

Kinetic Study of Cu (II) Adsorption on *Adenanthera pavonina* seeds

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Abstract: The powdered seeds of *Adenanthera pavonina* are used to study the biosorption of Cu(II) from aqueous solution. The batch experiments are conducted at different initial concentrations (10-70 mg/L) of Cu(II) over a contact period of 5-60 minutes. The biosorption equilibrium is established by 40 minutes. The pseudo-first order, the pseudo-second order, Elovich and intra-particle diffusion models have been analyzed to understand the kinetics of the biosorption process. The pseudo-second order kinetic model is found to be the best fit for the present experimental data. The maximum heavy metal ions adsorbed is found to be 10.917mg/g. The present study shows that the powdered *Adenanthera pavonina* seeds are efficient in biosorption of Cu(II) ions from aqueous solutions.

Keywords: Copper, Elovich, Intra-particle diffusion, Second-order kinetics.

I. Introduction

Over the past few decades, the release of metallic contents in the environment has been a major concern throughout the world. Heavy metals due to their toxic and persistent nature pose serious threat to the freshwater reserves [1]. Different industrial activities like mining, smelting, electroplating and agricultural activities like use of pesticides and fertilizers have contributed to the release of toxic heavy metals into the environment [2]. Most of the heavy metals are carcinogenic and can cause severe physiological damages to both plants and animals [3].

The treatment technologies that are available for the removal of heavy metals from wastewater include chemical precipitation, ion-exchange, membrane filtration, flotation, electrochemical treatment, coagulation and adsorption on activated carbons, engineered nanoparticles and biosorbents[4]. These technologies, with the exception of biosorption, are not economically viable and demand high maintenance and operational costs. Biosorption is an effective process for the removal of heavy metals from aqueous solutions. This is an emerging alternative to the conventional methods of metal removal and involves the usage of biological materials like fungal biomass [5,6], algal biomass [7,8], bacterial adsorbents [9] and several agricultural products and wastes like hazelnut shell [10], *Azadirachta indica* (Neem) leaf powder [11], tree fern [12], orange peel [13], rice husk [14], coffee husks [15], pomegranate peel [16]. Biosorption enables the reuse of biomaterials and requires low operating costs. The process can be completed within a short duration without the generation of any secondary pollutants [17]. Thus the technology has gained importance over the past decades.

Copper is an important trace metal that plays a significant role in human body. It helps in the synthesis of enzymes and in development of bones and tissues [18]. However, the carcinogenicity of Cu(II) has become a serious issue. Cu(II) is also a potential mutagen in human beings [19]. Copper is also an essential micronutrient in plants and acts as the electron donor in photosynthesis [20]. But, excess of copper accumulates in the plant bodies and retards growth of plants and causes leaf chlorosis [21]. Untreated industrial wastes have been found to contain large quantities of Cu(II) [22]. Thus the removal of Cu(II) from industrial waste water is an important issue. The present study uses *Adenanthera pavonina* seeds as the biosorption material and aims at investigating the adsorption kinetics of Cu(II) on powdered *Adenanthera pavonina* seeds. The study is conducted at different initial Cu(II) concentrations over a range of contact duration (5-60 minutes) and the biosorption data is analyzed by pseudo- first order, pseudo second order, Elovich and intra-particle diffusion kinetic models.

II. Materials And Methods

In order to study the adsorption kinetics of Cu(II) on powdered seeds of *Adenanthera pavonina*, batch adsorption experiments consisting of a series of conical flasks containing desired adsorbent dose of 5g/L and a predetermined concentration of Cu(II) (10-70mg/L) solution are agitated at 120 rpm for a definite duration of contact time (5-60 minutes). The procedure for the preparation of the adsorbent is similar to that described elsewhere [23]. The pH of the experimental system is maintained at 5, using 0.1 N HNO₃ or 0.1N NaOH. At 5, using 0.1 N HNO₃ or 0.1N NaOH. After agitation, the mixture is filtered using Whatman 41 filter paper and the filtrate is analyzed using Atomic Adsorption Spectrophotometer (AAS) so as to determine the heavy metal concentration after adsorption. The percent removal of heavy metal is calculated using the following equation:

$$\% \text{ Removal of Cu(II)} = \frac{(C_0 - C_i)}{C_0} \times 100 \quad (1)$$

Where, C_0 is the initial concentration of heavy metal, C_i is the final concentration of heavy metal. The adsorption capacity, q_e (mg/g) after equilibrium is calculated from the following equation.

$$q_e = \frac{(C_0 - C_e)}{W} \times V \quad (2)$$

Where, V is the volume of the solution in litres, W is the mass of adsorbent in grams and C_e is equilibrium concentration.

The efficiency of adsorption process is determined by the adsorption kinetics. Mass transport and chemical reaction processes are the rate controlling steps in a solid- solution interface [24]. In order to understand the mechanism of adsorption, the experimental data in the current study, have been tested using various kinetic models. The values of the constants obtained from these models can be utilized to prescribe the optimum conditions required to design heavy metal removal system through batch mode of experiments. In this study, the pseudo first-order [25], pseudo-second order [26], Elovich [27] and intra-particle diffusion [28] kinetic models have been applied to investigate the experimental data.

III. Results And Discussions

The adsorption kinetics of Cu(II) on powdered *Adenanthera pavonina* seeds have been studied. The effect of contact time at different initial metal ion concentrations (10-70mg/L) and the kinetic models exploited have been discussed in the following paragraphs.

1.1 Effect of contact time:

In the present study, the removal of Cu(II) increases with time and becomes saturated at 40 minutes. The rate of adsorption is faster in the initial 20 minutes until it attains equilibrium, at all initial concentrations of Cu(II). Fig. 1 shows the plot of percentage removal of Cu(II) versus the contact time for the initial metal concentrations. The maximum percent removal is attained at about 40 minutes of contact duration for all initial concentrations. Larger surface area of the adsorbent is available in the initial stage of adsorption. Thus the rate of adsorption is also higher initially. The capacity of the adsorbent for adsorption diminishes after the formation of a mono-molecular layer of the adsorbate. At this stage, the rate of adsorption is controlled by the rate of transportation of the sorbate from the exterior to the interior sites of the adsorbent. Thus the rate of increase in percent removal of metal ions becomes insignificant. This shows that the adsorption mechanism in the present study has two phases, the initial rapid phase and the second slower phase. Similar results have been extensively reported in literature [29, 30].

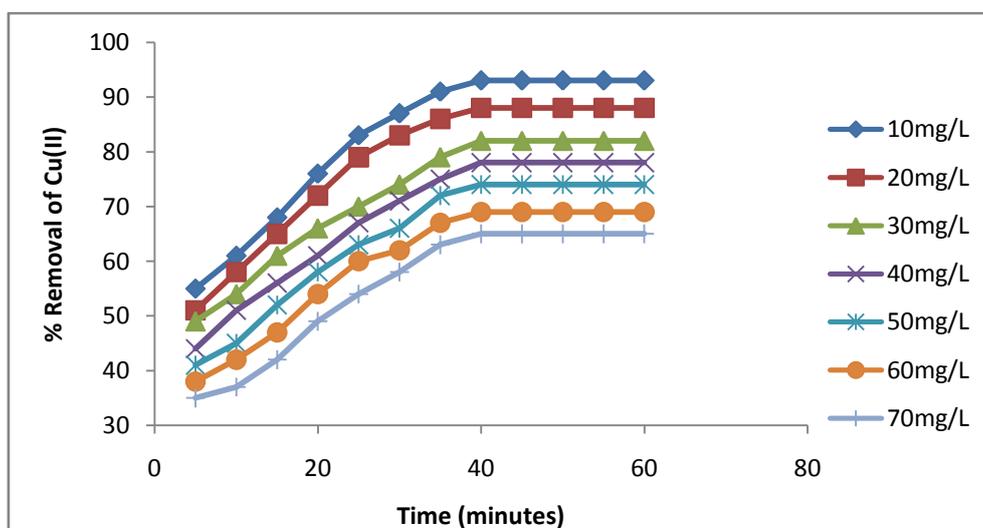


Figure1: Effect of contact time on removal of Cu(II)

1.2 Adsorption kinetics:

Adsorption kinetic models like pseudo-first order kinetic model, pseudo- second order kinetic model, Elovich model and the intra-particle diffusion model have been investigated in the present study in order to understand the adsorption kinetics and determine the rate limiting steps.

1.2.1 Pseudo first-order kinetics:

The Lagergan first-order rate expression can be written linearly as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

Where, q_e and q_t are the adsorption capacity (mg/g) at equilibrium time and at any instant of time, t , respectively and k_1 ((L/min) is the rate constant of pseudo first-order adsorption process. From the plot of $\log(q_e - q_t)$ versus t , the adsorption rate constant, k_1 , is estimated. The values of k_1 , R^2 and the calculated uptake capacity, q_e , are shown in Table 1.

1.2.2. Pseudo second-order kinetics:

The pseudo-second order model takes into consideration the adsorption equilibrium capacity. It can be expressed in the form:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \tag{4}$$

Where, $h = k_2 q_e^2$, is the initial sorption rate as $t \rightarrow 0$. The constants can be estimated by plotting of t/q_t against t . Table 1 displays the values for the second order rate constant, k_2 , the estimated equilibrium capacity, q_e , and the coefficient of correlation, R^2 .

1.2.3. Elovich model:

The Elovich equation is also based on adsorption capacity. It can be expressed linearly as,

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{5}$$

Where, α (mg/g min) is the initial adsorption rate and β (g/mg) is the desorption coefficient. The kinetic constants are estimated from the slope and intercept of the straight line plot of q_t versus $\ln t$ and the values of α , β and R^2 are shown in Table 1.

The values displayed in Table 1 show that the pseudo-second order model fits the biosorption data better than both pseudo-first order and Elovich kinetic models. Thus chemisorption may be considered the rate limiting step in the present study. The maximum q_e of 10.917 mg/g is calculated for a concentration of 70mg/L. The q_e values are higher than those calculated for pseudo-first order model at all concentrations of Cu(II).

Table1: Calculated kinetic model parameters for biosorption of Cu(II) on powdered *Adenanthera pavonina* seeds

Sl No.	C ₀ (mg/L)	Pseudo first-order kinetic			Second-order kinetic model			Elovich kinetic model		
		k ₁	q _e (exp) (mg/g)	R ²	k ₂	q _e (exp) (mg/g)	R ²	β	α	R ²
1	10	0.0933	1.684	0.9107	0.0761	2.088	0.9962	2.803	1.349	0.9548
2	20	0.103	3.488	0.927	0.0423	3.918	0.9965	1.479	2.525	0.9549
3	30	0.075	3.55	0.9177	0.0281	5.498	0.9958	1.095	3.867	0.9623
4	40	0.078	4.97	0.9339	0.0202	7.032	0.9951	0.811	3.765	0.9616
5	50	0.091	7.816	0.8745	0.0135	8.621	0.9956	0.578	2.556	0.9736
6	60	0.083	7.52	0.9201	0.013	9.542	0.9935	0.561	3.701	0.9497
7	70	0.075	8.492	0.9013	0.0092	10.917	0.9881	0.469	3.05	0.932

1.2.4. Adsorption mechanism:

The adsorption mechanism involves formation of metal-organic or metal-inorganic complexes due chemical reaction between the functional groups present on the surface of the adsorbents or due the cation-exchange capacity of the adsorbent [31]. Adsorption involves three important steps viz. film diffusion, pore diffusion and intra-particle transport. The last step is considered to be the equilibrium step. It is very rapid and is considered to be negligible. In a continuous flow system, film diffusion is considered to be the rate limiting step, whereas, in a batch mode of experiment, pore diffusion and intra-particle diffusion are the rate-limiting steps [32]. The intra-particle diffusion model helps to understand the mechanism governing the adsorption process. Literature review has revealed that the plot of q_t versus $t^{0.5}$ is multilinear in nature which suggests that adsorption may involve two or more steps [33]. The intra particle diffusion coefficient, K_{id} (mg/g min^{0.5}), can be obtained from the slope of the plot of q_t versus $t^{0.5}$. The intra-particle diffusion model can be explored as

$$q_t = K_{id}t^{0.5} + I \tag{6}$$

If the plot of q_t versus $t^{0.5}$ is linear, intra-particle diffusion governs the adsorption process and is the rate controlling step if the line passes through the origin [34]. The thickness of the boundary layer can be assumed from the values of I , which is the intercept of the intra-particle diffusion plot. The larger the value of I , the greater is the boundary layer effect [35]. Table 2 shows the values of K_{id} and I obtained in the present study.

Table 2: Calculated parameters for intra-particle diffusion model for biosorption of Cu(II) on powdered *Adenanthera pavonina* seeds

Sl. No.	C_0 (mg/L)	K_{id}	I	R^2
1	10	0.1513	0.8183	0.9176
2	20	0.2846	1.5537	0.9041
3	30	0.3908	2.1786	0.9416
4	40	0.5262	2.5464	0.9362
5	50	0.7276	2.3715	0.9211
6	60	0.7609	2.9944	0.924
7	70	0.9209	2.7248	0.9318

The plot of q_t versus $t^{0.5}$ (square root of time) (figure not shown) is found to follow two phases, a linear portion and a curve that gradually becomes constant. This suggests that both surface sorption and intraparticle diffusion take part in the adsorption mechanism. The curved portion can be related to boundary layer/ film diffusion effect whereas, the linear portion can be assigned to intraparticle/ film diffusion effect [36]. Moreover, the plot is not found to pass through the origin which shows that intraparticle diffusion is not the rate limiting step for the biosorption of Cu(II) on powdered *Adenanthera pavonina* seeds.

IV. Conclusion

The experiments to study the adsorption kinetics of Cu(II) on powdered seeds of *Adenanthera pavonina* is conducted as a function of contact time. The contact time of 40 minutes is required to attain equilibrium for the present study. The second-order kinetic model fits the experimental data and thus the process is mainly chemisorptions. The intraparticle diffusion model shows that intraparticle diffusion is not the rate-controlling step in the present experimental system. The results show that Cu(II) is effectively adsorbed on powdered *Adenanthera pavonina* seeds and can be employed in designing wastewater treatment plants for copper.

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