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Equilibrium and kinetic studies on the adsorption of copper onto carica papaya leaf powder

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Abstract. The possibility of using carica papaya leaf powder for removal of copper from wastewater as a low cost adsorbent was explored. Different parameters that affect the adsorption process like initial concentration of metal ion, time of contact, adsorbent quantity and pH were evaluated and the outcome of the study was tested using adsorption isotherm models. A maximum of 90%-94.1% copper removal was possible from wastewater having low concentration of the metal using papaya leaf powder under optimum conditions by conducting experimental studies. The biosorption of copper ion was influenced by pH and outcome of experimental results indicate the optimum pH as 7.0 for maximum copper removal. Copper distribution between the solid and liquid phases in batch studies was described by isotherms like Langmuir adsorption and Freundlich models. The adsorption process was better represented by the Freundlich isotherm model. The maximum adsorption capacity of copper was measured to be 24.51 mg/g through the Langmuir model. Pseudo-second order rate equation was better suited for the adsorption process. A dynamic mode study was also conducted to analyse the ability of papaya leaf powder to remove copper (II) ions from aqueous solution and the breakthrough curve was described by an S profile. Present study revealed that papaya leaf powder can be used for the removal of copper from the wastewater and low cost water treatment techniques can be developed using this adsorbent.

Keywords: adsorption; biosorption; carica papaya; freundlich isotherm; langmuir; pseudo-second order

1. Introduction

Water pollution by various heavy metals is one of the major environmental problems worldwide. Heavy metals (e.g., copper, lead, cadmium, chromium, zinc, etc.) are toxic even at low concentrations. They are non-biodegradable and through the food chain accumulate in the environment. Copper is one of such heavy metal which is most commonly present in the effluents from brass manufacture, petroleum refining, electro-plating, mining and different agrochemical industries (Dutta and Basu 2014). Many heavy metals including copper (Cu) is responsible for causing haemolysis, gastrointestinal disturbance, irritation of upper respiratory tract, liver and kidney damage, diarrhoea etc. The maximum acceptable concentration of copper in effluent discharge to water bodies as per The Environment (Protection) Rules, 1986, India is 3 mg/L. Therefore it is imperative to develop an easily and economically feasible method for wastewater treatments.

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Conventional methods for heavy metal removal from aqueous solution include chemical precipitation, ion exchange/chelation, electrolytic recovery, photocatalysis, membrane separation and solvent extraction. Almost all these processes are limited by technical and economical barriers for low metal ion concentration (< 100 ppm) (Abdel-Ghani and El-Chaghaby 2014). These techniques have inherent limitations such as sensitive operating conditions, low metal removal efficiency and production of secondary sludge which is costly to dispose. Small and medium industries lack the capital to afford these costly methods especially for fine purification when the metal concentration is low and may illegally release their partially or untreated wastewater into rivers. To avoid these problems, adsorption which is very effective and environmentally safe method is preferred for wastewater treatment. When comparing with alternative technologies, adsorption is attractive for its relative simplicity of design, operation and scale up, high capacity and favourable rate, insensitivity to toxic substances, ease of regeneration and low cost (Uslu *et al*. 2014). However the high cost of activated carbon which is commonly used as an adsorbent limits its use in adsorption. Recent research has focused on biosorption for the removal of heavy metals (Tang *et al*. 2012).

Biosorption is a property of certain types of inactive biomass to bind and concentrate heavy metals from even very dilute aqueous solutions. Biosorbents have great potential to replace conventional treatment technologies since they are highly efficient for heavy metal removal (Ang *et al*. 2013). Biosorption removal of toxic heavy metals is especially suited as a ‘polishing’ wastewater treatment step because it can produce close to drinking water quality (from initial metal concentrations of 1-100 mg/ L to final concentration < 0.01-0.1 mg/ L) especially in packed bed flow-through applications. Biosorption also offers several advantages over conventional treatment methods including working under a broad range of conditions (temperature, pH), cost effectiveness, efficiency, minimization of chemical/biological sludge, and regeneration of biosorbent with possibility of metal recovery. Several studies carried out on the absorption of heavy metals have revealed that plant materials like Firmiana Simplex Leaf (Tang *et al*. 2012) Neem leaves (Innocent *et al*. 2009), Pineapple leaf powder (Weng and Wu 2012), Ashoka leaf powder (Shelke *et al*. 2009), Agricultural adsorbents (Abia and Asuquo 2006), Agricultural wastes (Singha and Das 2013, Hernáinz *et al*. 2009), Basella alba leaves (Babalola *et al*. 2008), Neem bark (Naiya *et al*. 2009), Gmelina Arborea leaves (Jimoh *et al*. 2011), Erythrina variegata orientalis leaf powder (Venkateswarlu *et al*. 2008), Jatropha seed (Bose *et al*. 2011), Rice straw (El Sayed *et al*. 2010, Mousa *et al*. 2013), Kenaf fibres (Hasfalina *et al*. 2012) and Tree fern (Ho 2003) can be used for wastewater treatment.

The major constituents of papaya leaf is lignin and cellulose and may also contain other polar functional groups of lignin, which include alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have ability to some extent to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution (Sai Seetha *et al*. 2012). The number of sites in the biosorbent material, the accessibility of the sites, the chemical state of the site (i.e., availability), and affinity between site and metal (i.e., binding strength) are some of the important parameters deciding biosorption. The extent to which the site can be used by a given metal depends on its binding strength and concentration as compared to the metal already occupying the site. For electrostatic metal binding, a site is only available if the metal is ionized (Vieira and Volesky 2000).

Metal ions, adsorption onto carboxyl and hydroxyl groups can be illustrated as follows

$$M^{2+} + 2ROH \leftrightarrow (RO)_2M + 2H^+ \tag{1}$$

$$2RCOO^{-} + M2^{+} \rightarrow (RCOO)_2M \quad (2)$$

In which, M = metal ion, ROH and RCOO represents hydroxyl group and carboxylate ion that arising from the papaya leaves (Subramanian *et al*. 2010).

The disposal of adsorbent after adsorption can be easily carried out by incineration method and in landfilling also since the volume of metal laden bio sorbent is less than the volume of wastewater (Naja *et al*. 2010). The adsorbent is very cheap and also regeneration need not be done since here biosorption is done as a polishing treatment only and the amount of adsorbed metal on the adsorbent is comparatively less. Another option for the disposal of biosorbent is to use it as manure for non-consumable plants especially in parks and also can be neutralized prior to disposal. Also it can be safely disposed in hard rocks and clay rich soils, owing to their impervious properties.

The preparation of biosorbent does not require any expensive methods like pyrolsis which is again non environment friendly (Hossain *et al*. 2014). The procedure of biosorbent manufacture is very simple, easy to prepare, hazard free and is in tune with sustainable development which is the novelty of this study. The treatment techniques may include either a batch reactor using papaya powder as the adsorbent or a fixed bed column containing the adsorbent with upflow/downflow process.

India leads the world in papaya production with an annual output of about 3 million tonnes. Due to the high production, massive amounts of leaves are readily available to be used as bio sorbents. The objective of the present study was to investigate the ability of papaya leaves for adsorption of Cu (II) from aqueous solutions. Due to its low cost and easy availability, papaya leaves could be useful for additional applications, such as sequestration, the removal of ions from aqueous solutions, and similar separations in other industrial processes. The ability of the leaves for Cu (II) adsorption was evaluated by considering a variety of factors, including dosage, equilibrium duration and pH of the solution etc.

2. Materials and methods

2.1 Copper stock solution

1000 ppm of copper solution was prepared by dissolving 3.93 gm of copper sulphate pentahydrate ($CuSO_4.5H_2O$) in one litre distilled water. For conducting batch studies and dynamic mode studies, this stock solution was diluted to varied initial concentrations.

2.2 Papaya leaf powder

Leaf from papaya plants were collected, washed several times, dried in sunlight and then in oven at 80℃ for 4-5 hours. After that, it was powdered and utilized for absorption application.

2.3 Study on batch adsorption

Study on batch adsorption was conducted using synthetic solutions of known initial concentrations with papaya leaf powder in magnetic stirrer at normal temperature. Initial concentration, pH, contact time, and adsorbent quantity were varied and the final concentrations of metal ion in solution were measured in Atomic Absorption Spectrophotometer (AAS).

2.4 Column adsorption

A column having length 35 cm and diameter 5.5 cm was used for dynamic mode studies. The column was filled with known quantity of adsorbent and adsorbent length within the column was recorded. Solutions of Copper with various known initial concentrations were prepared and are allowed to pass into the column from an overhead tank. Both inflow and outflow was adjusted for maintaining the constant head. At fixed interval of time effluents were collected from the column and their concentration was analysed using AAS.

3. Results and discussions

3.1. Contact time effects

Out of all the parameters which affect the adsorption studies, the contact time which the adsorbent needs with the adsorbate particles is very important. To analyse the effect of time of contact on Cu sorption process, adsorption experiments were done over different contact times and for various initial concentrations of the adsorbent. Aqueous Cu solution with different initial concentrations were kept in contact with different amounts of adsorbent (1, 2, 5 and 10 g/L) for different time periods ranging from 15 minutes to 120 minutes. The residual concentration of Cu beyond 60 minutes showed hardly any further adsorption. Further, it was analysed that the adsorption kinetics increased rapidly up to 1 h at low adsorbate concentrations (10 mg/L) and beyond that the increase was marginal. For high adsorbate concentration (30 mg/L), the adsorption kinetics increased upto 15 min. Therefore, approximation of a steady state was assumed after 1 hour of contact time and a quasi-equilibrium situation was attained for Cu concentration of 10 mg/L and the same assumption is valid after 15-30 min for concentration of copper ranging from 20 mg/L to 30 mg/L. The sites for adsorption of the adsorbent are vacant during the starting phase of sorption and hence sites available for adsorption are more. After that adsorption is not easy since the adsorbate molecules in the bulk phase are repelled by the already adsorbed molecule on the solid surface. The kinetic data shows clearly two phases. Rapid adsorption phase comes first which is followed by second phase in which equilibrium occurred after continuous adsorption and

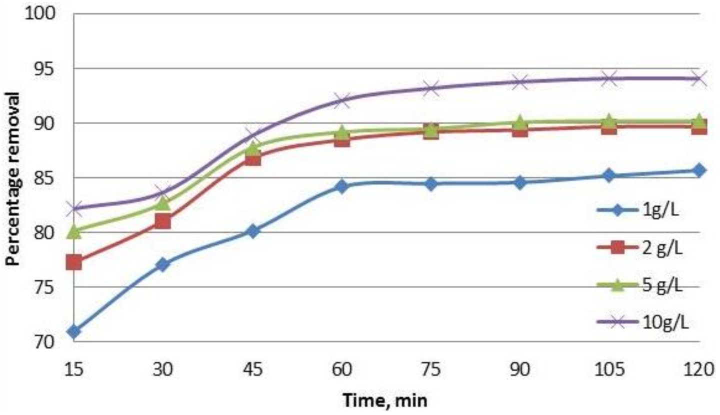

Fig. 1 Variation of percentage removal with contact time at different dosages of adsorbent (Initial concentration 10 mg/1)

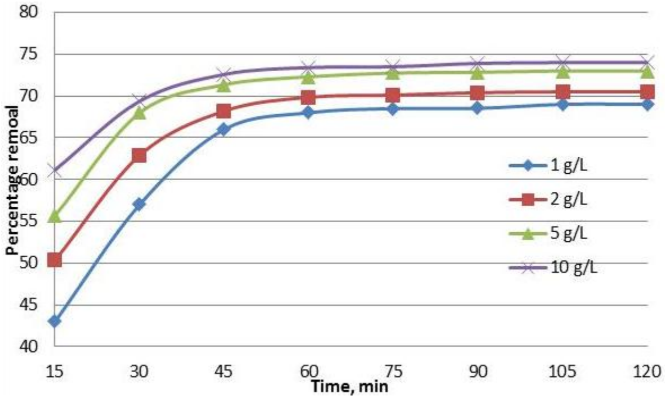

Fig. 2 Variation of percentage removal with contact time at different dosages of adsorbent (Initial concentration 20 mg/1)

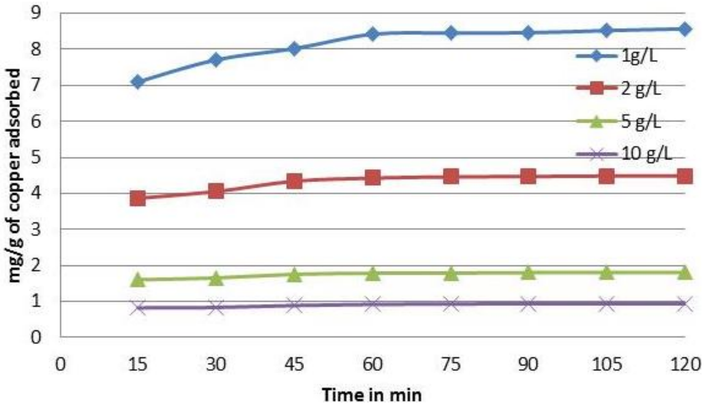

Fig. 3 Variation of uptake of Cu with contact time at different dosages of adsorbent (Initial concentration 10 mg/1)

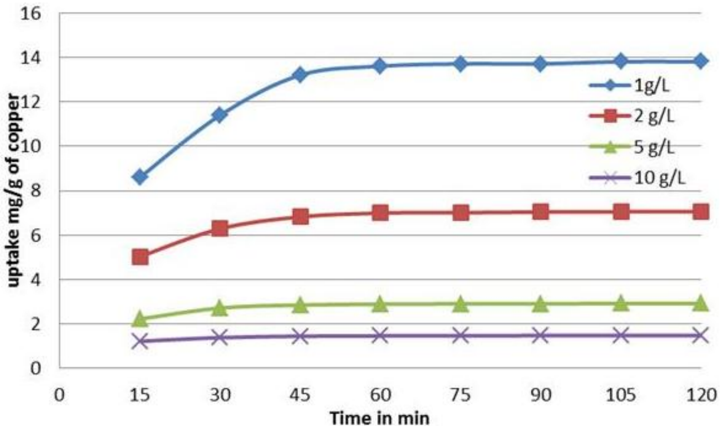

Fig. 4 Variation of uptake of Cu with contact time at different dosages of adsorbent (Initial concentration 20 mg/1)

remaining constant thereafter. Cu ions are rapidly attached on to activate sites on the surface of the papaya leaf powder by mass transfer through surface in the first phase. In the second phase, diffusion happens on to the pores of the adsorbent and the process is very slow. The interior pore spaces of leaf powders are getting filled with the solute which is the slow adsorption phase (Weng and Wu 2012). The variation of removal percentage of copper and uptake of copper with time of contact for different initial concentrations is presented in Figs. 1 to 4.

3.2 Effect of adsorbent dosage

Research Work on batch adsorption was done for different concentrations of Cu with different dosage of adsorbent to analyse the effect of adsorption of copper with various dosages of adsorbent. As the amount of adsorbent increases, percentage of adsorption increases due to escalation in surface area which gives rise to more vacant binding sites for adsorption. Fig. 5 shows the variation of equilibrium concentrations for various initial concentration of copper and the variation of percentage removal and uptake of copper for different dosage of adsorbent are

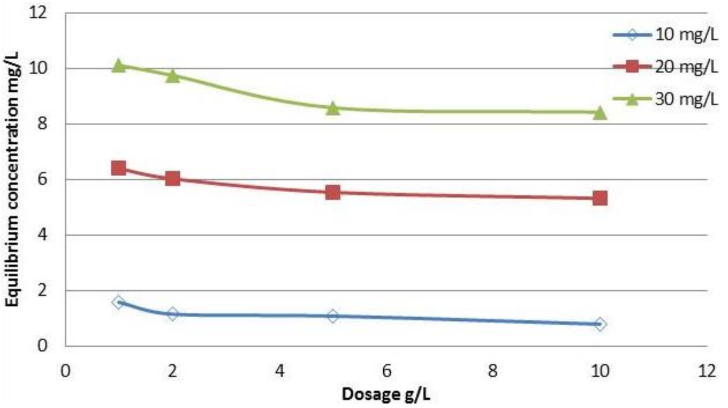

Fig. 5 Variation of equilibrium concentrations with adsorbent dosage for initial concentrations of 10 mg/l, 20 mg/l and 30 mg/l

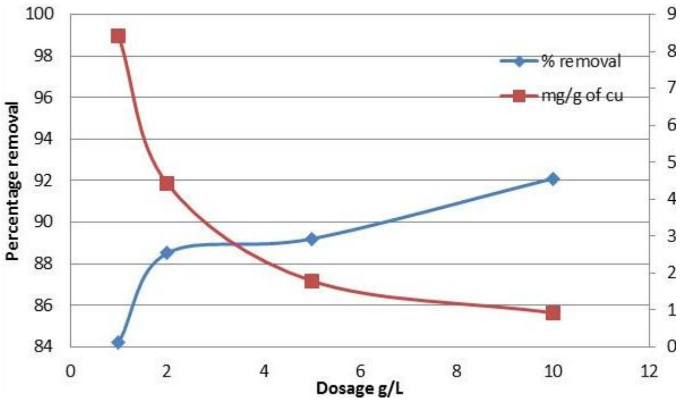

Fig. 6 Variation of percentage removal and copper uptake with adsorbent dosage for initial concentrations of 10 mg/l

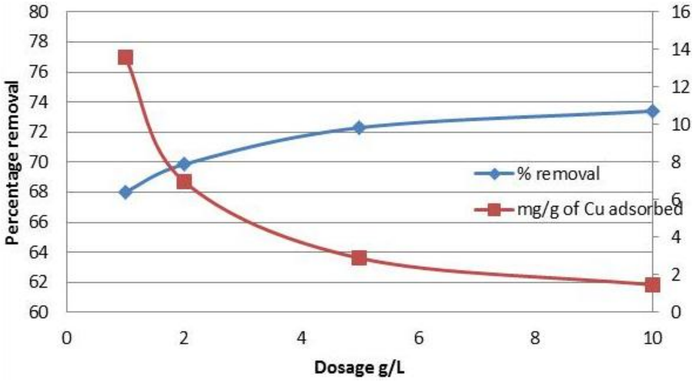

Fig. 7 Variation of percentage removal and Cu uptake with dosage of adsorbent (Initial concentrations of 20 mg/1)

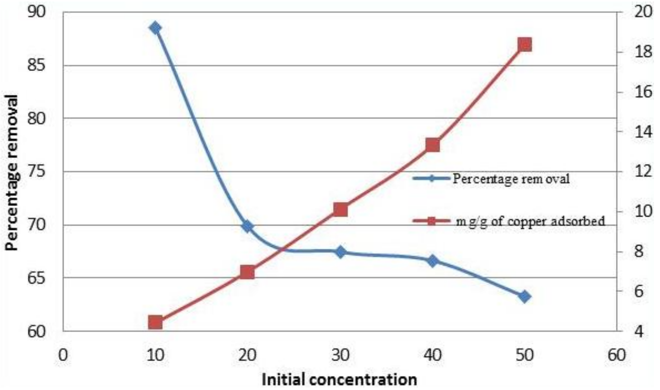

Fig. 8 Variation in percentage removal and Cu uptake for dosage of adsorbent of 2 g/1 and contact time of l h

presented in Figs. 6 to 7.

3.3 Initial concentration effects

Initial metal ion concentration in aqueous solutions effects the metal ions removal. There is a decrease in the percentage removal of Cu from aqueous solutions when the initial concentration escalates from 10 mg/L to 30 mg/L at constant pH. At low metal concentrations, vacant surface sites adsorbed the metal more rapidly. One explanation for this observation may be the fact that low metal concentrations are adsorbed very quickly on the outer surface. Further increase in the initial metal concentration led to fast saturation of adsorbent and thus, most of the metal adsorption took place slowly inside the pores by intra-particle diffusion (Kalpaklı 2015). Fig. 8 shows the variation of removal percentage and uptake of copper with different initial metal concentrations.

3.4 pH effect

Solutions acidity (pH less than 7) controls the removal of metal from aqueous solution and hence the pH of solution plays an important role in the uptake of heavy metal. By conducting experiments at various pH ranging from 2 to 9 it was seen that the amount of copper ions adsorbed on the solid phase of biosorbent powder were different as shown in Fig. 9. There is a strong force of attraction between the bio sorbent powder and copper ions and hence H+ ion could be an important factor deciding the capacity of biosorption. The biosorption of metal ion increases with pH owing to the reduction in electrostatic repulsion due to the reduction in the positive charge density on the sorption edges (Beena *et al*. 2011). The Copper adsorption was found maximum on to the surface of adsorbent at pH 7 (neutral).

3.5 Study of rate constant

The changes in effluent concentration of Cu with time at various initial copper concentrations are shown in Fig. 10. When initial Copper concentration rises, the equilibrium duration was found to increase.

The pseudo - first order equation of Lagergren is expressed as follows

$$\text{Log}\ (qe - qt) = \log qe - \frac{K1t}{2.303} \quad \text{(Shelke } et\ al.\ \text{2009)} \qquad (3)$$

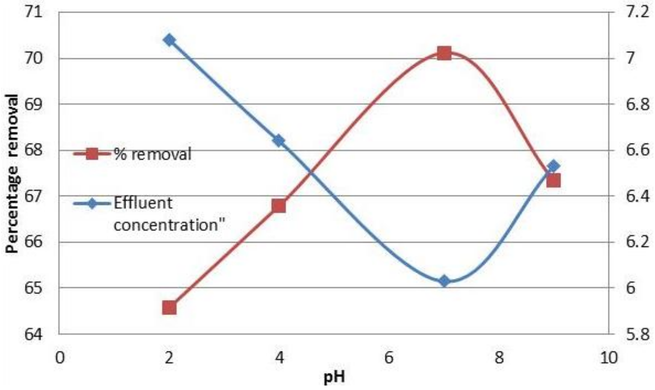

Fig. 9 Variation in concentration of effluent and percentage removal with pH for initial concentration of 20 mg/1, adsorbent quantity 2 g/1 and contact time l hour

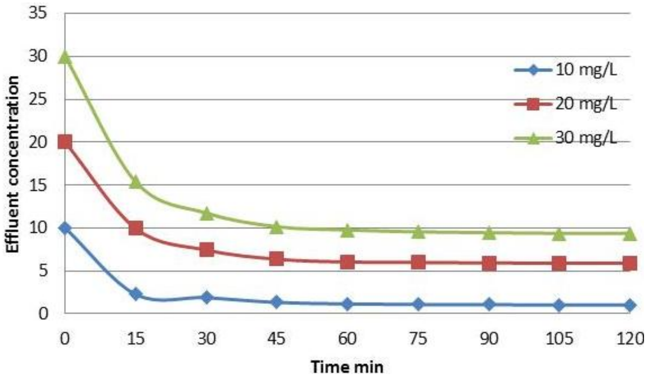

Fig. 10 Changes in concentration of effluent with time for various initial concentrations

where K_1 is the specific rate constant and *qe* is the amount of metal adsorbed till equilibrium is reached and *qt* is the amount of metal adsorbed at any time *t*.

For pseudo-first-order kinetics, a graph was obtained by plotting log (*qe* – *q*) against *t* but the model was not fitting well for the biosorption. The correlation coefficient values for pseudo-first-order model are less than that of pseudo second order model and was also reported by Tang *et al*. (2012), Beena *et al*. (2011), Gerçel and Gerçel (2007), Venkateswarlu *et al*. (2008), and Mehmet *et al*. (2007).

The data was well represented by pseudo-second-order model. The pseudo second-order model depends on the rate by which the adsorbent occupies the vacant sites on the adsorbent is proportional to the square of the number of unoccupied sites. The *t*/*qt* vs. '*t*' are plotted and presented in Figs. 11 to 12 for different adsorbent dosages and initial concentration of 10 mg/L which give a linear relationship with a slope of 1/*qe* and an intercept of 1/kqe^2. From the R^2 values given in Table 1, it can be predicted that process of adsorption follows pseudo second order kinetics. As seen from the Table 1 the rate constant *k* value for pseudo second order kinetics decreases when the initial solute concentration increases. From this it can be assumed that the

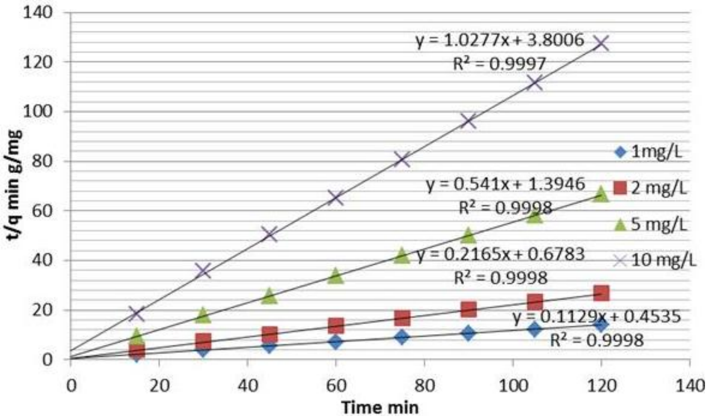

Fig. 11 Pseudo second order plot for Cu adsorption (Initial concentration of 10 ppm)

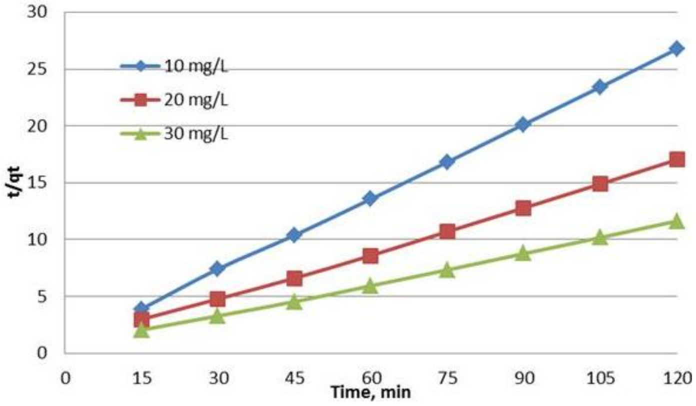

Fig. 12 Pseudo second order plot for Cu adsorption for various initial concentrations for adsorbent dosage of 2 g/1

Table 1 Diffusion model rate constants for different concentrations

Kinetic models	Initial concentration		
	10 mg/L	20 mg/L	30 mg/L
Pseudo second order model			
qe (mg/g)	4.6189	7.4294	10.8932
k (g min $^{-1}$mg^{-1})	0.0691	0.0256	0.0162
R^2	0.9998	0.999	0.9992
Intraparticle diffusion model			
k_p (mg/g/min$^{0.5}$)	0.0889	0.2457	0.3694
c	3.6218	4.7208	6.7886
R^2	0.8474	0.7177	0.743

solution will equilibrate more quickly when initial concentration was low. The same result was obtained by batch adsorption experiments.

The intra particle diffusion model was tested to find the possibility of the presence of intra-particle diffusion process in the adsorption of copper ions onto the surface of the biosorbent. The equation for intraparticle diffusion is given by

$$q_t = k_p\, t^{0.5} + c \tag{3}$$

where q_t is the amount of adsorbent adsorbed in time t, c is the intercept and k_p is the intra particle diffusion rate constant (Kannan and Veemaraj 2009). The value of q_t is found to have a straight line relationship with values of $t^{0.5}$ as shown in Fig. 13.

The value of c is an indication of the thickness of the boundary layer. None of the plots passed through the origin. Hence it can be assumed that even though intra particle diffusion was involved in the adsorption process it was not the rate controlling step. The value of rate constants for pseudo second order model and intraparticle diffusion model are given in Table 1.

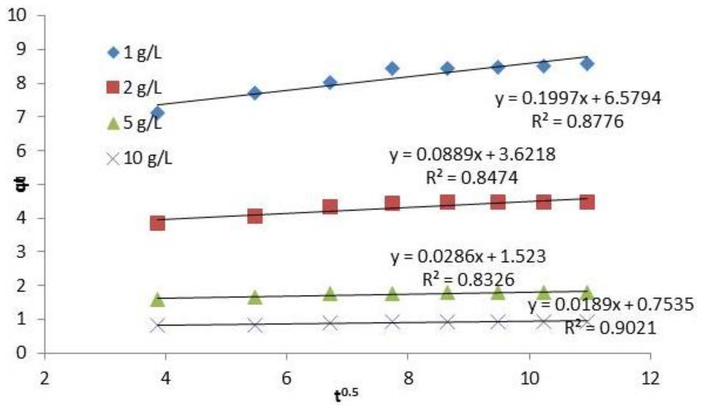

Fig. 13 Intra-particle diffusion model for copper adsorption (Initial concentration of 10 mg/1) with different dosages of adsorbent

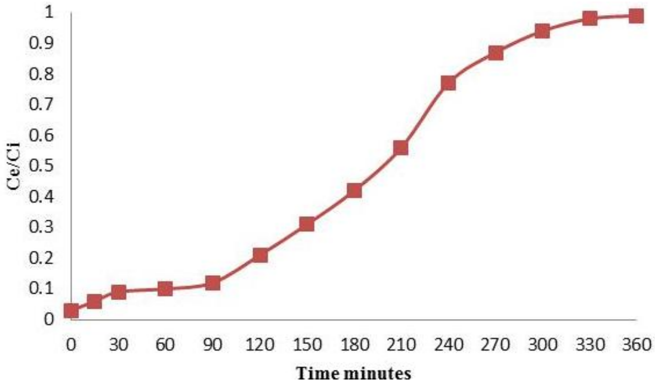

Fig. 14 Breakthrough analysis curve (Initial concentration of 20 mg/l)

3.6 Column studies

The breakthrough curve showing the changes in effluent concentration with time on a fixed bed of adsorbent is shown in Fig. 14. It is having a typical "*S*" shaped profile.

3.7 Adsorption isotherm

The adsorption isotherm gives an idea about adsorption capacity. It also describes the functional dependence of capacity on the concentration of pollutant. It can be used for determining the maximum adsorption capacity.

For investigation of the adsorption isotherm the Langmuir and the Freundlich isotherms were analyzed. The theoretical Langmuir isotherm which describes the adsorption of a solute from an aqueous solution is as follows

$$\frac{Ce}{qe}=\frac{1}{Qob}-\frac{Ce}{Qo} \tag{5}$$

where *qe* represents the equilibrium adsorption capacity in mg/g, *Ce* is the concentration at equilibrium in mg/ L, *Qo* and *b* are Langmuir constants which are related to adsorption capacity

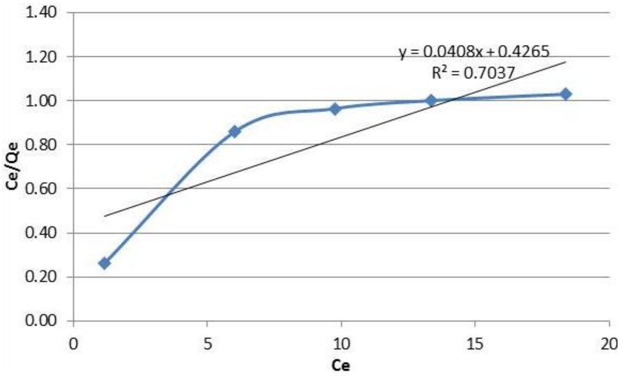

Fig. 15 Langmuir plot for copper adsorption (Adsorbent quantity of = 2 g/1, contact time = l h)

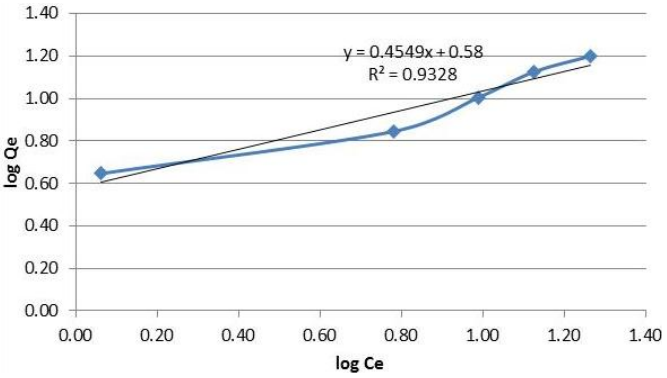

Fig. 16 Freundlich isotherm for copper adsorption (Adsorbent quantity = 2 g/1, contact time = l h)

and adsorption rate respectively. The slope and intercept of the Langmuir plot *Ce* vs *Ce*/*qe* gives the value of *Qo* and *b* respectively as shown in Fig. 15. The adsorption isotherms for removal of Cu were studied by varying the initial concentration between 10 mg/L and 50 mg/L and at a dosage of 2 g/L of the adsorbent. The Langmuir constants *Qo* and *b* are 24.51 mg/g and 0.0957 mg/1 respectively and isotherm plot is having a regression coefficient of 0.7037.

The constants of Freundlich isotherm were calculated using the following equation

$$\ln qe = \ln Kf + 1/n \ln Ce \tag{6}$$

where *qe* is the amount of the metal adsorbed at equilibrium in mg/L and *n* and *Kf* are Freundlich constants related to adsorption intensity and capacity of adsorption respectively (Papita *et al*. 2010). Log *qe* was plotted against Log C_e and the Freundlich isotherm coefficients were determined as shown in Fig. 16. The Freundlich model can be used to determine the intensity of adsorption of the sorbent towards the adsorbate. The plot was linear which describes the representative nature of adsorption on the adsorbents tested. Copper ions adsorption was favourable as per the value of correlation coefficient of regression R^2 (0.9328). The parameter n is a characteristic constant for the adsorption system. Values of *n* between 2 and 10 indicate good adsorption (Wang 2009). The values of 1/*n* and *Kf* from the plot are 0.4549 and 3.81 which indicate that adsorption was favorable. The disposal of bio absorbents is essential; these wastes can be safely disposed in hard rocks and clay rich soils, owing to their impervious properties. These wastes can also be incinerated or neutralized prior to disposal.

4. Conclusions

By conducting batch and column experiments using carica papaya leaf powder it was observed that a maximum of 90%-94.1% of copper (II) removal from the wastewater can be obtained under optimum conditions for small initial concentrations of copper. Therefore it can be utilized in treatments like polishing by reducing levels of copper to safe limits. When the metals, initial concentration in test solution was 10 mg/L the equilibrium duration was about 60 min and slightly increased with higher initial concentrations. The optimum pH was found to be 7. Pseudo second order reaction fits the experimental data well with R^2 value of 0.9998 whereas experimental data does not fit well with pseudo-first-order model for batch experiments. Based on the correlation coefficients ($R^2 = 0.9328$) the Freundlich model better fit the test data and the adsorption process was demonstrated better by this model. The adsorption on papaya leaf powder takes place between Cu ions in solution and carboxyl and hydroxyl groups that are abundant in the papaya leaves. Papaya leaf is easily available in India and is cheap. Hence papaya leaf powder can be used as a good adsorbent to treat wastewater for Cu removal and also for the design of low cost wastewater treatment techniques for heavy metal removal.

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