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Kinetics and equilibrium studies for the removal of cadmium ions by ion exchange resin

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ABSTRACT

Cadmium is a highly toxic metal which is found in the effluent of battery manufacturing plants. In this study, the ability to remove cadmium ions using an ion exchange resin has been studied in single component sorption-exchange systems.

The maximum sorption capacity of resin for cadmium ions has been reached at pH 5 and the value is 2.20 mmole/g resin. This value shows that resin can effectively remove cadmium ions. The equilibrium isotherms have been analyzed using the Langmuir, Freundlich and Redlich–Peterson isotherm equations and the experimental data are best described by the Redlich–Peterson model.

A series of kinetics studies have been conducted in an agitated batch reactor. Two variables have been studied under two different pH values, namely, 2.5 and 5.0, – different initial metal ion concentrations and different masses of resin. The kinetics of sorption of the cadmium ions have been analyzed by three kinetic models, the pseudo-first order, pseudo-second order and Elovich models. The rate constants and the correlation coefficients of the three kinetic models have been calculated. The experimental data were compared on the basis of SSE values and the pseudo-second model order provides the best fit to the experimental data.

Introduction

Heavy metal ions are one of the major pollutants to human water resources. Some heavy metal ions are extremely toxic, such as lead, mercury and cadmium, even in relatively low concentrations. They are non-biodegradable, so these pollutants will accumulate in plankton and plants and eventually, transfer to humans via the food chain.

A major source of heavy metal pollution in the environment is industrial wastewater, including effluents from electroplating, metal finishing and printed circuit board industries. Cadmium has been found especially in the wastewater from battery manufacturing plants, as it is a major component in the lead–acid battery and nickel–cadmium battery industry [1,2]. These industries produce large amounts of wastewater containing heavy metal ions every year. The wastewater generates a fatal risk to the environment if the wastewater is discharged to the environment without any treatment. An effective and economical treatment is necessary for those kinds of industries.

There are several treatment methods which can effectively treat the metal ion contaminated water. Chemical precipitation is conventionally used for metal ion removal by utilizing chemical precipitation and gravity separation of metal hydroxides. It is suitable when the composition of the wastewater is very consistent. But it is very sensitive to pH changes, changes in composition, and is not compatible with soaps or surfactants [1].

Membrane filtration has become a mature wastewater treatment technique in recent years, however, the size of the pores has to be carefully calculated to exclude undesirable particles, and the size of the membrane has to be designed for optimal operating efficiency. Membranes are also prone to clogging as the pores slowly fill with trapped particles, which means that the system must provide facilities for easy cleaning and maintenance so that it can be kept in good working order [1].

Adsorption and ion exchange systems utilize the ability of special resins to adsorb metals from solution in ionic form at a specific pH. This process is very effective for continuous metal removal [2] from high flow wastewater with low concentrations of heavy metals at a reasonably low cost. Exchange systems allow the treatment of relatively small amounts of wastewater with high concentration of metals (regeneration) [1].

Due to the importance of cadmium pollution from wastewaters a significant amount of research has been dedicated to the search for effective cadmium adsorbents and ion exchangers. Several natural adsorbents have been studied to determine their capacity for cadmium, including peat and lignin [3–5], beech leaves and tree

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fern [6,7], waste bagasse and grains [8–18], rice husk and coconut copra [19–22]. Other more common adsorbents include woods [23–25], hydroxyapatite [26], activated carbons [27–29], fly ash [30,31], algae and biomass [32,33]. In spite of all this research, most of the cadmium adsorption capacities of these natural and agricultural derived materials are of the order of 1 mmole/g of adsorbent material or less.

Research has also been carried out on several naturally occurring mineral ores such as chabazite and clinoptilolite [34], montmorillonite [35], goethite [36,37], perlite [38] and activated alumina [39] with capacities of the order of 1.5 mmol/g adsorbent/exchanger.

Synthetic exchangers have been found to have higher capacities around 2mmole cadmium/g exchange material, including modified MCMs [40] and Amberlite [41]. Only a few papers report kinetic studies on the uptake of cadmium by modified kaolinite clay [42], anaerobic sludge [43] and most of the kinetic studies relate to the hydroxyapatite structure in bone char where chelation and adsorption are both thought to occur [44–49].

In this research, the performance of a chelating ion exchange resin to remove cadmium ions from wastewater has been investigated. The sorption capacities of the resin for cadmium metal ions were determined by adsorption isotherm experiments at two different pH values using the sodium form of an imminodiacetate ion exchange resin. Moreover, the kinetics of the rate of cadmium removal by this system have been investigated by agitated batch kinetic studies using three kinetics models, namely, the pseudo-first-order, the pseudo-second-order and the Elovich models.

Based on the sorption capacity and sorption rate of the resin, the effectiveness of cadmium ion removal by the resin in wastewater treatment can be evaluated.

Theory

Equilibrium isotherm

Adsorption equilibrium isotherms are used to determine the maximum capacity of each sorbent for different sorbates. Furthermore, a best fitting isotherm model is determined in order to correctly represent the results of single component adsorption isotherm experiment. The predicted values from the models are compared with the experimental data.

Each isotherm model is developed under different theories and assumptions. Three of the most widely used isotherms, namely, the Langmuir, Freundlich and Redlich–Peterson have been used.

Langmuir isotherm

Langmuir [50] developed a theoretical equilibrium isotherm in 1916 to calculate the amount of gas adsorbed onto a solid surface at a fixed temperature. It is suitable for describing numerous homogenous, constant energy sorption systems. The mathematical expression is:

$$q_e = \frac{K_L C_e}{1 = a_L C_e} \qquad (1)$$

$$K_L = X_m a_L (\mathrm{dm}^3 \ \mathrm{g}^{-1})$$

where ^{a}ve is the cadmium ion concentration on resin at equilibrium (mmole Cd/g resin); C_e is an equilibrium concentration of cadmium ions in solution (mmole Cd/dm^3); K_L is the Langmuir equilibrium constant (dm^3/g); a_L is the Langmuir constant (mmole/dm^3); $K_L = X_m a_L(\mathrm{dm}^3 \ \mathrm{g}^{-1})$; X_m is the maximum (monolayer) cadmium adsorption capacity (mmole/g ion exchanger)

Freundlich isotherm

The Freundlich equation [51] is the earliest recognized sorption isotherm model. It is usually used to describe the adsorption of organic components in solution onto activated carbon. It could be applied to heterogeneous surfaces and multilayer sorption of the sorbate. The equation is:

$$q_e = a_F C_e^{b_F} \qquad (2)$$

where b_F is the constant related to the enthalpy of adsorption; a_F is the Freundlich constant.

Redlich–Peterson isotherm

The Redlich–Peterson equation incorporates the Langmuir and Freundlich equations. In 1978, Jossens et al. [52] modified the three parameter isotherm proposed by Redlich–Peterson and established the Redlich–Peterson isotherm equation.

The mathematical equation is:

$$q_e = \frac{K_R C_e}{1 = a_R C_e^{b_R}} \qquad (3)$$

where K_R is the Redlich–Peterson equilibrium constant; a_R is the Redlich–Peterson constant; b_R is the parameter to reflect heterogeneity in the adsorption process

And the exponent, b_R, lies between 0 and 1. There are two limiting behaviors: the Langmuir form for $b_R = 1$, and Henry's law form for $b_R = 0$. Because of the three unknowns, a_R, K_R and b_R, the isotherm parameters cannot be found by linearization. Therefore, a minimization procedure using Excel Solver has been adopted to solve the above equation by maximizing the correlation coefficient.

Batch kinetic models

The sorption kinetics of a sorbent depends on the sorbate properties, sorbent properties, the pH of the solution, temperature and the sorbent to sorbate ratio. The sorption process can be divided into a reaction kinetic process, mass transfer process or a combination of the two processes.

In this research, we have concentrated on analyzing the reaction kinetics of the sorption process, three kinetic models (pseudo-first order, pseudo-second order and Elovich equation) have been applied to determine the rate constant of the reaction between resin and the metal ions in the solution.

Pseudo-first-order model

The pseudo-first order equation was proposed by Lagergren [53] is often used in liquid sorption modeling [5]. The mathematical equation is:

$$\frac{dq_t}{st} = k_1 (q_e - q_t) \qquad (4)$$

where q_e and q_t are the sorption capacities (mmole/g resin) at equilibrium and time, t, respectively, k_1 is the rate constant for pseudo-first order equation (L/min). Integrating the Eq. (4), and substituting with the condition: $(q_e - q_t) = 0$ at $t = 0$, Eq. (4) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

By plotting $\ln(q_e - q_t)$ against t, k_1 and $\ln q_e$ can be found from the graph. However, the experiment data is generally different from the equation predicted value, it is because the parameter k_1