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Letter to Editor

Removal of Cadmium from Wastewater Using Ion Exchange Resin Amberjet 1200H Columns

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Abstract

The aim of this study was to remove Cd^{2+} by ion-exchange resin Amberjet 1200H in flow condition. The adsorption characteristics of metal onto the resin were accurately described by Freundlich isotherms. The ion exchange of cadmium on resin follows pseudo-second-order kinetics. Ion exchange capacities of the cadmium on the ion exchange resin was studied in metal solution. The capacities of sorption were 3.0 meq Cd/g, and the resin can be generated by HCl.

Keywords: heavy metal, ion-exchange, resin, regeneration, column

Introduction

Cadmium is a toxic heavy metal present in wastewaters from a variety of industries. Therefore, it is necessary to remove it before discharge into the environment. Different methods can be used for removing metals, including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption [1-5]. Ion exchange is the most common and effective process, particularly in drinking water purification and the concentration and removal of hazardous substances at very low concentrations in chemical process industries. Therefore, ion exchange appears to be a promising candidate for this purpose [6]. Different types of ion-exchange resins are often used in adsorption processes. A gel resin containing sulfonate groups (Dowex 50W) was investigated for removal of Cd^{2+}. The amount of sorbed metal ion was 4.7 meq/g dry resin [7]. Another investigated that the sorption capacity of the Amberlite IR-120 resin for Cd was 3.3 meq/g [8]. Purolite S-950, commercially available, can also be applied for removal of Cd^{2+} from the solutions containing Ni^{2+} ions by Koivula. R. This ion exchanger of the polystyrenedivinylbenzene matrix includes weak acidic aminophosphonic groups [9].

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Amberjet 1200H is a strong acidic resin with sulphonate functionality. The ion-exchange interactions that may occur during metal removal can be expressed as follows:

$$nRSO_3 - H^+ + M^{n+} \leftrightarrow nRSO_3^- - Mn^+ + nH^+ \qquad (1)$$

...where ($-RSO_3^-$) and M represent the anionic group attached to the ion exchange resin and the metal cation, respectively, while n is the coefficient of the reaction component, depending on the oxidation state of metal ions.

In the present study, Amberjet 1200H cation exchange resin was used for removal of cadmium from solution. Batch Cd^{2+} ion exchange, kinetic studies, fixed column experiments as well as desorption studies of resin have been investigated.

Material and Methods

Characteristics of the Cation Exchange Resin

The strong acid cation exchange resin 1200H (Rohm and Haas USA) was characterized with regard to its adsorption properties for specific heavy metals. Physical and chemical properties of the resin are shown in Table 1.

Table 1. Characteristic properties of the ion exchange resin used[a].

Amberjet 1200H	
Matrix	Styrene divinylbenzene copolymer
Functional groups	$-SO_3^-$
Physical form	Insoluble amber beads
Ionic form as shipped	H^+
Total exchange capacity	≥1.8 eq./l (H^+ form), ≥2.0 eq./l (Na^+ form)
Moisture-holding capacity	49-55% (H^+ form)
Shipping weight	800 g/l
Specific gravity	1.18-1.22 (H^+ form)
Uniformity coefficient	≤1.2
Harmonic mean size	630 ± 50 μm
Fine content	<0.300 mm (0.1% maximum)
Coarse beads	>0.850 mm (10% maximum)
Maximum reversible swelling	$Na^+ \rightarrow H^+$ (10%)

[a] Manufacturer supplied

Chemical

The pH-meter was calibrated using standard buffer solutions of known pH. pH adjustment was done by 0.1M NaOH or HCl.

A stock of 1,000 mg/l of cadmium was prepared by dissolving 2.2822 g, $3CdSO_4 .8H_2O$ in 1000 ml distilled water. Distilled water was used throughout the work. No other salts were added to adjust ionic strength.

Instrumentation

A Unicam 919 atomic adsorption spectrometer (AAS Unicam, England) was used for Cd^{2+} analysis. A pH meter CI-316 (ELMETRON, Poland) was used for pH measurement. A peristaltic pump was used (pp1B-05A ZALiMP, Poland) for column tests.

Batch Methods

Batch experiments are carried out with resin Amberjet 1200H to investigate the adsorption kinetics, effect of pH, and adsorption isotherms. This procedure involved using working solutions with Cd^{2+} concentration of 5 mg/l prepared from the standard solution of cadmium sulfurate, diluted to 100 ml with distilled water.

To develop adsorption isotherms, the method of adding different quantities of adsorbent (0.03 g, 0.04 g, 0.05 g, 0.1 g, 0.2 g, 0.5 g dry matter) to a constant solution volume (100ml) at the same initial concentration (C_0=const) was used, investigated pH value aeffected (pH=2.0, 3.0, 4.0, 5.86, 7.0), and pH value corrected by 0.1M HCl.

Preliminary runs showed that approx. 3 h were needed to reach equilibrium.

After equilibrium, the solution and resin were separated and the solution was analyzed by AAS.

Fixed-Bed Column Studies

The glass column of Cd^{2+} filled with 12.3 g of resin Amberjet 1200H, the column used the 1min empty bed contact time and with a loading rate of 10 m/h. The initial concentration of 40 mg/l, operated for a period of some days continuously without interim back washing as fixed-bed down-flow reactors. Inflow pH was not adjusted.

The columns are first filled with distilled water and run through the column prior to starting the experiments in order to wet the columns and to establish equilibrium between the adsorbent and the water.

Regeneration Studies

The loaded column was regenerated after the first loading by cycling 6%HCl solution. For reconditioning, columns were rinsed with deionized water and the pH was readjusted before reloading.

Fundamental Principle

In a system such as this, the metal concentration on the sorbent will increase until equilibrium is reached between the solid and liquid phases in the system. The concentration of metal on the medium is calculated as the difference between the original concentration of the solution and the measured concentration in the liquid phase after contact. The mass balance may be expressed as:

$$m(N_e - N_0) = V(C_0 - C_e) \tag{2}$$

...where: $N_0 = 0$ typically, let $x = V(C_0 - C_e)$

...so, $$N_e = \frac{V(C_0 - C_e)}{m} = \frac{x}{m} \tag{3}$$

The N_e value the mass/mass ration of metal/sorbent, single-component mass-basis isotherms for the Cd^{2+} investigated is presented in Figs. 2-4.

The most frequently used isotherms for the mathematical representation of this type of data is Freundlich Eq (4) [10]:

$$N_e = K_F C_e^{1/n} \tag{4}$$

...which can be linearized as:

$$\log N_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

...where:

V – volume of solution (l),

x – mass of metal captured by media (mg),

C_0 – initial liquid phase metal concentration (mg/l),
C_e – equilibrium liquid phase metal concentration (mg/l),
N_e – equilibrium metal concentration on media (mg/g),
m – media mass (g),
K_F – Freundlich isotherm constant (l/g).

Result and Discussion

Equilibrium Adsorption Isotherms

In Fig. 1 shows that isotherm data were fitted with the Freundlich model, $N_e=K_F\ C_e^{1/n}$. Resulting K_F values was 8.6012 and 1/n value was 0.6048. The satisfactory correlation (R^2) was 0.9976, indicating an excellent fit for the observed data.

Effect of pH on Ion Exchange Resin Amberjet 1200H

The effect of pH on the removal of Cd^{2+} by the ion exchange resin were studied at room temperature by varying the pH of metal solution-resin suspension from 2.0 to 7.0. The results are shown in Fig. 2.

The removal of Cd^{2+} exhibited that the greater increase in the sorption rate of metal ions on resin were observed in a pH range from 4 to 7. Metals were poorly adsorbed at pH<2. This may be due to increasing Cd^{2+} adsorption with decreasing pH lead to fewer OH^- ions in low pH conditions that could compete with the cadmium anions. It is noted that other results were obtained in a previous study by S. Rengaraj et al. [12], on the removal of trivalence chromium by the resin Amberjet 1200H, 1500H. The greater percentage was adsorbed in the pH range 2-6, more than 90% Cr^{3+} was removed.

Packed Columns

The adsorption column was operated until no further cadmium removal was observed (i.e. solute concentration in influent $C_0 \approx$ solute concentration in effluent C. The results are shown in Fig. 3.

From the reported data it can be observed that the initial adsorption is very high, decreases sharply and progressively over time in an almost vertical trend. The average capacity of Cd^{2+} is approx. 3.0 meqCd/g.

The Adsorption Kinetic Model

It is necessary to predict batch kinetics for the design of sorption systems. Previously several researchers used different kinetic models to predict the mechanism involved in the sorption process. These kinetic models can either be based on the concentration of solute or such as the first order [12] or second order [13]. In our studies we applied the first order and second order to compare the results.

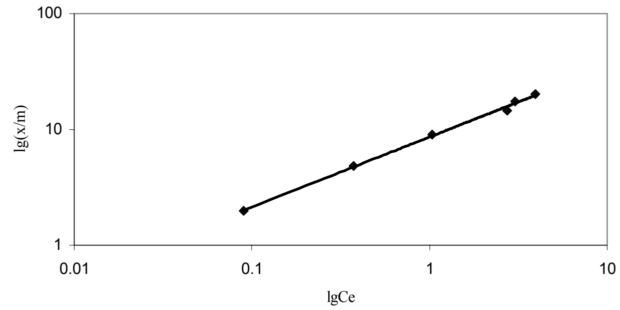

Fig. 1. Linear isotherm plot for the ion exchange of Cd^{2+} on Amberjet 1200H.

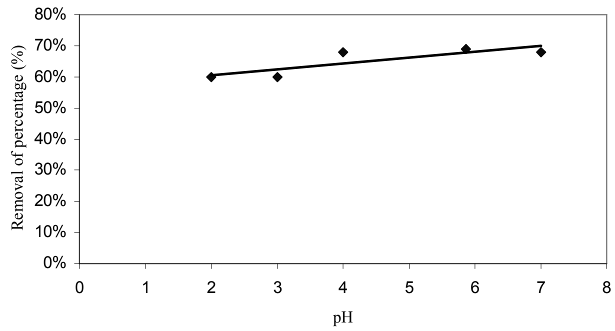

Fig. 2. Effect of pH on resin Amberjet 1200H.

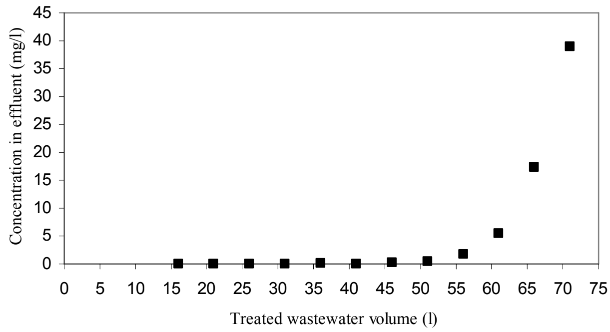

Fig. 3. Effluent of Cd^{2+} removed by resin Amberjet 1200H column.

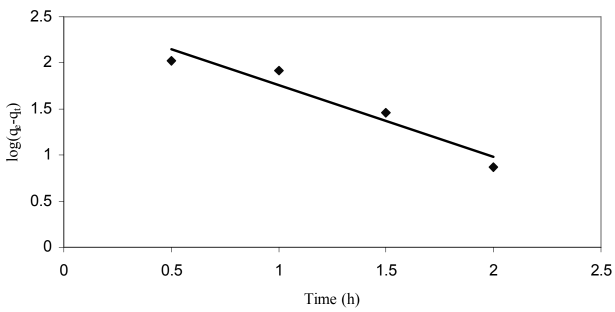

Fig. 4. Lagergren and Svenska plot for the adsorption of Cd^{2+} on ion exchange resin Amberjet 1200H.

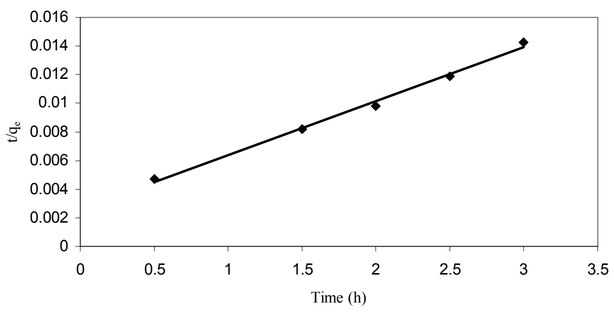

Fig. 5. Ho plot for the adsorption of Cd^{2+} on ion exchange resin Amberjet 1200H.

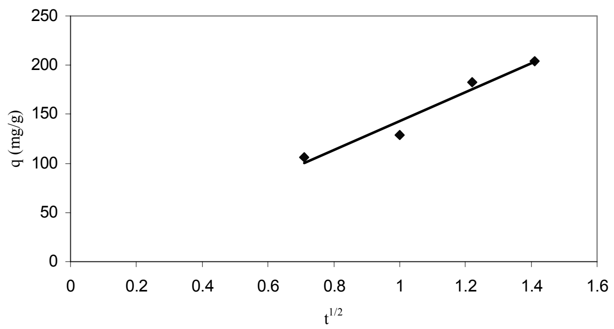

Fig. 6. Plot for the adsorption of Cd^{2+} on ion exchange resin Amberjet 1200H.

The rate constant k can be evaluated by the following pseudo-first-order. Lagergren and Svenska give the following expression:

$$dq/dt=k_{ad}(q_e-q) \quad (6),$$

...integrating Eq. (6) for boundary at time t = 0, and if at the same late time t the concentration has fallen to q, they give:

$$lg(q_e-q)=lgq_e-(k_{ad}/2.303)t \quad [12] \quad (7)$$

From Eq(7), it is evident that for a first-order reaction plot $lg(q_e-q)$ versus t yielded a straight line. The rate constant k can be evaluated by multiplying the slope of the plotted line, $k_{ad}=1.8$. $R^2=0.93$.

Expression of the Ho pseudo second order rate has been present for the kinetics of adsorption as follows [13]:

$$q_t=kq_e^2t/(1+kq_et) \quad (8)$$

...where k is the pseudo second order rate constant (g/mg·min), q_e is the amount of Cd^{2+} adsorbed at equilibrium (mg/g), and qe is amount of Cd^{2+} on the resin Amberjet 1200H at any time, t, (mg/g).

The common used linear form of Eq. (1) is as:

$$t/q_t=1/kq_e^2+t/q_e \quad (9)$$

The rate constant k can be evaluated by multiplying the slope of the plotted line k=0.009, $r^2=0.99$.

Comparing r^2, we concluded that the pseudo second order is well fitted to the reported data.

Intraparticle Diffusion Model

The rate constant for intraparticle diffusion can be evaluated by the following [12]:

$$q= k_{id}\, t^{1/2} \quad (10)$$

The rate constant for intraparticle diffusion, $k_{id}=147.27$. $R^2=0.95$.

Metal ion adsorption is often described as a two-step mechanism. During the first step rapid metal uptake takes place involving external and internal diffusion. Subsequently, a slow step prevails; intraparticle diffusion controls the adsorption rate and, finally, the metal uptake reaches equilibrium.

Conclusion

Ion exchange resin 1200H has been identified as a potentially efficient material for use in the treatment of water contaminated with select heavy metals. Heavy metals removal by ion exchange works effectively in such conditions with pH ranging from 4 to 7. Ion-exchange resin recycled, the heavy metals can be concentrated in a small volume that facilitates waste discharge.

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