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Biosorption of cadmium(II) and lead(II) ions from aqueous solutions onto dried activated sludge

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Abstract: The removal of heavy-metal ions from aqueous solutions by using dried activated sludge has been investigated in batch systems. Effect of solution pH, initial metal ion concentration, and temperature were determined. The results of the kinetic studies showed that the uptake processes of the two metal ions(Cd(II) and Pb(II)) followed the pseudo-second-order rate expression. The equilibrium data fitted very well to both the Langmuir and Freundlich adsorption models. The FT-IR analysis showed that the main mechanism of Cd(II) and Pb(II) biosorption onto dried activated sludge was their binding with amide I group.

Keywords: biosorption; adsorption isotherm; cadmium; lead; activated sludge

Introduction

Toxic metal compounds are frequently used in industrial processes and are widely distributed in the environment. Due to their extended persistence in biological systems and tendency to bioaccumulate as they move up the food chain, they represent important environmental and occupational hazards. The methods which have been used to remove heavy metal ions, such as chemical precipitation, redox, membrane, ion-exchange, solvent extraction and so on, are both costly and ineffective, particularly when there is a very low concentration of heavy metals (Gulnaz *et al.*, 2005).

Adsorption is a well-established technique for heavy metal removal. Activated carbon is the most efficient and popular adsorbent and has been used with great success for the removal of heavy metal, but due to its high regeneration cost and losses in the application processes, it cannot be used on a great scale (Lee *et al.*, 1998; Reed *et al.*, 1996). At present, there is growing interest in using low cost, non-conventional alternative materials including yeast biomass, clays, siderite, sawdust, fly ash, etc., instead of activated carbon for heavy metal removal from wastewaters (Vasudevan *et al.*, 2002; Tsai *et al.*, 2004; Erdem and Ozverdi, 2005; Li *et al.*, 2003; Jiang *et al.*, 2004). The use of activated sludge biomass as adsorbent also offers a potential alternative to existing methods for heavy metal removal (Aksu *et al.*, 2000, 2002). The cell walls of activated sludge biomass, essentially consisting of various organic compounds such as chitin, lipids, amino acids and other cellular components offer many functional groups which can bind metal ions such as carboxylate, hydroxyl, sulphate, phosphate and amino groups. In the concept of biosorption, several physical or chemical processes may be involved such as physical and/or chemical adsorption, ion exchange, coordination, complexation, chelation and microprecipitation.

In this paper, the use of dried activated sludge as a biosorbent for the removal of Cd(II) and Pb(II) ions from aqueous solution was investigated through batch experiments and the influence of some parameters on the biosorption process, such as solution pH, initial metal ion concentration and temperature has been examined. The pseudo-second-order model was adopted to evaluate its usefulness for describing the adsorption system. The mechanism of Cd (II) and Pb(II) biosorption on dried activated sludge was also studied.

1 Experimental

1.1 Preparation of the biosorbent and adsorbate

Activated sludge, a complex consortium of micro-organisms mainly containing bacteria was derived from a Qu Yang (Shanghai) municipal biological wastewater treatment system (aerobic activated sludge system). Biosorbed divalent cations by activated sludge in the activated sludge system were investigated and Cd(II) and Pb(II) ions were not detected on dried activated sludge. Activated sludge biomass was centrifuged at 2000 r/min for 5 min, washed twice with deionized water to remove easily suspended materials, dried at 60℃ until constant weight and then ground to a gritty consistency to yield granular biosorbent samples. Analytical grade $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ were used as adsorbates. The stock solutions of Cd(II) (500 mg/L) and Pb (II) (500 mg/L) were prepared by dissolving the adsorbates in distilled water, which were further

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diluted to the required concentrations before being used. Before mixing the dried activated sludge with solution, the pH of each test solution was adjusted to the required value with HCl and NaOH solutions.

1.2 Biosorption experiments

Adsorption of the heavy metals was carried out by batch experiments. The effect of pH on biosorption was investigated in pH ranges of 2.0—8.0 and 2.0—6.0 for Cd(II) and Pb(II), respectively. The pH of each solution was adjusted with 1.0 mol/L HCl or NaOH solutions. In each case 0.1 g of dried activated sludge was added to 100 ml of Cd(II) and Pb(II) solutions containing 50 mg/L of the desired metal in Erlenmayer flasks. The tightly stopperred flasks were agitated on a shaker at 150 r/min at 20 ℃ for 2 h. Samples were filtered and Cd(II) and Pb(II) concentrations in the filtrate were analysed by means of atomic adsorption spectroscopy (Vario 6 AAS).

The effect of initial metal ion concentration on biosorption, at the optimum pH, was determined using solutions with concentrations ranging from 20 to 100 mg/L for both Cd (II) and Pb (II). The effect of temperature on biosorption was investigated at temperatures of 20, 30, 40℃ at 50 mg/L initial metal concentration for both Cd(II) and Pb(II). In each case, 1.0 g dried activated sludge was added to 1 L of Cd(II) and Pb(II) solutions and agitated at 150 r/min. At predetermined time intervals, samples were collected and analyzed by AAS. The biosorption experiments were done in duplicates. The data were the mean values of two replicate determinations.

Metal uptake (q_t) was determined by the following equation:

$$q_t = (C_0 - C_t)V/W \quad (1)$$

where q_t is the amount of metal ions adsorbed on the biosorbent (mg/g); C_0 and C_t are the metal concentrations contained in the original solution and after the incubation period, respectively (mg/L); V is the volume of the solution (ml) and W represents the weight of the dried activated sludge used (g).

1.3 FT-IR analysis of biomass

FT-IR analysis of dried activated sludge was determined as follows: KBr pellet was prepared. The proportion of activated sludge biomass/KBr is 1/100. Nexus 470 FT-IR system was used for FT-IR analysis of dried activated sludge.

2 Results and discussion

2.1 Effect of pH

It is well known that pH is one of the major parameters controlling the sorption of metals with biosorbents. Fig.1 shows the effect of pH on the adsorption capacity of dried activated sludge. As can be seen from the figure, the removal of both Cd(II) and Pb(II) ions from aqueous solution was strongly affected by medium pH. There was an increase in biosorption capacity of biomass with increasing pH from 2.0 to 4.0 and 6.0 for Pb(II) and Cd(II), respectively. The maximum biosorption of heavy metal ions on the biomass is 26.5 mg/g at pH 6.0 for Cd(II) and 39.3 mg/g at pH 4.0 for Pb(II), respectively. At lower pH values, the biosorption of Cd(II) and Pb(II) are low because large quantities of proton compete with metal cations for biomass surface. As the pH increased, the overall surface charge of the dried activated sludge became negative and adsorption increased. At pH values higher than 6.0 and 4.0 for Cd(II) and Pb(II), respectively, biosorption studies could not be performed due to the precipitation of Cd(II) and Pb(II) ions.

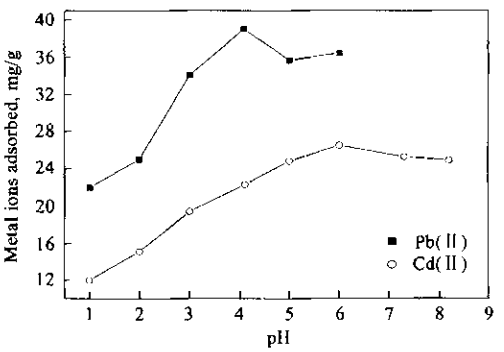

Fig.1 Effect of pH on adsorption of metal ions by the dried activated sludge
Initial concentration of metal ions: 50 mg/L; temperature: 20℃

2.2 Study of biosorption kinetics

Adsorption kinetics, expressed in terms of the rate of solute removal, that controls the residence time of the sorbate in the solid-solution interface, is one of the most important aspects of the operation defining the efficiency of the process. Several kinetic models have described the reaction order in sorption systems. However, over the past few years, a pseudo-second-order kinetic model has been considered to be among the most appropriate (Wang *et al.*, 2004).

The pseudo-second-order kinetic model is expressed as (Ho and McKay, 1999):

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \quad (2)$$

where k_2 (g/(mg·min) is the rate constant of pseudo-second-order sorption, q_e and q_t are amounts of metal ions adsorbed at equilibrium and time t (mg/g), respectively.

Integration Eq.(2) for the boundary conditions t $(0 - t)$ and q_t $(0 - q_t)$, gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (3)$$

Eq. (3) can be rearranged to obtain a linear form:

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

The straight line plots of t/q_t against t at different concentrations and temperatures suggest the applicability of the equation to the present system and also explain that the process of adsorption follows pseudo-second-order kinetics. The values of k_2 and q_e were calculated from the slop and intercept of the plots.

2.2.1 Effect of initial concentration

Initial metal concentration provides important driving force to overcome all mass transfer resistances of the metal between the aqueous and solid phase (Aksu and Akpinar, 2000). The influence of initial concentrations on adsorption of Cd(II) and Pb(II) ions by dried activated sludge were studied by changing the concentration of system from 20 to 100 mg/L. pH 6.0 and 4.0 were used for Cd(II) and Pb(II) ions biosorption experiments, respectively. As seen in Fig.2, the metal uptake is rapid for all the concentration in the first 15 min, since about 83.7% and 85.5% of the Cd(II) and Pb(II) present in the solutions was removed, respectively. The rate of adsorption decreased with time until it gradually approached a plateau due to the continuous decrease in the concentration driving force. Time required for attaining equilibrium for both metal ions was about 60 min. The short contact time of biosorbent with metal solution for biosorption suggests that the binding of the Cd(II) and Pb(II) ions to active sites occurs preferably onto the solid surface, with no significant ion diffusion towards the inside of the particle of the dried activated sludge (Mashitah *et al.*, 1999).

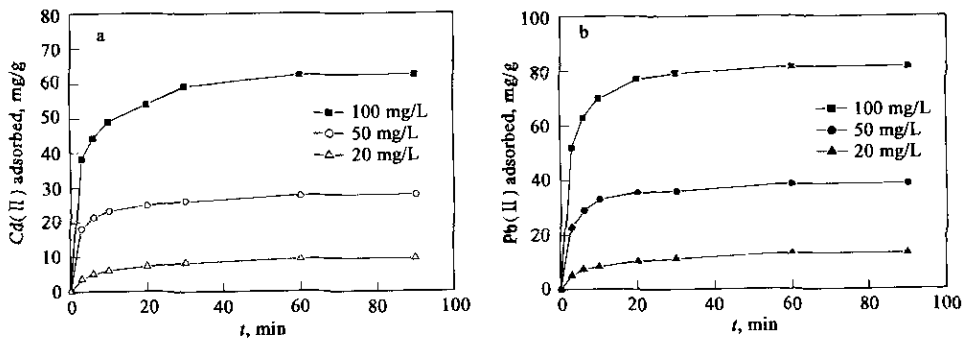

Fig.2 Effect of initial metal concentration on (a) Cd(II) and (b) Pb(II) adsorption by dried activated sludge at pH 6.0 for Cd(II) and 4.0 for Pb(II); temperature, 20℃

The kinetic data obtained has been analyzed by using the pseudo-second-order model and various rate parameters were calculated (Table 1). From Table 1 it can be seen that the correlation coefficients for the pseudo-second-order kinetic model obtained at all the studied Cd(II) and Pb(II) concentrations were higher than 0.98. Also the calculated q_e values agreed very well with the experimental date ($q_{e,exp}$). These suggest that the kinetics of Cd(II) and Pb(II) adsorption onto dried activated sludge follows the pseudo-second-order model. From Table 1 it also can be seen that equilibrium adsorption capacities increased from 9.8 to 61.3 mg/g for Cd(II) and 13.8 to 83.5 mg/g for Pb (II) as their concentrations varied from 20 to 100 mg/L. This difference in the maximum level of uptake of Cd(II) and Pb(II) ions has been explained in terms of difference in the ionic size of metals, the nature and distribution of active groups on the biosorbent, and the mode of interaction between the metal ions and the biosorbent (Okieimen *et al.*, 1985).

Table 1 Pseudo-second-order equation parameters for different initial concentrations of Cd(II) and Pb(II) and temperatures

	Cd (II)				Pb (II)			
C_0, mg/L (T = 20℃)	$q_{e,exp}$	q_e	k_2	R^2	$q_{e,exp}$	q_e	k_2	R^2
20	9.5	9.8	0.0157	0.995	14.1	13.8	0.0113	0.994
50	25.9	26.4	0.0151	0.997	38.9	39.4	0.0119	0.991
100	60.7	61.3	0.0053	0.983	82.8	83.5	0.0062	0.993
T, ℃ (C_0 = 50 mg/L)								
20	25.9	26.4	0.0151	0.997	38.9	39.4	0.0119	0.991
30	24.2	24.5	0.0193	0.997	28.6	28.9	0.0147	0.997
40	22.5	22.7	0.0265	0.999	13.2	13.7	0.0187	0.998

2.2.2 Effect of temperature

The plots of q_t vs. t at various temperatures of metal ions solutions under the initial concentration of 50 mg/L and pH of 6.0 for Cd(II) and 4.0 for Pb(II) are shown in Fig.3. From this study it can be seen that the amounts of Cd(II) and Pb(II) adsorbed decrease with increase in temperature of the systems, which indicates the biosorption of Cd(II) and Pb(II) on dried activated sludge is an exothermic reaction. It was interesting to note that Pb(II) uptake showed a stronger temperature dependence than that of Cd(II). A reasonable explanation might be that the actual attachment of the metal ions on the cellular surface included not only chemisorption and ion exchange, but also physical adsorption. The latter might play a greater role in the biosorption process of Pb(II) ions than Cd(II) ions because the ionic radius of the Pb(II)

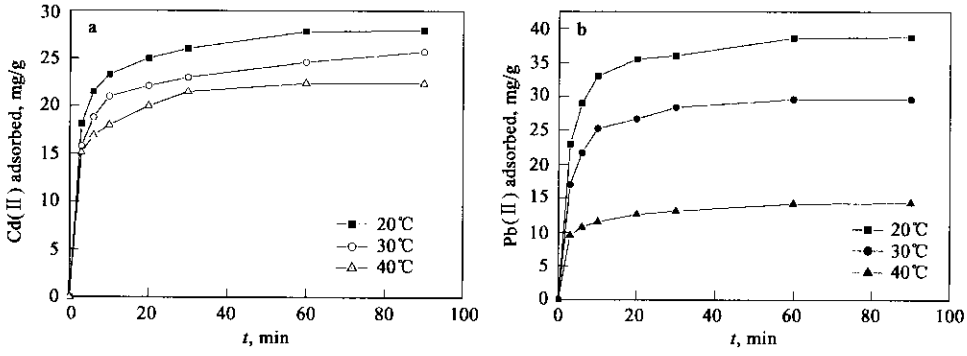

Fig.3 Effect of temperature on (a) Cd(II) and (b) Pb(II) adsorption by dried activated sludge at pH 6.0 for Cd(II) and 4.0 for Pb(II) and initial metal concentration 50 mg/L

ion (121 pm) was larger than that of Cd(II) ion (97 pm) (Weast *et al.*, 1988).

The values of various pseudo-second-order rate constants for different temperatures have been calculated from Eq. (4) and the results are listed in Table 1. The adsorption process still confirms to fit the pseudo-second-order rate model with high correlation coefficient (>0.99). The values of the rate constant, k_2 varies from 0.0158 to 0.0265 g/(mg·min) for Cd(II) ions and 0.0119 to 0.0187 g/(mg·min) for Pb(II) in the temperature range studied. The increase in the pseudo-second-order rate constant may be described by Arrhenius equation:

$$k_2 = k_0 \exp\left(\frac{-E}{RT}\right) \tag{5}$$

where k_0 is the temperature independent factor (g/(mg·min)), E is the activation energy of sorption (kJ/mol), R is the gas constant (8.314 J/(mol·K)) and T is the solution temperature (K). When the $\ln k_2$ values are plotted versus $1/T$, activation energy value can be calculated from the slope of the line obtained. The Arrhenius plots for Cd(II) and Pb(II) adsorption onto dried activated sludge are presented in Fig.4, where an acceptable linear relationship can be seen, with a regression coefficient, $R_2 > 0.99$. The activation energy obtained were 21.4 kJ/mol and 17.21 kJ/mol for Cd (II) and Pb (II), respectively. These values confirm that the physical adsorption play a greater role in the biosorption processes of Cd(II) and Pb(II) ions.

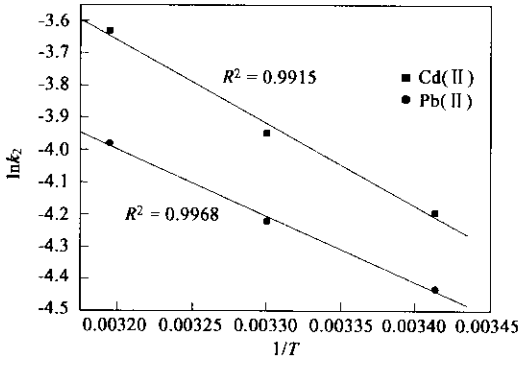

Fig. 4 Arrhenius plots for Cd(II) and Pb(II) adsorption onto dried activated sludge

2.3 Isotherm biosorption analysis

Isotherm experiments were carried out at initial pH of 6.0 for Cd(II) and 4.0 for Pb(II) at 25℃ by varying the initial Cd(II) and Pb(II) concentrations in the range of 20—200 mg/L. The experimental data obtained were plotted in a line arised form of Langmuir and Freundlich adsorption isotherms(Eqs.(6) and (7), respectively).

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{6}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{7}$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed metal ions per unit weight of biosorbent and metal ions concentration in solution at equilibrium, respectively. q_m, K_L, K_F and n are the isotherm constants.

The correlation coefficients and isotherm parameters derived from the fitting of experimental points are given in Table 2. The results show that the experimental data fit both the isotherm equations. For both metal ions, the Langmuir model yields a little better fit than the Freundlich model, which implied that monolayer adsorption existed for the experimental conditions used. Higher q_m and K_L values for Pb(II), as compared to Cd(II) confirm the stronger bonding affinity of dried activated sludge to Pb (II) than to that of Cd(II).

Table 2 Langmuir and Freundlich parameters for adsorption of Cd(II) and Pb(II) at 25℃

Metal ions	Langmuir			Freundlich		
	q_m	K_L	R^2	K_F	n	R^2
Cd(II)	84.3	0.021	0.997	2.12	1.17	0.988
Pb(II)	131.6	0.032	0.994	4.57	1.20	0.977

2.4 Mechanism of Cd(II) and Pb(II) biosorption by dried activated sludge

In order to find out which functions are responsible for the Cd(II) and Pb(II) adsorption, FT-IR analysis of dried activated sludge was carried out. Fig.

5 shows the IR spectra and the various functional groups corresponding to the absorption bands. The bands at 3224 cm^{-1} could be —OH and —NH stretching of activated sludge polymeric compounds, and the adsorption band at 2925 cm^{-1} could be asymmetric vibration of —CH. The adsorption band at 1651 cm^{-1} could be attributed to C=O stretching conjugated to a —NH deformation of —CN (amide I) group of protein peptide bond and chitisan-chitosan. A 1532 cm^{-1} band could be stretching vibration of —CN of peptidic bond of proteins. A 1424 cm^{-1} is of phenolic —OH and —C=O stretching of carboxylates. A 1396 cm^{-1} band could be stretching vibration of —COO. A 1027 cm^{-1} band could be vibration of —C—O—C and —OH of polysaccharides. Spectra analysis of FT-IR spectrum after divalent cations Cd (II) and Pb (II) adsorption showed that there was a substantial decrease in the adsorption intensity of amide I group at 1651 and 1532 cm^{-1} and this indicated that amide I group played the most important role in binding Cd (II) and Pb (II). The groups of —OH, and C—O—C also involved in Cd (II) and Pb(II) binding to some extent.

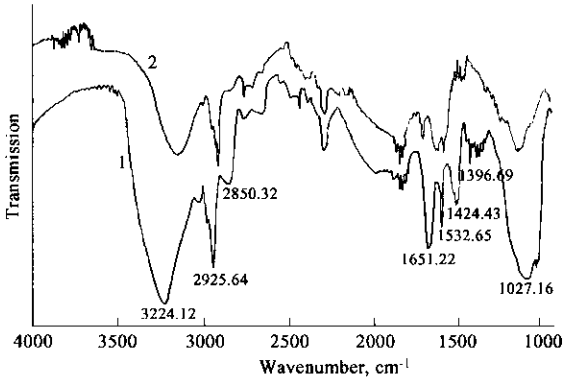

Fig.5 FT-IR spectra of dried activated sludge (1) before Cd(II) and Pb (II) adsorption and (2) after both divalent cations adsorption

3 Conclusions

The biosorption properties of dried activated sludge were studied for Cd(II) and Pb(II) removal. For the metal ions investigated the optimum adsorption was achieved at pH 6.0 and 4.0 for Cd(II) and Pb(II) ions, respectively. The adsorption kinetics were well described by the pseudo-second order kinetic model equation. The FT-IR analysis showed that amide I group plays an extremely important role in binding of Cd(II) and Pb(II). This study demonstrated that the use of readily available waste activated sludge biomass offers an alternative in the removal of metals from wastewaters.

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