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Adsorption Study of Aluminium onto Curcuma Longa

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Abstract: This study was conducted to determine the isotherm and kinetics of aluminium adsorption on *Curcuma longa. 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. Uptake of Al^{3+} ion onto *Curcuma longa* was shown on a pH dependent profile. Overall uptake of *Curcuma longa* was at the maximum when pH ranged between 5 to 9 and the optimal removal was 91.2%. Optimal removal of 95.8% was achieved at the 90th minute for 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 Freudlinch adsorption model (R^2 = 0.9458) as opposed 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 (R^2 = 0.9888), and this result suggests that chemical adsorption process was more dominant.

Key words: Aluminum, *Curcuma longa*, turmeric, adsorption.

INTRODUCTION

Aluminium can be found all around the environment such as water, plants and also in food (Amorim *et al.,* 1997; Solyak *et al*., 1997). According to Krewski *et al* (2006), aluminium compounds were used in industrial and pharmaceutical sectors as food additive, cosmetics and household products. According to Yokel and McNamara (2001), the main source of aluminium uptake into human was through food, drinking water and medicine. Neurotoxicity of aluminium to human health was discovered a few decades ago (Zatta, 2000), aluminium accumulation may increase the risks to neurological disorder and bone disorder such as Alzheimer's disease, Parkinson's disease, dementia and osteomalacia (Buratti *et al.,* 2006)

Adsorption is referred to as the ability of certain solid to concentrate a compound selectively from a solution onto its surface. Adsorption process generally can be divided into two parts i.e. physical and chemical adsorption depending on the type of bond that binds the molecule and the adsorbent surface (Pehlivan *et al.,* 2008). Adsorption isotherm is an equilibrium plot of concentration in the solid phase concentration (q_e) versus in the liquid phase (C_e) that is usually explained via two adsorption models namely Langmuir Model and Freudlinch Model. Adsorption kinetics refer to the relationship between adsorption capacity with time (Cooney, 1998).

Adsorbent material is any solid that has the ability to selectively adsorb certain molecules through the liquid phase onto its surface. *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). According to Duke (2002), cucurmin (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. The present work investigates the adsorption properties of soluble aluminum onto *Curcuma longa* powder. The factor that effect adsorption capacity such as pH, contact time and adsorbent dosage were examined.

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MATERIAL AND METHODS

Preparation of Adsorbent:

Fresh Curcuma longa pieces were weighed and dried in the Protech Model BS240 oven for 24 hours at 60ºC. 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:

Sulfuric 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 6 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 Whattman filter paper followed by 0.45um cellulose nitrate filter membrane. The final aluminium concentration in the filtrates is then measured by ECR method (APHA, 2005)

Effect of Contact Time:

Eight conical flasks containing 50 mL of aluminum 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 respectively. After leaving the solution to stabilize for 5 minutes, the solutions were filtered and aluminum 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 o f aluminium solution and shaked for 120 minutes at 200 rpm. After a 5-minute settling time, the solution was then filtered through a size 40 Whattman filter paper followed by 0.45um 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 amount 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 to 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 to 9 (Figure 1). Optimum removal rate was recorded to be 91.2% with the mean value ranged from 85.95 ± 5.02 % to 91.65 ± 0.63 %. This result showed that pH plays an important role in determining adsorption capacity of *Curcuma longa* to aluminium. According to Ozacar and co-workers (2005), pH influences the binding sites of metal to the adsorption surfaces. In addition, pH also influences the chemical structure of the metal in aques solution, hence influences its bioavailability.

Effects of Dosage:

Adsorption capacity of *Curcuma longa* to aluminium increased by increasing its dosage, as shown in Figure 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 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 (Figure 3) until it reached equilibrium. Optimal contact time for aluminum adsorption 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 (Hussin *et al.,* 2006).

Adsorption Isotherm:

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

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (1)$$

Where q_e is the adsorption capacity at equilibrium, K_F and n are 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 Figure 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;

$$q_e = \frac{QbC_e}{1+bC_e} \qquad (2)$$

This equation can be transformed into linearized forms as follows;

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e} \qquad (3)$$

The Q constant denotes the maximum adsorption capacity or maximum number of aluminum ion per mass unit of *Curcuma longa* that can form a complete monolayer that covers the whole adsorbent surface at high aluminium ion equilibrium. Figure 4(b) showed the Langmuir plot for this experiment. Based on the correlation coefficient, R^2 values of both Freundlich and Langmuir models as listed in Table 1, we found out that Freundlich model is more suitable to explain the adsorption isotherm. Aluminum 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 a 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).

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}\left(t\right) \qquad (5)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (6)$$

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

Where q_t and q_e are the amounts of aluminium adsorbed at 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 α and β are Elovich coefficients representing initial sorption rate and desorption constants, respectively. Figure 5 showed the kinetic adsorption plot for aluminum adsorption onto *Curcuma longa*.

Kinetic adsorption for pseudo-second-order model occurs chemically 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 kinetics model showered the strongest correlation (R^2 = 0.999). This suggests that aluminium adsorption occurs in a monolayer fashion and its adsorption pattern occurs via chemical adsorption or via ion exchange. Aluminum ions react chemically with the specific binding sites on the surface of *Curcuma longa.* The kinetic study results as shown in Table 2 indicated that the adsorption of aluminum was suited to pseudo second-order kinetic model by possessing the highest R^2 value (R^2 = 0.999). These results were also been supported by the values of adsorption capacity at equilibrium time, q_e (24.57 mg/g) from both calculated and experimental values. The results have been shown that the calculated q_e values that obtained from pseudo-second-order kinetics model show a good agreement with the experimental value (20.12 mg/g, obtained from Figure 3) which indicates that the second-order kinetic model describes well for the adsorption of aluminum onto *Curcuma longa*.

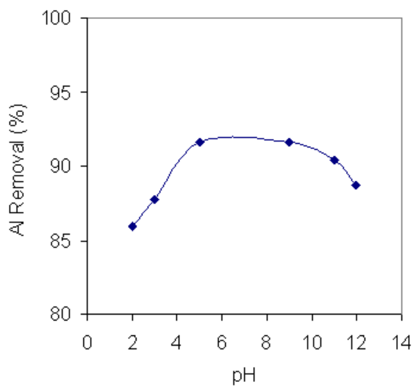


Fig 1: Optimization of pH for Al removal from aqueous solution using *Curcuma longa* powder.

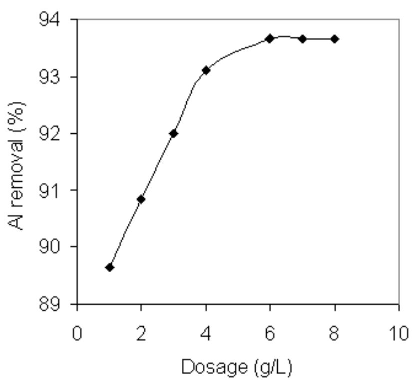


Fig. 2: Dosage effect for Al removal from aqueous solution using *Curcuma longa* powder.

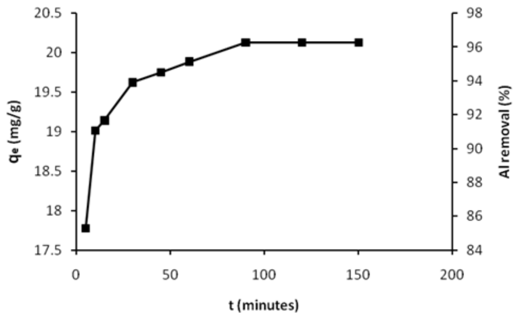
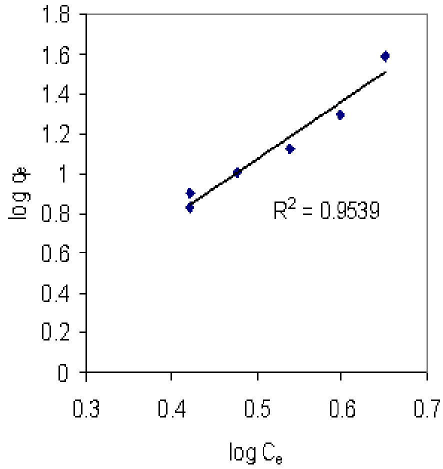
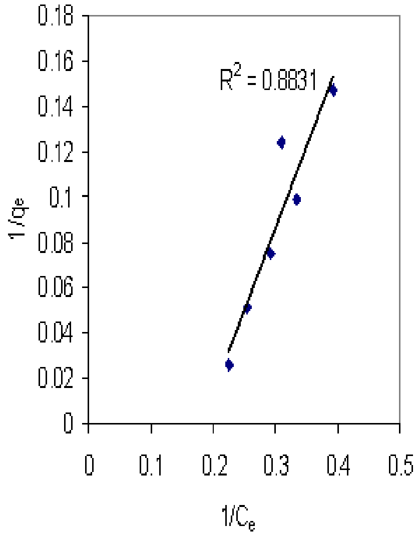


Fig. 3: Optimum contact time determination for Al removal.



(A)



(B)

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

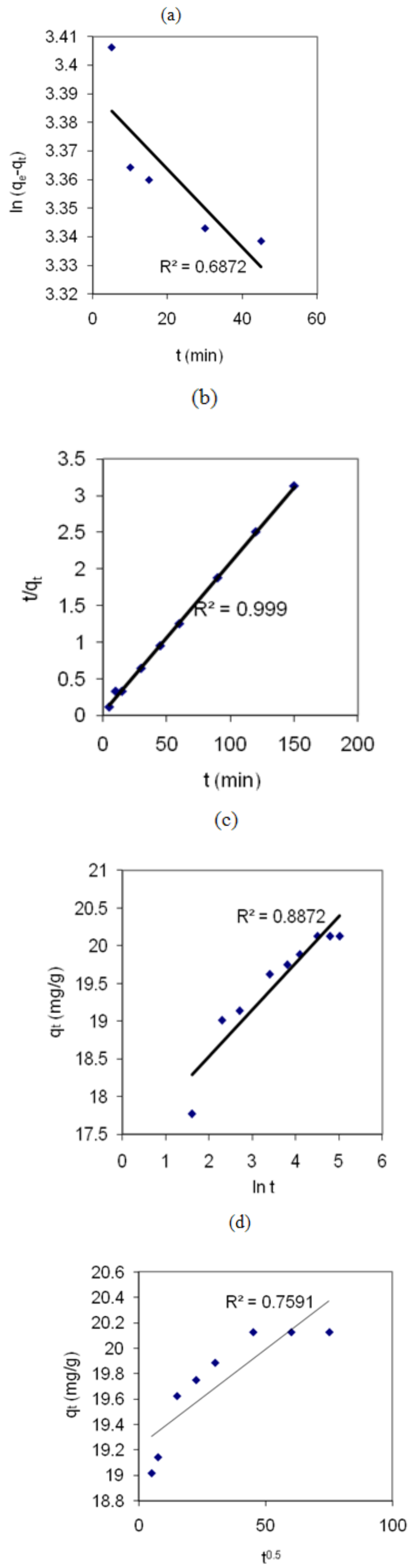


Fig. 5: Kinetic adsorption study for Al adsorption onto *Curcuma longa* powder according to (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich and (d) Intra-particle kinetic models.

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

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

Table 2: Constant values for adsorption kinetics models.

Constant	Value
Pseudo-first-order model	
R^2	0.6872
k_1 (min^{-1})	0.0014
q_e (mg/g)	29.69
Pseudo-second-order model	
R^2	0.9999
k_2 (g/mg min)	0.0407
q_e (mg/g)	24.57
Elovich model	
R^2	0.8872
α (mg/g min)	3.16 x 10^8
β (g/mg)	1.18
Intraparticle diffusion model	
R^2	0.7591
K_i (mg/g min$^{1/2}$)	0.0152
c (mg/g)	19.232

According to Thomas and Thomas (1997), the Elovich equation has been used to further explain the second order kinetic's model with the assumption that the actual adsorption surface is energetically heterogeneous. The plot of intraparticle model was expressed by q_t versus $t^{0.5}$ as shown in Figure 5. 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 the boundary layer diffusion of solute molecules. The second portion describes the gradual adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage (Aharoni & Ungarish, 1977).

Conclusion:

The result and discussions 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 kinetic of aluminium onto *Curcuma longa* (R^2 = 0.9888). This suggests that aluminium adsorption occurs in the multi-layer mode, and it occurs chemically between the phenolic functional groups in *Curcuma longa* with aluminium ion.

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