Removal of Cu (II) from Aqueous Solution Using Chromolaena Leaf Powder as Adsorbent

D. Krishna[a*] and Diwakar Shende[b]

[a]*Department of Chemical Engineering, M.V.G.R. College of Engineering, Vizianagaram, Andhra Pradesh, India*
[b]*Department of Chemical Engineering, Visvesvaraya National Institute of Technology, Nagpur, India*

Abstract: This paper reports the feasibility of chromolaena odorata leaf powder as adsorbent for the adsorption of Cu (II) metal ions from aqueous solutions at various conditions. Various industries discharges heavy metals in water bodies, affect the aquatic life, human health and overall ecosystem adversely. So, it is needed to remove the heavy metals present in water using low cost techniques. In this direction, bio-sorption is identified. Batch experimental studies were carried out for the removal of Cu (II) from waste water by adsorption on chromolaena odorata leaf powder. The effect of several process parameters like the agitation time, the adsorbent size, adsorbent dosage, initial copper concentration, and the effect of solution pH on adsorption are studied. Both Langmuir and Freundlich models for Cu (II) adsorption onto chromolaena odorata leaf powder are proved to be best fit based on high regression coefficient R2 value. The adsorption kinetic models follow the second order. The maximum metal uptake observed at pH 6 for copper removal is 10.416 mg/g.

Keywords: Adsorption; batch technique; isotherms; kinetics; chromolaena odorata leaf powder.

1. Introduction

Various industries discharge heavy metals which contaminate water bodies and severely affect on aquatic life, human health and environment [1]. Largely various human activities such as weathering of rocks and volcanic activities release heavy metals which are primary concern about pollution [2, 3]. Heavy metals such as manganese (Mn), mercury (Hg), lead (Pb), Cadmium (Cd), arsenic (As), copper (Cu) are treated as toxic due to their non-biodegradability and oxidation nature [4, 5]. Out of these heavy metals, copper is treated as one of the most toxic one. Several industries like paper and pulp, fertilizer, wood preservatives, refineries, metal cleaning and painting bath etc are primary source of copper metal ions which discharges into the environment. The intake of copper beyond limit may cause renal and hepatic damage, severe mucosal, irritation, wide spread capillary damage, gastrointestinal irritation and possibly necrotic changes in kidney and liver. World Health Organization (WHO) has recommended that maximum acceptable limit for Cu (II) concentration in drinking water should be 1.5 mg/l [6]. It is needed that water bodies containing heavy metals should require low cost treatment for domestic supply as water is essential element for humans.

Several methods for removal of copper from water bodies include reduction followed by

chemical precipitation [7], ion exchange [8], reduction [9], electrochemical precipitation [10], solvent extraction [11], membrane separation [12], evaporation [13] and foam separation [14]. Above cited conventional copper elimination processes are costly or ineffective at lower concentrations. In recent years biosorption research was given more importance on removal of heavy metals using readily available agriculture waste materials. This process can be applied as a low cost technique for purifying industrial waste water whereby drinking water quality can be improved. Considerable research was carried out on usage of naturally abundantly available bio-adsorbent materials which have efficacy for removal of heavy metals from water bodies. Still there is need to focus more on naturally available agriculture waste materials for removal of heavy metals as latest development in industries, urbanization and mining leads to discharge of heavy metals in the environment. So far, several bio-materials have been used as adsorbents to remove Cu (II) from aqueous solutions [15]. These include low cost adsorbents prepared with paddy straw powder [16], Tea waste adsorbent [17], onion and garlic skin [18], natural clay [19] coconut shell and neem leaves [20], Ceiba pentandra hulls [21], walnut shell [22] and spent tea leaves [23].

The objective of present study is the use of Chromolaena odorata leaf powder as an effective and inexpensive material for the removal of copper from aqueous solution in a batch mode. Adsorption isotherms like Langmuir isotherm, Freundlich isotherm, Tempkin isotherms and adsorption kinetics like first order, second order and intra particle mechanism were studied.

2. Materials and methods

2.1. Preparation of synthetic copper coluation

All chemicals used here are analytical grade. Stock solution of 1000 mg/l was prepared by adding distilled water in measured quantity of copper (II) sulfate placed in 1 L volumetric flask upto the mark. $CuSO_4.5H_2O$, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck. Various concentrations of test solution of Cu (II) ranging from 20-100 mg/l were prepared by subsequent dilution of the stock solution

2.2. Preparation of the adsorbent

The biosorbents used were chromolaena odorata leaf powder. The chromolaena odorata leaf has been collected in Andhra university college region in Visakhapatnam, Andhra Pradesh, India; materials were washed, dried for the removal of unwanted materials and also for the removal of moisture. After drying, it was crushed in roll crusher. The material obtained through crushing and grinding was screened through BSS meshes. Finally the products obtained were stored in air tight plastic bottle for further use. All the materials were used as such and no pretreatment was given to the materials.

2.3. Batch experimental procedure

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dosage, agitation time and pH. The range of different parameters studied in the present work is given in Table 1. Solution containing adsorbate and adsorbent have been taken in 250 ml capacity conical flasks and agitated at 180 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper.

Table 1. Various parameters and its ranges investigated in present experimentation

Parameter	Range of parameters
Agitation time, t, min	5, 10, 15, 20, 25, 30, 40, 50, 60 and 90
Adsorbent dosage, w, g	0.3, 0.4 and 0.5
Initial copper concentration,C_0, mg/L	20, 40, 60, 80 and 100
pH	2, 3, 4, 5, 6, 7, 8, 9 and 10

Final residual metal concentration after adsorption was measured by Atomic absorption Spectrophotometer. The percentage removal of copper from aqueous solution is estimated as under

$$\text{Removal of Cu (II)} = \frac{C_0 - C_e}{C_0} \times 100$$

Metal uptake (q_e) at equilibrium is calculated as under

$$q_e = \frac{(C_0 - C_e)v}{1000w}$$

where q_e (mg/g) is the amount of copper adsorbed per unit mass of adsorbent, C_0 and C_e are the initial and equilibrium metal ion concentration (mg/l), v is the volume of aqueous solution (ml), and w is the mass of adsorbent (g).

3. Results and discussion

3.1. Effect of contact time and copper concentrations

The agitation time profile for adsorption of Cu (II) metal for solution of 20 ppm for different adsorbent dosages is shown in Figure 1. The data shows that an equilibrium agitation time of 40 minutes is required for the percentage removal of copper. After equilibrium time, no further change in percentage removal of copper metal is observed. Figure shows that percentage removal of copper increases with increase in adsorbent dosage.

3.2. Effect of pH

The literature reveals that pH is the most important physical factor influencing the process of adsorption, the degree of ionization and the species of the adsorbate. Figure 2 shows the effect of pH on adsorption of copper at different initial concentrations. Percentage removal of copper increases with increase in pH values from 1 to 6, after words it decreases when pH is greater than 6. The maximum percentage removal of copper was noticed at pH 6.

3.3. Adsorption Isotherms

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbent. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.
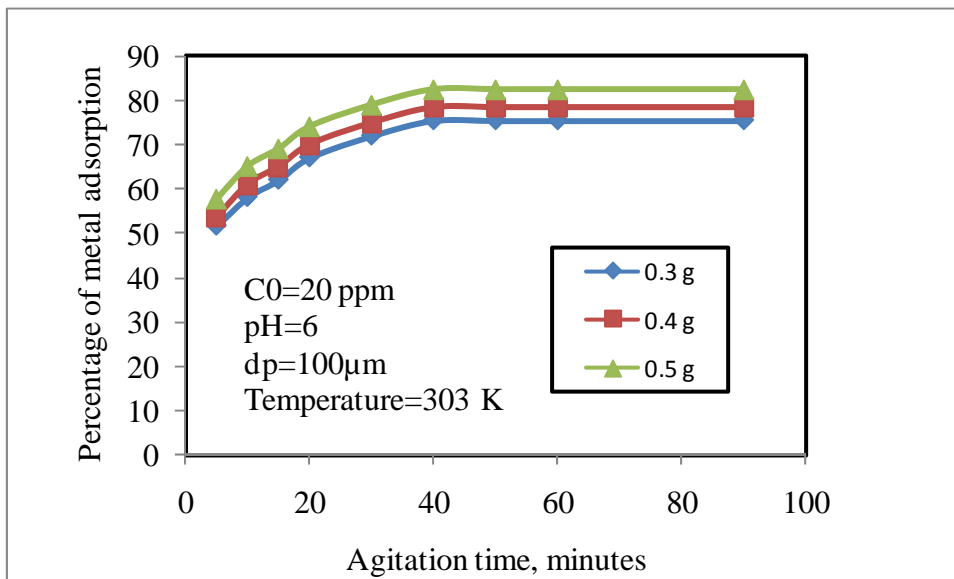
Figure 1. Effect of agitation time on adsorption of Cu (II) by chromolaena odorata leaf powder.
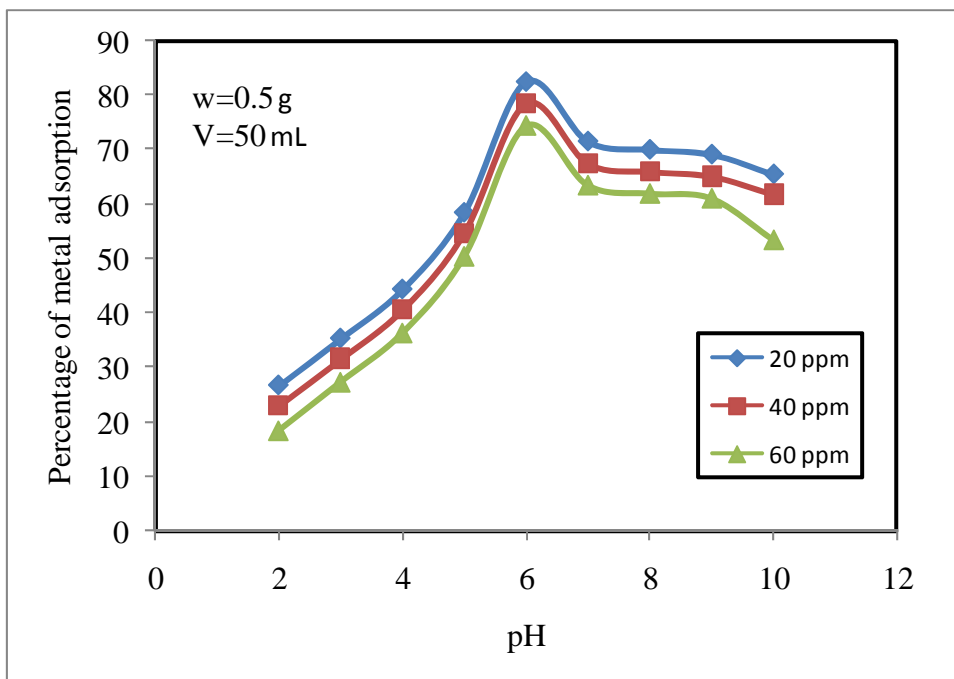

Figure 2. Effect of pH on adsorption of Cu (II) at different initial concentrations by chromolaena odorata leaf powder.

3.3.1. Langmuir model

The Langmuir isotherm [24] was used to estimate the maximum metal uptake and indicates that metal uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The model of this is presented as

$$q_e = \frac{q_{max}bC_e}{1+bC_e} \tag{1}$$

where q_e is the metal uptake (mg/g), C_e is the equilibrium metal concentration (mg/L), q_{max} is the maximum metal uptake at saturation sites, and b is the ratio of adsorption/desorption rates. The linear form of Langmuir isotherm is represented as follows

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}bC_e} \tag{2}$$

Figure 3 shows linearity for Langmuir isotherm for the adsorption of copper on chromolaena odorata leaf powder. q_{max} and b calculated from the slope and the intercept are 10.416 mg/g 0.0509 respectively at 303 K. It is noticed that there was strong binding of copper ions onto the surface of chromolaena odorata leaf powder. The separation factor, R_L determined from $\dfrac{1}{1+bc_0}$ at Temperature 303 K and pH 6 is in between 0.1642-0.4955 for various concentrations shows favorable adsorption ($0<R_L<1$).
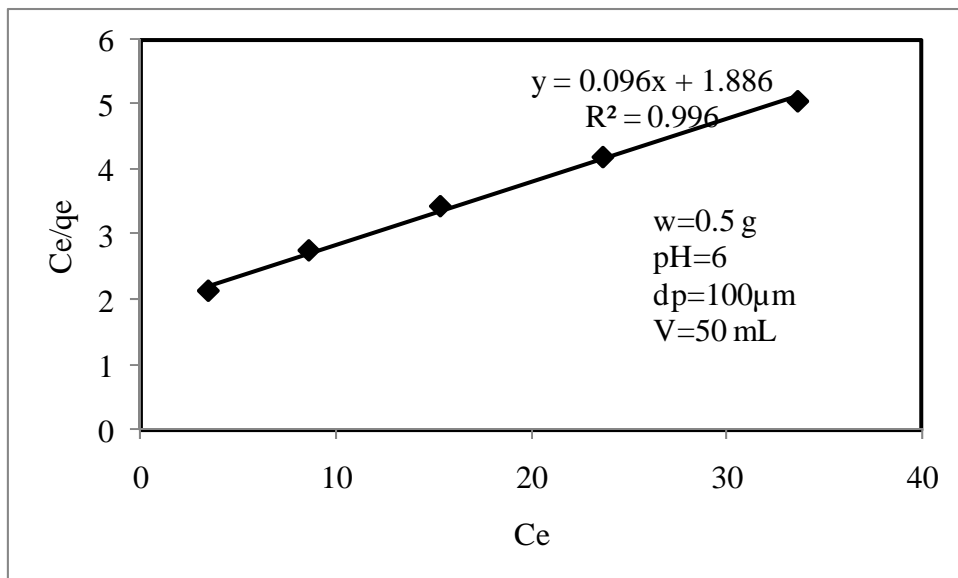

Figure 3. Suitability of experimental data to Langmuir isotherm for adsorption of copper.

3.3.2. Freundlich model

The Freundlich isotherm [25] is the most widely used nonlinear multilayer adsorption model with heterogeneous energetic distribution active sites and reversible adsorption, followed by interaction between adsorbed molecules. The general form of this model is represented by:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

K_f stands for Freundlich adsorption capacity and n stands for adsorption intensity, q_e is the metal uptake at equilibrium and C_e is the equilibrium copper concentration. The Freundlich equation is presented linearly as.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

The values of K_f and n obtained from intercept and slope of a plot of $\log q_e$ versus $\log C_e$ are 0.787 and 1.6129 respectively. Figure 4 shows good linearity with regression coefficient of 0.993 for Freundlich Isotherm for the adsorption of copper on chromolaena odorata leaf powder and Linearity of the relationship reveals strong binding of copper to on the surface of the adsorbent. As the slope of isotherm (n) is 1.6119, it is fulfilling the condition of n>1 for favorable condition.
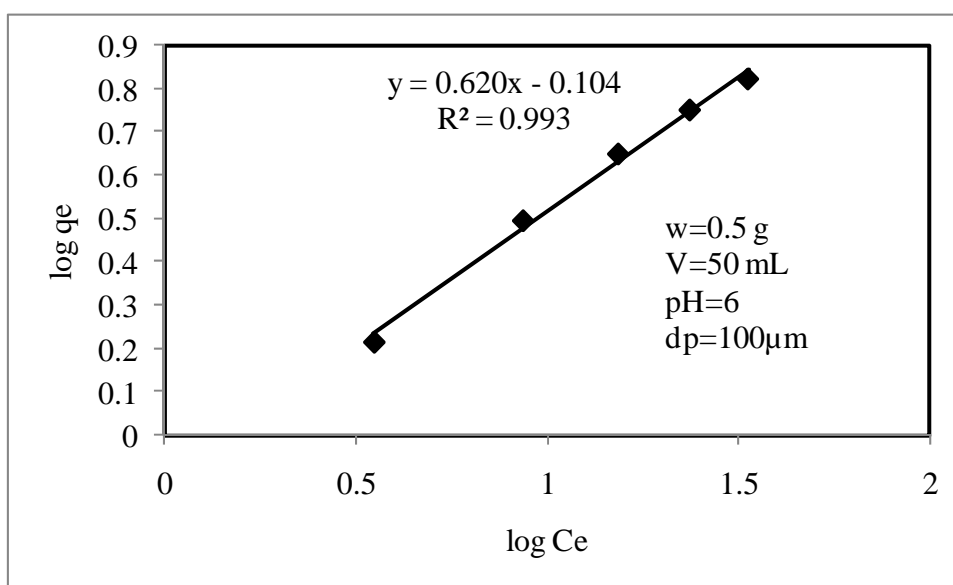

Figure 4. Suitability of experimental data to Freundlich isotherm for adsorption of copper.

3.3.3. Tempkin model

The Tempkin isotherm model [26] represents direct/indirect the adsorbent-adsorbate interactions through a factor. Tempkin has noticed that heats of adsorption would more often decrease than increase with increasing coverage through experimentation. Both the nonlinear and linear form of Tempkin equations are given below.

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{5}$$

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{6}$$

Here $B_T = (RT/b_T)$. T is the absolute temperature (K) and R is the ideal gas constant. Constant b_T is related to the heat of adsorption. A_T is the equilibrium binding constant corresponding to the maximum binding energy. A plot of q_e versus $\ln C_e$ at a fixed temperature will give Tempkin isotherm constants, A_T and b_T, obtained from equation are 0.5396 and 1140.39 respectively.

Figure 5 shows linearity for Tempkin Isotherm for the adsorption of copper on chromolaena odorata leaf powder with regression coefficients of 0.985 and Linearity of the relationship of figure reveals that strong binding of copper to the adsorbent.
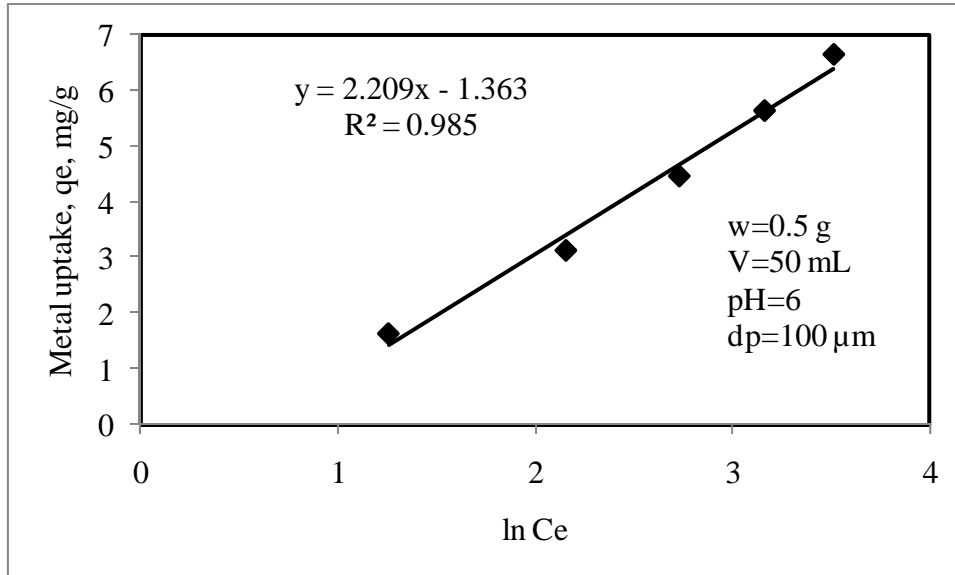

Figure 5. Suitability of experimental data to Tempkin isotherm for adsorption of copper.

3.4. Studies on kinetics of adsorption

The adsorption kinetic models describe the metal uptake, the rate, it controls the process time of metal uptake on the solid –solution interface along with reaction pathways and time to reach equilibrium. Two kinetic models have been tested to investigate the mechanism of adsorption using pseudo first order and pseudo second order kinetic models at various parameters. Based on regression coefficient (R^2 value), the closeness of experimental data to the model predicted values was decided A relatively high R^2 value (close or equal to one) is preferred for better adsorption of copper on adsorbent.

3.4.1. Pseudo-first order or Lagergren kinetic model

The pseudo first order model is presented as

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{7}$$

where q_e and q_t are the metal uptake at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo first order adsorption (min^{-1}). Equation (7) can be arranged to obtain the more useful form

$$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t \tag{8}$$

The plot of $\log(q_e - q_t)$ vs. t is linear from which k_1 can be determined from the slope. Figure 6 shows the first order kinetics for adsorption of copper by chromolaena odorata leaf powder. The

model equations with regression coefficients are shown in Table 1. From the graph, the q_e is estimated for different process parameters and the estimated value is checked with the experimental value. From Table 1, it can be seen that q_{ecal} and q_{eexp} are not the same. Therefore, first order kinetics may not represent the adsorption kinetics. The above model is not fit for copper removal on chromolaena odorata leaf powder adsorbent.

Table 1. Verification of Lagergren pseudo first order coefficients

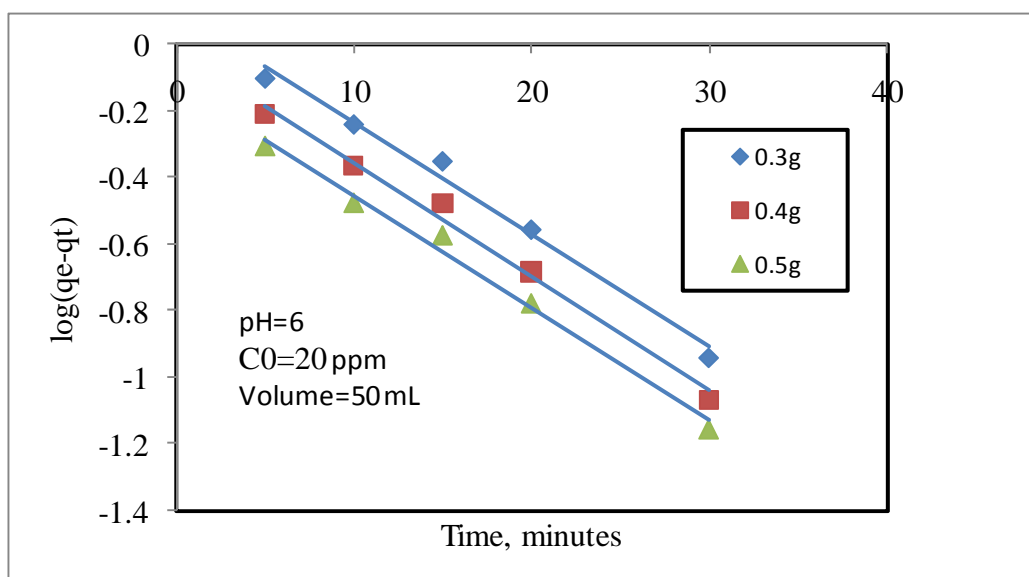| Process parameters (adsorbent dosage and initial concentration of Cu (II))	Model equations	q_{ecal}	q_{eexp}	R^2	Rate constants, K_1, min^{-1}
0.3 g and 20ppm	$\log(q_e - q) = -0.033t + 0.101$	1.2618	2.514	0.987	0.0759
0.4 g and 20ppm	$\log(q_e - q) = -0.034t - 0.012$	0.9727	1.959	0.990	0.0783
0.5 g and 20ppm	$\log(q_e - q) = -0.033t - 0.118$	0.7621	1.6482	0.990	0.0759

Figure 6. Suitability of experimental data to first order kinetics for adsorption of copper

3.4.2. Pseudo–second order kinetic model

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

where k_2 is the rate constant of pseudo second order adsorption (g mg^{-1}min^{-1}). The linear form of Equation (9) after integration is given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

And k_2 is obtained from the intercept of the plot of t/q_t vs. t. Figure 7 shows the second order kinetics for adsorption of copper by chromolaena odorata leaf powder. The model equations with correlation coefficients are shown in Table 2, it can be seen that q_{ecal} and q_{eexp} are almost the same. Therefore, the second order kinetic model fit for copper removal by chromolaena odorata leaf powder adsorbent.

Table 2. Verification of Lagergren pseudo second order coefficients

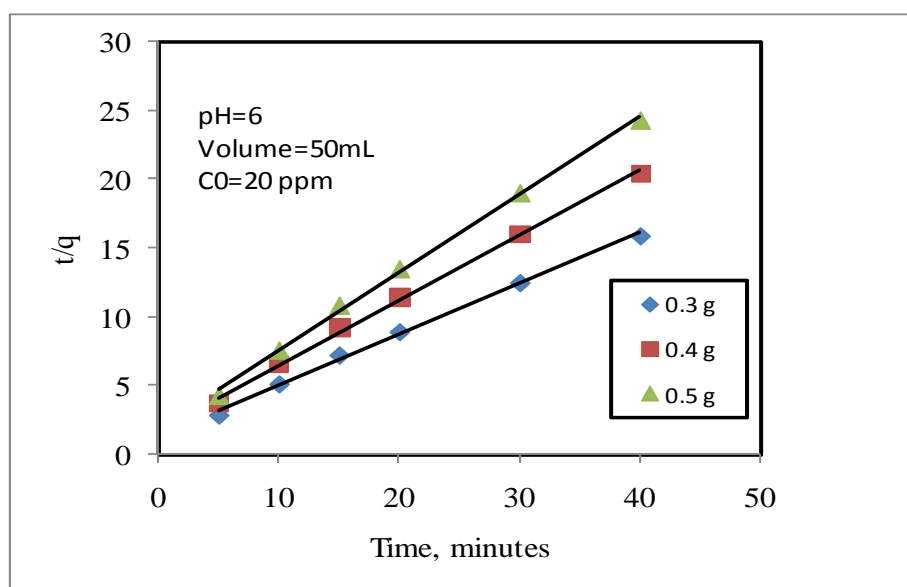| Kinetics	Process parameters (adsorbent dosage and initial concentration of copper)	Model equations	q_{ecal}	q_{eexp}	R^2	Rate constants, K_1, g mg^{-1} min^{-1}
2nd order	0.3 g and 20ppm	$\dfrac{t}{q} = 0.366t + 1.443$	2.732	2.514	0.997	0.0928
	0.4 g and 20ppm	$\dfrac{t}{q} = 0.471t + 1.788$	2.1231	1.959	0.997	0.1240
	0.5 g and 20ppm	$\dfrac{t}{q} = 0.564t + 1.969$	1.773	1.6482	0.998	0.1616

Figure 7. Suitability of experimental data to second order kinetics for adsorption of copper.

3.4.2 Intra-particle diffusion model

The combination of four consecutive steps [27] are used for adsorption of copper on a porous adsorbent; diffusion in the bulk solution, then diffusion across the thin film surrounding the adsorbent particles, followed by intra-particle diffusion and adsorption within the particles. According to Meena *et al.* [28] if the rate limiting step is the intra-particle diffusion, then amount of adsorbed at any time should be directly proportional to the square root of contact time t and shall pass through the origin which is represented mathematically in Equation (11),

$$q_t = K_{diff} t^{0.5} + C \qquad (11)$$

where q_t is the metal uptake (mg/g) and t is the contact time (min). K_{diff} is the intra-particle diffusion coefficient. A plot of q_t against $t^{0.5}$ should give a straight line with a positive intercept for intra particle diffusion controlled the adsorption process. The value of K_{diff} is calculated from slope. The higher values of K_{diff} represents an enhancement in the rate of adsorption.

Figure 8 shows good linearity for intra particle diffusion model based on the regression coefficients. The R^2 values (refer to Table 3) are close to unity, conforming that the rate-limiting step is actually the intra-particle diffusion process. The values of K_{diff} calculated from slope provide information about thickness of the boundary layer, i.e. the resistance to the external mass transfer. The larger slope indicates higher external resistance.
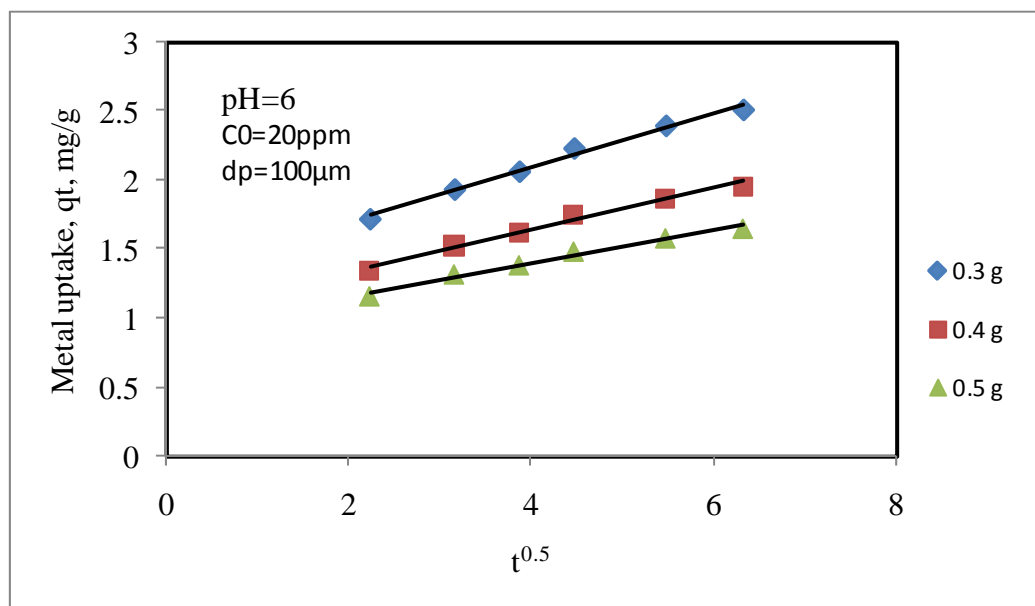

Figure 8. Suitability of experimental data to intra particle diffusion model for adsorption of copper.

Table 3. Verification of intra particle diffusion model and constants.

S. No.	Process parameters (adsorbent dosage and initial concentration of copper)	Model equations	R^2	K_{diff}	Constant, C
1.	0.3 g and 20ppm	$q_t = 0.195t^{0.5} + 1.311$	0.989	0.195	1.311
2.	0.4 g and 20ppm	$q_t = 0.151t^{0.5} + 1.037$	0.985	0.151	1.037
3.	0.5 g and 20ppm	$q_t = 0.119t^{0.5} + 0.916$	0.982	0.119	0.916

4. Conclusions

Biosorption is a relatively new technique which has shown significant attention on removal of heavy metals from aqueous solutions. The effective use of the chromolaena odorata leaf powder was studied in a batch mode and proved as capable of maximum metal uptake of 10.416 mg/g. The adsorption of copper on chromolaena odorata leaf powder is found strongly to be affected by parameters such as contact time, initial copper concentration, pH, adsorbent dosage and adsorbent particle size. The experimental results indicated that Langmuir model for copper adsorption on

adsorbent fits better than Freundlich and Tempkin model and also it follows the pseudo second-order kinetics. The performance of chromolaena odorata leaf powder is studied in the batch process as this gives a platform to do research further in continuous flow systems for industrial application at large scale in economical way.

References

[1] Tong, K.S., Kassim, M. J. and Azraa, A. 2011. Adsorption of copper ion from aqueous solution by novel biosorbent Uncariagambir: Equilibrium, kinetics and thermodynamic studies. *Chemical Engineering Journal*, 170, 1: 145-153. doi: 10.1016/j.cej.2011.03.044

[2] Yisa, J. 2010. Heavy metals contamination of road-deposited sediments. *American Journal of Applied Science*, 7, 9: 1231-1236. doi: 10.3844/ajassp.2010.1231.1236

[3] Ong, M. C. and Kamruzzaman, B. Y. 2009. An assessment of metals (Pb and Cu) contamination in bottom sediment from South China Sea coastal waters, Malaysia. *American Journal of Applied Science*, 6, 7: 1418-1423. doi: 10.3844/ajassp.2009.1418.1423

[4] Ghalay, A. E., Snow, A., and Kamal, M. 2008. Kinetics of manganese uptake by wetland plants. *American Journal of Applied Science*, 5, 10: 1415-1423. doi: 10.3844/ajassp.2008.1415.1423

[5] Omar, W. and Al-Itawi, H. 2007. Removal of Pb^{2+} ions from aqueous solutions by adsorption on Kaoline clay. *American Journal of Applied Science*, 4, 7: 502-507. doi: 10.3844/ajassp.2007.502.507

[6] World Health Organisation. 2004. *Guidelines for drinking water quality*, 3rd ed., WHO, Genrva. 1: 334.

[7] Zhou, X., Korenaga, T., Takahashi, T., Moriwake, T., and Shinoda, S. 1993. A process monitoring/controlling system for the treatment of waste water containing (VI), *Water Research*, 27, 6: 1049-1052. doi: 10.1016/0043-1354(93)90069-T

[8] Tiravanti, G., Petruzzelli, D., and Passino, R. 1997. Pretreatment of tannery wastewaters by an ion-exchange process for Cr (III) removal and recovery. *Water Science and Technology*, 36, 2-3: 197-207. doi: 10.1016/S0273-1223(97)00388-0

[9] Seaman, J. C., Bertsch, P. M. and Schwallie, L. 1999. In-Situ Cr(VI) reduction within coarse-textured, oxide-coated soil and aquifer systems using Fe(II) solutions. *Environmental Science and Technology*, 33, 6: 938-944. doi: 10.1021/es980546+

[10] Kongsricharoern, N. and Polprasert, C. 1996. Chromium removal by a bipolar electro-chemical precipitation process. *Water Science and Technology*, 34, 9: 109-116. doi: 10.1016/S0273-1223(96)00793-7

[11] Pagilla, K. R. and Canter, L. W. 1999. Laboratory studies on remediation of chromium-contaminated soils. *Journal of Environmental Engineering*, 125, 3: 243-248. doi: 10.1061/(ASCE)0733-9372(1999)125:3(243)

[12] Chakravathi, A. K., Chowadury, S. B., Chakrabarty, S., Chakrabarty, T. and Mukherjee, D. C. 1995. Liquid membrane multiple emulsion process of chromium(VI) separation from waste waters. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 103, 1-2: 59-71. doi: 10.1016/0927-7757(95)03201-N

[13] Aksu, Z., Özer, D., Ekiz, H. I., Kutsal, T., and Çaglar, A. 1996. Investigation of biosorption of chromium(VI) on cladophora crispata in two-staged batch reactor. *Environmental Technology*, 17, 2: 215-220. doi: 10.1080/09593331708616379

[14] Huang, S.-D., Fann, C.-F., and Hsieh, H.-S, 1982. Foam separation of chromium(VI) from aqueous solution. *Journal of Colloid Interface Science*, 89, 2: 504-513. doi: 10.1016/0021-9797(82)90201-6

[15] Park, D., Yun, Y.-S. and Park, J. M. 2010. The past, present, and future trends of biosorption. *Biotechnology and Bioprocess Engineering*, 15, 1: 86-102. doi: 10.1007/s12257-009-0199-4

[16] Varma, V. G. and Misra, A. K. 2016. Equilibrium and kinetics studies on the adsorption of copper onto paddy straw powder. *Desalination and Water Treatment*. 57, 28: 13081-13090. doi: 10.1080/19443994.2015.1057536

[17] Thapak, H. K., Trivedia, S. S., and Pandey, L. K. 2015. Removal of copper from synthetic waste water by tea waste adsorbent. *STM Journal of Water Pollution & Purification Research*. 2: 5–9.

[18] Chowdhury, A., Bhowal, A., and Datta, S. 2012. Equilibrium, thermodyanamic and kinetic studies for removal of copper (II) from aqueous solution by onion and garlic skin. *Water*. 4: 37-51. doi: 10.14294/WATER.2012.4

[19] Veli, S. and Alyüz, B. 2007. Adsorption of copper and zinc from aqueous solutions by using natural clay. *Journal of Hazardous Materials*, 149, 1: 226–233. doi: 10.1016/j.jhazmat.2007.04.109

[20] Singha, B. and Das, S. K. 2013. Adsorptive removal of Cu(II) from aqueous solution and industrial effluent using natural/agricultural wastes. *Colloids and Surfaces B: Biointerfaces*. 107: 97-106. doi: 10.1016/j.colsurfb.2013.01.060

[21] Rao, M. M., Ramesh, A., Rao, G. P. C., and Seshaiah, K. 2006. Removal of copper and cadmium from aqueous solution by activated carbon derived from *Ceiba pentandra* hulls. *Journal of Hazardous Materials*. 129, 1-3:123–129. doi: 10.1016/j.jhazmat.2005.08.018

[22] Kamar, F. H. and Nechifor, A. C. 2015. Removal of copper ions from industrial wastewater using walnut shells as natural adsorbent materials. *U.P.B. Scientific Bulletin, Series B*, 77, 3: 141-150

[23] Bajpai, S. K. and Jain, A. 2010. Removal of copper(II) from aqueous solution using spent tea leaves (STL) as a potential sorbent. *Water SA*, 36, 3: 221-228.

[24] Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. *Journal of the American Chemical Society*, 40, 9: 1361-1403. doi:10.1021/ja02242a004

[25] Freundlich, H. M. F. 1907. Uber die adsorption in losungen. *Zeitschrift fur Physikalische Chemie (Leipzig)*, 57: 385-470.

[26] Tempkin, M. J. and Pyzhev, V. 1940. Recent modifications to Langmuir Isotherms. *Acta Physiochim URSS*, 12: 217-222.

[27] Baral, S. S., Das, N., Choudhury, G. R., and Das, S. N. 2009. A preliminary study on the adsorptive removal of Cr(VI) using seaweed, *Hydrilla verticillata*. *Journal of Hazardous Material*, 171, 1-3: 358-369. doi: 10.1016/j.jhazmat.2009.06.011

[28] Meena, A. K., Mishra, G. K., Rai, P. K., Rajagopal, C., and Nagar, P. N. 2005. Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. *Journal of Hazardous Materials*, 122, 1-2: 161-170. doi: 10.1016/j.jhazmat.2005.03.024