

Equilibrium and kinetic studies for the adsorption of cadmium ion on Zeolite 4A

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Abstract

In the present study batch removal of cadmium ion from aqueous solution using Zeolite 4A was investigated. The influence of pH, sorption time, adsorbent dosage and initial metal ion concentration had been evaluated. The adsorption parameters were determined using both Langmuir and Freundlich isotherm models. The pseudo second order kinetic model was found to correlate the experimental data well with correlation coefficient R^2 value of 0.9987. The results of the study showed that Zeolite 4A can be efficiently used for removal of cadmium ion from waste water.

Keywords: Zeolite 4A, Cadmium, adsorption, Isotherms, kinetics

Introduction

The removal of toxic and polluting heavy metal ions from industrial effluents and water supplies in an effective manner is the need of the day. In the present study, cadmium ion (Cd (II)) is considered due to its toxicity and high disposal rate. Toxic effects of cadmium on humans include both chronic and acute disorders. Adsorption as a waste water treatment process is found to be one of the most cost effective and safe methods (Volesky 1995; Ahalya 2003).

Adsorptions of heavy metals by using Zeolites have been intensively studied recently because of its excellent binding properties. Zeolites are a special class of molecular sieves with alumino silicates as skeletal composition. The removal of metal ion takes place in Zeolite in two steps i.e., by adsorption and by ion exchange process (Panneerselavam et al. 2009). The present work deals with the assessment of the potential of Zeolite 4A for removal of cadmium ion in a batch system.

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Materials and methods

Adsorbent and preparation of metal ion solutions

Zeolite 4A used in this study, was procured in the form of cylindrical pellets with 1.5mm diameter, from National chemicals, Vadodara (India). The metal stock solutions were prepared from cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$) of analytical grade by dissolving in double distilled water. The concentration of metal ions was measured using atomic absorption spectrometer (GBC 932 plus) at the wavelength of 326.1nm. The pH of the solution was adjusted with dilute nitric acid and sodium hydroxide solution.

Adsorption studies

The batch adsorption experiments were carried out in 250ml conical Erlenmeyer flasks with 100ml cadmium ion solution on a rotary shaker. The effect of pH on the adsorption capacity of Zeolite 4A for Cd (II) was evaluated in the pH range of 3 – 8. The initial pH of metal solution was adjusted by using dilute NaOH and HNO_3 . Then 1g of adsorbent was added to the cadmium ion solution and the reaction mixture was shaken on an orbital shaker at 150 rpm for 2hr at ambient temperature, to reach equilibrium. Similarly, the effect of adsorbent mass (0.1 to 2.0g i.e. 1to20g/l), initial metal ion concentration (100 – 1000 mg/l), contact time (0 – 180 min) on the metal species adsorption was performed. In the adsorption experiments, unless otherwise conditions stated, adsorbent dose, temperature and initial metal ion concentration were 10g/l, 28°C and 100mg/l, respectively. After the adsorption, the samples were centrifuged, filtered to analyze the metal ion concentrations. All the experiments were conducted in duplicate and the mean values were used in the data analysis.

The amount of adsorbed cadmium ion by Zeolite 4A was calculated as follows.

$$q = \frac{v(C_i - C)}{m} \quad \text{----- (1)}$$

Where q is the metal uptake (mg metal/ gram of the adsorbent), v is the initial volume of the adsorption medium (l), C_i is the initial concentration of the metal in the solution (mg/l), C is the final concentration of metal in the solution and m is the amount of the added adsorbent on the dry basis (g) (Wang 2006).

Percentage removal of cadmium ions were calculated by

$$\% \text{ adsorption} = \frac{(c_i - c)}{c_i} * 100 \quad \text{---- (2)}$$

Results and Discussions

Effect of initial pH

Solution initial pH is a critical parameter for adsorption experiments. This parameter is directly related with the competition of hydrogen ions with metal ions to active sites on the adsorbent surface.

At low pH, the adsorption capacity for all metal ions is very low, because large quantities of hydrogen ions compete with metal ions at sorption sites. As the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake (Fan et al. 2008). The pH was varied from 3 to 8 during study and the results are shown in Figure 1. As the pH increased from 3.0 to 7.0, the adsorption efficiency of zeolite 4A to remove cadmium ion also increased from 85.29% to 92.83%. However, metal precipitates at high pH values i.e. above pH of 7.0 inhibit the contact of metal ion with the adsorbent. Decrease in sorption was noted with further increase in pH and this may be attributed to low solubility of cadmium at high pH.

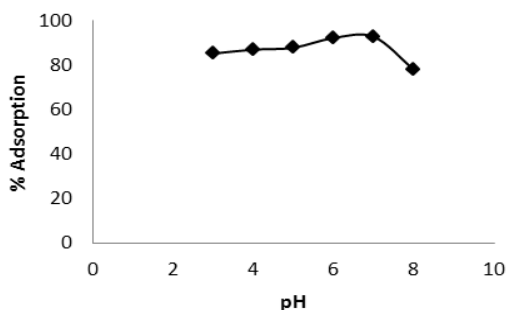


Figure 1: Effect of pH on adsorption of cadmium by Zeolite 4A at temperature 28 °C, adsorbent dosage 10g/l, 2hr contact time, 100mg/l initial metal ion concentration

Effect of contact time

Contact time plays an important role in the efficient removal of heavy metals using Zeolite 4A. The effect of contact time on cadmium uptake capacity by Zeolite 4A is shown in Figure 2. Removal efficiency has increased from 60.46% to 92.83% as the contact time increased from 10 min to 180 min and a large amount of cadmium ions were removed in the first 1hr and equilibrium was reached in 2hr. These results indicate that adsorption is rapid in the initial stages but slowed in the later stages until the attainment of equilibrium.

Effect of adsorbent dose

The effect of adsorbent dosage on the adsorption of cadmium by Zeolite 4A is shown in Figure 3. It is clearly seen that the percentage removal of cadmium by Zeolite 4A increases with increase in adsorbent dosage. With increase in adsorbent mass, the number of binding sites for the ions also increases (Ajaykumar et al. 2009). It was observed that the adsorption efficiency increased from 41.38% to 92.83% as adsorbent dosage varied from 1 to 10g/l.

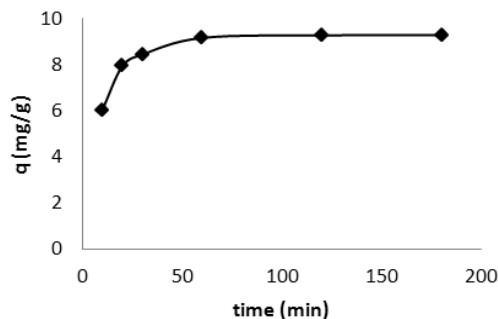


Figure 2: Effect of time on adsorption of cadmium by Zeolite 4A at temperature 28 °C, adsorbent dosage 10g/l, pH 7.0, 100mg/l initial metal ion concentration

At higher dosage 20g/l, the percentage removal of metal ion has decreased to 72.87%. This may be due to blockage of active sites with increase in adsorbent dosage. The metal uptake decreased from 41.38 to 3.64 mg/g with increase in adsorbent dosage.

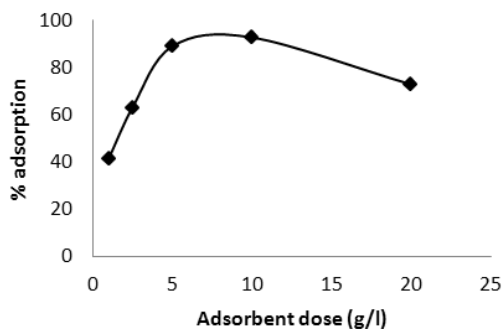


Figure 3: Effect of adsorbent dose on adsorption of cadmium by Zeolite 4A at temperature 28 °C, pH 7.0, 2hr contact time, 100mg/l initial metal ion concentration

Effect of Initial metal ion concentration

The initial metal ion concentration provides an important driving force to overcome all mass transfer resistances of the metal between aqueous and solid phase. Figure 4 indicates the effect of initial metal ion concentration on the removal of cadmium by Zeolite 4A. The removal efficiency has decreased from 92.83% to 43.79% with increase in metal ion concentration from 100 to 1000mg/l. The metal uptake increased from 9.28 to 43.79mg/g.

Adsorption isotherms

The equilibrium adsorption isotherm is of importance in the design of adsorption system. Langmuir and Freundlich isotherms are selected in this study.

Langmuir adsorption isotherm model is given by

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad \text{---- (3)}$$

Where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/l), b is a constant related to the energy or net enthalpy of adsorption (l/mg) and q_{\max} is the maximum adsorption capacity of adsorbent (mg/g). The values of Langmuir constants q_{\max}

and b were calculated from the slope and intercept of the linear plot of $1/q_e$ vs $1/C_e$

The Freundlich model is represented by

$$q_e = KC_e^{1/n} \quad \text{---- (4)}$$

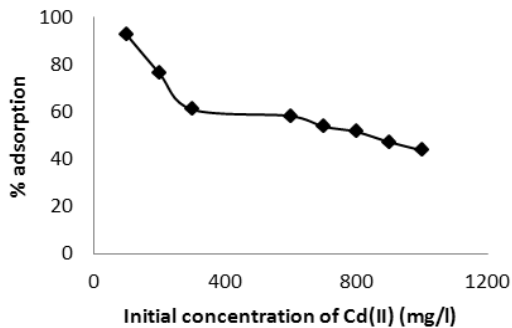


Figure 4: Effect of initial metal ion concentration on adsorption of cadmium by Zeolite 4A at temperature 28 °C, pH 7.0, 2hr contact time, adsorbent dose 10g/l

Where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/l), K and n are equilibrium constants indicative of adsorption capacity and adsorption intensity respectively (Wang 2009). The Freundlich constants were determined from the slope and intercept of linear plot of $\ln q_e$ vs $\ln C_e$.

The Langmuir and Freundlich constants calculated from linearized form of the corresponding isotherms are listed in Table.1. The data fit well with Langmuir isotherm than Freundlich isotherm as evident from the regression coefficients.

Table 1: Adsorption isotherm constants for cadmium ion adsorption

etal ion	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	b (l/mg)	R^2	K	n	R^2
Cd (II)	80.640	0.0198	0.936	2.076	5.154	0.907

Adsorption kinetics

The time dependent experimental adsorption data was used for kinetic modeling. The model equation used for fitting the data is pseudo second order equation given by

$$\frac{t}{q} = \frac{1}{h} + \frac{t}{q_e} \quad \text{---- (5)}$$

where $h = k_2 q_e^2$

k_2 is pseudo second-order rate constant. k_2 can be determined from the intercept of linearized plot of t/q versus t (Volesky 2001). The process of sorption follows second order kinetics with $k_2=0.032\text{g/mg.min}$. The correlation coefficient R^2 has an extremely high value of 0.9987 indicating the adsorption process is chemisorption.

Conclusion

The high potential of Zeolite4A for removal of Cadmium ion from aqueous solution was demonstrated in this study. The initial pH

significantly influenced cadmium uptake. The sorption capacities of cadmium increased with initial metal ion concentration but decreased with the increase in biomass dose. The data fit well with Langmuir model while the kinetic data were represented by pseudo second order kinetic model. The results indicated that Zeolite 4A can be used as an inexpensive effective adsorbent for cadmium removal.

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