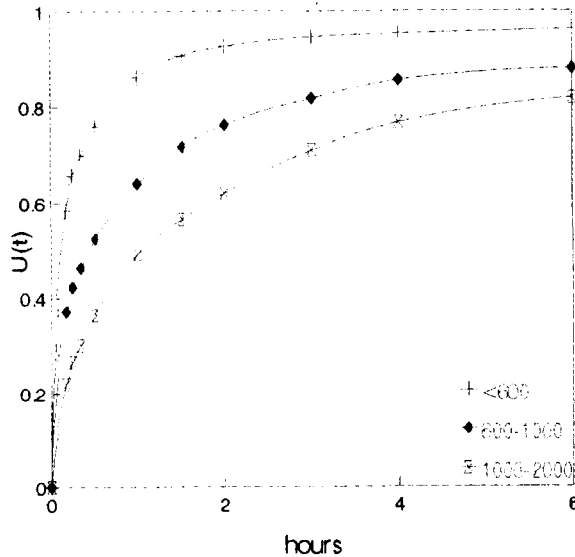


Fig. 8. Fractional attainment of equilibrium for Cd/Na-CLI at 50°C.

Table 2
Variation of diffusion coefficients with particle size

Particle size (μm)	Diffusion coefficients ($\text{cm}^2 \text{s}^{-1}$)			
	Pb^{2+}		Cd^{2+}	
	25°C	50°C	25°C	50°C
< 600	2.388×10^{-10}	3.888×10^{-10}	2.087×10^{-10}	3.892×10^{-10}
160–600	2.514×10^{-9}	—	1.489×10^{-9}	—
600–1000	1.363×10^{-8}	2.343×10^{-8}	8.989×10^{-9}	1.469×10^{-8}
1000–2000	2.068×10^{-8}	3.864×10^{-8}	1.665×10^{-8}	3.447×10^{-8}

decreased. Contrary to the kinetic profiles, the exchange rate is increased with decreasing grain size. The observed decrease of the diffusion coefficients indicates that the ions mobility is reduced with decreasing clinoptilolite particle size. A similar phenomenon has been reported for the Na/NH_4 exchange of clinoptilolite (Neveu et al., 1985) and the discrepancy was attributed to the assumption that zeolite grains are spherical. In this study, such an explanation is not satisfactory due to the significant differences in the values of the diffusion coefficients. It must be emphasized that the calculated diffusion coefficients are the effective ones, which express the ions diffusion through the zeolite pores and the channels of the lattice.

The corresponding activation energies for the systems examined are shown in Table 3. The values obtained are quite close to the values reported for the diffusion of monovalent ions into clinoptilolite (Araya et al., 1981), but are much lower than the activation energy values reported (Dyer et al., 1984) for the diffusion of cadmium into synthetic zeolite A.

Table 3
Activation energy of the ion exchange systems for various particle sizes

Particle size (μm)	Activation energy (kJ/mol)	
	Pb^{2+}	Cd^{2+}
< 600	15.61	19.95
600–1000	17.34	15.72
1000–2000	20.01	23.29

4. Conclusions

At the initial stage of exchange, lead ions substitute sodium ions that are present in the lattice and eventually potassium. The increase in the external solution temperature affects mainly the exchange between lead and potassium. On the contrary, cadmium ions cannot replace potassium ions.

The metal uptake by the zeolite and the rate of exchange are increased by decreasing the particle size of the zeolite though the diffusion coefficients are decreased. Generally, clinoptilolite can remove, to a significant degree, the metal ions lead and cadmium and the exchange is very rapid. It must be emphasized that particle size can differentiate significantly the amounts of metal removed. This must be taken into consideration when designing systems for water purification, so that optimum results are obtained.

5. References

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