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Equilibrium and kinetic studies on the adsorption of copper onto paddy straw powder

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ABSTRACT

Batch adsorption studies were conducted in the laboratory to explore the possibility of paddy straw powder as a low-cost adsorbent for the removal of copper from wastewater. The parameters affecting adsorption process such as time of contact, metal ion concentration, quantity of adsorbent and pH are also evaluated, and the results are fitted using adsorption isotherm models. It is observed from the experimental results that almost 90–95% copper can be removed from the solution using paddy straw powder. Biosorption of metal ion depends on pH, and the results indicated the optimum pH for the removal of copper as 7.0. To describe the distribution of copper between the liquid and solid phases in batch studies, Langmuir adsorption isotherm and Freundlich isotherm model have been used and it has been observed that Freundlich isotherm better represents the phenomenon. Using the Langmuir model, the maximum copper adsorption capacity was calculated to be 37.17 mg/g. The adsorption process is found to adhere to the pseudo-second-order rate equation. The ability of paddy straw powder to remove copper(II) ions from aqueous solution was also investigated in a packed bed column and an S-shaped profile was achieved for the breakthrough curve. Hence, paddy straw powder can be effectively used for future practical applications in industries considering the high copper adsorption capacity, perspective of waste utilization and freely abundant availability of this low-cost adsorbent.

Keywords: Adsorption; Biosorption; Freundlich; Isotherm; Langmuir; Paddy straw; Pseudo-second order

1. Introduction

The presence of heavy metals in water is a worldwide environmental problem. The concentration of heavy metals such as lead, copper, cadmium, zinc and chromium is toxic even at low concentrations. They accumulate in the environment through the food chain as they are non-biodegradable. Heavy metals are discharged by all metal processing activities. The practice of removal/recovery of metals using cheap methods should be implemented to decrease the environmental hazard of toxic metal-containing effluents [1].

Copper which is one of the principal heavy metals enters the water bodies through wastes from

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industrial processes such as dyeing, paper, petroleum, copper/brass-plating and copper–ammonium rayon. It is responsible for causing haemolysis, liver and kidney damage, irritation of upper respiratory tract, gastrointestinal disturbance, diarrhoea, etc. The U.S. Environmental Protection Agency (EPA) has set the maximum contaminant level for copper at 1.3 milligrams per litre (mg/L).

Conventional methods for the removal of metal ions from effluents include electrolytic recovery, ion exchange/chelation, chemical precipitation and solvent extraction/liquid membrane separation which are costly and have inadequate efficiencies at low metal concentrations, particularly in the range of 1–100 mg/L. The technologies for the removal of heavy metal ions are divided into three categories, chemical, physical and biological. Chemical methods involves conventional oxidation methods by oxidizing agents, irradiation, electro-chemical processes, coagulation combined with flotation and filtration, electro-flotation and electro-kinetic coagulation. The main drawback of chemical technologies is that they are very expensive and have disposal problems. Also, there is a demand for high electrical energy and chemical reagents. Physical methods are adsorption and membrane filtration processes such as nano-filtration, reverse osmosis and electrodialysis. Almost all membrane filtration processes have choking problems and hence have limited lifetime. Biological methods have less flexibility in design and operation and require large area. Precipitation cannot be used for fine purification, and pH plays an important role in precipitation.

Adsorption is an economically feasible, versatile, effective, simple and environment friendly method and has been widely used. Proper design of the adsorption process will produce high-quality treated effluents, and hence, it is one of the most popular methods for the removal of pollutants from effluents. This process will have much more impact if the adsorbent is inexpensive and does not require an additional pre-treatment step before application. Actually, adsorption can be used as a polishing treatment for the removal of heavy metals when the concentration of the pollutant is very less. Recently, biosorption is coming up as the latest technology for the removal of heavy metals [2].

The biosorption process involves a biosorbent which is in solid phase and a solvent normally water which is in liquid phase containing a dissolved species of the sorbate which may be a metal ion to be adsorbed. There is a high affinity of the sorbent for the sorbate species, and hence, the sorbate is attracted and bound with different mechanisms on the sorbent due to the imbalance between the two environments until equilibrium is established between the amount of solid-bound sorbate species, and its portion remaining in the solution. The biosorbent becomes enriched with metal ions in the sorbate since the heavy metals are adsorbed on the surface of biomass [3].

Heavy metal removal by biosorption can produce close to drinking water quality (from initial metal concentrations of 1–100 mg/L to final concentrations <0.01–0.1 mg/L), and hence it is especially suited as a polishing wastewater treatment step. Pre-treatment by different techniques such as precipitation or electrolytic recovery can be done in order to prevent unnecessarily rapid exhaustion of the sorption capacity when the metal concentrations in the waste water to be treated are very high (>100 mg/L). Recent studies have shown that heavy metals can be removed using plant materials such as *Firmiana simplex* leaf [2], neem leaves [4], pineapple leaf powder [5], Ashoka leaf powder [6], agricultural adsorbents [7], agricultural wastes [8], *Basella alba* leaves [9], neem bark [10], *Gmelina arborea* leaves [11], *Erythrina variegata* orientalis leaf powder [12] and tree fern [13].

Rice straw is one of the abundant lignocellulosic waste materials in the world. Rice is the third most important grain crop in the world in terms of total production behind wheat and corn. In terms of chemical composition, the straw predominantly contains cellulose (32–47%), hemicellulose (19–27%) and lignin (5–24%). The interaction of lignin with cations is by exchanging protons and subsequently by chelating with the metallic ion [14]. It possesses high oxygen which is largely fixed in hydroxyl group polysaccharides. These groups help in biosorption process by making a complex between metal ions present in aqueous solution and oxygen of hydroxyl group. The oxygen contains two lone pairs of electrons which it may donate to the metal ions [15].

The biosorption process depends on factors such as the number of sites in the biosorbent material, the accessibility of the sites, the availability of the site and binding strength between site and metal. Even an already occupied site is theoretically available for covalent metal binding. If a metal is already occupying the site, the binding strength and concentration decide whether the site can be used by the given metal. A site is available for electrostatic metal binding only if the metal is ionized [16].

Adsorption of metal ions onto hydroxyl and carboxyl groups can be represented as follows:

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

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

where M = metal ion, ROH and $RCOO^-$ are hydroxyl group and carboxylate ion arising from the paddy straw.

The advantage of biosorption is that it can be operated under a broad range of pH and temperature as compared to conventional wastewater polishing techniques such as ion exchange, activated carbon treatment or membrane technologies. Also, it is economically attractive due to the cheap raw materials that can be used as biosorbents. Biosorption is also efficient, cost effective and produces minimum sludge, and there is a possibility of regeneration of the biosorbent with possibility of metal recovery. The used-up metal-laden biosorbent is less in volume and can be disposed off by either incineration or landfilling [17]. In India, out of 130 metric tonnes of rice production, rice straw accounts to 100 metric tonne per year [18]. As rice straw is a marginal feed compared to other cereal grain straw and a problematic fuel source due to high ash generation, exploring more viable options to utilize rice straw is pressing, particularly as an environment concern [19]. Hence, it is a good initiative to make efforts in this study to convert rice straw as a waste material into valuable industrial product. The objective of this study was to investigate the ability of paddy straw for Cu(II) adsorption from aqueous solutions. Paddy straw is very cheap and easily available and hence could be useful for separations in other industrial processes. A variety of factors, including dosage, equilibrium duration and pH of the solution, were considered for the ability of the paddy straw powder for Cu(II) adsorption. The equilibrium data were analysed using Langmuir and Freundlich adsorption isotherm models. Pseudo-first-order and pseudo-second-order equations were used for evaluating kinetics. Raw paddy straw powder has been used here without any treatment since any type of treatment would have increased the cost of the adsorbent and will not be in line with the objective of developing a low-cost adsorbent.

2. Materials and methods

2.1. Stock solution of copper

Synthetic stock solution of copper was made by diluting 3.93 gm of copper sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$) in 1 l distilled water which is equivalent to 1,000 ppm of copper. Stock solution was diluted to obtain copper solutions of known initial concentrations for batch and column studies.

2.2. Paddy straw powder

Paddy straw was collected from agricultural field and washed several times with water after chopping into small pieces and dried in sunlight for several days. Dried sample biomass was kept in oven at 800°C for 3–4 h. After that, it was powdered and passed through fine sieves to obtain fine size mesh particles and kept for further use.

2.3. Batch adsorption studies

Batch adsorption studies were conducted using paddy straw powder with copper solutions of different initial concentrations in magnetic stirrer at normal temperature. Time of contact, initial concentration, pH and quantity of adsorbent were varied. The final concentrations were measured in atomic absorption spectrophotometer.

2.4. Column adsorption

Column studies were conducted in a column having diameter of 5.5 cm and length of 35 cm. Known quantity of adsorbent was filled in the column, and the length of adsorbent in the column was noted. Solutions of known concentration of copper was prepared and taken in a tank from which it is allowed to pass into the column. The rate of flow was adjusted to be around 60 ml/min at constant head. Constant head was maintained by adjusting inflow and outflow equal. The effluent from column was collected at various fixed time intervals, and final concentration was measured using atomic absorption spectrophotometer. The column arrangement is shown in Fig. 1.

3. Results and discussions

3.1. Effect of contact time

Time of contact between the adsorbent and the solution containing heavy metal is one of the important parameters which decide the removal of the adsorbent. To find out the effect of contact time, varying amounts of adsorbents ranging from 1 to 10 mg/L were mixed with the solution containing heavy metal and shaken for different contact periods ranging from 15 to 120 min. The concentration of Cu in solution was noted after different contact periods. The concentration of Cu in solution after 90 min was almost the same.

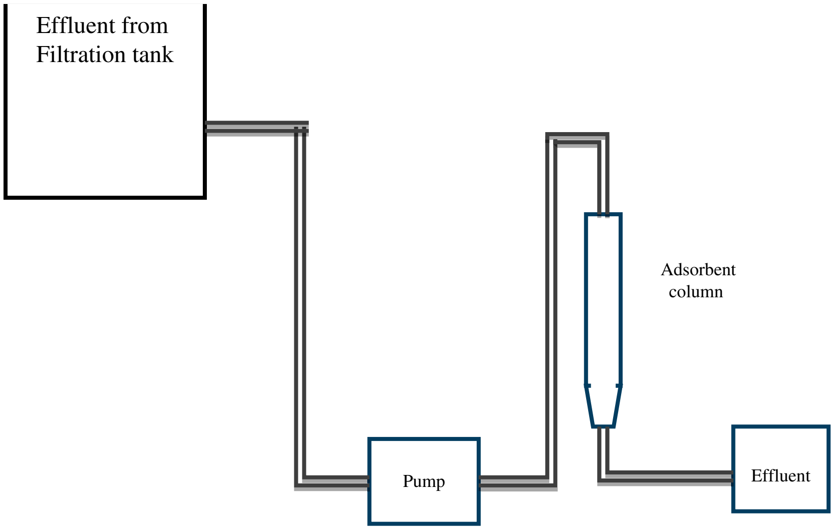

Fig. 1. Column arrangement for adsorption.

Also, the speed of adsorption was very fast up to about 90 min. Therefore, 90 min of contact time was taken as equilibrium time. A large number of vacant surface sites are available for adsorption during the initial stage of sorption. Further adsorption is difficult since the already adsorbed molecules on the solid surface repel the adsorbate molecules in the bulk phase. Two phases were observed in viewing these kinetic data. First one is the rapid adsorption phase and the second phase is in which a progressive adsorption occurs reaching equilibrium and remaining constant thereafter. In the first stage, Cu ions are rapidly attached on to the surface active sites of the paddy straw powder by surface mass transfer. In the second phase, slow adsorption is influenced by diffusion into the pores of the adsorbent. Around 90% Cu removal was achieved in all cases in the fast adsorption stage. The first phase which is very fast can facilitate the adsorption process by shortening the operating period. Consequently, the slow adsorption phase occurred in which the solute is adsorbed into the interior pore spaces of adsorbent [5]. The effect of contact time on percentage removal of copper and uptake of copper for various initial concentrations are shown in Figs. 2–7.

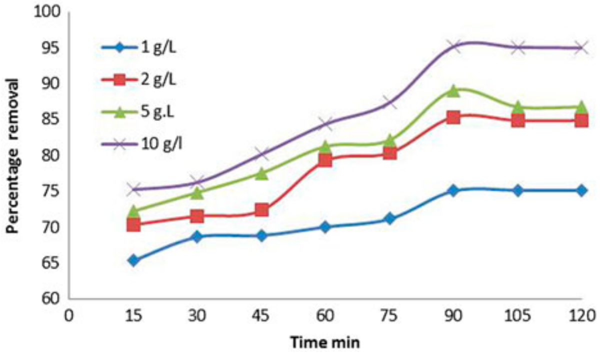

Fig. 2. Effect of contact time on percentage removal at various adsorbent dosages for initial concentration of 10 mg/L.

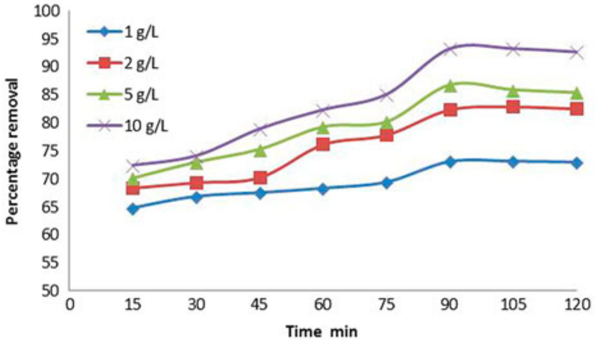

Fig. 3. Effect of contact time on percentage removal at various adsorbent dosages for initial concentration of 20 mg/L.

3.2. *Effect of adsorbent dose*

Adsorption studies were carried out at different initial Cu concentrations with different adsorbent doses at different time intervals to find out the effect of adsorbent dose for the adsorption of Cu from aqueous solution. The percentage of adsorption increased from 73.1 to 93.25% for an increase in adsorbent dose

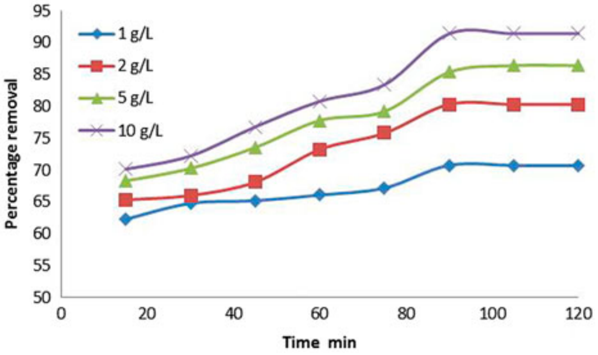

Fig. 4. Effect of contact time on percentage removal at various adsorbent dosages for initial concentration of 30 mg/L.

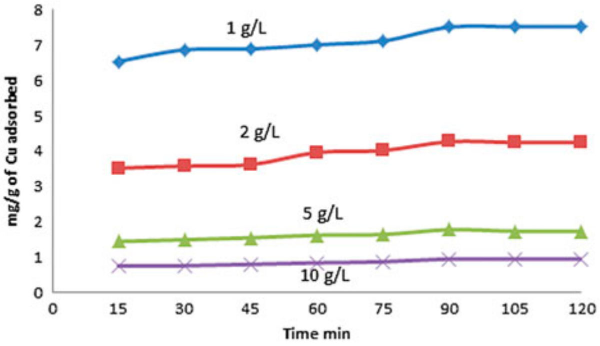

Fig. 5. Effect of contact time on uptake of Cu at various adsorbent dosages for initial concentration of 10 mg/L.

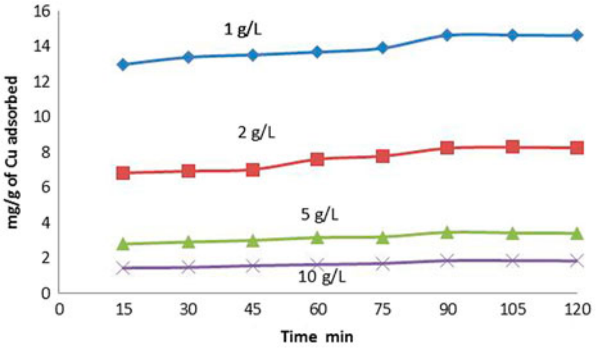

Fig. 6. Effect of contact time on uptake of Cu at various adsorbent dosages for initial concentration of 20 mg/L.

from 1 to 10 g/L, whereas the Cu uptake decreased from 14.62 to 1.87 mg/g for the same initial concentration. As the amount of adsorbent increases, surface area increases and higher percentage of adsorption happens due to the availability of more binding sites for adsorption. The decrease in uptake with increase in adsorbent dose may be due to overlapping of adsorption sites as a result of over-crowding of adsorbent particles. Effect of adsorbent dosage for equilibrium concentration for various initial concentrations is shown in Fig. 8, and the effect of adsorbent dosage on percentage removal and uptake of copper for various initial concentrations are shown in Figs. 9–11.

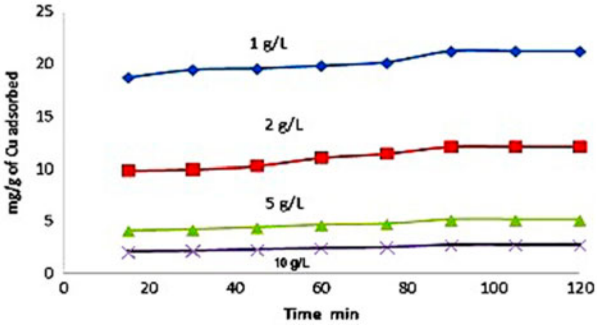

Fig. 7. Effect of contact time on uptake of Cu at various adsorbent dosages for initial concentration of 30 mg/L.

3.3. *Effect of initial concentration*

Initial concentration of metal ions in aqueous solution affects the metal ions removal. Removal percentage of Cu from aqueous solutions decrease as concentration increases from 10 to 30 mg/L at constant pH. The ratio of number of moles of metal in solution to the available surface area is low at lower metal concentration, and hence, adsorption is independent of initial concentration. The available sites for adsorption are less at higher initial concentrations, and hence, metal removal is dependent on initial concentration [20]. The effect of initial metal concentration on percentage removal and uptake of Cu is shown in Fig. 12.

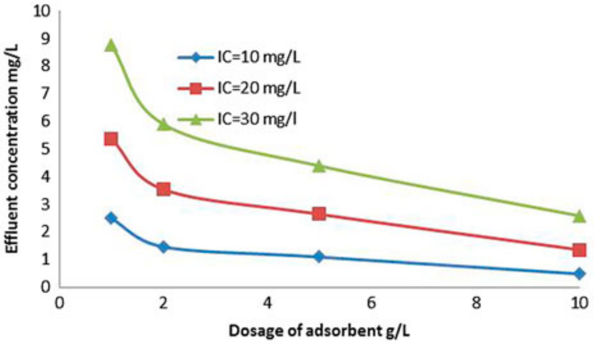

Fig. 8. Effect of adsorbent dosage for equilibrium concentration for initial concentrations of 10, 20 and 30 mg/L.

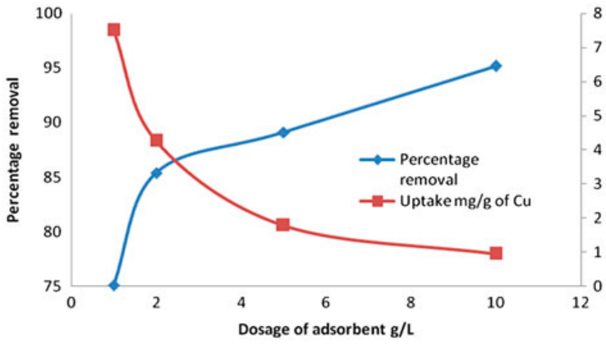

Fig. 9. Effect of adsorbent dosage on percentage removal and uptake of copper for initial concentration of 10 mg/l.

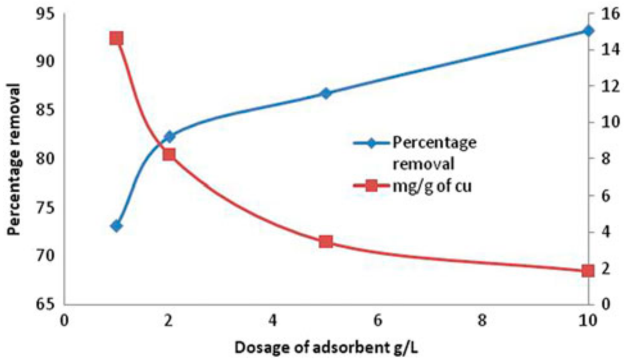

Fig. 10. Effect of adsorbent dosage on percentage removal and uptake of copper for initial concentration of 20 mg/l.

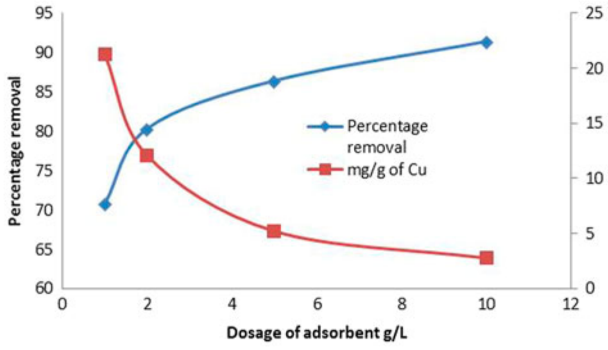

Fig. 11. Effect of adsorbent dosage on percentage removal and uptake of copper for initial concentration of 30 mg/l.

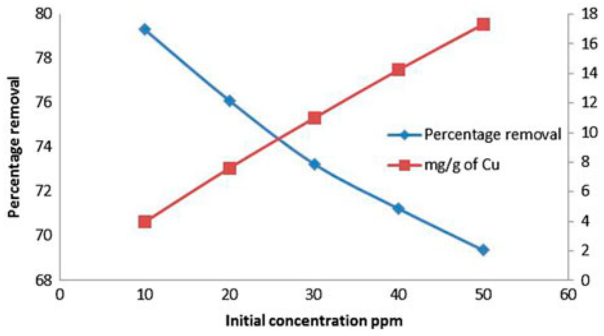

Fig. 12. Effect of initial metal concentration on percentage removal and uptake of Cu for adsorbent dosage of 2 g/L and contact time of 1 h.

3.4. Effect of pH

The acidity of solution is one of the most important factors for controlling the uptake of heavy metals from wastewater, and hence, the solution pH plays a vital role in the removal of heavy metals. It was found that there was a change in the quantity of adsorbed copper ions on the solid phase of biosorbent powder over the entire pH range of 2–9 by conducting experiments carried out at different pH as shown in Fig. 13. This indicates that H^+ ion could influence the biosorption capacity because of the strong force of interaction between the copper ions and the biosorbent powder. As pH increases, biosorption of metal increases because of the reduction of positive charge density on the sorption edges leading to reduction in electrostatic repulsion [21]. As pH increases, the negative charge density on the paddy straw powder surface increases, enhancing the Cu adsorption capacity because of the increase in the electrostatic attraction force between the adsorbent surface and Cu ions. More H^+ ion competes with free Cu^{2+} ion at lower pH levels for the active surface sites of adsorbent and less functional groups, i.e. OH is ionized (deprotonated) leading to difficulty in Cu adsorption [5]. The maximum adsorption of Copper on to the surface of adsorbent was found to be at pH 7 which was rather neutral.

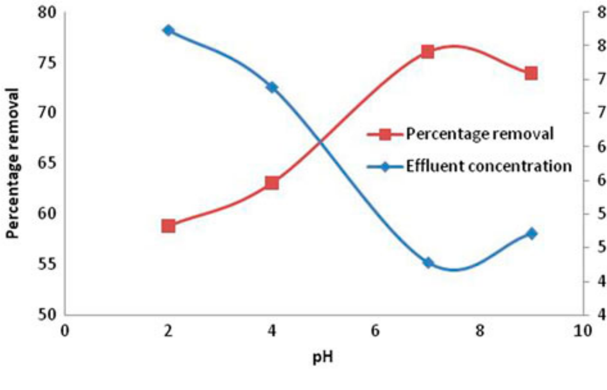

Fig. 13. Effect of pH on effluent concentration and percentage removal for initial concentration of 20 ppm, quantity of adsorbent 2 g/L and for contact time 1 h.

3.5. Study of rate constant

The variation of effluent concentration of Cu with duration at different initial solute concentrations is shown in Fig. 14. Adsorption was seen to take in two steps, one a very fast one followed by a slow adsorption step during which equilibrium is obtained. The duration required for equilibrium was found to increase with increasing initial Cu concentration.

Adsorption of Cu from liquid phase into the solid phase can be considered as a reversible process with equilibrium established between the two phases. For studying the adsorption kinetics, the pseudo-first-order equation of Lagergren was employed. The pseudo-first-order equation of Lagergren [6] is generally expressed as follows:

$$\log(q_e - q_t) = \log\ q_e - \frac{K_1 t}{2.303} \tag{3}$$

where q_e and q_t are the amount of metal adsorbed during equilibrium time and any time, respectively, and K_1 is the specific rate constant.

The pseudo-first-order model was found not to achieve a good fitting for the biosorption of metal when $\log(q_e - q)$ was plotted against t. The value of correlation coefficient for pseudo-first-order model is less than that of pseudo-second-order model and was also reported by different authors [2,12,21–23].

The best fits were found to be the pseudo-second-order model. The pseudo-second-order model is based on the assumption that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. A linear relationship was obtained by plotting t/q_t vs. t and shown in Figs. 15–17 for various adsorbent dosages and initial concentrations with a slope of $1/q_e$ and an intercept of $1/kq_e^2$. From the R^2 (Table 1) values, it can be concluded that the adsorption process follows pseudo-second-order kinetics. The pseudo-second-order kinetics rate constant k decreased rapidly from 0.029 to 0.0092 g/mg/min when the initial solute concentration was increased from 10 to 30 mg/L. This indicated that the solution with the smallest solute concentration is likely to equilibrate most quickly which is obtained by batch adsorption experiments.

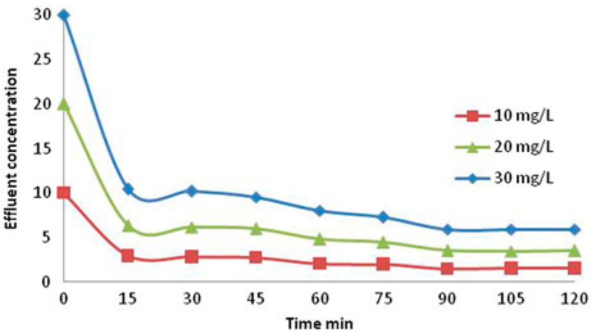

Fig. 14. Variation of effluent concentration with time for different initial concentrations.

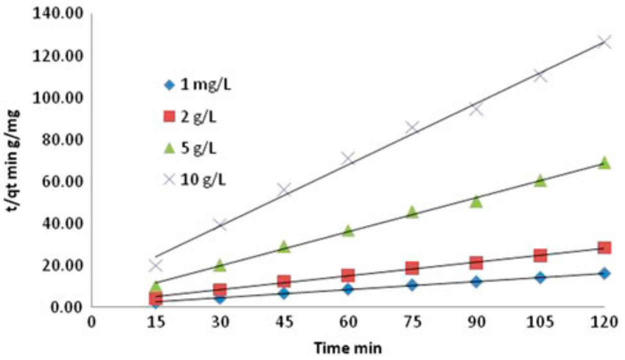

Fig. 15. Pseudo-second-order plot for adsorption of Cu for initial concentration of 10 mg/L.

The intraparticle diffusion model was also explored for the adsorption process using the formula:

$$q_t = k_p \cdot t^{0.5} + c \tag{4}$$

where q_t is the amount adsorbed in time t, c is the intercept, and k_p is the intraparticle diffusion rate constant. The value of q_t is found to be linearly correlated with values of $t^{0.5}$ as shown in Fig. 18. The value of intercept c gives an idea about the boundary layer thickness. The graph was not passing through origin. This indicates that intraparticle diffusion was not the rate-controlling step but involved in the adsorption process.

The correlation coefficients for the intraparticle diffusion model was 0.9089 for initial concentration of 10 mg/l. The value of rate constants for pseudo-second-order model and intraparticle diffusion model is given in Table 1.

3.6. Column studies

The effect of effluent concentration on a fixed bed of adsorbent is presented in the breakthrough curve depicted in Fig. 19. The breakthrough curves somewhat follow the ideal "S"-shaped profile that is characteristic of adsorbents of small molecular sizes and also of adsorbents comprised of small sized particles.

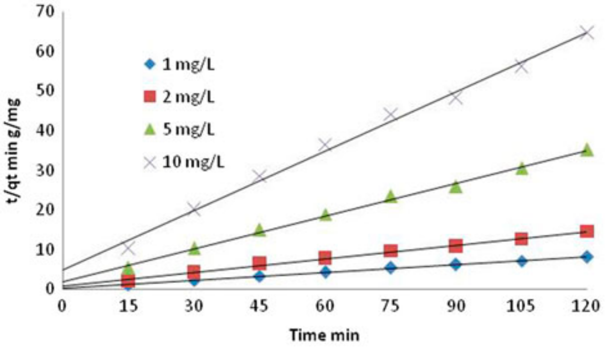

Fig. 16. Pseudo-second-order plot for adsorption of Cu for initial concentration of 20 mg/L.

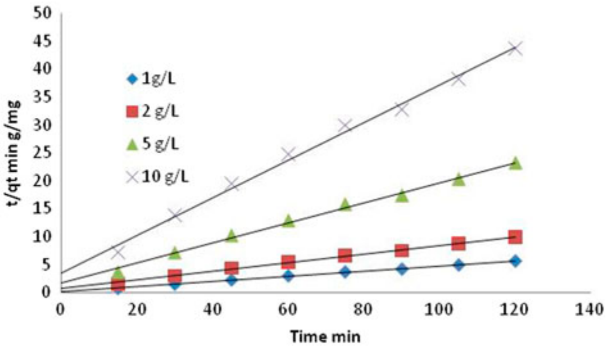

Fig. 17. Pseudo-second-order plot for adsorption of Cu for initial concentration of 30 mg/L.

Table 1
Values of rate constants for pseudo-second-order and intraparticle diffusion models

Kinetic models	Initial concentration 10 mg/L	 20 mg/L	 30 mg/L
Pseudo-second-order model			
q_e (mg/g)	4.5106	8.7719	12.8866
k (mg/g/min)	0.029	0.0147	0.0092
R^2	0.9965	0.9963	0.9961
Intraparticle diffusion model			
k_p (mg/g/min$^{0.5}$)	0.1247	0.2435	0.3861
c	2.9483	5.694	8.005
R^2	0.9089	0.9187	0.9301

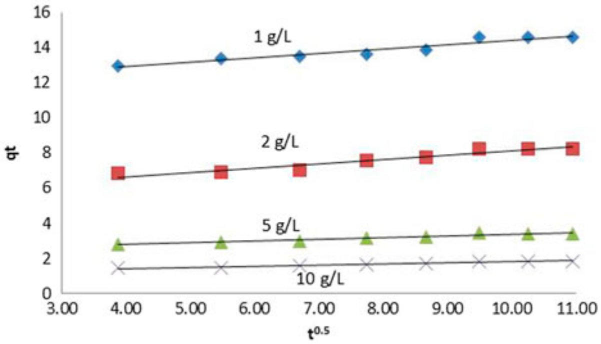

Fig. 18. Intraparticle diffusion model for adsorption of copper for initial concentration of 20 mg/L for adsorbent dosage of 2 g/L.

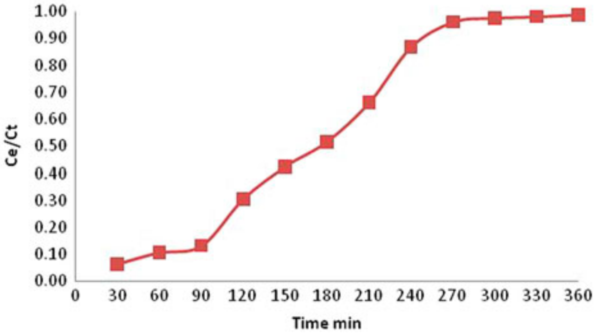

Fig. 19. Breakthrough curve for an initial concentration of 20 ppm and column height of adsorbent 12 cm.

3.7. Adsorption isotherm

Experimental adsorption isotherms are the most common ways of describing adsorption phenomena and play an important role in the determination of the maximum capacity of adsorption. It is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium. The models which are widely used for describing adsorption process are Langmuir and Freundlich models. The Freundlich model is an empirical relation equation based on the distribution of solute between the solid phase and the aqueous phase at equilibrium and is perhaps the most popular adsorption model for a single-solute system [6].

In order to investigate the adsorption isotherm, the Langmuir and the Freundlich isotherms were analysed. The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{5}$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium liquid phase concentration (mg/L), Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively, and are calculated from the slope and intercept of the Langmuir plot C_e vs. C_e/q_e (Fig. 20). The adsorption isotherm for Cu removal was studied using initial concentration between 10 and 50 mg/L at an adsorbent dosage of 2 g/L. The Langmuir constant Q_o is 37.17 mg/g and b is 0.0550 L/mg with a regression coefficient of 0.9795.

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter [24]. The separation factor R_L can be calculated using the equation:

$$R_L = \frac{1}{1 + bC_o} \tag{6}$$

where C_o = initial concentration mg/L and b = Langmuir constant.

R_L is a positive number whose magnitude determines the feasibility of the adsorption process. R_L is found to be less than 1 and greater than 0 which indicates the adsorption reaction as favourable.

For the Freundlich isotherm constants were calculated using the following equation:

$$\ln\ q_e = \ln\ K_F + 1/n\ \ln\ C_e \tag{7}$$

where q_e is the amount of copper(II) adsorbed at equilibrium (mg/L) and K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively [25]. The Freundlich isotherm coefficients were determined by plotting $\log q_e$ against $\log C_e$ (Fig. 21). The adsorption intensity of the sorbent towards the adsorbate can be found out by Freundlich model. The correlation regression coefficient R^2 from the graphs (0.9994) showed that copper ions adsorption was favourable. The constant K_F is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process. A value of $1/n$ below 1 indicates a normal adsorption and from the value obtained here (0.7367) indicates the adsorption as favourable.

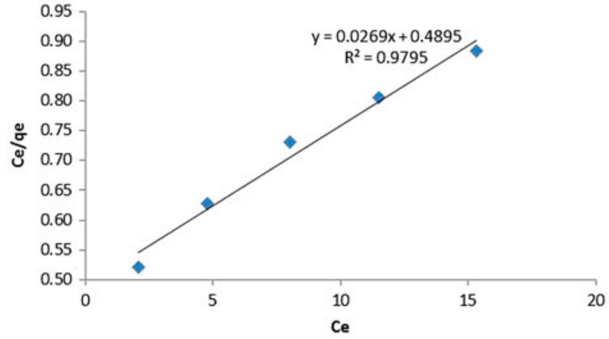

Fig. 20. Langmuir plot for Cu adsorption (quantity of adsorbent = 2 g/L, time of contact = 1 h).

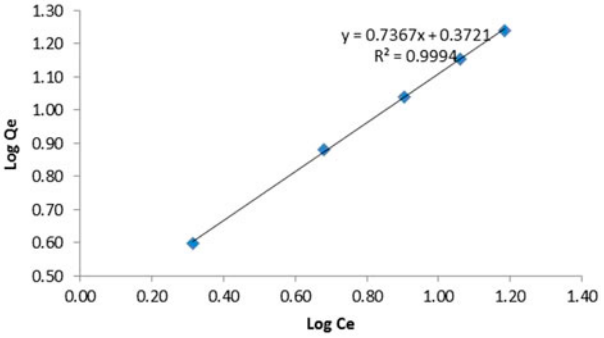

Fig. 21. Freundlich isotherm for adsorption of copper (quantity of adsorbent = 2 g/L, time of contact = 1 h).

4. Conclusion

It was found that almost 90–95% copper(II) can be removed from the wastewater using paddy straw powder by conducting batch experiments. Paddy straw powder has the potential adsorption capacity to remove copper(II) and can be used also in polishing treatment reducing copper levels to safe levels. The time to reach equilibrium was about 90 min. The kinetics data were approximated quite well by the pseudo-second-order kinetics equation with R^2 value of 0.9963, whereas pseudo-first-order model does not fit the experimental data well for batch experiments. The correlation coefficient for Freundlich model was 0.9994, and it fit the test data better than Langmuir model. The optimum pH was found to be 7. The adsorption occurred between copper ions and hydroxyl and carboxyl groups which are abundant in the paddy straw. Paddy straw powder is not costly, and it is easily available in India. Therefore, it can be concluded that paddy straw powder can be effectively used as a low-cost adsorbent to remove copper(II) from wastewater and would be useful for the design of wastewater treatment techniques for removal of heavy metals.

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