



Removal of CU (II) from aqueous solution using custard apple peel powder as adsorbent

D. Krishna*, V.V.L.Srividya, P.Aswini Naidu and S.K.Mastan Vali

Department of Chemical Engineering, M.V.G.R. College of Engineering, Vizianagaram, India-535005.

ARTICLE INFO

Article history:

Received: 22 March 2013;

Received in revised form:

17 April 2013;

Accepted: 8 May 2013;

Keywords

Adsorption,
Batch technique,
Isotherms,
Kinetics,
Custard apple peel powder.

ABSTRACT

Heavy metal accumulation in waste water could affect aquatic life, human health and overall ecosystem adversely. Therefore, in recent years much emphasis has been given for the use of agricultural waste as low cost adsorbents for the removal of metallic contaminants from waste water. In this paper, the studies on removal of Cu (II) by adsorption on custard apple peel powder as adsorbent have been investigated in a batch type experiments. The agitation time, the adsorbent size, adsorbent dosage, initial copper concentration, and the effect of solution pH are studied. The Freundlich model for Cu (II) adsorption onto Custard apple peel powder is proved to be the best fit followed by Langmuir model and Tempkin model based on high regression coefficient R^2 value. The adsorption kinetic behavior is best described by second order. The maximum percentage removal of metal efficiency is found to be 93.97 %. The results obtained in this study illustrate that custard apple peel powder is expected to be an effective and economically viable adsorbent for Cu (II) removal from industrial waste water.

© 2013 Elixir All rights reserved.

Introduction

Aqueous effluents emanating from many industries contain heavy metals dissolved in it. If these discharges are emitted without purification, they may have severe impact on environment [1]. Primarily some anthropogenic activities such as weathering of rocks and volcanic activities play a vital role for enriching the water reservoirs with heavy metals [2, 3]. Numerous metals such as manganese (Mn), mercury (Hg), lead (Pb), Cadmium (Cd), arsenic (As), copper (Cu) are known to be significantly toxic due to their non-biodegradability and toxicity [4, 5]. Among these heavy metals, copper is considered as one of the most toxic one. The potential source of copper in industrial effluents includes paper and pulp, fertilizer, wood preservatives, refineries, metal cleaning and painting bath etc. The excessive intake of copper 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]. Consequently, it is essential that the potable water should be given some treatment before domestic supply.

Several methods are used to remove copper from the industrial wastewater. These 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 small concentrations. In recent years biosorption research is focused on using readily available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective way of purifying industrial waste

water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can efficiently remove heavy metals from aqueous bodies. These materials are identified as biosorbents and the binding of metals by biomass is referred to as biosorption.

In the present investigation, the use of Custard apple peel powder as an effective and inexpensive material for the removal of copper from aqueous solution was described. The paper is organized as follows: next section deals with the material and methods used for the estimation of copper.

Materials and methods

Chemicals

Copper (II) sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck. Stock solution of Copper (II) sulfate having concentration of about 1000 mg/l was prepared by using double distilled water. Various concentrations of test solution of Cu (II) ranging from 20-100 mg/l were prepared by subsequent dilution of the stock solution while the initial pH was adjusted to 6, using a pH meter. Fresh dilution of the stock solution was done for each sorption study. All reagents used here were of AR grade chemicals.

Preparation of the adsorbent

The sorbents used were crushed Custard apple peel powder. The Custard apple peel was obtained from local market; materials were washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it is crushed in roll crusher and hammer mills. The material obtained through crushing and grinding is screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use. All the materials were used as such and no pretreatment was given to the materials. The average particle sizes were maintained in the range of 63 to 125 μm .

Batch mode adsorption studies

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 was 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 (Whatman No-1).

Table 1. Range of different parameters investigated in the present study

Parameter	Values Investigated
Agitation time, t, min	5, 10, 15, 20, 25, 30, 40, 50, 60, 90 and 120
adsorbent dosage, w, g	0.25, 0.5, 0.75, 1.0, 1.25, 1.5 and 1.75
Initial copper concentration, C_0 , mg/L	20, 40, 60, 80 and 100
pH of aqueous solution	2, 3, 4, 5, 6, 7, 8, 9 and 10

Metal analysis

Final residual metal concentration after adsorption was measured by Atomic absorption Spectrophotometer.

To estimate the percentage removal of copper from aqueous solution, the following equation was used.

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

Metal uptake (q_e) at equilibrium time was calculated from the following equation

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

Where q_e (mg/g) is the amount of copper adsorbed per unit weight 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 adsorbent weight (g).

Results and discussion

Effect of agitation time and initial copper concentrations

The equilibrium agitation time is determined by plotting the percentage removal of copper against agitation time for different adsorbent dosages as shown in Figure 1. The percentage removal of copper increases up to 50 min of the agitation time and thereafter no further increase is recorded by custard apple peel powder as adsorbent. Adsorption equilibrium time is defined as the time required for heavy metal concentration to reach a constant value. It is observed that percentage removal of copper decreases with increase in adsorbent dosage.

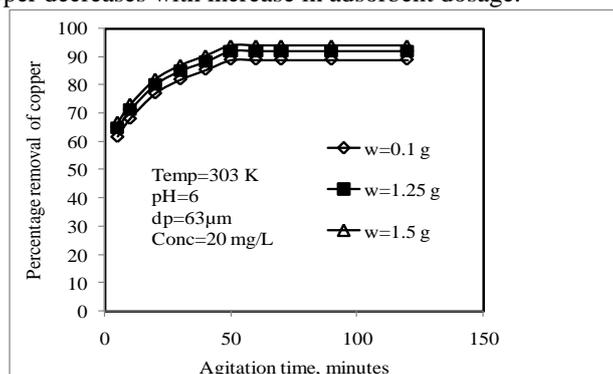


Figure 1. Variation of percentage removal of copper with agitation time by custard apple peel powder for different initial concentration of copper in solution

Effect of adsorbent dosage and adsorbent size in aqueous solution

The variations in percentage removal of copper and also metal uptake in aqueous solution with adsorbent dosage are shown in Figure 2. The percentage removal of copper from aqueous solution increases from 52.67% to 93.97% and also metal uptake decreases from 2.1068 to 0.5179 mg/g with an increase in the adsorbent dosage from 0.25 g to 1.75 g in 50 ml solution at 303 K for 63 μ m size. The percentage removal of copper from aqueous solution with adsorbent size is reported in Table 1. The percentage removal of copper increases from 82.07 % (0.5471 mg/g) to 93.97 % (0.6265 mg/g) for 1.5 g of dosage in 50 ml for the initial copper concentration of 20 mg/L at 50 min equilibrium agitation time with decrease in the adsorbent size from 125 to 63 μ m. This phenomenon is expected as the decrease in size of adsorbent results in the increase of the surface area of it, thereby the number of active sites are better exposed to the adsorbate.

Table 1. Effect of adsorbent particle size, $C_0=20$ mg/L; Temp=303 K; v=50mL; t=50 min; pH=6 and w=1.5 g.

S.No.	Adsorbent average particle size, μ m	Final concentration, mg/L	Percentage adsorption	Metal uptake (mg/g)
1	63	1.206	93.97	0.6265
2	89	2.138	89.31	0.5954
3	125	3.586	82.07	0.5471

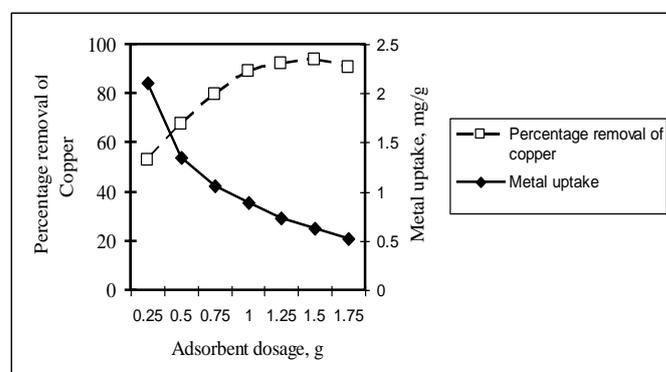


Figure 2. Variation of percentage removal of copper and metal uptake with adsorbent dosage by custard apple peel powder

Effect of pH of the aqueous solution

pH is an important factor for controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorbate. The effect of pH on adsorption of copper at different initial concentrations is shown in Figure 3. The maximum percentage removal of copper for various initial concentrations is reported at pH value of 6. It is confirmed that adsorption of copper increases with increase in pH values from 1 to 6, after words it decreases when pH is greater than 6.

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.

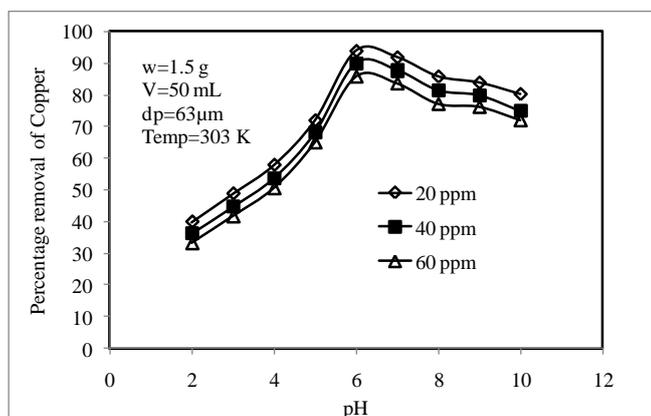


Figure 3. Effect of pH of aqueous solution on percentage removal of copper for different initial concentrations by custard apple peel powder

Langmuir model

The Langmuir isotherm [15] was derived originally from studies on gas adsorption to activated carbon. The Langmuir isotherm model is used to estimate the adsorption of adsorbent used and suggests that 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 Langmuir adsorption isotherm is of the form:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (1)$$

Here q_e is the metal concentration adsorbed in solid (biomass), C_e is the metal residual concentration in the solution. q_{\max} is the maximum specific uptake corresponding to sites saturation, and b is the ratio of adsorption/desorption rates. The Langmuir isotherm in Eq (1) can be written as

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \quad (2)$$

The adsorption data for adsorption of copper on custard apple peel powder is plotted in Figure 4 shows good linearity for Langmuir isotherm. The equations with correlation coefficients are shown in Table 2. q_{\max} is calculated from the slope and b is calculated from the intercept. It is observed that strong binding of copper ions to the surface of custard apple peel powder. The separation factor, R_L obtained (from Table 3) between 0.0601-0.2424 for various concentrations shows favorable adsorption ($0 < R_L < 1$).

Table 2. Langmuir isotherms and its coefficients

S. No	Parameters	Equations	q_m	b	R_L	R^2
1	T=303 K	$\frac{C_e}{q_e} = 0.308 C_e + 1.971$	3.2468	0.1563	<1	0.984

Table 3. $R_L = \frac{1}{1 + b C_0}$ values at pH=6; T=303 K

Initial concentration, C_0 (mg/L)	R_L
20	0.2424
40	0.1379
60	0.0963
80	0.0741
100	0.0601

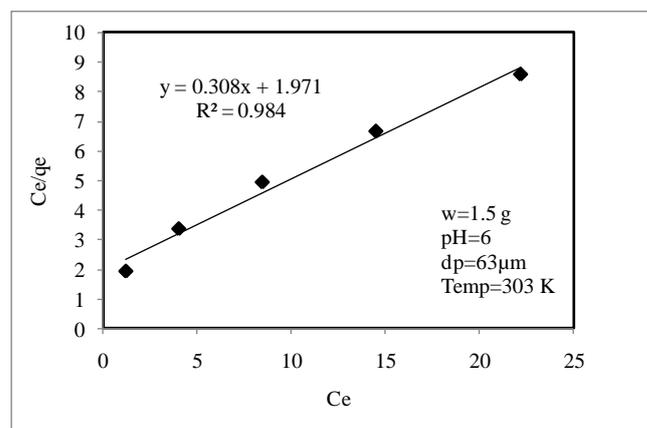


Figure 4. Langmuir isotherm for adsorption of copper by custard apple peel powder

Freundlich model

The Freundlich isotherm [16] is based on multilayer adsorption with interaction between adsorbed molecules. The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. This relation can be reasonably applied to the low or intermediate concentration ranges. For adsorption from solution, the Freundlich isotherm is represented by:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

Here K_f is the Freundlich constant and is also known as Freundlich capacity and n stands for adsorption intensity. q_e is the amount of copper adsorbed at equilibrium and C_e is the residual concentration of Copper in solution. The Freundlich equation is expressed linearly as.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

The values of K_f and n can be obtained from intercept and slope of a plot of $\log q_e$ versus $\log C_e$.

The adsorption data for the adsorption of copper on custard apple peel powder was plotted in Figure 5 shows good linearity for Freundlich Isotherm. The equations with correlation coefficients are shown in Table 4. Linearity of the relationship indicates strong binding of copper to the adsorbent. As the slope of isotherm (n) is 2.0449, it is fulfilling the condition of $n > 1$ for favorable condition.

Table 4. Freundlich isotherm and its coefficient

S. No.	Parameters	Equations	K_f	n	R^2
1	T=303 K	$\log q_e = 0.489 \log C_e - 0.230$	0.5889	2.0449	0.997

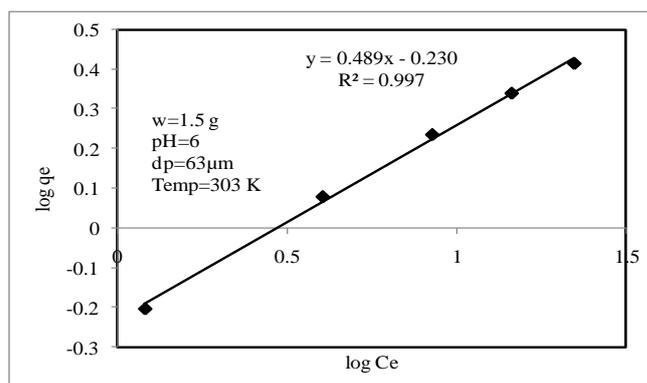


Figure 5. Freundlich isotherm for adsorption of copper by custard apple peel powder

Tempkin model

The Tempkin isotherm model [17] contains a factor that takes care of the adsorbent-adsorbate interactions. Tempkin considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. Tempkin noted experimentally that heats of adsorption would more often decrease than increase with increasing coverage. The nonlinear form of Tempkin equation is given by Eq (5) and the linear form in Eq (6).

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

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (6)$$

Here $B_T = (RT/b_T)$. T is the absolute temperature and R is the universal 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 .

The adsorption data for adsorption of copper on custard apple peel powder was plotted in Figure 6 shows good linearity for Tempkin Isotherm. The equations with correlation coefficients are shown in Table 5. Linearity of the relationship indicates strong binding of Copper to the adsorbent.

Table 5. Tempkin isotherm and its coefficient

S. No.	Parameters	Equations	b_T	A_T	R^2
1	T=303 K	$q_e = 0.67 \ln C_e + 0.392$	3759.913	0.5851	0.977

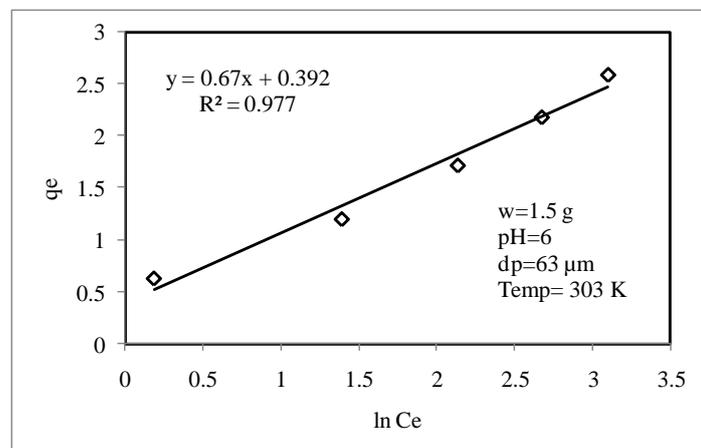


Figure 6. Tempkin isotherm for adsorption of copper by custard apple peel powder

Dubinin and Radushkevich (D-R) isotherm

Dubinin and Radushkevich equation [18] is represented in a linear form by equation

$$\ln q_e = \ln Q_0 - K_{DR} \varepsilon^2 \quad (7)$$

Where K_{DR} ($\text{mol}^2 \text{KJ}^{-2}$) is a constant related to mean adsorption energy and ε is the Polanyi potential which can be calculated from the following equation

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

The slope of plot of $\ln q_e$ versus ε^2 gives K_{DR} ($\text{mol}^2 \text{KJ}^{-2}$) and the intercept yields the sorption capacity Q_0 (mg/g). T is the absolute temperature in Kelvin and R is the universal gas constant ($8.314 \text{ Jmol}^{-1} \text{K}^{-1}$).

The sorption energy can also be worked out using the following relationship [19]

$$E = \frac{1}{(2 \times K_{DR})^{\frac{1}{2}}} \quad (9)$$

Where, E is the mean free energy of adsorption. If the value of E is between 1 and 16 KJ/mol, then physical adsorption prevails; and if the value of E is more than 16 KJ/mol, then chemisorption prevails. The adsorption data for adsorption of copper on custard apple peel powder was plotted in Figure 7 shows non-linearity for D-R isotherm. The equations with correlation coefficients are shown in Table 6. From regression coefficient R^2 value, the present data is not fit for D-R isotherm.

Table 6. Dubinin and Radushkevich (D-R) isotherms and its coefficients

S. No.	Parameters	Equations	K_{DR}	E(KJ/mole)	R^2
1	T=303 K	$\ln q_e = -5 \times 10^{-07} \varepsilon^2 + 0.681$	5×10^7	1.00	0.829

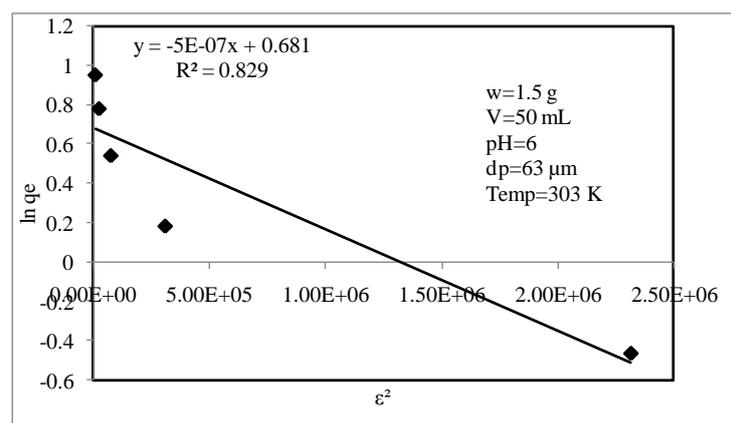


Figure 7. Dubinin and Radushkevich (D-R) isotherm for adsorption of copper by custard apple peel powder

Studies on kinetics of adsorption

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbate uptake at the solid –solution interface. Chemical kinetics gives information about reaction pathways and time to reach equilibrium. Sorption kinetics shows a large dependence on the physical and /or chemical characteristics of the sorbent material. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (R^2 value). A relatively high R^2 value (close or equal to one) indicates that the model successfully describes the kinetics of copper adsorption.

Pseudo-first order or Lagergren kinetic model

It is the first equation for sorption of liquid/solid system based on solid capacity. The pseudo first order equation is generally expressed as

$$\frac{dq}{dt} = k_1 (q_e - q_t) \quad (10)$$

Here q_e and q_t are the adsorption capacities at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of pseudo first order adsorption (min^{-1}). Eq (10) can be arranged to obtain the more useful form

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad (11)$$

The plot of $\log(q_e - q_t)$ vs t is linear from which k_1 can be determined from the slope. First order kinetics for adsorption of copper by custard apple peel powder is shown in Figure 8. The equations with correlation coefficients are shown in Table 7.

Table 7. Lagergren pseudo first order coefficients

Parameters pH=6, Temperature=303 K (adsorbent dosage and initial concentration of Cr(VI))	Model equations	q _{ecal}	q _{eexp}	R ²	Rate constants, K ₁ , min ⁻¹
1.0 g and 20ppm	$\log(q_e - q) = -0.0245t - 0.432$	0.3698	0.8891	0.998	0.0576
1.25 g and 20ppm	$\log(q_e - q) = -0.024t - 0.534$	0.2924	0.7364	0.999	0.0553
1.5g and 20ppm	$\log(q_e - q) = -0.025t - 0.608$	0.2466	0.6265	0.998	0.0576

Table 8. Lagergren pseudo second order coefficients

Parameters pH=6, Temperature=303 K (adsorbent dosage and initial concentration of copper)	Model equations	q _{ecal}	q _{eexp}	R ²	Rate constants, K ₁ , g mg ⁻¹ min ⁻¹
1 g and 20ppm	$\frac{t}{q} = 1.067t + 3.832$	0.9372	0.8891	0.998	0.2971
1.25g and 20ppm	$\frac{t}{q} = 1.292t + 4.422$	0.7739	0.7364	0.998	0.3775
1.5g and 20ppm	$\frac{t}{q} = 1.52t + 5.063$	0.6578	0.6265	0.998	0.4563

Table 9. Intra particle diffusion model and constants

S. No.	Dosage, g	Model equations	R ²	K _{diff}	Constant, C
1.	1.0 g and 20ppm	$q_t = 0.055t^{0.5} + 0.504$	0.988	0.055	0.504
2.	1.25 g and 20ppm	$q_t = 0.044t^{0.5} + 0.428$	0.988	0.044	0.428
3.	1.5 g and 20ppm	$q_t = 0.037t^{0.5} + 0.37$	0.988	0.037	0.370

From the graph, the q_e is estimated for different process parameters and the estimated value is checked with the experimental value. From Table 7, it can be seen that q_{ecal} and q_{eexp} are not the same. Therefore, first order kinetics may not represent the adsorption kinetics, though the R^2 value is close to 1. The above model is not fit for copper removal on custard apple peel powder adsorbent.

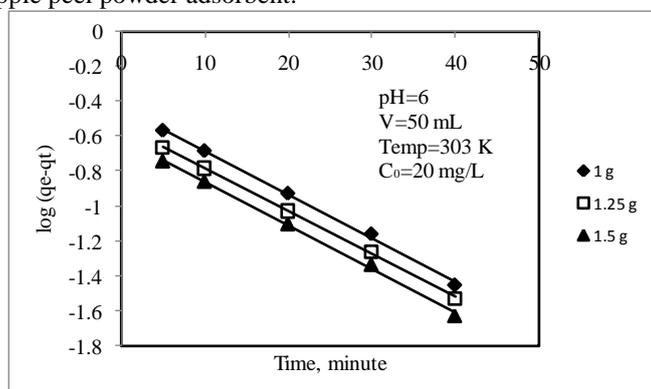


Figure 8. First order kinetics for adsorption of copper by custard apple peel powder

Pseudo-second order kinetic model

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

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (12)$$

Where k_2 is the rate constant of pseudo second order adsorption ($g \text{ mg}^{-1} \text{ min}^{-1}$). Eq (12) can be rearranged to obtain more useful form as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (13)$$

The linear form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

And k_2 is obtained from the intercept of the plot of t/q_t vs t . The second order kinetics for adsorption of copper by custard apple peel powder is shown in Figure 9. Their equation with correlation coefficients are shown in Table 8, it can be seen that q_{ecal} and q_{eexp} are almost the same. Therefore, the second order kinetic model is fit for copper removal by custard apple peel powder adsorbent.

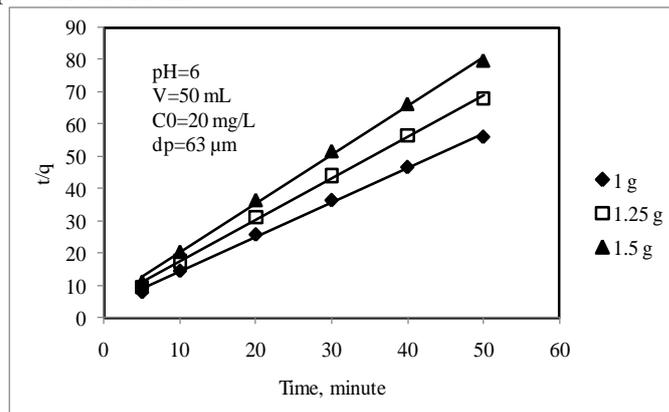


Figure 9. Second order kinetics for adsorption of copper by custard apple peel powder

Intra-particle diffusion model

The adsorption of copper on a porous adsorbent is the combination of four consecutive steps [20]; 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 [20]. According to Weber and Moris [21] 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 defined mathematically in Eq (15)

$$q_t = K_{diff}t^{0.5} + C \quad (15)$$

where q_t is the amount of Copper adsorbed and t is the contact time. 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 adsorption process. The value of K_{diff} can be calculated from slope. The higher values of K_{diff} illustrate an enhancement in the rate of adsorption.

The adsorption data was plotted in Figure 10 shows good linearity for intra particle diffusion model. The equations with correlation coefficients are shown in Table 9. The R^2 values (refer to Table 9) 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.

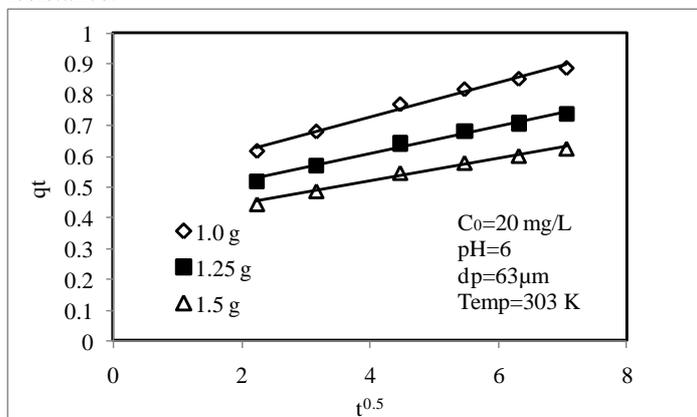


Figure 10. Intra particle diffusion model for adsorption of copper by custard apple peel powder

Conclusions

The custard apple peel powder is capable of removing copper from aqueous solution, up to 93.97% for an initial concentration of copper 20 mg/L, adsorbent dosage of 1.5 g (in 50mL solution), adsorbent size of 63 μ m, pH=6 and at a temperature of 303 K. The Copper adsorption performance by custard apple peel powder is strongly affected by parameters such as contact time, initial copper concentration, pH, adsorbent dosage and adsorbent particle size.

- The percentage adsorption of copper is increased from 66.84% to 93.97% for 20 mg/l with increase in contact time from 5 to 120 minutes for an adsorbent dosage of 1.5 g. Percentage Adsorption is reached equilibrium stage at 50 minutes of contact time.

- With an increase in pH from 2 to 10, the percentage adsorption of copper is decreased from 93.97% to 39.98% for 20 mg/L solution. The optimum pH is taken at pH of 6 for an adsorbent dosage of 1.5 g.

- With an increase in initial concentration of copper from 20 to 100 mg/L (for 1.5 g dosage, pH of 6 and a particle size of

63 μ m), the equilibrium percentage adsorption of copper is decreased from 93.97% to 77.79%.

- With the increase in adsorbent dosage from 0.25 to 1.75 g (for 50 mL of solution with initial concentration of 20 mg/L, pH of 6 and particle size of 63 μ m), the percentage adsorption of copper is increased from 52.67 % to 93.97 %.

- The percentage removal of copper increases from 82.07 % (0.5471 mg/g) to 92.15% (0.6265 mg/g) for 1.5 g of dosage in 50 mL (initial concentration of 20 mg/L, pH of 6) of solution at 50 min equilibrium agitation time with decrease in the adsorbent size from 125 to 63 μ m

- The Freundlich models for copper adsorption onto custard apple peel powder is proved to be the best fit followed by the Langmuir and Tempkin model for the experimental data. However, the data cannot be described by Dubinin-Radushkevich-isotherm, since the correlation coefficient is very low.

- The kinetics of the adsorption of copper on custard apple peel powder can be better described with pseudo second-order kinetics.

The present study is performed in the batch process as this gives a platform for the designing of continuous flow systems with an industrial application at a commercial level also. Further, research is to be carried out to make the process economically viable at industrial scale with focus on copper removal and regeneration of custard apple peel powder.

References

1. L.Krim, S.Nacer & G.Bilango, Kinetics of chromium sorption on biomass fungi from aqueous solution, Am.J.Environ.Sci., 2 (2006) 27-32.
2. J.Yisa, Heavy metals contamination of road deposited sediments, Am.J.Environ.Sci., 7 (2010) 153-159.
3. M.C.Ong & B.Y.Kamruzzaman, An assessment of metals (Cu and Pb) contamination in bottom sediment from south china sea coastal waters, Malaysia, Am.J.Environ.Sci., 6 (2009) 1418-1423.
4. A.E.Ghalay, A.Snow & M.Kamal, Kinetics of manganese uptake by wetland plants, Am.J.Environ.Sci., 5 (2008) 1415-1423.
5. W.Omar & H.Al-Itawi, Removal of Pb²⁺ ions from aqueous solutions by adsorption on kaoline clay, Am.J.Environ.Sci., 4 (2007) 502-507.
6. World Health Organisation, Guidelines for drinking water quality, 3rd ed., Genrva Vol.1. 2004, p 334.
7. X. Zhou, T. Korenaga, T. Takahashi, T. Moriwake, S. Shinoda, A process monitoring/controlling system for the treatment of waste water containing (VI), Water Res., 27 (1993) 1049.
8. G. Tiravanti, D. Petruzzelli, R. Passino, Pretreatment of tannery wastewaters by an ion-exchange process for Cr (III) removal and recovery, Water Sci.Technol., 36 (1997), 197-207.
9. J.C. Seaman, P.M. Bertsch, L. Schwallie, In-Situ Cr (VI) reduction within coarse -textured oxide-coated soil and aquifer systems using Fe (II) solutions, Environ.Sci.Technol., 33 (1999) 938-944.
10. N. Kongsricharoen, C. Polprasert, Chromium removal by a bipolar electro-chemical precipitation process, Water Sci.Technol., 34 (1996) 109-116.
11. K.R. Pagilla, L.W. Canter, Laboratory studies on remediation of Chromium -contaminated soils, J.Environ.Eng., 125 (1999) 243-248.

12. A.K. Chakravathi, S.B. Chowadary, S. Chakrabarty, T. Chakrabarty, D.C. Mukherjee, Liquid membrane multiple emulsion process of chromium (VI) separation from waste waters, *Colloids, Surf. A.*, 103 (1995) 59-71.
13. Z. Aksu, D. Ozer, H.I. Ekiz, T. Kutsal, A. Calar, Investigation of Biosorption of Chromium (VI) on *Cladophora Crispata* in Two-Stage Batch Reactor, *Environ. Technol.*, 17 (1996) 215-220.
14. S.D. Huang, C.F. Fann, H.S. Hsieh, Foam separation of chromium (VI) from aqueous solution, *J. Colloid Interface Sci.*, 89 (1982) 504-513.
15. I. Langmuir, Adsorption of gases on glass, Mica, and Platinum, *J. Am. Chem. Soc.*, 40 (1918) 1361-1403.
16. H. Freundlich, Veber die adsorption in loesungen (adsorption in solution), *Z. Phys. Chem.*, 57 (1907) 385.
17. Tempkin, M.J., Pyzhev, V. (1940). Recent modifications to Langmuir Isotherms, *Acta Physicochim. URSS*, 12, 217-222.
18. Hall, K.E., Eagleton, L.C., Acrivos, A., Vermeulen, T. (1996). Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, *Ind. Eng. Chem. Fundam.*, 5, 212-223.
19. McKay, G., Otterburn, Sweny, A.G. (1981). Surface mass transfer processes during color removal from effluent using silica, *Water Res.* 15, 327-331.
20. Baral, S.S., Das, N., Roy Choudary, G., Das, S.N. (2009). A preliminary study on the adsorptive removal of Chromium (VI) using seaweed, *Hydrilla Verticillata*, *J. Hazard. Mater.*, 171, 358-369.
21. Weber, W.J., Jr. Morris, J.C. (1963). Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. AMSE*, 89, 31-59.