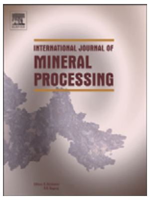
International Journal of Mineral Processing 97 (2010) 68–73

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro



Kinetics and equilibrium studies for the removal of cadmium ions from aqueous solutions using Duolite ES 467 resin

K. Srinivasa Rao *, G. Roy Chaudhury, B.K. Mishra

Institute of Minerals and Materials Technology, (Council of Scientific and Industrial Research) Bhubaneswar-751013, Orissa, India

ARTICLE INFO

Article history:
Received 19 July 2010
Accepted 6 August 2010
Available online 12 August 2010

Keywords:
Kinetics
Equilibrium
Sorption
Cadmium
Langmuir isotherm

ABSTRACT

Kinetic and equilibrium studies were conducted with cation exchange resin (Duolite ES 467) to investigate the effectiveness of removal of cadmium ions from aqueous solutions in a batch mode. The effect of various parameters was studied, such as contact time, agitation speed, sorbent mass, sorbate concentration, pH, competitive ion and temperature. The kinetic data were analyzed by finding their fitness to the well-known Lagergren and pseudo-second-order models using linear and non-linear curve fitting methods. Equilibrium isotherms generated were tested by applying Langmuir and Freundlich isotherm models using both linear and non-linear methods. The optimum contact time and agitation speed were found to be 60 min and 600 rpm, respectively. The presence of sodium chloride ions in solution drastically reduced the cadmium uptake. On the other hand, higher pH and temperature enhanced sorption. The non-linear curve fitting analysis method was found to fit the data better than the linear method. Similarly the Langmuir isotherm model has an edge over the Freundlich model. The calculated thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 indicate the effectiveness of Duolite ES 467 resin to remove cadmium from solution.

1. Introduction

Water and soil are contaminated due to indiscriminate discharge of hazardous solid wastes and liquid effluents. These wastes need to be treated to meet the stringent legislative standards before discharge. Cadmium is one of the toxic metals found in wastewater discharges of electro-plating, battery, photovoltaic cell, metallurgical and textile industries (Salim et al., 1992; Cheung et al., 2000; Grayson and Othumer, 1978). Cadmium is highly toxic and its accumulation in human body causes erythrocyte destruction, nausea, salivation, diarrhea, muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformation (Patterson and Passino, 1987; Lehoczky et al., 1998). Due to its toxicity the permissible limit of cadmium in industrial discharges is set at 0.2 mg L^{-1} by the Ministry of Environment and Forests (MOEF), Government of India, to (MINAS, 2001). The maximum permissible limit of cadmium in drinking water is 0.005 mg L^{-1} as recommended by the WHO. Therefore, the cadmium in the effluents needs to be removed before discharge. A number of techniques reported in the literature to treat cadmium contaminated water, namely chemical precipitation (Esalah et al., 2000), sorption (Kaikake et al., 2007; Mohan and Singh, 2002; Matheickal et al., 1999; Ozer and Pirincci, 2006; Singh et al., 2005; Singh et al, 2006; Mohapatra and Anand, 2007), ion exchange (Koivula et al., 2000; Kocaoba, 2007; Wang and Fthenakis, 2005; Demirbas et al., 2005; Pehlivan and Altun, 2006; Ayuso and Sanchez, 2007) and membrane separation process (Canet et al., 2002). Sorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater. Activated carbon is generally used as the sorbent; however, it is relatively expensive. Though there are some reports on the removal of cadmium using inexpensive agricultural waste materials (Ho, 2006; Ho and Wang, 2004; Benguella and Benaissa, 2002; Cheung et al., 2001; Nouri et al., 2007; Ghodbane et al., 2007), none of these have the potential of regeneration and reuse. Thus the process generates solid waste, which has to be disposed off safely. On the other hand, in the ion exchange process, the resin is reused for sufficient number of times and the metal ions are recovered in a useful form. Recently, Rao et al (Srinivasa Rao et al., 2002; Srinivasa Rao et al., 2005) showed the effectiveness of Duolite ES 467 resin containing aminophosphonic acid functional group to remove heavy metals such as copper, nickel, cobalt, zinc, iron and lead from wastewaters. Resins containing phosphonic acid functional groups like RSPO, Diaion CRP 200 and Purolite S-9500 reported (Dabrowski et al., 2004; Koivula et al., 2000) to remove cadmium from solutions. The kinetics and equilibrium studies of cadmium removal using Duolite ES 467 resin have not been reported so far to the best of our knowledge. Keeping in view the above factors, the present study was undertaken and the results are incorporated in this communication.

2. Materials and methods

2.1. Sorbate

Stock solutions of cadmium (1400 mg L^{-1}) were prepared by dissolving the appropriate amount of its sulfate ($3CdSO_4 8H_2O$) in

---

* Corresponding author. Tel.: +91 6742581635; fax: +91 6742581066.
E-mail address: srkaranam@yahoo.com (K.S. Rao).

0301-7516/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.minpro.2010.08.003

distilled water. The required concentration was prepared by suitably diluting the stock solution. All chemicals used in this study were of analytical grade. Before mixing with the resin, the pH of each solution was adjusted to the required value with either 2% H_2SO_4 or 0.1 M NaOH solutions.

2.2. Sorbent

The resin (Duolite ES 467) was obtained from Diamond Shamrock (I) Ltd. Mumbai, India. The resin has aminophosphonic groups with the general formula R-CH_2-NH-CH_2-PO_3Na_2, where R represents the resin matrix. The properties of the resin were reported elsewhere (Srinivasa Rao et al., 2002). In the present case, acid form of the resin was used.

2.3. Method

Sorption studies were carried out in a two-necked round bottom flask. The whole set-up was kept in a thermostatic water bath (Buchi make, model B480). Agitation was done using fractional HP Remi stirrer. Unless otherwise specified, all experiments were carried out under the following conditions: pH 4.9, adsorbent amount 2 g, sorbate concentration 140 mg L^{-1}, agitation speed 600 rpm, temperature 30 °C and solution volume 200 mL. The aqueous samples were collected at predetermined time intervals and analyzed for the remaining cadmium concentration with atomic absorption spectrophotometer (Perkin Elmer AA200). The pH_{PZC} of the resin was determined by the method of Balistrieri and Murray 1981. Accordingly, to a series of 100 mL polythene bottles containing 40 mL of the 0.01 M KNO_3 solution, different volumes of either 0.1 M HCl or 0.1 M NaOH solution were added to obtain wide range of pH values from 2 to 9.The total volume of the solution in each bottle was made up to 50 mL by addition of distilled water. After 2 h of equilibration, the pH values were noted (pH_i) and known amount of resin was added. After 72 h of equilibration at room temperature with intermittent shaking, the pH values of the supernatant liquid was measured (pH_f). The difference between pH_i and pH_f (ΔpH) were plotted against pHi. The solution pH at which ΔpH is zero is called pH_{PZC} of the resin. Similarly, pH_{PZC} of the Cd(II) loaded resin was determined.

Efficiency is calculated from the following Eq. (1)

$$\%\text{Adsorption or Adsorption Efficiency} = 100 \times (C_0 - C_f) / C_0 \quad (1)$$

where C_0 and C_f are the initial and final Cd(II) concentrations, respectively, in the solution.

Non-linear regression analysis was performed to determine the model parameters for the pseudo-second-order kinetic equation. A trial-and-error procedure was used for the non-linear method using the *solver* add-in with Microsoft Excel spreadsheet.

3. Results and discussion

3.1. Sorption kinetics

3.1.1. Effect of contact time

Sorption reaction was carried out using 200 mL solution containing 90 mg L^{-1} of cadmium and 2 g of resin. Fig. 1 shows cadmium uptake capacity of the resin at different time intervals. It was observed that the kinetics of sorption could be divided into two parts, i.e., the initial faster phase followed by the slower rate. The initial faster rate prevailed for about 15 min followed by the slower rate for 15–60 min. Beyond that there was hardly any sorption indicating attainment of equilibrium.

The rate equation can be modeled using Lagergren pseudo-first-order rate equation (Eq. (2)) or pseudo-second-order rate equation linear (Eq. (3)) or non-linear Eq. (4).

$$\ln(q_e - q) = -k_1 t + \ln q_e \quad (2)$$

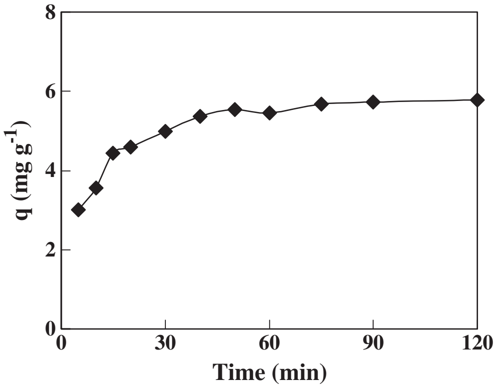


Fig. 1. Effect of time on sorption of cadmium (solution 200 mL, Cd 90 mg L^{-1}, pH 4.8, resin 2 g, rpm 600, Temp. 30 °C).

$$t/q = 1/k_2 q_e^2 + 1/q_e t \quad (3)$$

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where k_1 is the pseudo-first-order rate constant(min^{-1}), q_e the amount of cadmium sorbed at equilibrium(mg g^{-1}), q the amount of cadmium on the surface of the resin at any time (mg g^{-1}), t contact time(min) and k_2 the pseudo-second-order rate constant (g mg^{-1} min^{-1}).

The values of k_1 and q_e were obtained respectively from the slope and intercept of the plot (not shown) between ln ($q_e - q$) versus t, respectively. Though R^2 value was high (0.971) but the lower amount of cadmium sorbed at equilibrium (3.2 mg g^{-1}) as against the actual value of 5.77 mg g^{-1} determined using this model suggest that the Lagergren model does not fit well to the sorption of cadmium by Duolite ES 467.

Since Lagergren model failed to fit the experimental data, data were further tested using pseudo-second-order linear (Eq. (3)) and non-linear (Eq. (4)) models (not shown). Based on the R^2 values for linear (0.97) and non-linear (0.99) models, non-linear model describes the data better. Similar observations were reported in the literature (Ho, 2006; Nouri et al., 2007; Ghodbane et al., 2007).

3.1.2. Effect of stirring speed

In order to find out the effect of mixing, a series of experiments were carried out with 200 mL solution containing 140 mg L^{-1} of cadmium and 2 g of resin by varying the speed of agitation from 400 to 800 rpm. Results are shown in Fig. 2. It is observed that beyond 600 rpm, the rate of sorption increased marginally which indicated that 600 rpm is sufficient to minimize the bulk diffusion mass transfer coefficient.

3.1.3. Effect of initial Cd concentration

The initial concentration of Cd(II) was varied from 70 to 340 mg L^{-1} and the results are shown in Fig. 3. It was found that the cadmium uptake (q) increased with the increase of initial cadmium concentration. The sorption of cadmium increased gradually with increasing contact time and reached a plateau afterwards for all initial concentrations. An increase in cadmium concentration leads to an increase in the sorption capacity of cadmium by Duolite ES 467.

3.1.4. Effect of sorbent mass

The sorbent mass was varied from 5 to 20 g L^{-1} keeping the cadmium concentration constant (90 mg L^{-1}) and the results are shown in Fig. 4 The percentage of Cd(II) sorption increased from 48.4 to 60 with the increase of sorbent amount from 5 to 20 g L^{-1} but the uptake capacity of the resin decreased from 8.56 to 2.67. This may be attributed to the availability of more sorption sites due to higher