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Batch kinetics and isotherms for biosorption of cadmium onto biosolids

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ABSTRACT

A basic investigation into the removal of cadmium ions from aqueous solutions by municipal-wastewater biosolids was conducted in batch conditions. The influences of different experimental parameters such as initial pH, shaking rate, sorption time, equilibrium conditions and initial cadmium-ion concentrations on cadmium uptake were evaluated. According to our experimental results, a pseudo-second-order model was more suitable for describing the biosorption kinetics than the Lagergren model. Kinetic experiments showed that cadmium concentrations reached equilibrium within 2 h. We found that the biosorptive capacity of the biosolids was dependent on solution pH, with pH 4 being optimal. Investigation of the influence of the shaking rate on the biosorption capacity of the biomass showed that an optimum value was obtained between 150 and 250 rpm. The Langmuir isotherm model better represented the sorption process the Freundlich model. The maximum cadmium adsorption capacity of the biosolids (q_{max}) was 0.38 mm/g dry biosolid and the Langmuir constant (k_d) was 0.1044 mm/l.

Keywords: Biosorption; Cadmium; Biosolids; Kinetics; Isotherm

1. Introduction

Cadmium is a toxic heavy metal which is widely used in industry, particularly the electroplating and battery industries. The chronic toxicity of cadmium to humans and the environment has been well documented. In the United States, the safe level of cadmium in drinking water has been set at 0.01 mg/l [1]. The problem with the removal of such contaminants down to levels approved by national or international agencies has not totally been solved by conventional chemical-precipitation procedures [2]. The traditional approaches for removing or recovering metals, such as precipitation, oxidation/reduction, ion exchange, filtration, electrochemical processes, membrane separations and evaporation, all exhibit several disadvantages, such as high cost, incomplete removal, low selectivity, high energy consumption and the generation of toxic slurries that are difficult to dispose of [3]. Biological materials are known for their potential to adsorb heavy metals [4,5].

Biosorption is an emerging technology that uses biological materials to remove metals from solution through adsorption. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [6]. Biosorption mainly involves cell-surface complexation, ion exchange and microprecipitation [7]. The major advantages of biosorption over conventional treatment methods include [4]:

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- Low cost.
- A high efficiency of metal removal from dilute solutions.
- The minimization of chemical and/or biological sludge.
- No additional nutrient requirements.
- Regeneration of the biosorbent.
- The possibility of metal recovery.

Biological wastewater treatment produces a biological sludge (biosolids) consisting of inert materials and microorganisms. Currently, there are limited reuse/disposal options for biosolids due to their high concentrations of heavy metals and the risk of pathogens. Previous research has shown the ability of biosolids to remove metals from the wastewater stream [8]. Waste activated sludge (WAS) consists of the nonliving microorganisms which are no longer required in the wastewater-treatment process and are ready for disposal. Dewatered WAS has a solids content of 13%. To overcome the risk of pathogens as well as the transportation and storage issues associated with live return activated sludge (RAS), dewatered, nonliving WAS was chosen for this study.

2. Materials and methods

2.1. Preparation of biosolids

In this study the required biosolids were sourced from the waste sludge produced at the Ekbatan wastewater-treatment plant in Tehran. This treatment plant was chosen because the wastewater treated is of domestic origin and has low background concentrations of cadmium. Pretreatment of the biosolids included dewatering at 103–104 °C and grinding the biosolids to a grain size of between 50 and 120 standard mesh. The initial concentration of cadmium in the biosolids was measured by nitric acid digestion [9] and atomic-adsorption analysis. The initial value was 0.0000131 mm/g of dry biosolid.

2.2. Chemicals

All chemicals used were of analytical reagent grade and were used without further purification. Cadmium solutions were prepared according to the 'Standard Methods' [9] from analytical reagent-grade cadmium dust ($Ca(NO_3)_2 + 4H_2O$, Merck Company). Stock 0.1 m cadmium solutions were initially prepared and preserved with 1.5 ml of concentrated HNO_3 per liter [9] then diluted prior to use. In all cases where samples needed to be stored, they were preserved as detailed in the 'Standard Methods'. The solution pH was adjusted to the required value with HNO_3 or NaOH. Acid washing with a solution of $1\,HNO_3 + 1\,H_2O$ followed by a triple rinse with distilled water was conducted to avoid metal uptake onto the glassware [9].

2.3. Experimental procedure

The tests were conducted in laboratory scales in a batch reactor system of 800 ml volume. Cadmium solutions of different concentrations were prepared by adequate dilution of the stock solution with deionized distilled water. Batch equilibrium experiments were carried out by adding a measured amount of biosolids to the cadmium solutions. The solution was placed on an electric mixer and mixed until equilibrium was reached. The biosolids were removed by filtration through a 0.45 m membrane filter (Millipore) and the filtrates were analyzed for residual cadmium concentration by atomic-adsorption spectrophotometry (Unicam 919). The experiments were conducted in a temperature-controlled room (25 ± 1 °C). All experiments were conducted at least in duplicate and the average reported in the results.

2.4. Kinetic studies

In these studies, cadmium solutions at concentrations of 0.25, 0.75 and 1.5 mm were used in conjunction with 1.0 g (dry wt.) of biosolids at 25 ± 1 °C. Reaction times of 5, 10, 20, 30, 60, 120, 180, 300 and 420 min were investigated. A shaking rate of 200 rpm and the initial pH of 4 were used.

2.5. pH studies

When investigating the effect of initial pH value, metal concentrations of 0.25 and 0.75 mm were used in conjunction with 1.0 g (dry wt.) of biosolids at 25 ± 1 °C. Initial solution pH was adjusted to 2, 3, 4 or 6. The reaction time was 2 h and a shaking rate of 200 rpm was used.

2.6. Shaking-rate studies

In these studies, metal concentrations of 0.25 and 0.75 mm were used in conjunction with 1.0 g of biosolids at 25 ± 1 °C. Shaking rates of 50, 100, 200 and 300 rpm were investigated. The reaction time was 2 h and an initial pH of 4 was used.

2.7. Sorption equilibrium studies

Biosolids masses of 0.5, 1, 2 and 4 g (dry wt.) were used in conjunction with solution concentrations of 0.25 and 0.75 mm at 25 ± 1 °C. The initial pH was set to 4, the reaction time was 2 h and a mixing speed of 200 rpm was used. These results were used for adsorption isotherm studies and modeling.

3. Results and discussion

3.1. Biosorption kinetics of cadmium uptake onto biosolids

Cadmium-adsorption kinetic profiles at initial solution concentrations of 0.25, 0.75 and 1.5 mm are shown in Fig. 1; the cadmium-uptake equilibrium time at these concentrations was 2 h. With an increase of the initial concentration of cadmium solution, the relative adsorption rate increased in the first 5 min. However, the adsorption rate decreased afterwards.

With increased initial concentration of cadmium, the adsorption rate (adsorption to initial concentration ratio) decreased. More specifically, at the concentration of 0.25 mm, the adsorption was 82.1% of the total cadmium in the system, however, for concentrations of 0.75 and 1.5 mm the adsorption dropped to 44.8% and 28.8%, respectively. Nevertheless, an increase in the initial concentration of a solution will generally increase the total metal adsorption. In previous studies on zinc-ion adsorption by biosolids, Norton et al. [8] found that at concentrations of 0.076 and 0.3 mm equilibrium was achieved in 5 h at pH 4. In their studies the maximum adsorption was 0.006 and 0.026 mm/g of biosolids.

Two different kinetic models were used to fit the experimental data for cadmium biosorption on biosolids. The pseudo-first-order Lagergren model is generally expressed as [10]:

$$\frac{d_q}{d_t} = k_{1,ads}\left(q_e - q\right) \tag{1}$$

where q_e (mg/g) and q are the amounts of adsorbed metal ions on the biosorbent at equilibrium and at any time t, respectively, and $k_{1,ads}$ is the Lagergren rate constant for the first-order biosorption. Integrating (1) between the limits $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ provides:

$$\log(q_e - q) = \log q_e \frac{k_{1ads}}{2.303} t \tag{2}$$

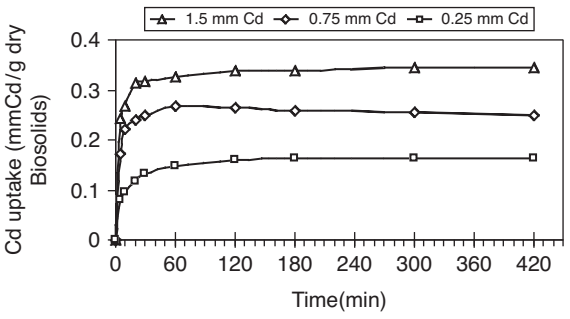

Fig. 1. Cadmium-adsorption kinetic profile at 0.25, 0.75 and 1.5 mm concentrations.

Linear plots of $\log(q_e - q)$ versus t indicated the applicability of this kinetic model. However, to adjust Eq. (2) to fit the experimental data, the value of q_e (the equilibrium sorption capacity) must be pre-estimated by extrapolating the experimental data to $t = \infty$ [10].

The pseudo-second-order model is based on the assumption that biosorption follows a second-order mechanism. Thus, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites:

$$\frac{d_q}{d_t} = k_{2,ads}\left(q_e - q\right)^2 \tag{3}$$

where $k_{2,ads}$ is the rate constant for the second-order biosorption (g/mg·min). Integrating (3) from $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$, and then linearizing it yields Eq. (4):

$$\frac{t}{q} = \frac{1}{k_{2ads}q_e^2} + \frac{1}{q_e}t \tag{4}$$

Here, q_e and $k_{2,ads}$ can be calculated from the slope and the intercept, respectively, of a plot of t/q versus t. It is important to note that it is not necessary to estimate the experimental value of q_e for the application of such a model [10].

The results showed a good fit for cadmium adsorption kinetics with the pseudo-second-order model; in fact, the correlation coefficient for the second-order kinetic model was equal to 1 (exactly 0.999). A value of q_e, 0.281 (mm Cd/g dry biosolid), was obtained which was almost equal to the 0.299 mm/g read from the adsorption diagram. The rate constant of the second-order biosorption, $k_{2,ads}$, was calculated as 0.0097.

In studies on copper biosorption by brown seaweed, it was shown that copper adsorption by *Sargassum chromophyta* followed a pseudo-first-order Lagergren model [10].

Yan and Viraraghavan [11] showed that biosorption of heavy metals like lead, nickel, cadmium and zinc by *Mucor rouxii* biomass did not follow the Lagergren equation; rather they conformed to the Ho false second-degree model.

3.2. Effect of pH on cadmium uptake

Fig. 2 shows the effect of pH on the adsorption of cadmium. As shown here, the effect of pH on adsorption with 0.25 and 0.75 mm cadmium was almost the same. The metal uptake at pH 2 was negligible, thus indicating the possibility of using this pH effect for metal elution and biomass regeneration. In fact, at pH 2, cadmium was leached out of the biomass and into solution. This clearly demonstrated that cadmium uptake increases with solution pH.

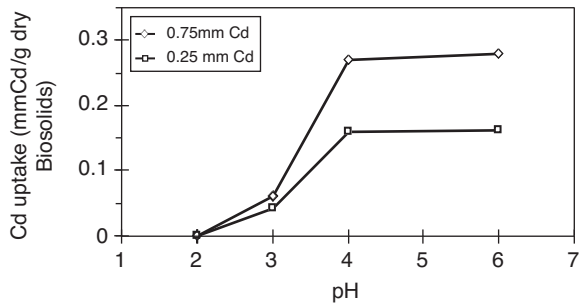

Fig. 2. The effect of pH on cadmium adsorption in 0.25 and 0.75 mm concentrations.

The increase of pH from 2 to 3 slightly increased the adsorption rate; however, from pH 3 to 4 the adsorption rate increased rapidly. At pH greater than 4 the adsorption rate increased insignificantly, therefore the maximum rate of adsorption was at a pH of slightly more than 4.

Norton et al. [8] showed that in zinc biosorption by biosolids, pH 2 was suitable for zinc elution, and with the increase of pH from 2 to 3, the adsorption rate increased exceedingly but afterwards (up to a pH of 6) the increase was insignificant.

Kaewsarn [12] showed that the biosorption of copper by a *Padina* sp. was affected by pH. At pH below 2 the adsorption was minimal and with an increase of pH up to 4 the adsorption increased exceedingly; again, above that value the increase was insignificant.

Mameri et al. [13] suggested that low pH could limit metal adsorption by biomaterial. The ion exchange between metal ions and hydronium ions of some constituent compounds in the biomaterial is believed to be involved in the biosorption mechanism (because at low pH there are more hydrogen ions). Different metals have different pH optima, due to the different solution chemistry of the metals [14]. The low biosorption capacity at pH values below 4.0 was attributed to hydrogen ions competing with metal ions on the sorption sites [15,16]. In other words, at lower pH, due to the protonation of the binding sites resulting from a high concentration of protons, the negative charge intensity on the sites was reduced, resulting in the reduction or inhibition of the binding of metal ions [17]. In fact, most microbial surfaces are negatively charged because of the ionization of functional groups, thus contributing to their metal binding [18,19].

Biosorbent materials primarily contain weak acidic and basic functional groups. It follows from the theory of acid–base equilibria that, in the pH range of 2.5–5, the binding of heavy-metal cations is determined primarily by the state of dissociation of the weak acidic groups. Carboxyl groups (–COOH) are the most important groups for metal uptake by biological materials [20,21]. The ionic states of cell-wall functional groups can be used to explain the pH dependence of biosorption. Low-pH conditions allow hydrogen and hydronium ions to compete with zinc for metal binding sites on the biomass, causing poor zinc uptake. At higher pH values, there are lower numbers of competing hydrogen ions and more ligands are exposed with negative charges, resulting in greater zinc sorption [8].

3.2. Effect of shaking rate on cadmium uptake

Investigation of the influence of the shaking rate on the biosorption capacity of the biomass showed that an optimum value was obtained at between 150 and 250 rpm (Fig. 3). This moderate shaking rate in gave the best homogeneity to the metal solution–biomass granule mixture.

Fig. 3 shows that the effect of shaking was more significant with higher concentrations of cadmium in solution. Here, the cadmium intake reached a peak at a shaking rate around 200 rpm for both 0.25 and 0.75 mm solutions; however, the impact of shaking rate on adsorption in the 0.75 mm was higher, as observed from the slopes of the curves.

In studies on zinc adsorption by inactive *Streptomyces rimosus* bacteria, Mameri et al. [13] showed that 250 rpm was the optimal shaking rate for zinc adsorption by 3 g of *Streptomyces rimosus* biomass at a pH of 6.5 at 20 °C and a concentration of 100 mg/l.

Norton et al. [8] chose the optimal shaking rate of 200 rpm in their studies on zinc adsorption by biosolids.

In his studies on nickel adsorption by sewage ash, Weng [22] selected the optimal shaking rate as 170 rpm.

The reason why adsorption decreased at lower shaking rates is because the biomass granulates agglomerated and thus took much more time to reach equilibrium. These results could be attributed to experimental conditions and to a too-short contact time; at higher speeds, the vortex phenomenon was encountered [13].

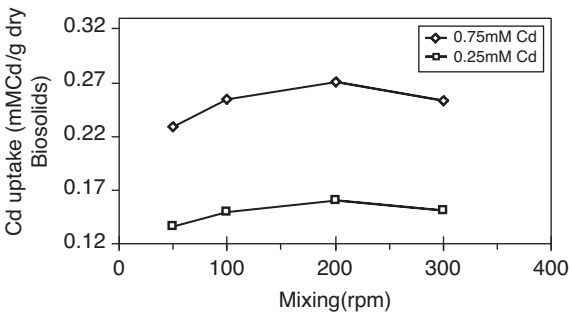

Fig. 3. The effect of shaking rate on cadmium adsorption at 0.25 and 0.75 mm concentrations.

3.3. Adsorption isotherm modeling studies

To examine the relationship between the sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption–isotherm models are widely employed for fitting the data [10].

Among several available adsorption isotherm equations, two isotherms (the Langmuir and Freundlich isotherms) were investigated. These isotherms are widely used to analyze data for water- and wastewater-treatment process [23]. The linear form of the Langmuir equation is:

$$\frac{C_{eq}}{q_{eq}} = \frac{K_d}{q_m} + \frac{1}{q_m} C_{eq} \quad (5)$$

where C_{eq} is the equilibrium metal solution concentration, q_{eq} is the amount of metal adsorbed onto the biosolids at equilibrium, q_{max} is the Langmuir constant for the maximum metal uptake and K_d is also the Langmuir constant related to the energy or net enthalpy of adsorption by the Arrhenius equation [11,24–26].

The Freundlich equation is given by:

$$q_{eq} = K_F (C_{eq})^{1/n} \quad (6)$$

where K_F and n are the Freundlich constants characteristic of the system, indicating the adsorption capacity and the adsorption intensity, respectively. To simplify the derivation of K_F and $1/n$, Eq. (6) can be linearized in logarithmic form as Eq. (7) [10]

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

The Langmuir and Freundlich constants, along with their R^2 values, were calculated from the plots of biosorption data for cadmium on the biosorbent (Figs. 4 and 5). The correlation regression coefficients showed that Langmuir isotherm best fit the experimental data over the studied range (the R^2 values for the Langmuir and Freundlich models were 0.9852 and 0.9239, respectively).

The maximum adsorption capacity (q_{max}) was determined to be 0.37 mm/g (41.5 mg/g) with a Langmuir constant of 0.1044 mm/l (11.73 mg/l). These values compare well with other data reported in the literature.

Akar and Tunali [27] reported a maximum cadmium uptake capacity of 17.03 ± 0.76 mg/g (Langmuir model) using the fungus *Botrytis cinerea*.

According to the results of Goksungur et al. [28], the maximum capacity of cadmium adsorption in the Langmuir model was 31.75 mg/g by *Saccharomyces cerevisiae*.

Hawari and Mulligan [29] reported a maximum cadmium uptake capacity of 0.53 mm/g (Langmuir model) using anaerobic sludge granules.

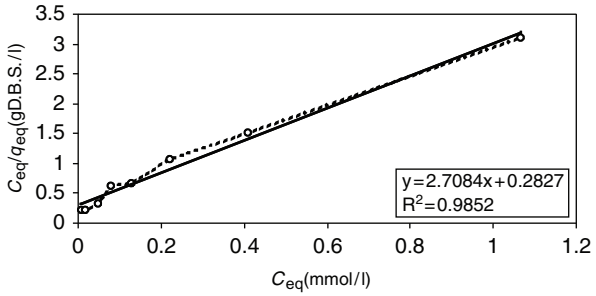

Fig. 4. Langmuir adsorption isotherm of cadmium ions on biosolids.

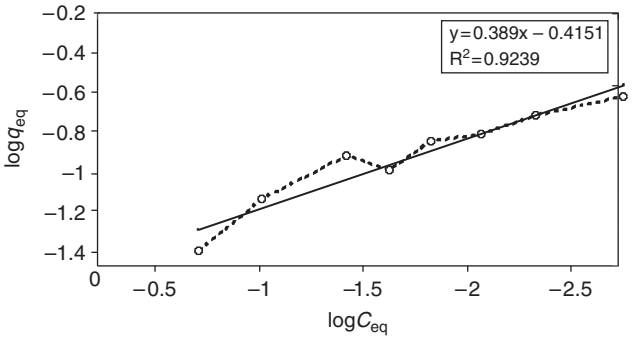

Fig. 5. Freundlich adsorption isotherm of cadmium ions on biosolids.

4. Conclusions

The following conclusions can be drawn from the laboratory experiments:

- The kinetic experiments showed that the metal-uptake equilibrium took 2 h for cadmium at concentrations of 0.25, 0.75 and 1.5 mm and its adsorption kinetics followed a pseudo-second-order model.
- The increase of pH from 2 to 3 increased the adsorption insignificantly, whereas the increase of pH from 3 to 4 increased the adsorption exceptionally. Also, at pH values over 4 the increase in adsorption was not significant. Therefore, the maximum cadmium adsorption was at a pH slightly over 4 and pH 2 would be suitable for metal elution.
- The optimum shaking rate for cadmium adsorption was 150–250 rpm at 0.25 and 0.75 mm concentrations.
- The Langmuir adsorption isotherms at pH 4 indicated the adsorption capacity of the dry biosolids was 0.37 mm/g dry biosolids (41.5 mg/g). This compares favorably with other biosorbents. This indicates the potential for further study on the use of biosolids for the biosorption of cadmium and other metals.

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