

Full Length Research Paper

## Second-order kinetic model for the adsorption of divalent metal ions on *Sida acuta* leaves

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The removal of metal ions from effluents is of importance to many countries of the world both environmentally and for water re-use. A comparison was made of the linear least-squares method of the widely used pseudo-second order kinetic model for the sorption of some divalent metal ions onto *Sida acuta* leaves. Four pseudo-second order kinetic linear equations were used for this study. The results obtained from the experimental data for *S. acuta* leaves of 1.0 g with particle size range of 0.25 to 0.5 mm and at 300 rpm with initial concentrations of 5.0, 4.0, 20 and 2.5 mg/dm<sup>3</sup> for Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions, respectively showed that when the four pseudo-second order kinetic linear equations were compared, the Type 2 model with regression values for Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions as 0.979, 0.995, 0.991 and 0.965 respectively showed best fit for the sorption onto *S. acuta* leaves. This provided the evidence that the divalent metal ions sorption unto *S. acuta* followed the pseudo-second – order kinetic expression.

**Key words:** *Sida acuta*, sorption, divalent metal ions, kinetic model, effluents.

### INTRODUCTION

Elements in every group of the periodic table have been found to be stimulatory to animals. Most metals in the fourth period are carcinogenic. It can be assumed that the carcinogenicity is related to the electronic structure of transition and inner transitional metals (Luckey and Venugopal, 1977). Sorption of pollutants from wastewater has long been studied. The rate at which sorption takes place is of the utmost importance when designing batch sorption systems, consequently it is important to establish the time dependence of such systems under various process conditions (Ho, 2006).

The sorption of metal ions from aqueous solution plays an important role in water pollution control, and in recent years there has been considerable interest in the use of low-cost sorbents such as peat for this purpose.

However, although the sorption kinetics of individual metal ions onto this type of material has been examined, the processes which occur are not completely understood, for instance, the rate limiting step and the bonding mechanism (Ho and McKay, 2000).

The application of low-cost sorbents including carbonaceous materials, agricultural products and waste by-products has been investigated. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, rice bran, soybean and cottonseed hulls, peanut shells, hazelnut shell, rice husk, sawdust, wool, orange peel and compost and leaves. Most of this work has shown that natural products can be good sorbents for heavy metals (Ho et al., 2002).

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**Table 1.** A comparison of the second order models.

References	Linear form	Plot
Sobkowsk and Czerwinski (1974)	$\frac{\theta}{1-\theta} = k_2 t$	$\frac{\theta}{1-\theta}$ vs. t
Ritchie (1977)	$\frac{q_\infty}{q_\infty - q} = \alpha t + 1$	$\frac{q_\infty}{q_\infty - q}$ vs. t
Blanchard et al. (1984)	$\frac{1}{n_0 - n} - \alpha_\beta = kt$	$\frac{1}{n_0 - n}$ vs. t
Ho (1995)	$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t$	$t/q_t$ vs. t

*Sida acuta* is a malvaceous weed that frequently dominates improved pastures, waste and disturbed places roadsides (Mann et al., 2003). The plant is native to Mexico and Central America but has spread throughout the tropics and subtropics (Holm et al., 1977). A comparison of the second order model is shown in Table 1. Sobkowsk and Czerwinski (1974) used a second-order rate equation based on the sorption capacity of a solid for a higher concentration of the solid for the rate of reaction of carbon dioxide sorption on a platinum electrode. Ritchie (1977) used a second-order empirical equation to test the sorption of gases onto a solid. The Ritchie equation has also been applied in solution/solid sorption systems. Blanchard et al. (1984) reported a similar rate equation for the overall exchange reaction of  $\text{NH}_4^+$  ions fixed in zeolite by divalent metallic ions in solution. The second-order expression of Blanchard et al. (1984) was used to describe the kinetics of exchange processes between the sodium ions from zeolite A and cadmium, copper, and nickel ions from solutions. In recent years, Ho (2006) described sorption, which included chemisorption and provided a different idea to the second-order equation called a pseudo-second-order rate expression.

The purpose for this study is to know if the sorption of some divalent metal ions onto *S. acuta* leaves used as sorbent follows the pseudo-second order kinetic expression.

## MATERIALS AND METHODS

### Preparation of *S. acuta* leaves

The leaves were dried at room temperature for a period of three days. The sorbent was screened to obtain a geometrical size of 0.25 - 0.5 mm. This was to allow for shorter diffusion path, thus allowing the sorbent to penetrate deeper into the effluent more quickly, resulting in a higher rate of adsorption (Adeyinka et al., 2007).

### Phytochemical screening

Phytochemical tests were carried out on the powdered plant material employing standard phytochemical procedures to establish the presence or otherwise of secondary metabolites such as alkaloids, steroids, flavonoids, tannins and saponin glycosides (Sofowora, 1982; Evans, 1989).

### Preparation of synthetic wastewater

Stock solutions of Nickel, Lead, Copper, Zinc and Aluminium were prepared with distilled water and Nickel (II) Sulphate, Lead (II) Nitrate, Zinc (II) Sulphate, and Copper (II) Sulphate respectively. All working solutions were obtained by diluting the stock solution with distilled water. The pH of the effluent was adjusted to a pH of 5 to prevent hydrolysis by the use of relevant acids and bases. The concentration of metal ions in effluent was analyzed by Atomic Absorption Spectrophotometer.

For quality control purpose, the diluted water were digested and analyzed with every sample group to track any possible contamination source. A duplicate was analyzed for every sample to track experimental error and show capability of reproducing results (Marshall and Champagne, 1995).

### Adsorption experiment

The experiments were carried out in the batch mode for the measurement of adsorption capabilities. The bottles with 500 ml capacity were filled with 50 ml of the synthetic wastewater, and 1 g of *S. acuta* dried leaves (ground). The bottles were shaken for a predetermined period at room temperature in a reciprocating shaker for 2 h at 300 rpm.

The separation of the adsorbents and solutions was carried out by filtration with Whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an Atomic Absorption Spectrophotometer (AAS).

## RESULTS AND DISCUSSION

Table 2 shows that *S. acuta* contained bioactive constituents such as alkaloids, flavonoids, cardiac and

**Table 2.** Results of phytochemical tests.

Test	Observation	Inference
Molisch's test for carbohydrates	Deep violet ring was observed at the interface	Carbohydrates present
Fehling's solution test for reducing sugar	A brick-red precipitate was observed	Glycoside present
Frothing test for saponin glycosides	Persistent frothing was observed	Saponin glycoside present
Blood haemolysis test for saponin glycoside	Clear zones of haemolysis was observed	Saponin glycoside confirmed
Borntrager's test for anthraquinone glycosides	No pink colouration was observed	Anthraquinone glycoside absent
Test for cyanogenetic glycosides	Yellow colour of sodium picrate paper retained.	Cyanogenetic glycoside absent
Keller-killiani test for deoxy-sugar	A brown ring was observed at the interface	Deoxy-sugar present in cardiac glycosides
Kedde's test for lactone ring	A violet colour that faded gradually with the deposition of whitish crystalline solid was observed	Lactone ring present in cardiac glycosides
Lieberman's test for steroidal ring	A colour change from violet to blue to green was observed	Steroidal ring present in cardiac glycosides
Salkowski's test for steroidal ring	A reddish-brown colour was observed at the interface	Steroidal ring present in cardiac glycosides
Tests for flavonoids	A yellow colour which turned to colourless was observed	Flavonoids present
Aqueous ferric chloride test for Tannins	No blue black, green or blue green precipitate or colouration observed	Tannins absent
Test for Phlobatannins	No red precipitate was observed	Phlobatanins absent
Test for alkaloids using water, methanol and chloroform as extracting solvents	Wagner's, Hager's and Dragendorff's reagent gave characteristic precipitates with methanol and chloroform extracts	Alkaloidal base present

saponin glycosides. An expression of the pseudo-second-order rate based on the solid capacity has been presented for the kinetics of sorption of divalent metal ions onto peat (Ho, 2006):

$$q_t = \frac{q_e^2 kt}{1 + q_e kt} \quad (1)$$

where  $k$  is the pseudo-second-order rate constant (g/mg min),  $q_e$  is the amount of cadmium ion sorbed at equilibrium (mg/g), and  $q_t$  is amount of cadmium ion on the surface of the tree fern at any time,  $t$ , (mg/g). Equation 1 can be rearranged to obtain

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

This has a linear form of

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

If the initial sorption rate, as  $h = q_t/t$  when  $t$  approaches 0,  $h$  (mg/g min), is

$$h = kq_e^2 \quad (4)$$

**Table 3.** Pseudo-second order kinetic model linear forms.

Type	Linear form	Plot	Parameter
Type 1	$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t$	$t/q_t$ vs. $t$	$q_e = 1/\text{slope}$ $k = \text{slope}^2 / \text{intercept}$ $h = 1/\text{intercept}$
Type 2	$\frac{1}{q_t} = \left( \frac{1}{kq_e^2} \right) \frac{1}{t} + \frac{1}{q_e}$	$1/q_t$ vs $1/t$	$q_e = 1/\text{intercept}$ $k = \text{intercept}^2 / \text{slope}$ $h = 1/\text{slope}$
Type 3	$q_t = q_e - \left( \frac{1}{kq_e^2} \right) \frac{q_t}{t}$	$q_t$ vs $q_t/t$	$q_e = \text{intercept}$ $k = -1/ \text{intercept} \times \text{slope}$ $h = - \text{intercept} / \text{slope}$  $q_e = - \text{intercept} / \text{slope}$
Type 4	$\frac{q_t}{t} = kq_e^2 - kq_e^2 q_t$	$q_t/t$ vs $q_t$	$k = \text{slope}^2 / \text{intercept}$ $h = \text{intercept}$

Equation 2 can be rearranged to obtain

$$q_t = \frac{t}{1/h + t/q_e}, \tag{5}$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t. \tag{6}$$

In order to distinguish the kinetics equation based on the concentration of a solution from the sorption capacity of solids, this second-order rate equation has been called a pseudo-second-order one since it was represented.

The pseudo-second-order rate constants can be determined experimentally by plotting  $t/q_t$  against  $t$ . Although there are many factors which influence the sorption capacity, including the initial sorbate concentration, the reaction temperature, the solution pH value, the sorbent particle size and dose, and the nature of the solute, a kinetic model is concerned only with the effect of observable parameters on the overall rate (Ho, 2006). In this study, regression,  $r^2$ , was used to test the best-fitting of the kinetic model to the experimental data.

The least squares method is used for finding the parameters for kinetic models. The pseudo-second-order kinetic model has been linearized into four different types which were shown in Table 3 and a simple linear

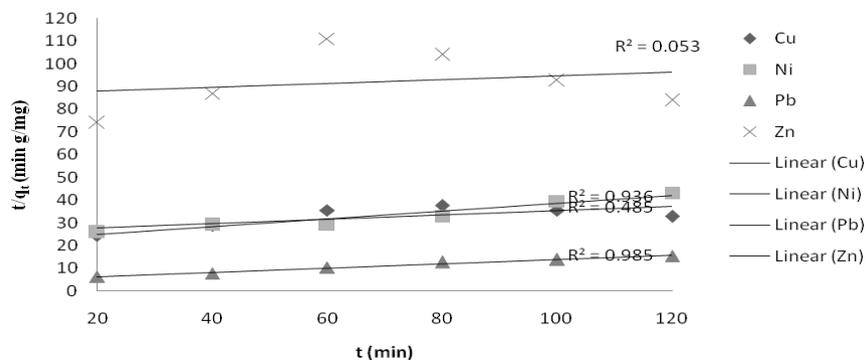
regression could result in different parameter estimates (Kinniburgh, 1986; Longhinotti, 1998; Ho, 2004). The most popular linear used is Type 1.

Figures 1 to 4 show experimental data with linear equations of the four pseudo-second-order kinetic models obtained by using the linear method for the sorption of the divalent metal ions under study onto *S. acuta*. Values of the pseudo-second-order kinetic model constant,  $k$ , the amount of the divalent metal ions under study sorbed at equilibrium,  $q_e$ , and the initial sorption rate,  $h$ , are listed in Table 4. The regression ( $r^2$ ) values obtained for Type 3 indicated that there was a strong positive evidence that the divalent metal ions sorption onto *S. acuta* followed the pseudo-second-order kinetic expression. It is clear that transformations of non-linear pseudo-second-order kinetic models to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least-squares method (Longhinotti et al., 1998; Ho, 2004). In a linear analysis, different linear forms of the same model would significantly affect calculations of the parameters.

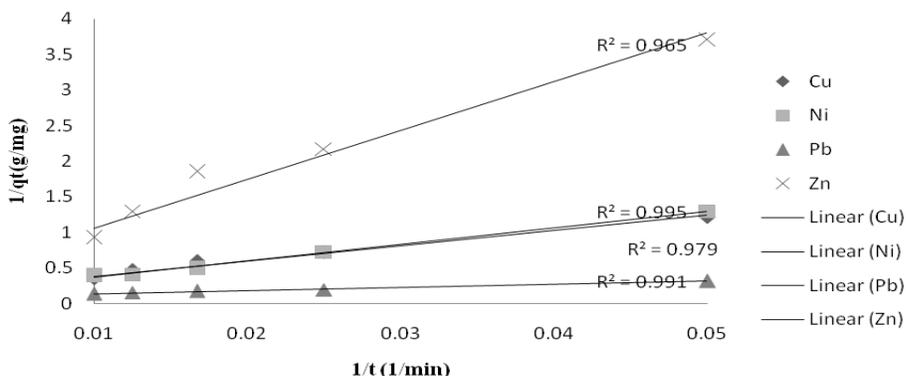
**Conclusion**

The following conclusion can be drawn as follows:

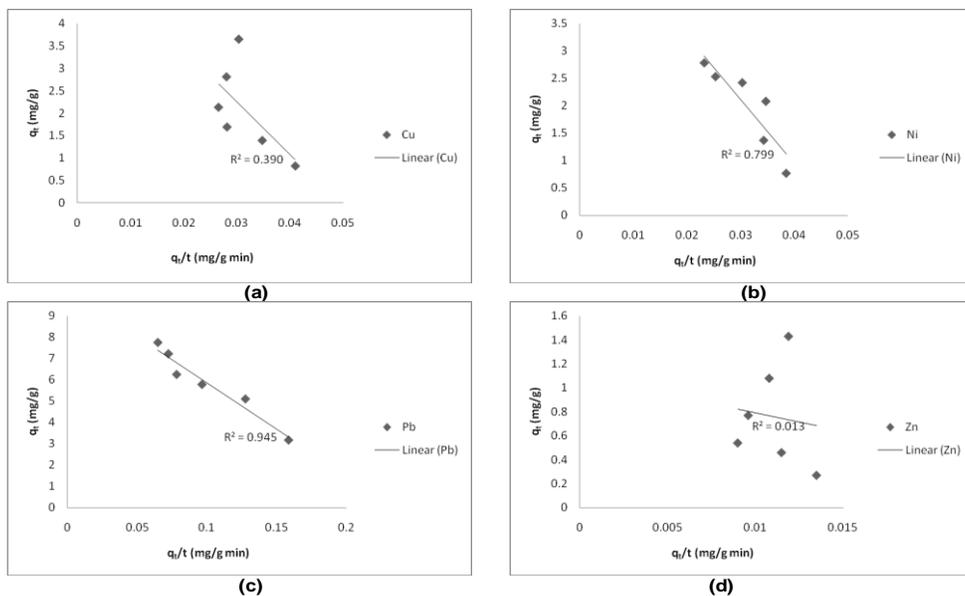
- (1) The results show sorption of divalent metal ions used



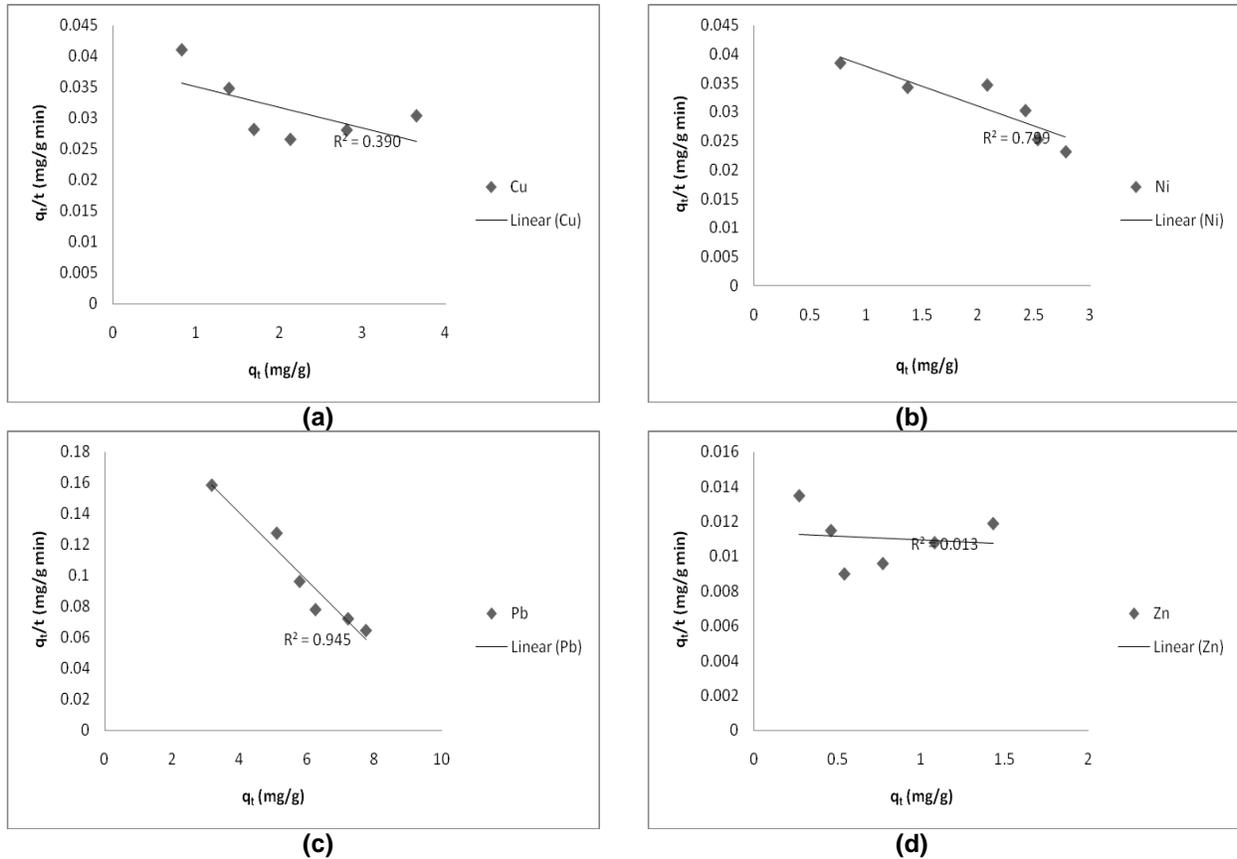
**Figure 1.** Type 1 pseudo-second- linear equations obtained by using the linear equations obtained from the linear method for the sorption of divalent metal ions onto sida acuta leaves.



**Figure 2.** Type 2 pseudo-second- linear equations obtained by using the linear equations obtained from the linear method for the sorption of divalent metal ions onto sida acuta leaves.



**Figure 3.** Type-3 pseudo-second- linear equations obtained by using the linear equations obtained from the linear method for the sorption of (a)  $\text{Cu}^{2+}$  ions, (b)  $\text{Ni}^{2+}$  ions, (c)  $\text{Pb}^{2+}$  ions, and (d)  $\text{Zn}^{2+}$  ions onto sida acuta leaves.



**Figure 4.** Type-4 pseudo-second- linear equations obtained by using the linear equations obtained from the linear method for the sorption of (a)  $\text{Cu}^{2+}$  ions, (b)  $\text{Ni}^{2+}$  ions, (c)  $\text{Pb}^{2+}$  ions, and (d)  $\text{Zn}^{2+}$  ions onto sida acuta leaves.

**Table 4.** Pseudo-second-order kinetic parameters obtained by using the linear methods for divalent metal ions.

Type	Parameter	$\text{Cu}^{2+}$	$\text{Ni}^{2+}$	$\text{Pb}^{2+}$	$\text{Zn}^{2+}$
Type 1	$q_e$ (mg/g)	10.783	5.805	10.556	11.884
	$k$ (g/mg min)	0.00033	0.00139	0.00200	0.00008
	$h$ (mg/g min)	0.0385	0.0469	0.2232	0.0116
	$r^2$	0.485	0.985	0.936	0.053
Type 2	$q_e$ (mg/g)	6.040	6.8630	10.315	2.668
	$k$ (g/mg min)	0.00127	0.00093	0.00217	0.00205
	$h$ (mg/g min)	0.0465	0.0436	0.2310	0.0146
	$r^2$	0.979	0.995	0.991	0.965
Type 3	$q_e$ (mg/g)	5.770	5.620	10.206	1.099
	$k$ (g/mg min)	0.00148	0.00152	0.00225	0.02955
	$h$ (mg/g min)	0.0493	0.0481	0.2347	0.0357
	$r^2$	0.390	0.799	0.945	0.013
Type 4	$q_e$ (mg/g)	11.522	6.529	10.456	25.850
	$k$ (g/mg min)	0.00029	0.00105	0.00208	0.00002
	$h$ (mg/g min)	0.0385	0.0447	0.2273	0.0114
	$r^2$	0.390	0.799	0.945	0.013

for the study on to *S. acuta* leaves by agitation; a pseudo-second order model can describe the sorption process. (2) The sorption equilibrium capacity, the sorption rate constant and the initial sorption rate can be a function of the metal ion present.

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