

Adsorption of Heavy Metals by Brewery Biomass

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Abstract—In this work, biosorption of lead, copper and cadmium by waste brewery yeast has been studied. The adsorption capacity for lead, copper and cadmium on the biomass increased with the increasing temperature and the maximum uptakes were 0.465 mmolPb/g (96.4 mg/g), 0.769 mmolCu/g (48.9 mg/g) and 0.127 mmolCd/g (14.3 mg/g) at 308 K. The Langmuir isotherm, favorable type, and the pseudo second-order kinetic model represent our experimental data very well. The heat of biosorption was evaluated from the Langmuir isotherm equation, and the biosorption of lead, copper and cadmium was endothermic reaction.

Key words: Biosorption, Brewery Yeast, Heavy Metal, Adsorption Capacity

INTRODUCTION

Toxic heavy metals are released into the environment from a number of industries such as mining, plating, dyeing, automobile manufacturing and metal processing. The presence of heavy metals in the environment has led to a number of environmental problems. In order to meet the water quality standards for most of countries, the concentration of heavy metals in wastewater must be controlled. Conventional physico-chemical treatment methods for removing heavy metals include precipitation, filtration, oxidation-reduction, ion exchange and membrane separation. However, when metals are dissolved in huge volumes at relatively low concentration, these methods become generally ineffective or expensive [Aderhold et al., 1996; Blanco et al., 1999; Lee and Suh, 2000; Eccles, 1995]. Therefore, there is a need for the development of a low cost process to remove heavy metals economically.

Biosorption is a process that utilizes biological materials as adsorbents, and this method has been studied by several researchers as an alternative technique to conventional methods for heavy metal removal from wastewater [Jeon et al., 2001; Sa and Kutsal, 2001; Volesky, 2001; Yu et al., 1999].

The binding mechanisms of heavy metals by biosorption could be explained by the physical and chemical interactions between cell wall ligands and adsorbates by ion exchange, complexation, coordination and microprecipitation. The diffusion of the metal from the bulk solution to active sites of biosorbents occurs predominantly by passive transport mechanisms [Veglio and Beolchini, 1997] and various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents can bind the heavy metals [Avery and Tobin, 1993]. Living or dead biomass can be used to remove metals, but maintaining a living biomass during metal

biosorption is difficult because it requires a continuous supply of nutrients and toxicity of metal for microorganism might take place. On the other hand, the use of dead biomass can avoid these problems and the used cells can be easily regenerated [Sudha and Abraham, 2001; Yan and Viraraghavan, 2001].

A variety of biomaterials such as bacteria, yeast, algae and fungi have been successfully used as biosorbents for the removal of heavy metals [Kapoor and Viraraghavan, 1995; Volesky, 1994]. Bailey et al. [1999] defined a low cost sorbent as one that is abundant in nature, or is a by-product or waste material from industries such as breweries and dairy products. The yeast has been studied by many investigators as a biosorbent since it can be obtained without additional cost or easily cultivated in substantial amounts using simple fermentation techniques and inexpensive growth media [Aksu and Dönmez, 2003; Avery and Tobin, 1992; Jianlon, 2002; Marques et al., 1999].

In this work, the waste brewery yeast was obtained from a fermentation process of a brewery plant, and the biosorption of lead, copper and cadmium was studied in a batch reactor with respect to the pH, initial metal concentration and temperature. Biosorption equilibria and kinetics over the temperature range of 288-308 K were investigated and the biosorption heat was evaluated.

MATERIALS AND METHODS

1. Preparation of Biosorbent

The biomass, collected from a brewery plant, was washed several times with distilled water, and then dried in a vacuum drying oven at 80 °C for 48 h. The dried biomass was grounded with a mortar and pestle. The particles were separated by using a US standard testing sieve (No. 100~No. 200) and stored in a sealed bottle with a silica gel to prevent readsorption of moisture.

2. Biosorption Equilibrium

Heavy metal solutions were prepared by dissolving metal nitrates,

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($\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), in distilled water. The mixture containing 0.1 g of biosorbent and 100 ml of metal nitrate solution was agitated on a shaking incubator at 150 rpm for 24 h in 300 mL an Erlenmeyer flask. The pH of solution (initial metal concentration of 200 mg/L) was adjusted between 2.5 and 6.0 with 1 N HNO_3 and 1 N NaOH , and the temperature was adjusted between 288 K and 308 K. The heavy metal concentration was varied over the range of 0.1–5.0 mmol/L. After equilibrium experiments, the biosorbent was separated from the solution by centrifugation for 10 min at 10,000 rpm and then the residual metal concentration in the solution was analyzed by ICP (Leeman 010-2106). The amounts of lead, copper and cadmium adsorbed onto the biomass at equilibrium were calculated from the following mass balance equation:

$$q = (C_i - C) \frac{V}{W} \quad (1)$$

Here q is the equilibrium amount adsorbed on the biomass (mol/kg), C_i is the initial concentration of bulk fluid (mol/m³), C is the equilibrium concentration of the solution (mol/m³), V is the volume of solution (m³), and W is the weight of biomass (kg).

3. Biosorption Kinetics

Biosorbent, 0.2 g, was suspended in 200 ml of metal nitrate solution and initial metal concentration was varied over the range 10–200 mg/L. For kinetic experiments, four different biosorbent concentrations varying between 0.5–4.0 g/L at an initial heavy metal concentration of 100 mg/L were used. The pH and agitation speed of this experiment were the same as those for equilibrium study. Samples were withdrawn at pre-determined time intervals, centrifuged and then analyzed for residual metal concentration.

RESULTS AND DISCUSSION

1. Effect of pH

The biosorption capacities of lead, copper and cadmium on vari-

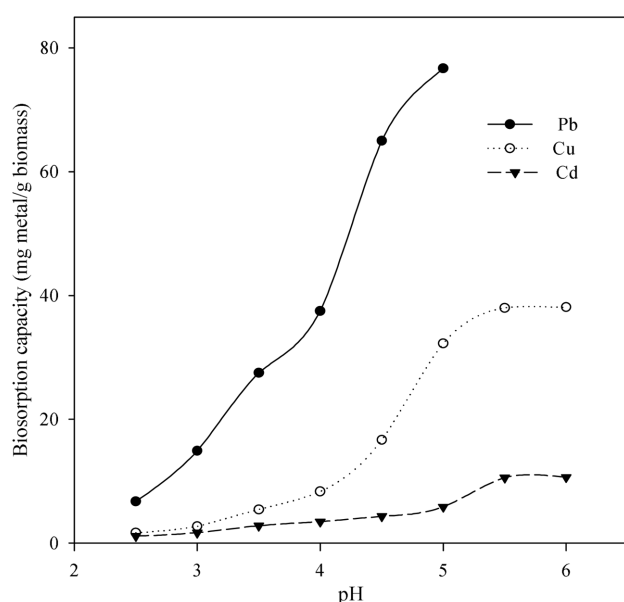


Fig. 1. Effect of initial pH on the biosorption capacity (Co: 200 mg/L, biomass conc.: 1 g/L, 150 rpm, 25 °C).

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ous pH values are shown in Fig. 1. The experiments were not conducted above pH 6.0 (5.0 for Pb) to avoid possible hydroxide precipitation. The biosorption capacity increased with increasing pH and the effect of pH was in the order of $\text{Pb} > \text{Cu} > \text{Cd}$. The effect of pH on the biosorption capacity can be interpreted by the competition of the hydronium ions $[\text{H}_3\text{O}^+]$ and metal ions for binding sites. At low pH values, the ligands on the cell are closely associated with the hydronium ions, but when the pH is increased, the hydronium ions are gradually dissociated and the positively charged metal ions are associated with the free binding sites. Similar findings were reported by other researchers [Benguella and Benaissa, 2002; Esposito et al., 2002; Yang and Volesky, 1999].

2. Biosorption Equilibrium

Adsorption isotherms are very important for the design of an adsorption-based process design. In this study, the Langmuir isotherm model was used to correlate our experimental equilibrium data. The Langmuir equations have two parameters in Eq. (2).

$$q = \frac{q_m b c_e}{1 + b c_e} \quad (2)$$

To find the parameters for adsorption isotherm equation, the linear least squares method and the pattern search algorithm (NMEAD) were used. The value of the mean percentage error, obtained from Eq. (3), has been used as a test criterion for the fit of the correlation.

$$\text{Error}(\%) = \frac{100}{N} \sum_{k=1}^N \left[\frac{|q_{\text{exp}} - q_{\text{cal}}|}{q_{\text{exp}}} \right] \quad (3)$$

The parameters and the average percent differences between the measured and calculated values are given in Table 1. The equilibrium adsorption data for lead, copper and cadmium at four different temperature are shown in Figs. 2–4 along with the Langmuir isotherm equation. As can be seen in this figures, the equilibrium isotherm was favorable type and the Langmuir equation represents our experimental data very well. The applicability of the Langmuir isotherm indicates good monolayer coverage of the metal ions on the surface of the biomass. The adsorption capacity for lead, copper and cadmium increased with increasing temperature and the maximum uptakes were 0.465 mmolPb/g (96.4 mg/g), 0.769 mmolCu/

Table 1. Adsorption equilibrium parameters of lead, cadmium and copper

Heavy metal	Parameters	Temperature			
		288 K	298 K	303 K	308 K
Lead	q_m	0.358	0.422	0.442	0.465
	b	4.27	9.87	11.31	12.40
	error (%)	6.36	7.99	6.70	1.10
Copper	q_m	0.608	0.707	0.754	0.769
	b	1.76	3.21	3.55	4.16
	error (%)	6.18	3.95	6.73	8.03
Cadmium	q_m	0.104	0.107	0.125	0.127
	b	1.74	3.15	5.62	6.61
	error (%)	6.45	6.50	4.84	6.78

$$\text{Error}(\%) = \frac{100}{N} \sum_{k=1}^N \left[\frac{|q_{\text{exp},k} - q_{\text{cal},k}|}{q_{\text{exp},k}} \right]$$

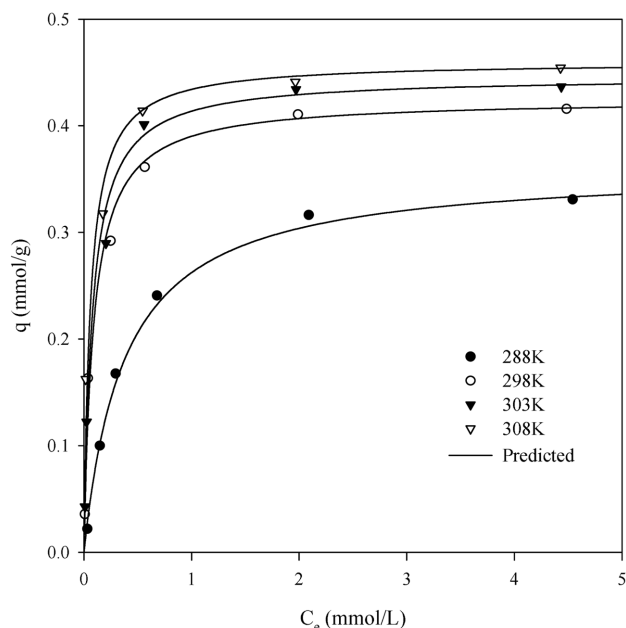


Fig. 2. Adsorption equilibrium isotherm of lead (pH 5.0).

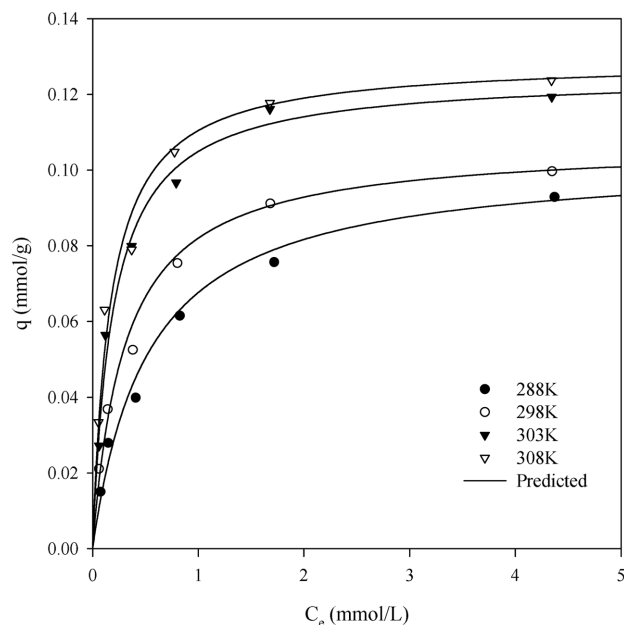


Fig. 4. Adsorption equilibrium isotherm of cadmium (pH 5.5).

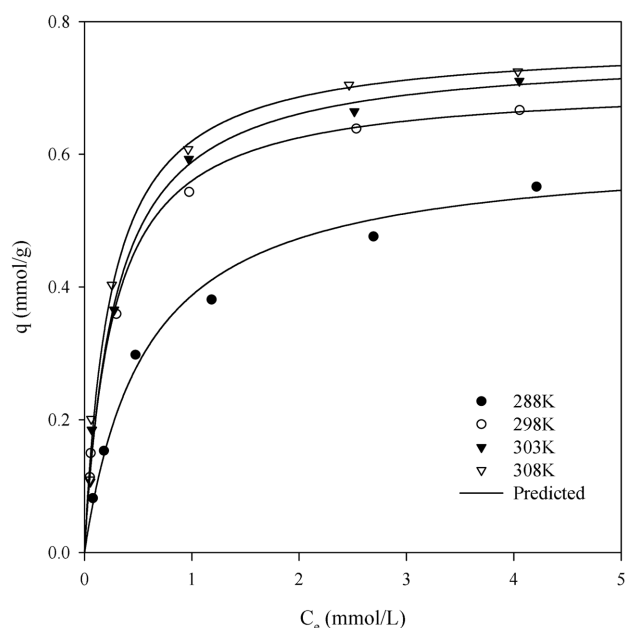


Fig. 3. Adsorption equilibrium isotherm of copper (pH 5.5).

g (48.9 mg/g) and 0.127 mmolCd/g (14.3 mg/g) at 308 K.

3. Heat of Adsorption

The heat of adsorption can be calculated by using the Langmuir parameter, b , and this parameter can be expressed as a function of temperature by the following Arrhenius type relationship:

$$b = b_0 \exp \left[-\frac{\Delta H}{RT} \right] \quad (4)$$

where b_0 is a constant, ΔH (kcal/mol) is the heat of adsorption, R is a universal gas constant and T is the absolute temperature (K). If b values are known for various temperatures, the heat of adsorption can be calculated from the plots of $\log b$ versus $1/T$ [Özer and Özer, 2003].

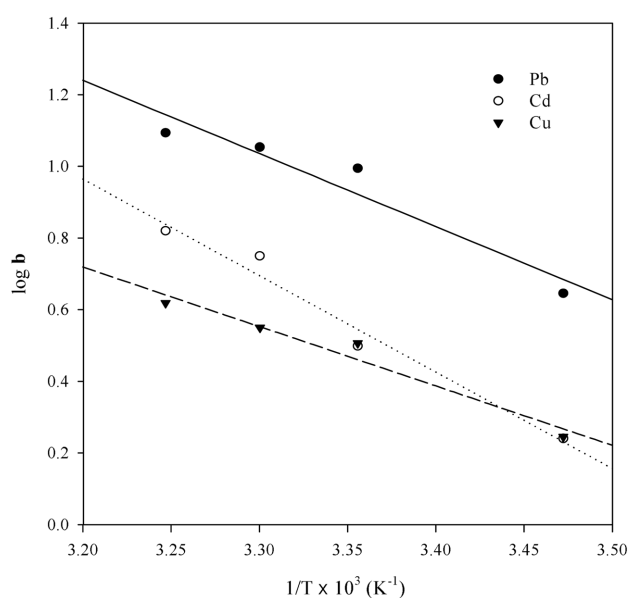
Fig. 5. Variation of the Langmuir constant (b) with temperature.

Table 2. The values of biosorption heat for lead, cadmium and copper and regression coefficients

Heavy metal	Biosorption heat (kcal/mol)	R^2
Lead	4.06	0.92
Copper	3.30	0.96
Cadmium	5.35	0.97

The variation of b with temperature is shown in Fig. 5, and the biosorption heats and regression coefficients obtained are summarized in Table 2. As shown in Table 2, the biosorption heats for lead, copper and cadmium are 4.06, 3.30 and 5.35 kcal·mol⁻¹, respec-

tively. The values of biosorption heat for the three heavy metals show that the reaction is endothermic. Nakajima et al. [1982] also reported that the biosorption of uranium by polyacrylamide-immobilized *S. viridochromogenes* and *C. regularis* was an endothermic reaction and similar results were reported for biosorption of cadmium and lead by spent grain [Low et al., 2000].

In general, the heat of physical adsorption is no more than $1 \text{ kcal} \cdot \text{mol}^{-1}$, and that of chemical adsorption is $20\text{--}50 \text{ kcal} \cdot \text{mol}^{-1}$ [Smith, 1981]. Since the heats of adsorption for the heavy metals of our study are $3.3\text{--}5.4 \text{ kcal} \cdot \text{mol}^{-1}$, we believe that both physical and chemical adsorptions are involved in the biosorption. Sağ [1993] also reported that the adsorption heats for the biosorption of Pb(II) ions on *Z. rami-*

gera and Ni(II) ions on *R. arrhizus* have values between physical adsorption and chemical adsorption.

4. Kinetic Studies

The effects of initial metal concentration (10, 50, 100, 200 mg/L) and biosorbent concentration (0.5, 1.0, 2.0, 4.0 g/L) on the adsorption kinetics of heavy metals are studied. Figs. 6-8 show the amounts of the metal adsorbed onto biosorbent, biosorption capacity, with reaction time for different metal concentration. The adsorption capacities of lead and copper increased rapidly in the beginning of the reaction and reached equilibrium in about 60 min, but that of cadmium reached at equilibrium in about 120 min. The figures also show that the adsorption capacities of lead, copper and cadmium

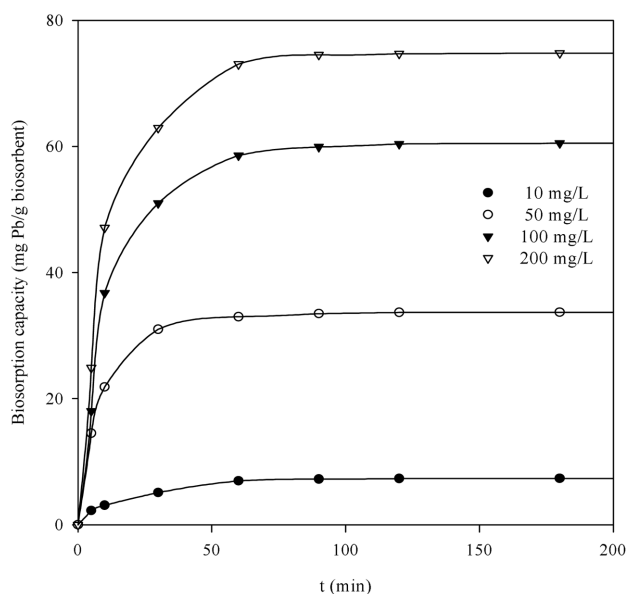


Fig. 6. Biosorption capacity of lead for different metal concentration (pH 5.0).

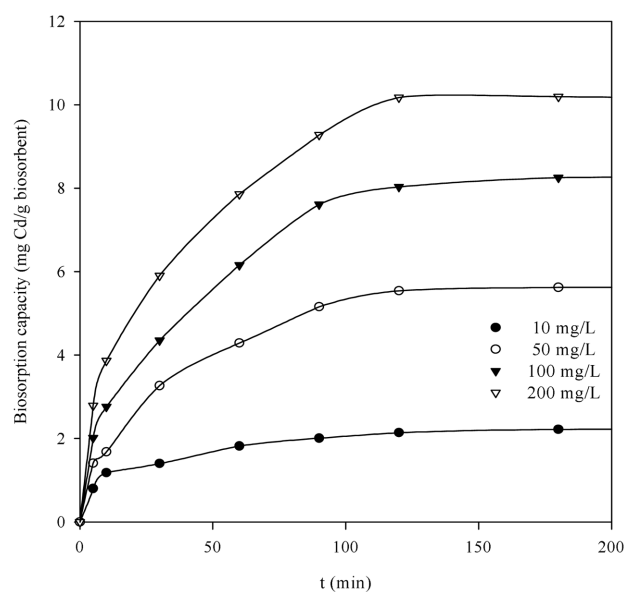


Fig. 8. Biosorption capacity of cadmium for different metal concentration (pH 5.5).

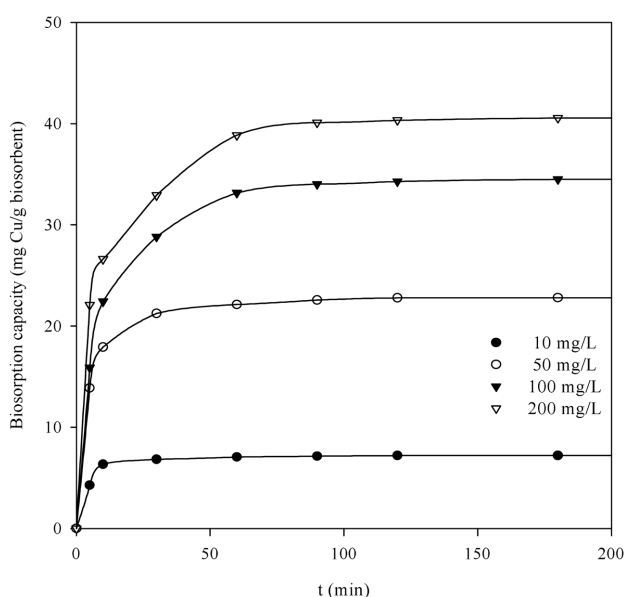


Fig. 7. Biosorption capacity of copper for different metal concentration (pH 5.5).

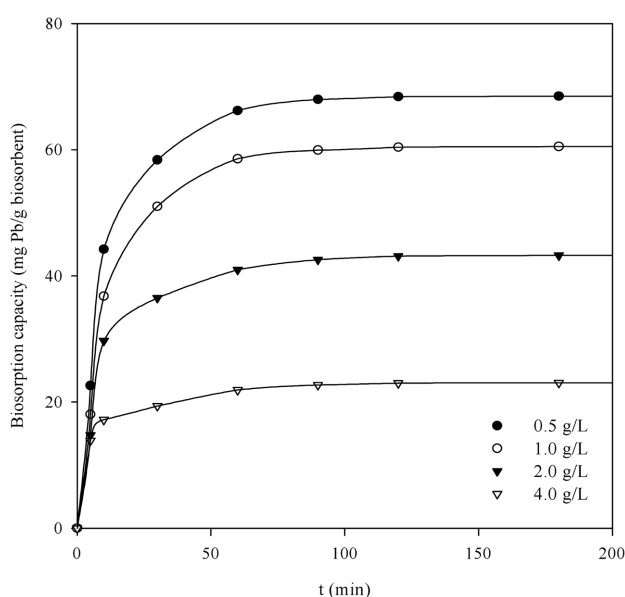


Fig. 9. Biosorption capacity of lead for different biosorbent concentration (pH 5.0).

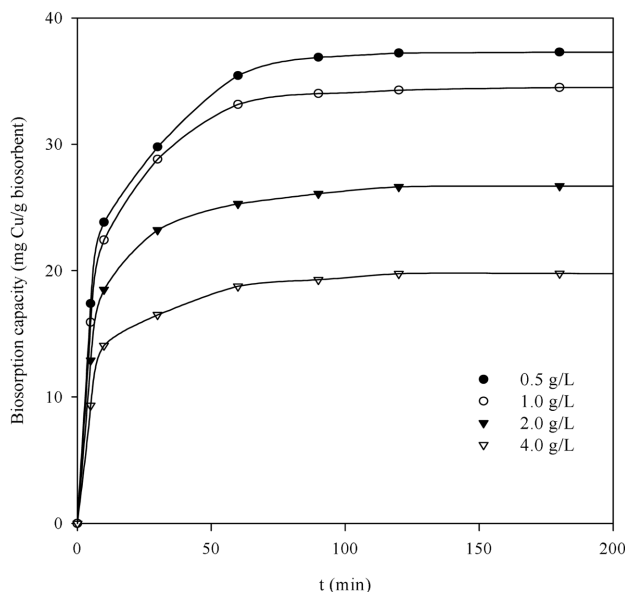


Fig. 10. Biosorption capacity of copper for different biosorbent concentration (pH 5.5).

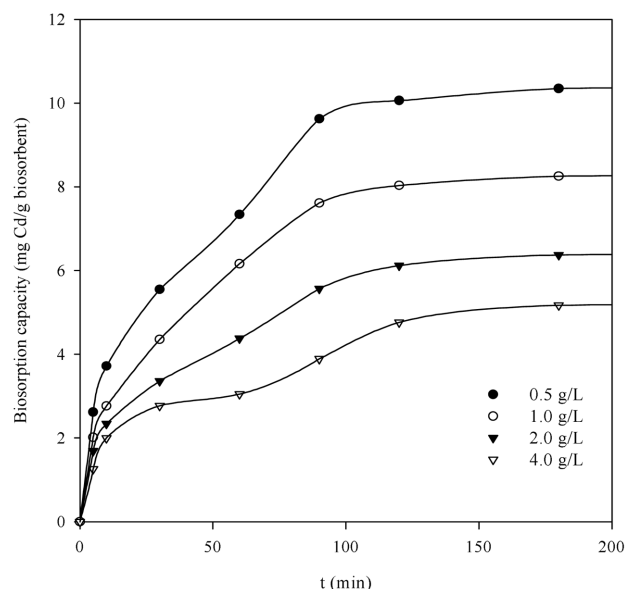


Fig. 11. Biosorption capacity of cadmium for different biosorbent concentration (pH 5.5).

increased with increasing initial metal concentration.

Figs. 9-11 show the variation of biosorption capacity for different biosorbent concentration. As shown in Figs. 9-10, the biosorption capacity profiles of lead and copper are very similar and the capacities increase rapidly in the beginning of the reaction. The biosorption capacities of lead and copper for higher biomass concentrations (2 and 4 g/L) reach equilibrium within 10 min, but more than 60 min was required to reach equilibrium capacities for lower biomass concentrations (0.5 and 1 g/L). Although the biosorption capacity profiles of lead and copper are very similar, the capacity of lead was substantially higher than that for copper. As for cadmium, Fig. 11, the profile as well as biosorption capacity are very different—longer time to reach equilibrium and much lower biosorption capacity.

In order to analyze the biosorption kinetics of lead, copper and cadmium, the pseudo first-order and second-order kinetic models

were applied to the experimental data.

The pseudo first-order rate expression of Lagergren [1898] can be expressed as:

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_{1,ad}}{2.303} t \quad (5)$$

where, q_{eq} and q_t are the amounts (mg/g) of adsorbed metal on the biosorbent at equilibrium and at time t , respectively. $k_{1,ad}$ is the rate constant (L/min). If Eq. (5) is applicable, the adsorption rate is the pseudo first-order reaction, and the rate constant $k_{1,ad}$ can be obtained from the slope of the plot of $\log(q_{eq} - q_t)$ against t .

The pseudo second-order rate equation [Ho and McKay, 1998] can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_{2,ad} q_{eq}^2} + \frac{1}{q_{eq}} t \quad (6)$$

Table 3. Comparison of the first-order and second-order rate constants for different initial metal concentration

Heavy metal	Initial concentration	First-order kinetic model			Second-order kinetic model			$q_{eq, exp}$ (mg/g)
		$K_{1,ad} \times 10^{-2}$ (min ⁻¹)	q_{eq} (mg/g)	R^2	$K_{2,ad} \times 10^{-2}$ (g mg ⁻¹ min ⁻¹)	q_{eq} (mg/g)	R^2	
Lead	10 mg/L	3.96	6.53	0.974	0.93	8.04	0.995	7.44
	50 mg/L	4.77	17.96	0.956	0.57	34.97	0.999	33.82
	100 mg/L	4.93	44.05	0.983	0.19	64.10	0.998	60.54
	200 mg/L	5.87	61.04	0.988	0.17	78.74	0.998	74.86
Copper	10 mg/L	3.75	1.83	0.859	5.81	7.32	0.999	7.22
	50 mg/L	3.94	7.73	0.963	1.45	23.26	0.998	22.83
	100 mg/L	4.24	20.12	0.991	0.53	35.71	0.999	34.52
	200 mg/L	4.33	23.58	0.993	0.42	42.02	0.997	40.58
Cadmium	10 mg/L	1.66	1.55	0.984	2.94	2.37	0.995	2.37
	50 mg/L	2.10	5.11	0.991	0.61	6.48	0.994	5.90
	100 mg/L	2.28	7.63	0.978	0.41	9.51	0.991	8.47
	200 mg/L	2.33	8.47	0.982	0.40	11.49	0.993	10.25

where $k_{2,ad}$ is the rate constant of pseudo second-order kinetic model (g/mg·min). If Eq. (6) is applicable, the plot of t/q_t against t should give a linear relationship, and q_{eq} and $k_{2,ad}$ can be determined from

the slope and intercept of the plot.

The values of model parameters $k_{1,ads}$, $k_{2,ads}$, q_{eq} and correlation coefficients (R^2) are obtained and presented in Tables 3 and 4. As

Table 4. Comparison of the first-order and second-order rate constants for different biosorbent concentration

Heavy metal	Initial concentration	First-order kinetic model			Second-order kinetic model			$q_{eq,exp}$ (mg/g)
		$K_{1,ad} \times 10^{-2}$ (min ⁻¹)	q_{eq} (mg/g)	R^2	$K_{2,ad} \times 10^{-2}$ (g mg ⁻¹ min ⁻¹)	q_{eq} (mg/g)	R^2	
Lead	0.5 g/L	5.09	48.38	0.992	0.19	71.94	0.994	68.50
	1.0 g/L	4.93	44.05	0.991	0.19	64.10	0.992	60.54
	2.0 g/L	3.98	24.87	0.980	0.68	43.29	0.995	43.30
	4.0 g/L	3.52	9.94	0.984	0.94	23.70	0.998	23.11
Copper	0.5 g/L	4.31	24.07	0.987	0.39	38.91	0.994	37.36
	1.0 g/L	4.24	20.12	0.983	0.47	35.84	0.999	34.52
	2.0 g/L	3.45	12.58	0.973	0.69	27.55	0.996	26.74
	4.0 g/L	3.36	9.56	0.965	0.86	20.49	0.998	19.83
Cadmium	0.5 g/L	2.37	9.62	0.889	0.33	11.83	0.987	10.52
	1.0 g/L	2.28	7.63	0.905	0.40	9.51	0.990	8.47
	2.0 g/L	1.91	5.28	0.916	0.53	7.22	0.985	6.41
	4.0 g/L	1.13	3.85	0.894	0.59	5.73	0.957	5.24

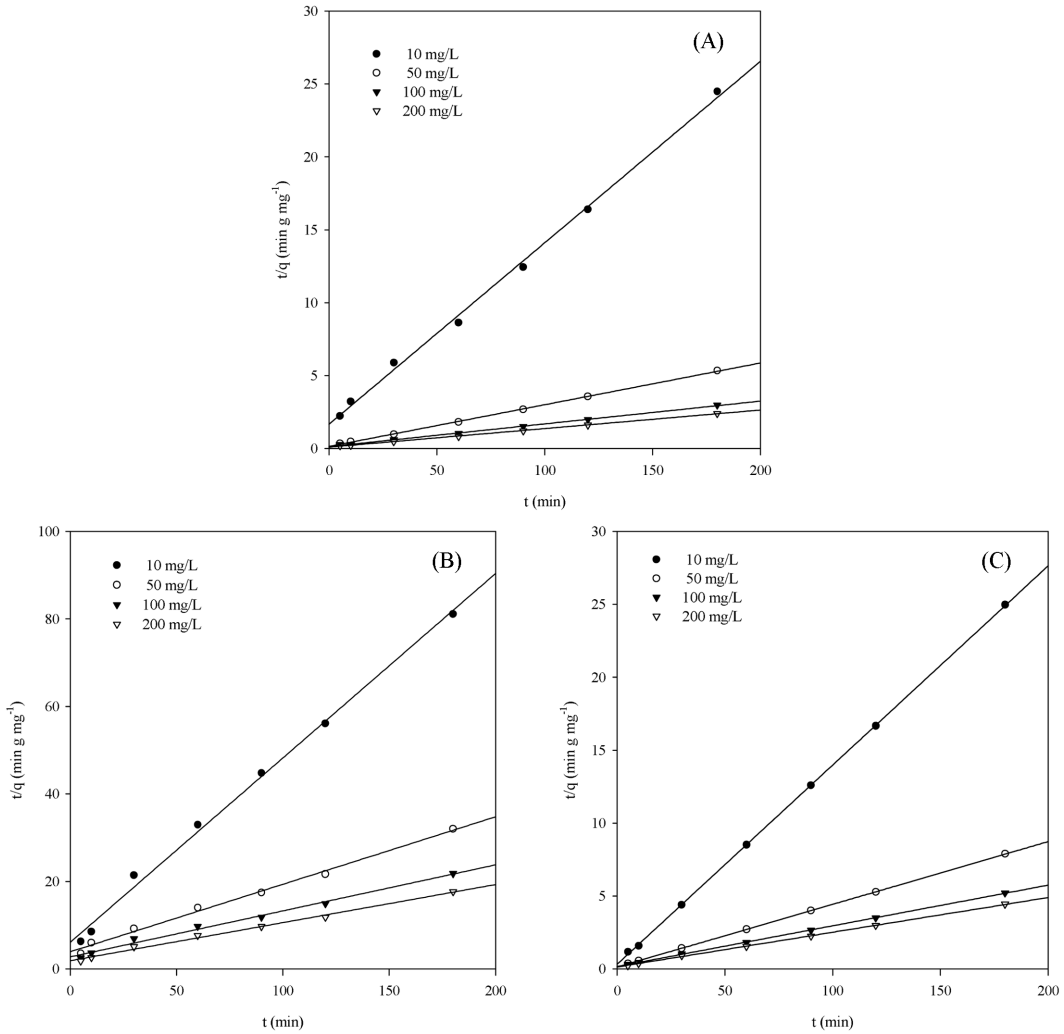


Fig. 12. t/q vs. t plot for the second-order kinetic model for different initial metal concentration. (A): lead, (B): cadmium, (C): copper.

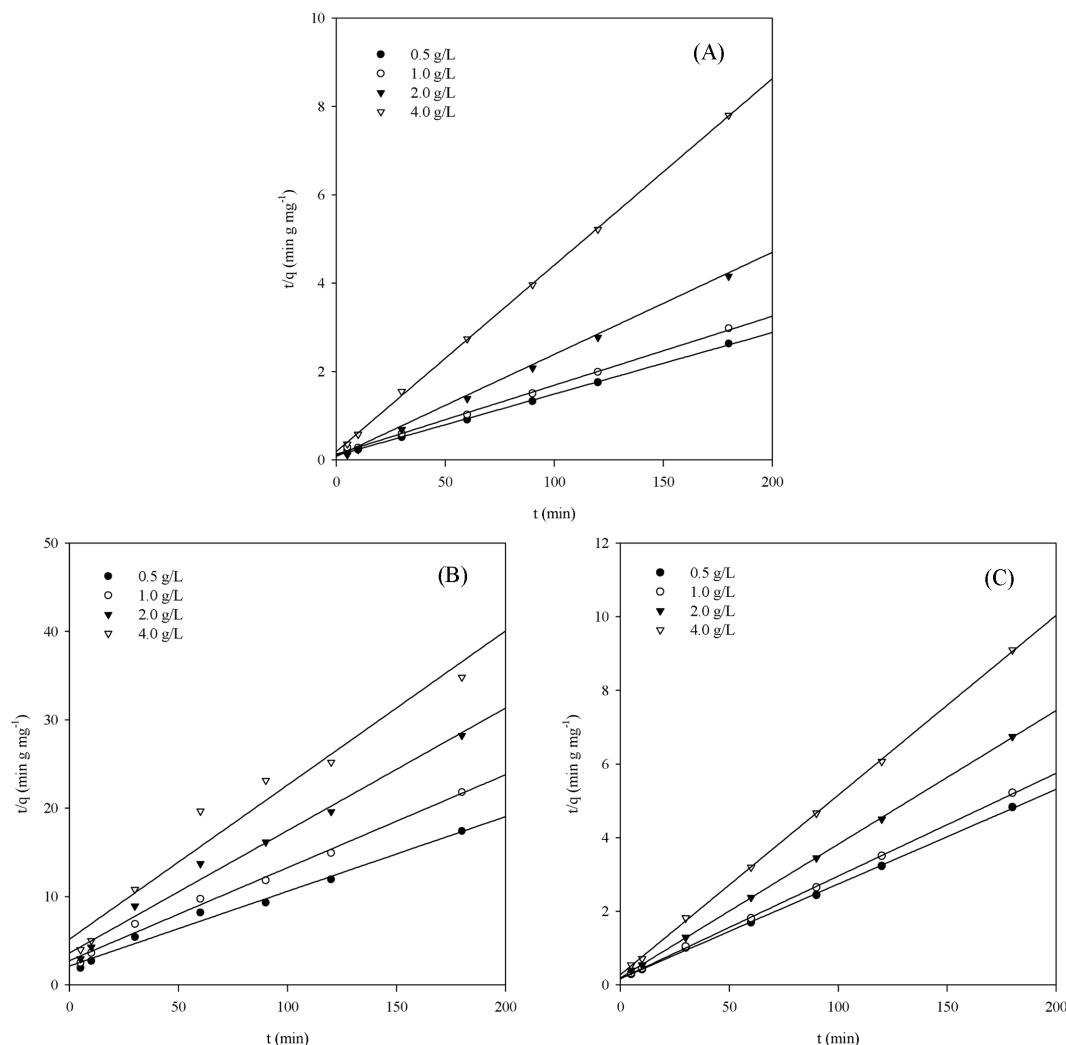


Fig. 13. t/q vs. t plot for the second-order kinetic model for different biosorbent concentration. (A): lead, (B): cadmium, (C): copper.

shown in these tables, the correlation coefficient for the second-order rate equation is greater than 0.99 and substantially higher than that for the first-order rate equation. And also, the q_{eq} values calculated from the second order kinetic model agree well with the experimental values. Figs. 12 and 13 show plots of the experimental data and the second-order model for initial metal concentration and biosorbent concentration, respectively. These show that the biosorption of lead, copper and cadmium can be represented by the pseudo second-order reaction.

CONCLUSIONS

In this study, the biosorption of lead, copper and cadmium was investigated and the following conclusions can be drawn.

1. The uptake capacity of lead, copper and cadmium increased with increasing initial metal concentration and decreased with increasing biosorbent concentration.

2. The uptake capacity increased with increasing pH and was maximum at pH 5.0 (for Pb) and 5.5 (for Cu and Cd). The metal uptake capacities and the effect of pH were in the order of lead >

copper > cadmium, and the maximum metal uptakes were 96.4 mgPb/g, 48.9 mgCu/g and 14.3 mgCd/g, respectively.

3. The biosorption isotherm was well described by Langmuir model of favorable type, and the pseudo second-order kinetic model represented the experimental data very well.

4. The biosorption of the heavy metals was endothermic reaction, and the heats of reaction were 4.06, 3.30 and 5.35 kcal·mol⁻¹ for lead, copper and cadmium, respectively.

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NOMENCLATURE

C_e : equilibrium adsorbates concentration in the liquid phase [mmol/L]

$K_{1,ad}$: rate constant of first-order biosorption [min⁻¹]

$K_{2,ad}$: rate constant of second-order biosorption [$\text{g mg}^{-1} \text{min}^{-1}$]
 q : adsorptive capacity per unit mass of adsorbent [mmol/g]
 q_m : Langmuir constant [-]
 q_{eq} : adsorbed amount on the biosorbent at equilibrium [mg/g]
 q_t : adsorbed amount on the biosorbent at time t [mg/g]
 R : correlation coefficient [-]
 V : volume of liquid [L]
 ΔH : heat of adsorption [kcal/mol]
 R : universal gas constant [cal/mol K]
 T : absolute temperature [K]

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