

## Journal of Advanced Scientific Research

ISSN **0976-9595** Research Article

Available online through http://www.sciensage.info

# KINETIC MODELLING FOR THE ADSORPTION OF CU (II) IONS ONTO CASSIA FISTULA (L) EPICARP ACTIVATED CARBON

Nandhakumar Vaiyapuri<sup>1</sup>\*, Rajeswari Murugavel<sup>2</sup>, Surya Samiya<sup>1</sup> & Rajappa Arumugam<sup>2</sup>

<sup>1</sup>Department of Chemistry, A.V.V.M Sri pushpam College (Affiliated to Bharathidasan University), Poondi, India. <sup>2</sup>Department of Chemistry, Sri Manakula Vinayagar Engineering College, Puducherry, India \*Corresponding author: vnchem14@gmail.com

## ABSTRACT

An activated carbon was prepared from Cassia fistula (L) Epicarps using phosphoric acid as an activating agent and designated as Cassia fistula Phosphoric acid Activated Carbon (CFPAC). Adsorption kinetics of copper (II) ion from aqueous solution onto the adsorbent CFPAC was investigated by taking different initial concentrations 10,20,30 and 40 mg/L at the temperature 303K.Kinetic data were fitted with Lagergren, Ho and Webber-Morris equations for pseudo first order and pseudo second order and intra particle diffusion models respectively. According to Mean of Sum of Squired Error (MSSE) tool, the adsorption followed pseudo second order kinetic equation. Intra particle diffusion was the rate determining step as per Webber Morris plot constant values.

Keywords: Adsorption, Cu (II) ion, Cassia fistula (L) Epicarp, Kinetics.Pseudo first order, Pseudo second order, Intra particle diffusion

## 1. INTRODUCTION

The presence of toxic heavy metals in environment through industrial waste disposal is currently an important environmental concern. The abatement of heavy metal ions from water is an essential process because they are not able undergo biodegradation and cause harmful effects to ecosystem by the accumulating in the tissues of living organisms causing various diseases. Copper ion is toxic heavy metal ion when it exceeds the threshold limit to living organisms and it is one of the most widespread heavy metal in the environment [1-2]. Copper is a very common substance that widely used in many industries. Sources of copper ion in effluents are due to plating bath metal cleaning, paper board, antifouling for paint and pigment, mining, fertilizer, etc. [3]. Excessive intake of copper ions by human leads to renal, liver, capillary and brain damage, several mucosal and gastrointestinal irritation, central nervous problems, depression and possible necrotic changes in the kidney and liver [4-6]. Among the ionic species of copper, Cu (II) ions in the aqueous solution can attach easily to organic and inorganic matter depending on solution pH [7]. Treatment technologies available for the abatement of heavy metal ions from aqueous solutions are precipitation, ion exchange, bioremediation and adsorption. Adsorption is preferred because of it is high efficient, easy to handle and cost effective [8-12]. The present study is undertaken to evaluate the efficiency of a carbon adsorbent prepared from a *Cassia fistulas* (L) Epicarps through phosphoric acid activation for the removal of copper (II) ion from aqueous solution.

# 2. MATERIAL AND METHODS

# 2.1. Preparation of Adsorbent

Phosphoric acid activation method was selected as this method produce activated carbon with more porosity from plant biomass which was used by many researchers [13-15]. The Cassia fistulas (L) Epicarps were washed with distilled water, dried in sun light for 5 days, chopped to get small pieces of few mm size (~1to2 mm) and powdered. 40 g of the powder was immersed in a solution of 40% of H<sub>3</sub>PO<sub>4</sub> for 2 hours with constant stirring to get impregnation ratio of 1:1 (w/w) and kept aside for 24 hours. At the end of 12 hours, the supernatant solution was decanted off and then oven dried for 24 hours. Then the material was carbonized in muffle furnace at 673K temperature for 30 minutes. The carbon material was powdered and further activated in a muffle furnace at 673K temperature for a period of one hour. Then the material was cooled, washed with plenty of water to remove residual acid, dried at 383K temperature, powdered and the particle sizes between 73

 $\mu$ m and 150  $\mu$ m were selected by sieving through proper sieves. Thus obtained carbon material was designated as *Cassia fistula* Phosphoric acid Activated Carbon (CFPAC).

#### 2.2. Preparation of Stock Solution

Cu(II) ion solution of 1000 mg/L concentration was prepared by dissolving 3.9266 g of (CuSO<sub>4</sub>.5H<sub>2</sub>O) in 1000 mL of de-ionised water. Required initial concentrations of the solution say 10, 20, 30 and 40 mg/L were prepared from the stock solution. Deionised water was used for all further experiments.

#### 2.3. Data Processing Tools

#### 2.3.1. Kinetics Studies

2.3.1.1. Pseudo first order kinetics

Pseudo first order rate expression given by Lagergren [16].

 $log(q_e - q_t) = log q_e - k_1/2.303 \times t$ 

Where,  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed (mg/g) at equilibrium and at time t (min) respectively,  $k_1$  is the rate constant of adsorption (1/min). A plot of log ( $q_e - q_t$ ) against t at various concentrations were drawn  $k_1$  and  $q_e$  are calculated from the slopes and intercepts respectively.

#### 2.3.1.2. Pseudo second order kinetics

The second-order kinetic model [17] given by 'Ho' is expressed as

$$t/q_t = 1/k_2 q_e^2 + 1/q_e \times t$$

Where,  $k_2$  is the second order rate constant.

The initial adsorption rate, h (mg/g min), as t/0 can be defined as

$$h = k_2 q_e^2$$

Equilibrium adsorption capacity  $(q_e)$  can be determined from the slope and the second-order constants  $k_2$  (g/mg min) can be determined from the intercept of plot t/q<sub>t</sub> versus t.

#### 2.3.1.3. Intra-particle diffusion study

In the rate of intraparticle diffusion is given by the following Webber –Morris equation [18]

$$q_t = k_{id} t^{1/2} + C$$

 $k_{id}$  is the intra particle diffusion rate constant (mg/g min<sup>1/2</sup>), and C is the thickness of boundary layer. The plot of  $q_t$  versus  $t^{1/2}$  obtained from  $k_{id}$  and C were calculated from the slope and intercept of the linear portion of plot suggest intra particle diffusion process.

#### 2.3.1.4. Statistical tool for kinetics models

Best fitting kinetic model was determined by using the statistical tool Mean of Sum of Squared Error (MSSE) [19] is as follows;

$$MSSE = \sqrt{\sum [(q_e) \exp -(q_e) cal]^2} / N$$

Where N is that the number data,  $(q_e)_{exp}$  is the experimental  $q_e$  and  $(q_e)_{cal}$  is the calculated  $q_e$ .

#### 2.3.1.5. Batch adsorption experiment

Batch adsorption experiments for the adsorption onto CFPAC were conducted by varying the operational parameters such as contact time and initial metal ion concentrations. Forty (40) mg of CFPAC was added to 50 mL of the Cu(II) ion solutions of known initial concentration. The solution pH was brought to 5 by adding Conc. HCl. The contents were shaken thoroughly using an orbital mechanical shaker with a speed of 150 rpm for pre-determined time. The solution was then centrifuged and the concentration of the centrifugate was determined spectrophotometrically using Systronics 2202 make UV-Visible spectrophotometer.

Percentage of removal and also the amount of adsorbate adsorbed were calculated by the following equations.

$$q_{t} = (C_{i} - C_{t}) \frac{V}{W}$$

% of Removal =  $((C_i - C_t)/C_i) \times 100$ 

Where;  $C_i$  and  $C_t$  are the concentration of adsorbate (mg/L) at initial stage and at time't' respectively

V is the volume of solution (L)

W is the mass of adsorbent (g).

Experimental result obtained from the effect of initial concentration and contact times were employed in testing the applicability of kinetic models.

#### 3. RESULT AND DISCUSSION

# 3.1. Effect of contact time and initial concentration

Cu (II) ions solution of concentrations of ranging from 10 mg/L to 40 mg/L was used in this experiment. The percentage removal of Cu (II) ions increased with the increase of time and remains constant after attaining equilibrium at 160 minutes. Fig.1 shows that percentage of removal was rapid at initial stages (within 50 minutes) and it becomes slow in later stages. At initial stages, the available adsorptive sites are plenty which make the adsorbed molecules to rush up towards the adsorptive sites. At later stages, most of those sites are exhausted and therefore the rate of adsorption was slow.



#### Fig.1: Effect of contact time

[pH :5; Dose :40 mg/ 50 mL; Agitation time : 200 min; Temp:303K] Further the figure shows that, at low concentration range, the percentage adsorption is high because the ratio of available reactive sites to the number of Cu(II) ions in the solution is high. At higher initial concentration of Cu (II) ion, that ratio is small. This leads to a fall in the percentage of Cu (II) ion adsorbed.

## 3.2. Kinetic models

The results obtained from effect of contact time experiments are fitted into pseudo first order and second order kinetic models and the values of the kinetic parameters evaluated are presented in Table 1 and 2. Concerned graphs are shown in fig. 2 and 3.

Tabl	e 1: ]	Intra	particle	diffusion	and	Pseudo	first	order	kineti	c parameters
------	--------	-------	----------	-----------	-----	--------	-------	-------	--------	--------------

Ci (mg/L)	k <sub>id</sub> (mg/g.min)	$k_1 \times 10^{-2} (min^{-1})$	$q_{e(cal)} (mg/g)$	$q_{e(exp)} (mg/g)$	∆qe	MSSE
10	0.05	3.80	4.7	11.9	7.2	
20	0.08	4.21	11.7	22.4	10.7	5 48
30	0.15	3.73	17.5	31.8	14.2	J. <b>T</b> 0
40	0.44	3.50	29.5	40.0	10.6	

Table 2: Pseudo	second	order	kinetic	parameters	

Ci (mg/L)	$k_2 \times 10^{-2}$ (g/mg.min)	$q_e(cal) (mg/g)$	h	$q_e(exp) (mg/g)$	∆qe	MSSE
10	2.77	12.1	4.073	11.9	-0.2	
20	0.89	23.0	4.751	22.4	-0.7	0.62
30	0.45	33.1	4.895	31.8	-1.4	0.65
40	0.28	42.0	4.861	40.0	-2.0	









The pseudo first order rate constant  $k_1$  (min<sup>-1</sup>) and pseudo second order rate constant k<sub>2</sub> (g/mg.min) are found to increase with the increase of initial concentrations of Copper (II) ion solutions. The initial sorption rate 'h' increased directly with an increase of (II)ion concentration. initial Copper Further experimentally determined  $q_{e(exp)}$  is found close to the  $q_e$ (cal) calculated from second order kinetics. The deviation parameter MSSE value is 5.48 for pseudo first order and it is 0.63 for the pseudo second order kinetic model. This confirms the applicability of the pseudo second order kinetic model. The determination coefficient  $(R^2)$  for pseudo first order model ranged between 0.94 and 0.98 where as these values for the second order model were 0.99. It indicates that the experimental data best fitted into pseudo second order. The results obtained from intra particle diffusion model are presented in Table 1 and concerned plots are shown in fig. 4. Intra particle diffusion rate constant K<sub>id</sub> values were increased with an increase of Copper (II) ion concentration that reveals the rate of adsorption is governed by the diffusion of Copper (II) ions within the pores of the adsorbent.



Fig. 4: Weber - Morris plots for intra particle diffusion

## 4. CONCLUSION

*Cassia fistula* Phosphoric acid Activated Carbon (CFPAC) found to have good absorption capacity for Cu(II) ion at pH 5. Equilibrium of adsorption attained at 160 minutes for the dosage of 40 mg per 50 mL for the studied initial concentrations 10,20,30,40 mg/L. The regression coefficient values showed that kinetic data best fitted to pseudo second order plots. Experimentally determined  $(q_{e(exp)})$  values were close to the theoretically calculated  $(q_{e(cal)})$  from second order kinetics. Therefore kinetic of the studied adsorption process was pseudo second order.

Intra particle diffusion rate constant values suggested the pore diffusion as the rate limiting step.

## 5. ACKNOWLEDGEMENT

This work was financially supported by University Grants Commission, New Delhi through Minor Research Project No. F MRP-66.49/16 (SERO/UGC)

### 6. REFERENCES

- Wan MW, Kan CC, Rogel BD, Dalida MLP. Carbohydr. Polym., 2010; 80:891-899.
- Villaescusa I, Fiol N, Martinez M, Mialles N, Poch J, Serarols J. Water Res., 2004; 38:992-1002.
- 3. Li N, Bai R, Sep. Purif. Technol., 2005; 42:237-247.
- Zhu CS, Wang LP, Chen W. J. Hazard. Mater., 2009; 168:739-746.
- Larous S, Meniai AH, Lehocine MB. Desalination, 2005; 185:483-490.
- Ajmal M, Khan AH, Ahmad S, Ahmad A. Water Res., 1998; 32:3085-3091.
- Hasan S, Ghosh TK, Viswanath DS, Boddu VM. Journal of Hazardous Materials, 2008; 152:826-837.
- Arivoli S. "Kinetic and Thermodynamic Studies on the Adsorption of Some Metal Ions and Dyes onto Low Cost Activated Carbons". Ph D. Thesis, Gandhigram Rural University, Gandhigram. 2007.
- Paul Chen J, Wu Shunnian Wu, Kai Hau Chong. Carbon. 2003; 41:1979-1986.
- Vijayaraaghavan K, Jegan J, Palanivel K, and Velan M. J. Chem. Engg., 2005; 106:177-184.
- Sekaran G, Shanmugasundaram KA, Mariappan M, Raghavan KV. J. Chem. Technol., 1995; 2:311.
- Selvarani K, "Studies on Low Cost Adsorbents for the Removal of Organic and Inorganics from Water", PhD.Thesis, Regional Engineering College, Thiruchirapalli, 2000.
- 13. Sych, N.V. et al 2012, M.M.S. Ali et al 2014, Javier Blanco Castro et al 2000
- Sych NV, Trofymenko SI, Poddubnaya OI, Tsyba MM, Sapsay VI, Klymchuk DO, Puziy AM. *Applied Surface Science*, 2012; 261:75-82.
- 15. Ali MMS, EL-SAI N, GIRGIS BS. International Journal of Computational Engineering Research, 2014; 4:70-78.
- Javier Blanco Castro, R Pablo Bonelli, Elsa G Cerrella, Ana Cukierman L. Ind. Eng. Chem. Res., 2000; 39:4166-4172.
- Lagergren S, Svenska BK. Zurtheorie der sogenannten adsorption geloesterstoffe. Vetenskapsakad. Handl. 1982; 24:1, 1898.
- 18. McKayG, HoYS. Process Biochemistry, 1999; 34:451.
- Weber Jr WJ, Morris JC. Journal of the Sanitary Engineering Division, American Society of Civil Engineers, 1963; 89:31.