UPTAKE OF CADMIUM IONS FROM AQUEOUS SOLUTION BY NATURAL AND IRON MODIFIED ZEOLITE

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ABSTRACT

In this study, a natural zeolite (NZ) sample has been used in preparation of iron modified zeolite (IMZ). The uptake of cadmium ions on NZ and IMZ has been examined. The experimental results have showed that the capacity of IMZ is four times higher than that of NZ. Almost complete Cd removal is achieved at the initial Cd concentration of 232.69 mg/l, which imposes IMZ as a good sorbent material. The balance between outgoing Na, K, Ca, Mg and ingoing Cd ions shows an almost complete stoichiometric relation, indicating ion exchange as the main process responsible for Cd uptake on IMZ.

Keywords: zeolite, iron modified zeolite, cadmium removal, ion exchange.

INTRODUCTION

The presence of heavy metals like cadmium in aquatic ecosystems is a serious problem because of their toxic properties. The main sources of cadmium pollution are wastewaters of various industries such as alkaline batteries, Cd plating, copper alloys, semi-conductors and electronic products [1]. Removal of Cd from wastewater is usually performed by precipitation, while lower concentrations are removed using different adsorbents such as natural zeolites, metal oxides, clay minerals [2-4]. The removal capacity of these materials is too low to be explored for practical application [5]. In this work, cadmium removal from an aqueous solution, using iron modified zeolite, has been examined and results have been compared with those for natural zeolite.

EXPERIMENTAL

Sample preparation

The natural zeolite (NZ) originated from the Zlatokop deposit, Vranjska Banja, Serbia. The sample was milled and sieved to two particle size fractions: < 0.043 mm and 0.6-0.8 mm. The samples were rinsed in ultrapure water in order to remove possible impurities. After drying at 60^{o}C, the samples were stored in a desiccator.

The iron modified zeolite (IMZ) sample was prepared from NZ of both particle sizes. 20.0 g of a natural zeolite sample was shaken with 100 ml of freshly prepared 0.1 mol/l $Fe(NO_3)_3 \cdot 9 H_2O$ in an acetate buffer at pH = 3.6, for 2 h in an incubator shaker at room temperature. After filtration the zeolite was shaken with 90 ml of 1 mol/l NaOH solution for an hour. Thereafter, the zeolite was rinsed for an hour at 50^{o}C with 50 ml of 4% $NaNO_3$ and then with 50% of ethanol. The prepared IMZ was dried for 24 hours at 40^{o}C, and kept in a desiccator [6].

Cadmium uptake experiments

Cadmium uptake on NZ and IMZ was examined using the incubator shaker, in the period of 24 hours at room temperature. 1g of zeolite sample was shaken with 100 ml of cadmium aqueous solutions with initial concentrations ranging from 2.07-13.94 mmol/l. The solutions were prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ in ultrapure water. After equilibration (24 h) at room temperature, the concentrations of remaining cadmium, as well as released Na, Ca, K and Mg ions, in supernatants were determined by ion chromatography and the complexometric method [7].

RESULTS AND DISCUSSION

Figure 1 shows the comparison of experimental results for equilibrium cadmium uptake on natural and iron modified zeolite vs. initial cadmium concentrations. The results show that the amount of cadmium removed on iron modified zeolite was approximately four times higher then on natural zeolite for both particle sizes (~0.4 mmol/g vs. ~0.1 mmol/g). Obviously, during preparation of IMZ, the number of exchangeable sites increases compared to NZ, which is responsible for higher uptake of cadmium ions. The amount of cadmium removed is slightly higher for the samples of the lower particle size, which can be attributed to the higher specific surface area.

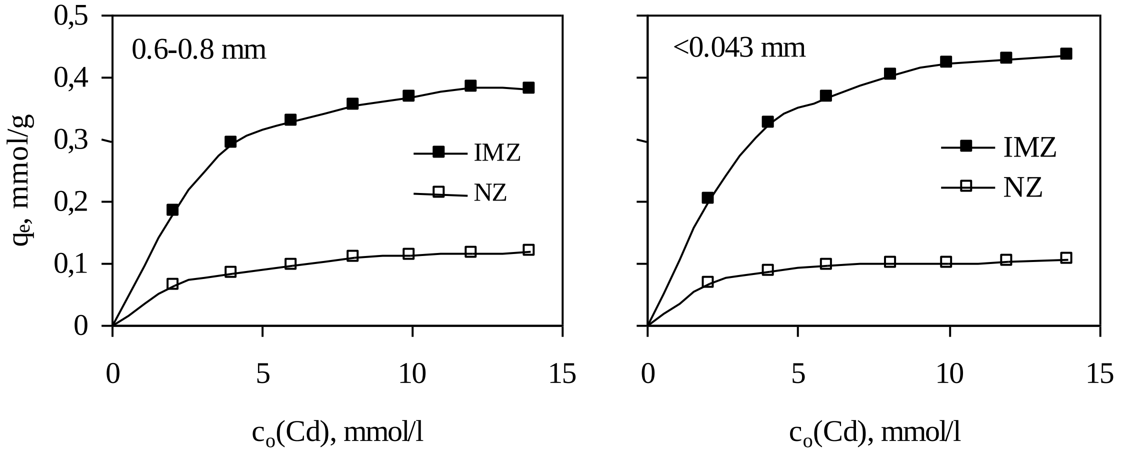

Figure 1. Cadmium uptake on natural (NZ) and iron modified zeolite (IMZ) vs. initial cadmium concentrations.

The percentage of cadmium removal onto natural and iron modified zeolite are calculated and shown in Fig 2.

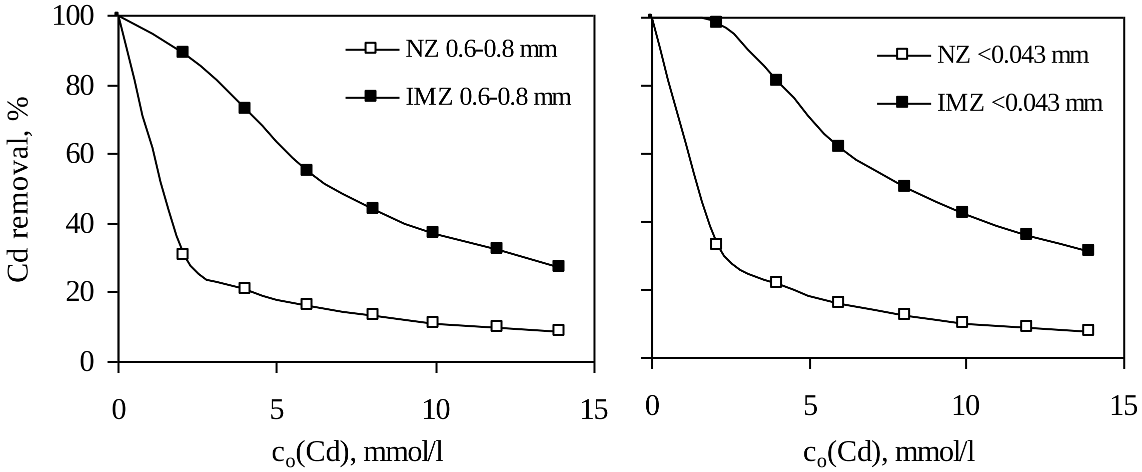

Figure 2. The removal efficiency of cadmium ions by natural (NZ) and iron modified zeolite (IMZ) as a function of initial cadmium concentration.

The percentage removal of cadmium onto both natural and iron modified zeolite increases with the decrease of initial cadmium concentration. Almost complete cadmium removal has been achieved for IMZ in the solution with the initial concentration of 2.07 mmol/l (232.69 mg/l), while less then 40% of cadmium removal has been observed at the same initial concentration for NZ. These results impose the IMZ as a good choice for removing of Cd from aqueous solutions. The experimental results for cadmium removal have been fitted to linearized Langmuir and Freundlich adsorption isotherms. Table 1 shows the calculated parameters.

Table 1. Calculated parameters of Langmuir and Freundlich isotherms.

Sample	Particle size mm	Langmuir isotherm parameters			Freundlich isotherm parameters		
		K_L l/mmol	q mmol/g	R^2	K_F (mmol/g)(l/mmol)$^{1/n}$	n	R^2
NZ	**0.6-0.8**	**0.085**	**0.130**	**0.986**	**0.059**	**3.470**	**0.982**
	<0.043	**0.123**	**0.113**	**0.998**	**0.067**	**5.178**	**0.948**
IMZ	**0.6-0.8**	**1.585**	**0.375**	**0.985**	**0.262**	**5.311**	**0.954**
	<0.043	**11.136**	**0.399**	**0.938**	**0.328**	**7.283**	**0.993**

The Langmuir isotherm shows better fitting of experimental results, therefore this equation was used to calculate the capacity of zeolite for cadmium ions.

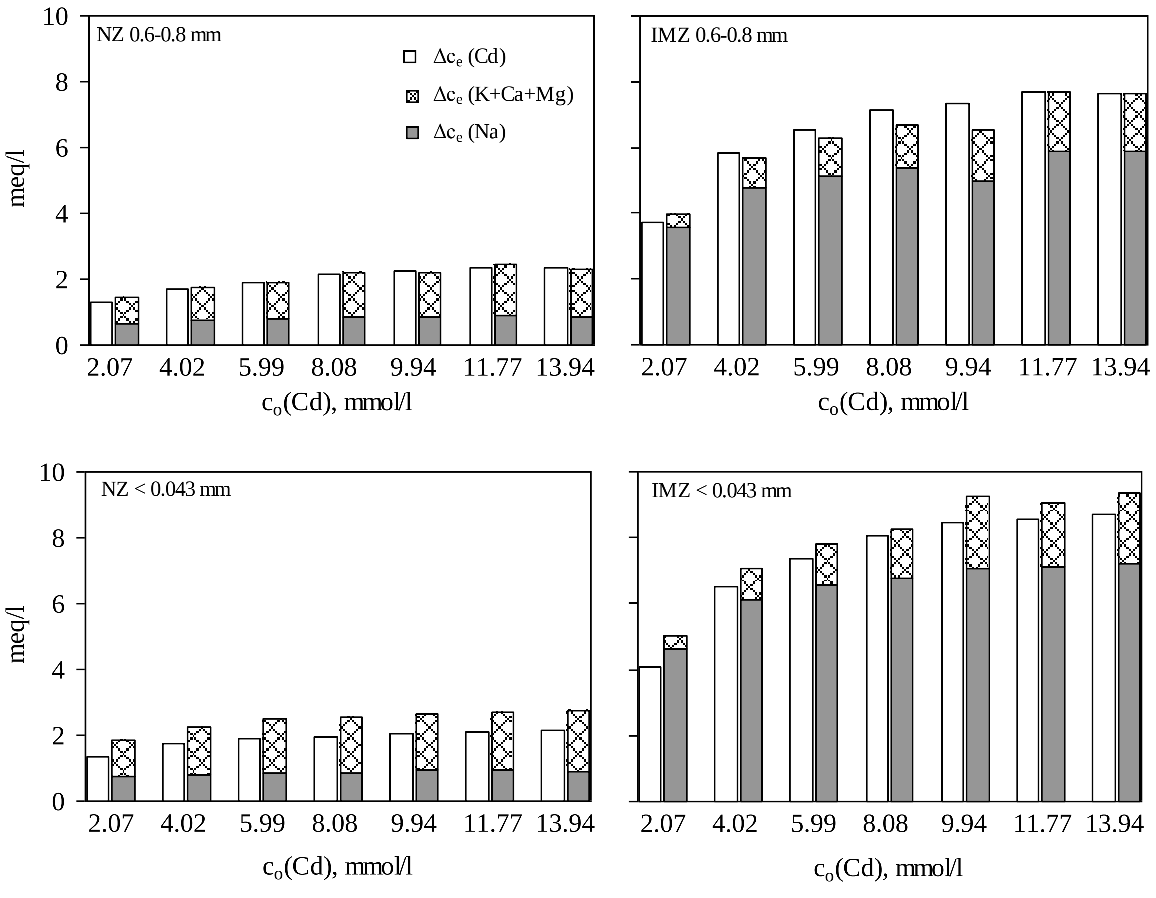

Figure 3. Relationship between the concentration of Cd bound and released exchangeable cations in the solution as a function of initial cadmium concentration. Note: $\Delta c_e = c_{initial} - c_{final}$.

The relation between the concentrations of Na, K, Ca, Mg ions leaving the zeolite structure and concentrations of Cd ions entering the zeolite structure has been calculated for different initial cadmium concentrations and is presented in Figure 3.

The balance of ions shows an almost complete stoichiometric relation for NZ and IMZ of both particle sizes, indicating ion exchange as the main mechanism responsible for Cd uptake. Among all exchangeable cations, Na ions are dominant for IMZ. As the amount of Na is 8-9 times higher compared to the sum of other exchangeable cations, this indicates Na ions are responsible for higher removal capacity of Cd onto IMZ.

CONCLUSION

The results show that the capacity of IMZ for cadmium ions is four times higher than that of NZ. The percentage of cadmium removal onto both NZ and IMZ increases with the decrease of initial cadmium concentration. Almost complete Cd removal is achieved at the initial Cd concentration of 232.69 mg/l (2.07 mmol/l), which imposes IMZ as a good sorbent material. The balance between outgoing and incoming ions on zeolite indicates ion exchange as the main mechanism responsible for cadmium uptake.

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