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Chemistry

EFFECTS OF KINETIC AND THERMODYNAMIC PARAMETERS ON THE SORPTION OF COPPER METAL IONS

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Abstract

The Earth's crust contain different components like heavy metals which are difficult be degraded or destroyed. However, some heavy metals are needed to maintain the physiological activity. The higher concentrations of such components may cause poisoning the biological organism. Therefore water containing such heavy metals must be treated before their discharge. For this, an efficient modified biomass was prepared from Kush plant. The proper modification was confirmed by Zeta potential measurement and Boehm titration. Its sorption capacity was evaluated with batch experiments. The maximum sorption capacity was found to be 72.10 mg/g. The optimum contact time for maximum sorption was obtained in between 120- 130 min. Thermodynamic study suggested that the process is feasible, spontaneous and endothermic in nature.

Keywords: *Biomass, zeta potential, thermodynamic study, adsorption capacity, heavy metal.*

Introduction

The Earth's crust contain different components including heavy metals (www.lenntech.com). Such compounds cannot be degraded or destroyed (Gupta 2000). Such compounds can easily pass into bodies *by* food, water and air (www.lenntech.com). However, some heavy metals are needed to maintain the physiological activity of the human body. Their higher concentrations may cause poisoning the biological organism (Alluri 2007). In the higher use of heavy metals in the past few decades has resulted in a high influx of such substances in biological organism causing the risk in health of human (Wasker 2010).

Therefore such water containing heavy metals must be treated before their discharge into water bodies, which can be accomplished with biosorption technique (Kratochvil 1998). It is cost effective, eco-friendly and efficient (Kratochvil 1998). In this study *Desmostachys bipinnata* (L.) Stapf, known as Kush in Nepali is used as biomass for the removal of metal ions and its efficiency is evaluated using some of the important parameters used in adsorption process.

Material and Methods

Preparation of biosorbent

Standard stock solution (1000mg/L) of Copper metal ions was prepared from its sulphate salts. All the working solutions of different concentrations were prepared by diluting standard stock solution with 0.1M nitric acid and 0.1M HEPES (2-[4-(2-Hydroxymethyl)-1-piperazinyl] ethanesulphonic acid) was used as the buffering agent (Ghimire 2008). The pH of the working solutions was adjusted by treating with dilute nitric acid and sodium hydroxide solutions. All the reagents and chemicals used in this study were of Fisher scientific analytical grade.

A typical herb, *Desmostachya bipinnata* was grounded into powdered and treated with concentrated sulphuric acid, followed by the treatment with hydrazine monohydrate. This is called modified biomass, used for adsorption experiments. The details of preparation of biomass were published in earlier paper (Kour 2013).

All the batch experiments were carried out in 50 mL, Erlenmeyer flasks with 25 mg of modified biomass and 20 mL of copper metal ion solutions at lab temperature at 150 rpm. Zeta Potential analysis was used to determine if a surface modification to the particle has been successful or if the processing step has modified the particle surface. The pH_{pzc} measurement were carried out at different pH ranging from 1- 12. A volume of 20 mL of distilled water was taken in separate flasks and pH was adjusted with the help of 0.1 M nitric acid and sodium hydroxide, respectively. 25 mg of biomass was added to each flask and allowed to equilibrate for 2 h by shaking. Then the mixtures were filtered and the optimum pH as well as the zeta potential of the solutions was measured using pH meter (Hanna instrument).

The chemical analysis was carried out using Boehm titration to find the amount of acidic and basic functional sites present on the surface of the raw as well as modified biomass. This method involves neutralization of surface acidic sites with base (NaOH) and surface basic sites with acid (HCl). In this method 200 mg of raw and modified biomass were agitated with 50 mL of 0.02 N sodium hydroxide and 0.02 N hydrochloric acid for 24 h in separate flasks.

The mixture was filtered and 5mL of filtrate was back titrated with 0.02 N HCl or 0.02 N NaOH using methyl orange as an indicator to determine the volume of base and acid consumed. On the basis of volume of acid or base consumed by the definite weight of biomass, the amount of functional group per gram biomass is calculated according to the Boehm procedure.[6] pH measurement were carried out at 50 mg/L copper metal ions as the function of pH from one to seven.

The adsorption capacity of modified biomass were measured at different concentration from 25 - 1000 mg/L respectively, at optimum pH -5 .The flasks were shaken in a shaker for 24 h to attain the equilibrium. Then the solutions were filtered, initial and equilibrium concentrations of the metal ions were measured using ICP-AES (SPECTRO, Analytical Instrument, Kleve, German). The sorption capacity of metal ions (q in mg/g) is the concentration of the metal ions onto the biomass, which can be calculated from the mass balance principle as shown in equation (1).

$$q = \frac{C_i - C_e}{W} \times V \qquad (1)$$

where, W and V represent weight of the sorbent (mg) and volume of solution (L).

The effects of contact time on to sorption of metal ions were studied from 5 -360 min. All the flasks were shaken for the desired time interval and at the end of each contact time, the solution was filtered, then their concentrations were measured. Thermodynamic study was carried out at 25, 35, 45 and 55ºC with 25 and 50 mg/L solution of copper metal ions to evaluate the nature of sorption process.

Results and Discussion

Zeta Potential Analysis

The pH_{pzc} is the pH at which the net charge of the surface of biomass becomes zero (Deng and Ting 2005). The zeta potential of raw and modified biomass in the solution at different pH values are shown in figure1.

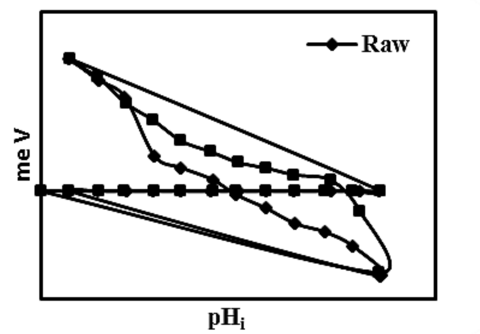

Figure 1. Zeta potential (pH_{pzc}) curve of raw and modified biomass.

The zeta potential of biomass is positive at pH< 6 and negative at pH> 6. The pH_{pzc} values had shifted towards higher pH ranges (around 11) after modification of the biomass, suggesting the proper modification with nitrogen functional groups.

Table 1. Results of Boehm titration.

Biomass	Volume consumed in mL		Functional group (meq/g)	
	NaOH	HCl	Acidic	Basic
Raw	19	11	1.9	1.1
Modified	10	38	1.0	3.8

Boehm titration

The acidic and basic functional sites on the surface of raw biomass were 1.9 and 1.1 m eq /g, respectively. After modification the values obtained for basic functional sites were increased suggesting the introduction of *N*-functional groups onto the surface of the modified biomass. The values of acidic and basic functional sites are given in table1.

Evaluation of sorption capacity

The equilibrium adsorption of metal ions onto the biomass could be best described with Langmuir isotherm and the sorption isotherms were evaluated using the most popular linearized Langmuir model represented by the following equation (2).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (2)$$

The Langmuir constant (q_m and b) can be calculated from plots of C_e/q_e versus C_e (b) and (c) respectively. The correlation coefficient (R^2) of the Langmuir plot is 0.99 which suggests that the equilibrium sorption of respective metal ions onto the modified biomass could be best described with the Langmuir isotherm equation. The maximum amount of metal ions adsorbed (q_m) is found to be 72.10 mg/g.

Evaluation of optimum contact time

Sorption kinetics is an important parameter to predict the rate and time at which the metal ions are removed from aqueous solution (Rao 2009). The experimental data showed an increase in sorption with the increase in time from 5 -130 min and then it almost reached a saturation level. As the contact time increased, the active sites on the biomass were filled and the sorption became slower and reached the plateau as shown in Figure 2(a).

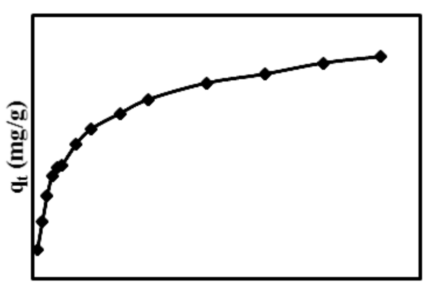

Figure 2(a). Adsorption kinetic for modified biomass.

From the figure 2(a) optimum contact time was found in between 120-130 min. All the kinetic data of copper metal ions were tested using the pseudo-first order and pseudo-second order rate equation. In case of the first-order rate equation, data were poorly fitted (data and figure not given) and the Lagergren correlation coefficient (R^2) value was very low.

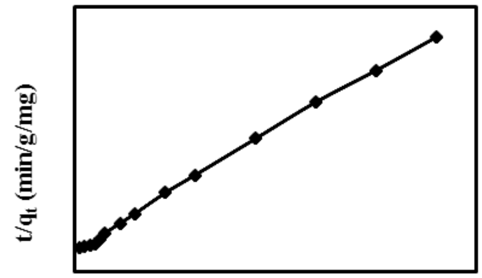

Figure 2(b). Pseudo-second order kinetic for modified biomass

Therefore, pseudo-second order kinetic model has been used to evaluate the experimental kinetics sorption data given by Ho and McKay.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where, q_t = amount of the adsorption at time t (min), (mg/g) , k_2 = rate constant of the pseudo-second order kinetic adsorption, (g/mg- min). The straight-line plot of t/qt versus t, as shown in figure 2 (b), is used to obtain the rate parameters.

Kinetic modeling of the data was studied using pseudo- second order rate equation, and its applicability was tested by linear plot of t/q_t versus t. The calculated values of k_2, q_e, and R^2 are given in table 2. The R^2 value obtained is close to 1.0, which indicates the applicability of the model for the entire sorption process and confirmed the chemisorptions of the copper metal ions onto the modified biomass.

Evaluation of thermodynamic parameters

The thermodynamic study provides the information on the nature of adsorption process. The important parameters used are the standard Gibb's free energy (ΔG^o), the enthalpy of sorption (ΔH^o) and the entropy (ΔS^o) changes due to transfer of one mole of solute from solution to solid- liquid interface.

Here, ΔH^o and ΔS^o were calculated from the slope and intercept of the plot, respectively.

Table 3. Thermodynamic parameters for sorption of Cu(II) ions onto the modified biomass

Cu(II) ions	Temp(K)	ΔG^o (J mol^{-1})	R^2	ΔH^o (J mol^{-1})	ΔS^o (J mol^{-1} K^{-1})
25 (mg/L)	298	-6082.91	0.990	29.89714	120.6361
	308	-7169.99			
	318	-8645.40			
	328	-9610.36			
50 (mg/L)	298	-1883.88	0.978	39.83237	140.6729
	308	-3789.59			
	318	-5023.32			
	328	-6128.78			

The thermodynamic parameters calculated by using above relationships are given in Table 3.

Table 2. Pseudo-second order kinetics for modified biomass.

Biomass	Metal ions	q_e (mg/g)	k_2(g/mg -min)	R^2
Modified	Cu(II)	33.84	0.96 x10^{-3}	0.99

The standard free energy change (ΔG^o) can be calculated from the following relation (4).

$$\Delta G^o = -RT \ln K_C \tag{4}$$

where, T(K) is the absolute temperature, R(JK^{-1}mol^{-1}) is gas constant and K_C is equilibrium constant. It can be calculated from the equation (5).

$$K_C = \frac{C_{ae}}{C_e} \tag{5}$$

where, C_{ae} and C_e are the equilibrium concentration of metal ions (mg/L) on the sorbent and in solution, respectively. The enthalpy change (ΔH^o) and entropy change (ΔS^o) can be obtained from equation (6).

$$\ln K_C = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{6}$$

The plot of ln K_C as a function of 1/T gives a straight line as shown in figure 3.

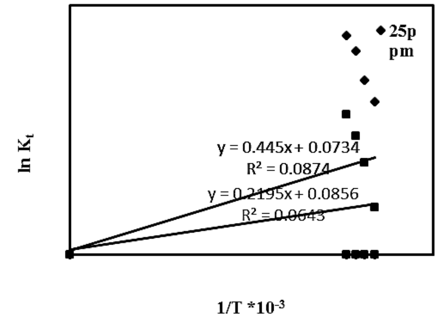

Figure 3. Thermodynamic parameters of Cu (II) sorption onto the modified biomass

The negative value of Gibbs free energy (ΔG^o) suggests that the process of sorption is spontaneous and feasible (Torres 2006). The positive value of enthalpy change (ΔH^o) indicates the endothermic nature of sorption process where as the positive value of entropy change (ΔS^o) shows the affinity of the biomass towards copper metal ions and suggests an increased randomness at the biomass and solution surface (Deng *et al.* 2003).

Conclusion

This research work has explored a new biomass *Desmostachya bipinnata*, which is cost effective, efficient and ecofriendly. It was characterized by zeta potential measurement and Boehm titration, which suggested the modification on the biomass. Batch adsorption experiments were performed at optimum pH 5 to evaluate the adsorption capacity, optimum contact time and thermodynamic parameter for the Cu metal ions. The sorption performance was fitted well with Langmuir model with correlation coefficient R^2 of 0.99 and the rate of sorption followed the pseudo second order kinetics. The results of thermodynamic study indicate the spontaneity and feasibility of the process.

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