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Methionine templated analcime for enhancing heavy metal adsorption

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ABSTRACT: Zeolites are effective adsorbents to remove heavy metals from aqueous solutions. To investigate the role of the template on enhancing the ability of zeolites to absorb metals, methionine amino acid was introduced to zeolite synthesis gel to produce a modified analcime zeolite. Afterwards, adsorption of Cu(II) and Ni(II) cations on template-free analcime and methionine-templated analcime were studied and the experimental data were fitted with Freundlich and Langmuir equations in order to obtain the sorption parameters. Batch experiments were carried out to evaluate Cu(II) and Ni(II) adsorption at different pH values, heavy metals concentrations, and removal intervals. The results showed that the metal removal efficiency was strongly dependent on the pH of the solutions. The analcime zeolites absorbed Cu(II) more readily than Ni(II). Furthermore, methionine-templated analcime exhibited a higher potential for heavy metal removal than the template-free zeolite. Raman spectra indicated that the presence of a methionine template during analcime zeolite synthesis could create a complex structure of Cu—S (methionine)/zeolite and Ni—S (methionine)/zeolite. Thus introducing a sulphur-containing template such as methionine may give further possibilities to improve the metal removal efficiency of zeolites.

KEYWORDS: organic additive, zeolite

INTRODUCTION

Heavy metals are the most important pollutants in the environment and widely found on water surfaces from natural and industrial sources[1]. Among metals, the two important pollutant are Cu and Ni cations. Cu ions can deposit in brain, skin, liver, pancreas, and myocardium causing serious toxicological effects on humans[2,3]. Ni is a commonly toxic metal in natural ecosystems. The most common adverse health effect of nickel in humans is an allergic reaction in direct contact with the skin caused by jewellery or other items containing nickel.

There are several methods for removing heavy metals from waste water such as adsorption, chemical precipitation, ion exchange, electrochemical treatment, solvent extraction, and membrane separation[4,5]. Nowadays, a number of low cost adsorbent materials such as zeolites are available to remove metal ions[6–8].

Zeolites are hydrated aluminosilicate minerals and have a micro-porous structure. Moreover, the zeolites can be modified by the introduction of new functional groups in order to improve its activity and selectivity for the removal of several substances[9]. There are several applications of pretreated natural zeolites for removing metals from wastewater. For example, natural and sodium pretreated zeolites can take up (remove by ion exchange) lead, nickel, cadmium, and barium ions[10]. Furthermore, the Na pretreated zeolite can be used to take up lead and cadmium from wastewater with an increased ion exchange capacity[11]. The removal efficiency of the metal Bulgarian zeolite pretreated with NaCl, CH_3COONa, and NaOH solutions is able to remove copper ions[12].

Methionine, an essential amino acid, is one of the two sulphur-containing amino acids. The data on the complexation of essential metal ions and the bioactive ligands methionine and cysteine give approach into many physicochemical processes[13]. Animal studies have shown that adding methionine to the drinking water of rats protect the animals from the toxic effects of lead[14]. In a separate experiment, it also protects the animals from the toxic effects of mercury and atrazine (a herbicide)[15].

In our previous work, the effect of D-methionine on the transformation of the structure of zeolite Y to analcime and zeolite P was investigated and these two zeolites were synthesized in the presence of D-methionine as a template[16]. In this study, the removal of Cu(II) and Ni(II) cations was studied to evaluate the effect of methionine amino acid on the adsorption ability of methionine template analcime with respect to template-free analcime.

MATERIALS AND METHODS

Methionine template analcime and template-free analcime were obtained according to the reported procedure[16]. The reagents D-methionine, silicic acid, NaOH, and aluminium powder (all purchased from Merck) were used in the synthesis. All aqueous solutions were prepared using deionized doubly distilled water. The sol-gel mixture was prepared by mixing an aluminate and a silicate solution. Aluminium powder (0.108 g) was dissolved in a 3.3 M caustic solution at 40 °C to yield the aluminate solution. NaOH (25 ml, 2.5 M) was mixed with silicic acid (5.9 g) in a Teflon bottle and stirred until the solid is completely dissolved to yield the silicate solution. Afterwards, the aluminate solution was added to the silicate solution with stirring to produce the sol gel. The amino acid D-methionine was dissolved in H_2O (4 ml) followed by heating to 50 °C. Subsequently, the warmed D-methionine solution was added to the aluminosilicate sol-gel. After the addition was completed, the Teflon bottle was transferred to a stainless-steel autoclave and the sealed autoclave was put into an air oven and heated for 96 h at 160 °C. The solid products were recovered by filtration or centrifugation and washed with deionized water, dried overnight at 100 °C, and calcinated at 550 °C for 4 h in an electric furnace.

Stock solutions were prepared by dilution of analytical grade $CuSO_4 \cdot 5\,H_2O$ and $NiSO_4 \cdot 6\,H_2O$ salts with distilled water.

Batch adsorption studies

The adsorption tests were performed by the batch technique at 30 °C. For isothermal studies, the amounts of pre-weighed zeolite (0.01 g) as adsorbents were placed in adsorption cells containing 10 ml of Cu(II) and Ni(II) solutions with a certain initial concentration. The solution pH was kept at 6 adjusted by 0.1 M HCl and NaOH solution. The cells were then agitated in an orbital shaker at 100 rpm and liquid samples were taken out at a given interval for Cu(II) or Ni(II) adsorption analyses.

The effect of pH on the adsorption of heavy metal ions was also investigated at different pH values. While the solution pH varied from 2–8, the amount of adsorbents, the initial concentration of heavy metal ions, and the solution temperature were fixed at 0.01 g, 20 mg/l and 30 °C, respectively.

Analytical Procedures

Energy dispersive X-ray (EDX) spectra were recorded on an EDX Genesis XM2 attached to FE-SEM. Raman spectra on the samples were obtained using the Nicolet Almega Dispersive Raman (Thermo Scientific, USA) spectrometer consisting of a laser operating at the maximum power of 100 mW at 532 nm.

RESULTS AND DISCUSSION

Although the modification of a zeolite increase its price, this work used methionine which is abundant and inexpensive. Because of methionine low price it can be used as a fairly common ingredient to pet food too.

Dynamic adsorption of Cu(II) and Ni(II)

The adsorption of Cu(II) and Ni(II) on the analcime zeolites was first investigated at different time intervals. As shown in Fig. 1, Cu(II) and Ni(II) adsorption approached maximum after 14 h and 10 h, respectively. At the same initial concentration, the amounts of adsorbed Cu(II) and Ni(II) on analcime zeolites were significantly different and followed the order of Cu(II) > Ni(II). In addition, methionine template analcime showed higher adsorption than template-free analcime.

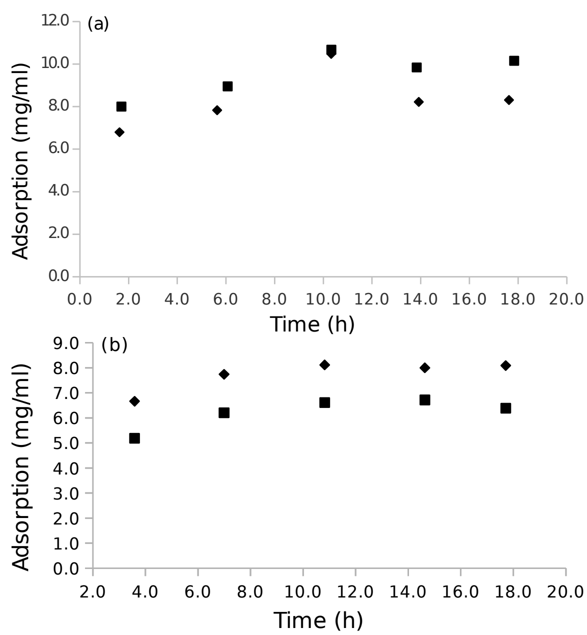

Fig. 1 Dynamic adsorption of (a) Ni(II) and (b) Cu(II) on methionine template analcime (squares) or free template analcime (diamonds).

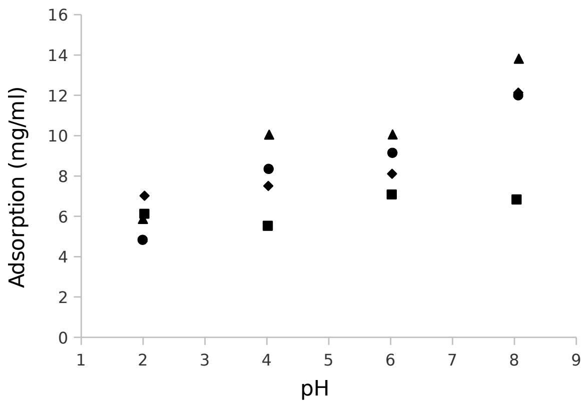

Fig. 2 Effect of pH on Cu(II) and Ni(II) adsorption on methionine template analcime (diamonds) and free template analcime zeolites (squares) and Cu(II) adsorption on methionine template analcime (triangles) and free template analcime zeolites (circles). Adsorption conditions: $T = 30\,°\mathrm{C}$, $[\mathrm{Cu(II)}] = 20$ ppm, and $[\mathrm{Ni(II)}] = 20$ ppm.

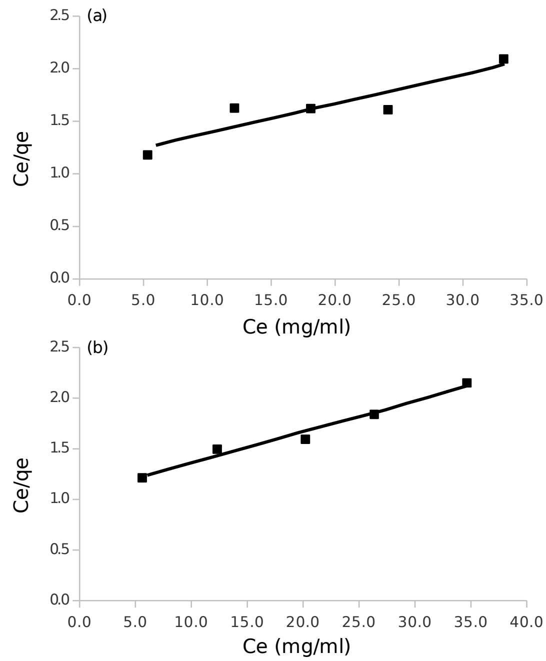

Fig. 3 Langmuir isotherm for Ni(II) adsorption on (a) methionine template analcime: $y = 0.025\,x + 1.024$ ($R^2 = 0.834$); and (b) free template analcime: $y = 0.031\,x + 1.056$ ($R^2 = 0.974$).

Effect of pH

Fig. 2 shows the effect of pH on Cu(II) and Ni(II) adsorption on methionine template analcime and template-free analcime zeolite. The removal of metals was highly dependent on pH. It was found that with increasing pH, adsorption of Ni(II) and Cu(II) exhibited the same trend; higher Ni(II) and Cu(II) adsorption were achieved in solutions of higher pH. Chemical precipitation was avoided by keeping the maximum pH below that of the metal hydroxide precipitation. It is well known that zeolites can adsorb heavy metals via ion-exchange mechanism. The pH level of the aqueous solution influenced the adsorption of metals to the zeolite via a competition with hydrogen ions. As the pH level increase, the concentration of the competing hydrogen ions decrease and this causes an increase in the amounts of adsorbed metals [17].

Adsorption isotherms

Two adsorption isotherms, Langmuir and Freundlich isotherms, were employed to calculate the adsorption capacity. Freundlich proposed the equation

$$\log q = \log K_{\mathrm{F}} + \frac{1}{n} \log C_{\mathrm{e}},$$

where q is the amount of adsorbed cations per gram of zeolite, C_{e} is the equilibrium concentration of cations, and K_{F}, the Freundlich constant, indicates the adsorption capacity of the zeolite [18]. The Langmuir model assumes that the adsorption occurred on surface sites where the energy in each site is equal. The linear form of Langmuir equation is

$$\frac{C_{\mathrm{e}}}{q_{\mathrm{e}}} = \frac{C_{\mathrm{e}}}{q_{\mathrm{m}}} + \frac{1}{K_{\mathrm{L}} q_{\mathrm{m}}},$$

where q_{e} is equilibrium concentration on adsorbent (mg/g), q_{m} is the saturation capability (mg/g), and K_{L} is the Langmuir adsorption constant (l/mg). The constant K_{L} and the saturation capability q_{m} can be evaluated by the regression analysis of the linear form of the foregoing equation. Capacity and $1/n$ is an exponent associated with the adsorptive strength as well as the favourability [2].

The experimental equilibrium data for Ni(II) and Cu(II) adsorption on methionine template analcime and template-free analcime were fitted by the Langmuir and Freundlich isotherms (Figs. 3 and 4). The adsorption data is listed in Table 1.

The results showed that both mathematical models, either Langmuir or Freundlich, fitted the data well. However, the regression coefficients obtained from the Freundlich isotherm were higher than that of the Langmuir isotherm, which suggested the heterogeneous adsorption of Ni(II) and Cu(II) on methionine template analcime and template-free analcime zeolite. From the Langmuir model, the calculated parameters at the maximum

Table 1 Calculated Langmuir and Freundlich constants of the adsorption isotherms of Ni(II) or Cu(II) on zeolites.

Cation	Adsorbent	Langmuir isotherm			Freundlich isotherm		
		q_m (mg/g)	K_L (l/mg)	R^2	K_F	$1/n$	R^2
Ni(II)	Methionine templated analcime	40	0.024	0.834	1.39	0.732	0.978
	Free template analcime	32.225	0.029	0.974	1.38	0.689	0.987
Cu(II)	Methionine templated analcime	62.5	0.019	0.903	1.53	0.812	0.984
	Free template analcime	45.45	0.022	0.901	1.37	0.756	0.99

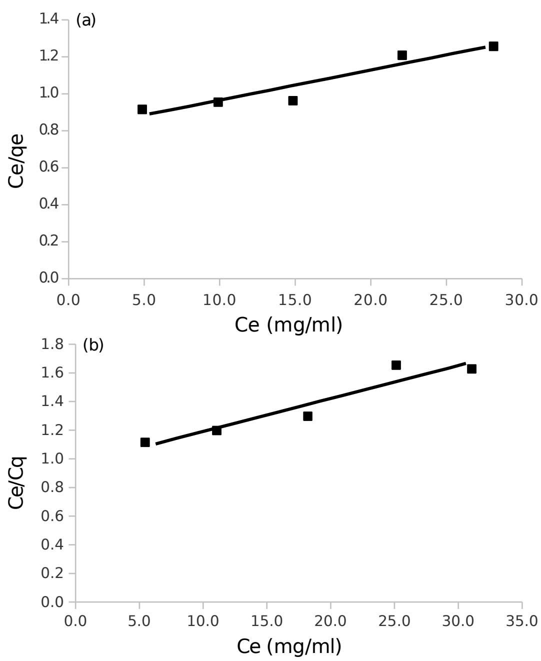

Fig. 4 Langmuir isotherm for Cu(II) adsorption on (a) methionine template analcime: $y = 0.016x + 0.802$ ($R^2 = 0.903$); and (b) free template analcime: $y = 0.022x + 0.970$ ($R^2 = 0.901$).

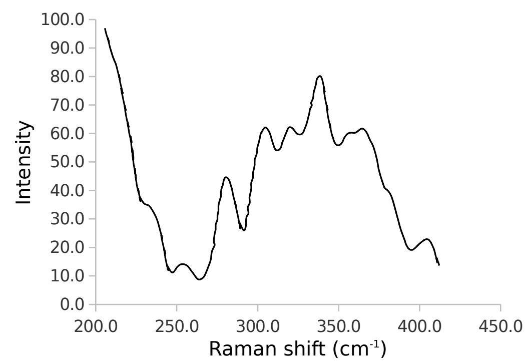

Fig. 5 Resonance Raman spectrum of copper-methionine template analcime.

uptake of Cu(II) and Ni(II) for methionine template analcime were 62.5 and 40 (mg/g) and for template-free analcime were 45.4 and 32.25, respectively. Based on the Freundlich isotherm, the maximum adsorption capacity of Cu(II) and Ni(II) were 1.44 and 1.42 for methionine template analcime while they were 1.38 for the both template and template-free analcime.

The results indicated that a greater uptake of Cu(II) took place compared to Ni(II) under the same conditions of pH, initial metal concentration, and adsorbent concentration. This affinity is in agreement with the reports for other hydrous solids such as activated carbon[19] and has been related to the first equilibrium hydrolysis constant ($-\log K_1$): Cu(II) = 7.9 and Ni(II) = 9.9. It has been confirmed that higher first hydrolysis constantly lowers the degree of solvation of metal ions[20]. Furthermore, the results indicated that methionine template analcime shows higher adsorption ability than template-free analcime.

Analysis of methionine template analcime adsorption by energy dispersive X-ray and Raman techniques

To investigate methionine effect on adsorption of Cu(II) and Ni(II) ions, the elemental analyses of the methionine template analcime were carried out by energy dispersive X-ray (EDX). In conclusion, a sulphur peak in the EDX spectrum of methionine template analcime confirmed the existence of sulphur atoms in this zeolite.

In addition, the Raman resonance technique was applied to characterize Cu—S and Ni—S bond stretching frequencies. The Raman spectrum of methionine template zeolite after adsorption of Cu(II) and Ni(II) reveals the existence of Cu—S and Ni—S linkage (Figs. 5 and 6).

The data provides strong evidence for the assignment of low-frequency (~350–400 cm^{-1}) peak in the resonance Raman spectra of the blue copper-methionine as a Cu—S (methionine) stretching vibration[20] and low-frequency (~412 cm^{-1}) peak as a Ni—S (methionine) stretching vibration[21].

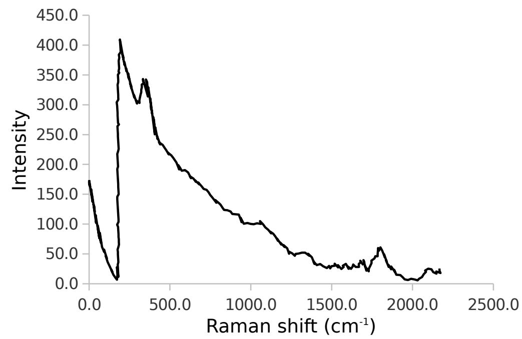

Fig. 6 Resonance Raman spectrum of nickel-methionine template analcime.

CONCLUSIONS

The results indicated that both methionine template analcime and template-free analcime zeolites effectively adsorb Ni(II) and Cu(II) ions in aqueous solution with an adsorption capacity in the sequence Cu(II) > Ni(II). In addition, these heavy metals exhibited an increased affinity to the methionine template analcime zeolite surface with respect to template-free analcime. The Cu—S and Ni—S bonds between methionine and heavy metals may be a good confirmation for the higher adsorption capacity of methionine template analcime.

It is believed that this new adsorption method, which is based on modifying the zeolite synthesis gel by adding the template containing sulphur in the gel system, could have a good potential for future applications of adsorption of pollutants on other zeolites.

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