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Original Research Paper

Adsorption Study of Aluminium onto *Curcuma longa*

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ABSTRACT

Curcuma longa or turmeric was used as adsorbent for aluminium removal. The effects of operational factors, including pH, contact time and dose were studied, and their optimal controls were proven. Overall uptake of *Curcuma longa* was at the maximum when pH ranged between 5 and 9 and the optimal removal was 91.2%. Optimal removal of 95.8% was achieved at the 90th minute for the batch experiment. A dose of 6 g/L was enough for optimal removal of 93.6%. Aluminium adsorption onto *Curcuma longa* was found to have a good correlation with Freundlich adsorption model contrary to the Langmuir model. Simple kinetic model such as pseudo-first order, pseudo-second order, Elovich equation and intra-particulate mixing models were employed to determine the adsorption mechanism. The adsorption kinetic study showed that the pseudo-second order kinetic was the most applicable, and this result suggests that chemical adsorption process was more dominant.

INTRODUCTION

Aluminium can be found all around the environment such as water, plants and also in food. Aluminium compounds are used in industrial and pharmaceutical sectors as food additive, cosmetics and household products (de Amorim et al. 2006, Krewski 2006). The main source of aluminium uptake into human was through food, drinking water and medicine (Yokel & McNamara 2001). Neurotoxicity of aluminium to human health was discovered a few decades ago. Aluminium accumulation may increase the risks of neurological disorders and bone disorder such as Alzheimer's disease, Parkinson's disease, dementia and osteomalacia (Zatta 2000, Buratti 2006).

Curcuma longa or turmeric belongs to the family Zingiberaceae and is in the same group with ginger and galangal. The genus *Curcuma* includes hundreds of species of plants with underground rhizome (Jayaprakasha et al. 2005). Curcurmin (an active ingredient commonly found in *Curcuma* sp.) has been used in traditional medicine to cure cuts, asthma, epilepsy, kidney stone, abdominal cramp, high cholesterol level and Alzheimer's disease. However, its pharmacological mechanism, especially for Alzheimer's disease is still not fully understood (Duke 2002).

There are many researches that study the relation between curcumin and aluminium in neurotoxicity. Previous study indicated curcumin's ability to bind redox active metals and cross the blood-brain barrier could be playing the crucial role in preventing against Al-induced neurotoxicity (Pallavi Sethi et al. 2009). Treatment with tannic acid and curcumin reduced the accumulation of the Al and Pb in rat's brain (Candan & Tuzmen 2008). Curcumin exerts a protective effect against aluminium-induced elevation of ageing-related changes by modulating the extent of oxidative stress (by upregulating the activities of antioxidant enzymes) and by regulating the activities of Na^+, K^+ ATPase, PKC and AChE. Therefore, it is suggested that curcumin counters aluminium-induced enhancement in ageing-related processes (Sharma et al. 2009). Hence, this study aims to investigate the adsorption properties of aluminium onto *Curcuma longa* powder in term of adsorption equilibrium and kinetics.

MATERIALS AND METHODS

Preparation of adsorbent: Fresh *Curcuma longa* pieces were weighed and dried in the Protech Model BS240 oven for 4 hours. The dried pieces were then grounded to become powder.

Batch adsorption experiments: Batch adsorption experiments were done to determine the effect of pH, contact time and adsorbent dose on aluminium removal.

Effect of pH: Sulphuric acid (37%) or sodium hydroxide (1 M) was added to a known concentration of aluminium solution to control its pH. Batch experiment was done by adding 0.1g of *Curcuma longa* powder in a series of six conical flasks containing aluminium solution with pH ranging from 2 to 12. The flasks were covered by parafilm and shook with Orbital shaker Model 719 at 200 rpm. After shaking for 120 minutes, the shaker was turned off to let the solution to stabilize for 5 minutes. The solution was then filtered through a size 40 Whatman filter paper followed by 0.45µm cellulose nitrate filter membrane. The final aluminium

concentration in the filtrates is then measured by Eriochrome Cyanine R method (ECR) (APHA 2005)

Effect of contact time: Eight conical flasks containing 50 mL of aluminium solution were prepared and their initial aluminium concentrations were determined. In each of the conical flasks, 0.1 g of *Curcuma longa* powder was added. The mixtures were then subjected to a shaking procedure at 200 rpm for 5, 10, 15, 30, 45, 60, 120 and 150 minutes. After leaving the solution to stabilize for 5 minutes, the solutions were filtered and aluminium concentrations in each flask were measured.

Effect of dose: In this experiment, the amount of *Curcuma longa* powder added into the aluminium solution was varied. The amount added were 0.05g, 0.10g, 0.15g, 0.20g, 0.25g, 0.30g, 0.35g and 0.40g respectively. Each determined mass of *Curcuma longa* was added into 8 separate conical flasks containing 50 mL of aluminium solution and shook for 120 minutes at 200 rpm. After a 5-minute settling time, the solution was then filtered through a size 40 Whatman filter paper followed by 0.45µm cellulose nitrate filter membrane. The final aluminium concentration in the filtrates is then measured by ECR method (APHA 2005).

Adsorption isotherm and kinetics: In isotherm study, the amounts of *Curcuma longa* powder used were 0.05g, 0.10g, 0.15g, 0.20g, 0.25g, 0.30g, 0.35g, and 0.40g respectively. In the kinetic studies, shaking time was varied for 5, 10, 15, 30, 45, 60, 90, 120 and 150 minutes.

RESULTS AND DISCUSSION

Effect of pH: This study found that aluminium removal was at its optimal rate at pH ranging between 5 and 9 (Fig. 1). Optimum removal rate was recorded to be 91.2% with the mean value ranging from 85.95±5.02% to 91.65±0.63%. This showed that pH plays an important role in determining adsorption capacity of *Curcuma longa* to aluminium. pH influences the binding sites of metal to the adsorption surfaces. In addition, pH also influences the chemical structure of the metal in aqueous solution, hence influencing its bioavailability (Ozacar 2005).

Effects of dosage: Adsorption capacity of *Curcuma longa* to aluminium increased by increasing its dosage as shown in Fig. 2. Optimal aluminium removal of 93.65% was obtained at the dosage of 6 g/L. With increased adsorbent dosage, aluminium increases because of the increased Al removal in ion exchange site ability, surface areas and the number of available adsorption sites (Naiya et al. 2009).

Effect of contact time: Adsorption capacity for aluminium increased with increased contact time (Fig. 3) until it reached equilibrium. Optimal contact time for aluminium adsorp-

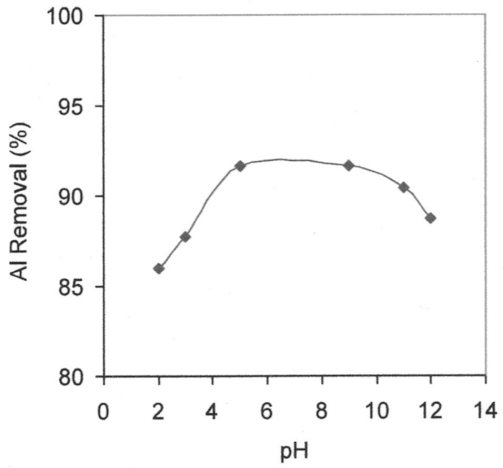

Fig. 1: Optimization of pH for Al removal from aqueous solution using *Curcuma longa* powder.

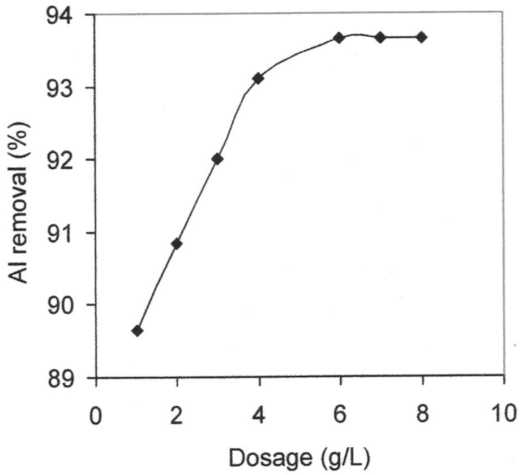

Fig. 2: Dosage effect for Al removal from aqueous solution using *Curcuma longa* powder.

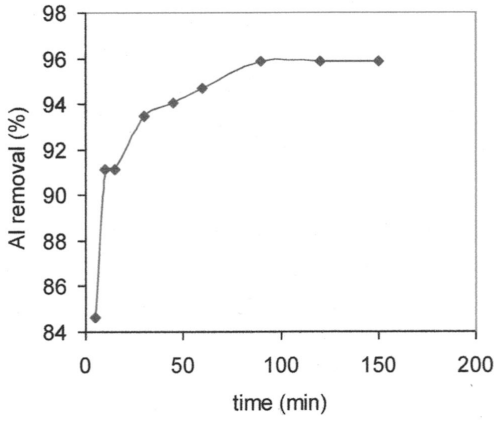

Fig. 3: Optimum contact time determination for Al removal.

tion was 90 minutes with 95.85% removal. Contact time is the time needed for adsorption process to achieve equilibrium when no more changes in adsorptive concentration were observed after a certain period of time. Long contact time was required to achieve equilibrium because of the differences in the characteristics and properties of the adsorbents (Hussein et al. 2006).

Adsorption isotherm: Freundlich isotherm model was used as a model for adsorption on heterogeneous surfaces. This isotherm is explained based on the following equation;

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad ...(1)$$

Where q_e is the adsorption capacity at equilibrium, K_F and n is the constant value in the equation was obtained from the y-intercept and slope of the log q_e versus log C_e plot as showed in Fig. 4(a).

The Langmuir adsorption isotherm assumed that maximum adsorption equals to the saturation of a monolayer of aluminium on the surface of the adsorbent at constant energy. Langmuir equation is commonly used for monolayer adsorption onto adsorbent with limited adsorption sites. The equation is as follows;

$$q_e = QbC_e /1+ bC_e \quad ...(2)$$

This equation can be transformed into linearized forms as follows;

$$\frac{1}{qe} = \frac{1}{Q} + \frac{1}{QbCe} \quad ...(3)$$

The Q constant denotes the maximum adsorption capacity or maximum number of aluminium ions per mass unit of *Curcuma longa* that can form a complete monolayer that covers the whole adsorbent surface at high aluminium ion equilibrium. Fig. 4(b) shows the Langmuir plot for this experiment. Based on the correlation coefficient, R^2 values of both Freundlich and Langmuir models are listed in Table 1. We found that Freundlich model is more suitable to explain the adsorption isotherm. Aluminium maximum adsorption capacity on *Curcuma longa* was up to 7.68 mg/g.

Adsorption kinetics: Most sorption processes take place by a multistep mechanism comprising: (i) diffusion across the liquid film surrounding the solid particles (a process controlled by an external mass transfer coefficient), (ii) diffusion within the particle itself assuming a pore diffusion mechanism (intraparticle diffusion), and (iii) physical or chemical adsorption at the site (Kumar et al. 2005). Four kinetic models were tested to fit the experimental data points; intraparticle diffusion, pseudo-first-order, pseudo-second-order and Elovich models. Mathematical expressions of these models are given in eqs. (4)-(7), respectively (Lagergren 1898, McKay et al. 1999, Chien & Clayton 1980, Weber & Morris 1963).

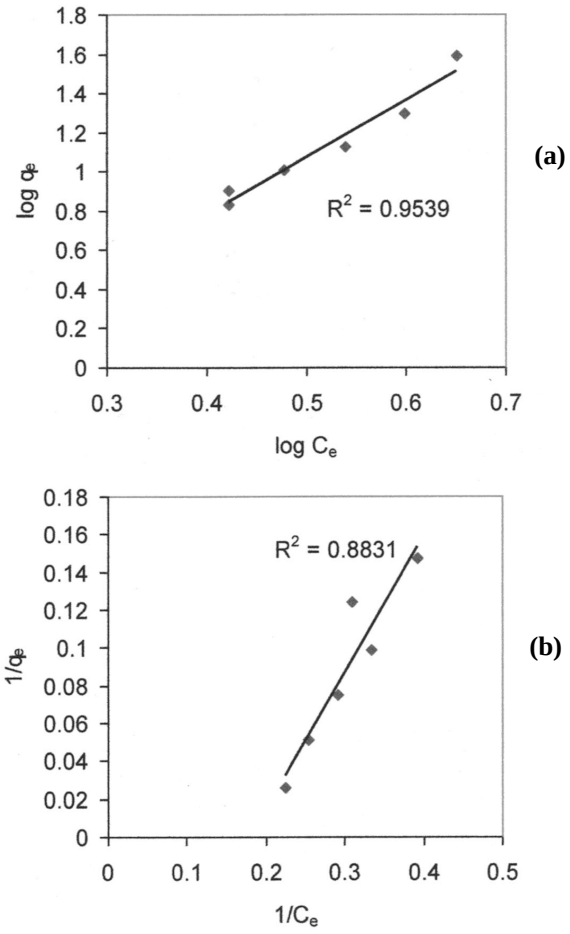

Fig. 4: Freundlich (a) and Langmuir (b) isotherm for Al adsorption onto *Curcuma longa* powder.

$$\ln q_e - q_t = \ln q_e - K_1 t \quad ...(4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad ...(5)$$

$$q_t = \frac{1}{b} \ln (ab) + \frac{1}{b} \ln t \quad ...(6)$$

$$q_t = k_i t^{0.5} + c \quad ...(7)$$

Where q_t and q_e are the amounts of aluminium adsorbed at a time t and at equilibrium, respectively. While k_i is the intraparticle diffusion constant, c is intercept; k_1 and k_2 are pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of a and b are Elovich coefficients representing initial sorption rate and desorption constants, respectively. Fig. 5 (d) showed the kinetic adsorption plot for aluminium adsorption onto *Curcuma longa*. Kinetic adsorption for pseudo-second-order model occurs chemically

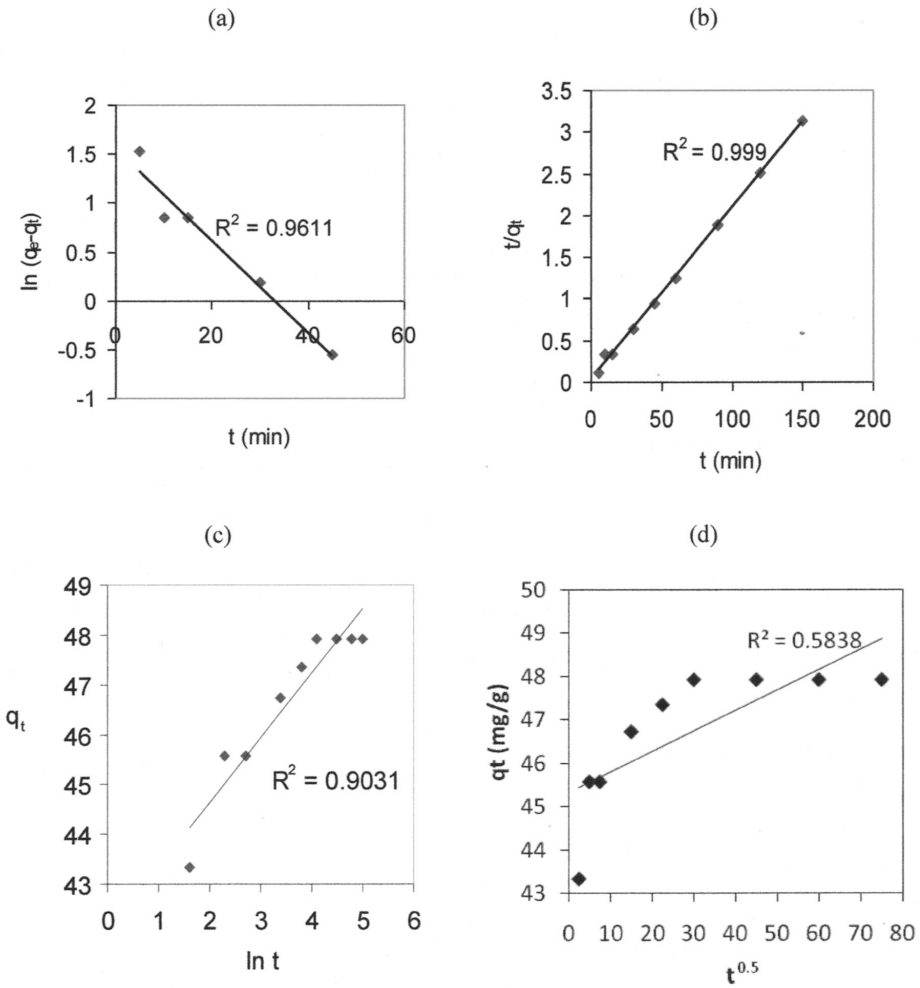

Fig. 5: Kinetic adsorption study for Al adsorption onto *Curcuma longa* powder according to (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich and (d) Intraparticle kinetic models.

Table 1: Constant values and R^2 for Freundlich and Langmuir models.

Freundlich	Constant values	Langmuir	Constant values
R^2	0.9539	R^2	0.8831
1/n	3.2345	Q_b (mg/g)	7.6839
KF (mg/g)(mg/L)^n	0.2519	b (ml/mg)	0.1805

and involves valence force through ion sharing or exchange between the adsorbent and the ions adsorbed onto it (Septhum et al. 2007). Pseudo-second-order kinetic model showered the strongest correlation ($R^2 = 0.9888$). This suggests that aluminium adsorption occurs in a monolayer fashion, and its adsorption pattern occurs via chemical adsorption or via ion exchange. Aluminium ions react chemically with the specific binding sites on the surface of *Curcuma longa.*

The Elovich equation has been used to further explain the second order kinetics model with the assumption that the actual adsorption surface is energetically heterogeneous (Thomas & Thomas 1997). Elovich kinetic model showed a good correlation for *Curcuma longa* ($R^2 > 0.9$) despite the correlation value being lower than the correlation coefficient for the first and second order kinetic models. Therefore, this could be used to explain that the adsorption surface is energetically heterogeneous. The plot of intraparticle model was expressed by q_t versus $t^{0.5}$ as shown in Fig. 5(d). It was present multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or

Table 2: Constant values for adsorption kinetics models.

Constant	Value
Pseudo-first-order model	
R^2	0.9611
k_1 (min^{-1})	0.0473
q_e (mg/g)	4.78
Pseudo-second-order model	
R^2	0.9999
k_2 (g/mg min)	0.0512
qe (mg/g)	48.78
Elovich model	
R^2	0.9031
α (mg/g min)	3.463
β (g/mg)	0.7849
q_e (mg/g)	7.0068
Intraparticle diffusion model	
R^2	0.5838
Ki (mg/g $min^{1/2}$)	0.0472
c	45.25
q_e (mg/g)	45.70

the boundary layer diffusion of solute molecules. The second portion describes the gradual adsorption stage, where intraparticle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage (Aharoni & Ungarish 1977).

Table 1 gives the constant values and correlation coefficients for both Freundlich and Langmuir models. On the other hand, Table 2 summarizes the constant values for the adsorption kinetics and their correlation coefficients.

CONCLUSION

The results and discussion presented in this paper showed that the optimal parameters determined in the experiment were effective in determining the efficiency of aluminium adsorption onto *Curcuma longa*. Comparison between two mathematical equations for the adsorption isotherm revealed that the strongest correlation was shown by the Freundlich model ($R^2 = 0.9458$). Therefore, the Freundlich model is used to represent the adsorption of aluminium onto *Curcuma longa*. Second order kinetic model is used to explain the adsorption kinetics of aluminium onto *Curcuma longa* ($R^2 = 0.9888$). This suggests that aluminium adsorption occurs in the multi-layer mode, and it occurs chemically or via ion exchange between the phenolic functional groups in *Curcuma longa* with aluminium ion.

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