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Removal of copper by adsorption on treated laterite

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Abstract

Copper is an essential element for human body and also micro nutrient for plants. Higher concentrations of copper in water cause severe health problems. Many process and metallurgical industries release significant quantities of copper into the environment. Several methods were suggested for removal of copper, most of which were either cost ineffective and/or release harmful chemicals. In that perspective, current paper is focused on the removal of copper from aqueous solution by using laterite as an adsorbent. The equilibrium, kinetics and adsorption behaviour under varied pH and temperature were studied in this investigation. It was found that the removal efficiency was about 90%. The kinetics obeyed pseudo second order model. The adsorption equilibrium isotherms could be described by Langmuir model satisfactorily.

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1. Introduction

Wide spread industrialization is the main cause for release of significant quantities of heavy metals into the environment. Now-a-days the presence of heavy metals like Cu, Zn, Pb, Cd, Cr and Hg in industrial wastes were of a major concern due to their inherent toxicity and hazardous effects. Also heavy metals are not susceptible to biological degradation. Therefore, the elimination of heavy metals from water and waste water is utmost important in the interest of public health. Copper is an essential trace element needed for human body and well known micronutrient for plants and animals but it is toxic if it exceeds the limit specified. Excessive concentration of copper may cause vomiting, diarrhea, stomach cramp coma, jaundice, gastrointestinal distress and nausea. Bureau

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of Indian Standards (BIS) recommended an acceptable limit as 0.05 mg/L of copper in drinking water. The U.S. Environmental Protection Agency (EPA) has set a guidance level for copper in drinking water at 1.3 mg/L. The National Academy of Sciences' Food and Nutrition Board (NASFNB) recommends that children need a minimum of 0.34 mg/day and the requirement for adults is 0.9 mg/day.

The effluents from metal plating, mining, smelting, electroplating, brass manufacture, paper and pulp, and fertilizer industries contain high concentration of copper. For removal of copper various methods such as precipitation [1], electrocoagulation [2], ion exchange [3], ultrafiltration [4], bio-filtration [5] and reverse-osmosis were suggested. Studies were also conducted using nanomaterials for removal of copper[6]. Removal of copper from aqueous solutions by adsorption using several adsorbents such as chemically activated sawdust [7], polypyrrole conducting polymer [8], carbon foam [9], activated carbon [10], biochar [11], modified coal fly ash [12], tree bark [13] and a multi-adsorbent system[14]. A close inspection of the literature reveals that most of the existing methods have drawbacks such as high cost, difficulty to make adsorbent, low efficiency and/or production of hazardous byproducts. In view of this the present study has been taken up where the laterite which is cheaper and abundantly available was used as an adsorbent.

2. Materials and Methods

Analytical grade chemicals of Merck (India) and triple distilled water were used for preparation of solutions. Concentrations of copper were measured by Atomic Absorption Spectrophotometer (AAAnalyst 400, Perkin Elmer, USA), pH measurements were made with Digital pH meter (Model No. 335, Systronics India). Orbital Shaker (Model No. CIS-24 plus Remi) for agitation purpose and a centrifuge were used.

2.1. Preparation of treated laterite

The raw laterite was procured from IIT Kharagpur, West Bengal, India (GPS location 25° 33' N/86° 33' E). The raw laterite was crushed, sieved and 50 ± 2 g of 0.25–0.5 mm particle size of raw material was treated with 200 mL of 2N HCl at 70 ± 10° C for 2–3 hours with constant stirring. The liquid part of treated mass was distilled at 110° C to recover 60% HCl and then the pH was adjusted to 6 – 8 by adding 4N sodium hydroxide dropwise. The contents were further stirred for 30 minutes and kept at rest for 24 hours for the solid matter to settle down. The supernatant liquid was decanted and the treated laterite was filtered and washed thoroughly with distilled water until it was free from chlorides. The filtered laterite was dried at 110°C and was used as an adsorbent for removal of Copper.

2.2. Procedure

The stock Copper(II) adsorbate solution (1000 mg Cu²⁺/L) was prepared by dissolving the analytical grade Cupric Sulphate (CuSO₄.5H₂O) in triple distilled water. Required concentrations (2 – 200 mg Cu²⁺/L) of Cu²⁺ solutions were prepared by proper dilutions of stock solution. A known amount (0.2 – 2.0 g) of treated laterite is taken in a conical flask and required volume (50 – 200 mL) of known concentration (2 – 200 mg Cu²⁺/L) of adsorbate solution is added. This mixture was agitated for 2 hours at constant temperature and pH. A portion of contents was withdrawn, filtered and analysed for copper. The copper present in the solution was estimated by using Atomic Absorption Spectrophotometer [15]. Each experiment was carried out three times and their average value was reported in this paper.

3. Results and discussion

Initially experiments were conducted to determine the optimum values for contact time, pH, initial concentration, adsorbent dosage and temperature. Further experiments were carried out at these conditions to estimate order of reaction and isotherm model.

3.1. Effect of contact time

The optimum time required for adsorption of Copper on laterite adsorbent was first investigated. For this study, 200 mL of 100 mg/L Cu²⁺ solution and 1.0 g of treated laterite were taken in a conical flask and agitated at room temperature (30°C) for three and half hours. A portion (5.0mL) of the contents was withdrawn at regular time intervals (15 minutes) and then filtered. The concentration of copper present was estimated by using atomic adsorption spectrophotometer. The adsorption intake was calculated by using formula:

$$\% \text{ of adsorption} = \frac{(C_i - C_t)}{C_i} \times 100 \quad \dots(1)$$

Here C_i is the initial copper concentration in mg/L and C_t is the concentration of copper in mg/L at time t.

The effect of contact time on the adsorption of copper on laterite was shown in Fig.1. From the graph it was observed that the concentration of copper in the solution got gradually decreased and attained equilibrium after

120 minutes i.e the percentage of adsorption of copper gradually increased and reached a maximum. This may be due to the occupation of the active sites of adsorbent with Cu ions.

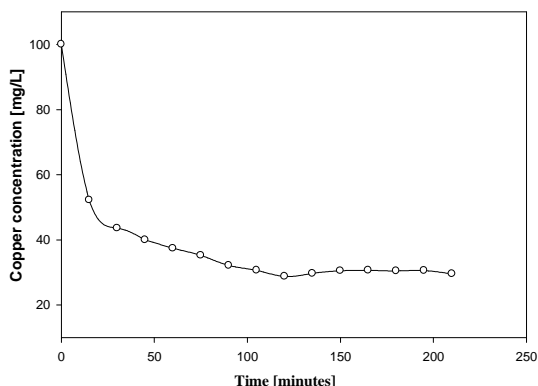


Fig.1 Effect of contact time

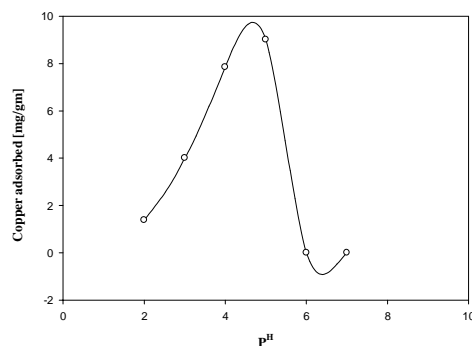


Fig.2. Effect of pH

3.2. Effect of pH

The optimum pH at which maximum % of adsorption occurs was also determined. For this study, 8 flasks, each with 50 ml of 100 mg/L Cu^{2+} solutions were taken separately in flasks and the pH was adjusted to the required value by adding either HCl or NaOH solution drop wise. 0.5 g of treated laterite was added to each flask and all the flasks were agitated for 120 minutes (optimum time). A portion of sample from each flask was centrifuged and analysed for copper. The effect of pH on adsorption of Copper was shown in Fig.2.

From the graph it was observed that the optimum pH was around 5.0 at which the maximum adsorption of Cu on laterite was found. Lower pH values are favourable to adsorption and pH values higher than 6 favoured the precipitation of copper as copper hydroxide. So a value of 5 was chosen for pH as the optimum one.

3.3. Effect of initial concentration

The adsorption of copper ion on adsorbent depends on initial concentration of copper. The effect of concentration of copper on the adsorption of copper was also investigated. For this study, 50.0 mL of different concentrations of copper solutions ranging from 5.0 mg/L to 1000.0 mg/L were taken separately; the pH of each solution was adjusted to 5.0 + 0.1. About 0.5 g of treated laterite was added to each flask and then agitated for 120 minutes. 1.0 mL portion of each sample was centrifuged, diluted properly and analysed for Cu as mentioned in the experimental procedure. The adsorption scenario was shown in the Fig.3.

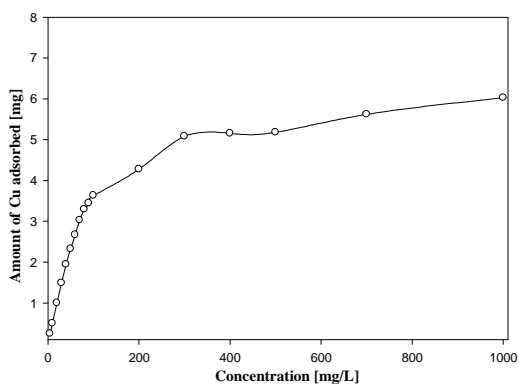


Fig.3. Effect of Concentration

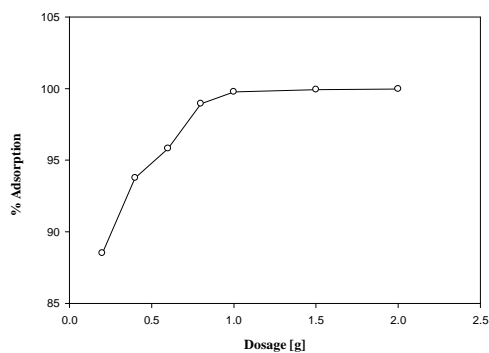


Fig.4. Effect of Dosage

From the graph it was observed that the extent of Cu adsorption increases with increase in initial concentration of Cu and reaches a maximum at around 300 mg/L. However 200 mg/L can be considered as optimum. This is because, at lower concentrations of Cu, most of the active sites of laterite unoccupied at any time.

As the concentration of Cu is increased the number of active sites that occupied with Cu is also increased. However, at higher concentrations of Cu all active sites get occupied and so that further increase in the concentration of Cu, no further increase the occupied active sites with Cu.

The adsorption of copper ion on adsorbent depends on initial concentration. Copper ions have smaller hydrated radii (8.38 Å) and hence can enter into smaller pores on the surface of the adsorbent. Copper has high electro negativity (1.9) and standard reduction potential (0.34 V) which shows a trend with sorption capacity. At lower concentrations, metal ions are easily adsorbed on vacant active sites. As the metal ion concentration increases, the vacant sites are filled up and no further adsorption occurs due to saturation of vacant sites of adsorbent. Figure 3 shows the effect of metal ion concentration on percent removal of copper. Almost all the copper that is present is adsorbed at lower concentrations of copper.

3.4. Effect of adsorbent dosage

For this study, laterite adsorbent ranging from 0.2 g to 2.0 g and 50.0 mL of 50.0 mg/L copper solution were taken separately; pH is adjusted to 5.0 + 0.1 and agitated for 120 minutes. A portion of solution from each dosage was centrifuged and analysed for copper. The dosage of adsorbent is another important parameter in adsorption studies, which influences the extent of metal uptake from the solution and the results of the present investigation were shown in Fig.4. An examination of the plot revealed that the adsorption was maximum at a dosage of 1.0 g. Thereafter, the removal of copper remained constant with increasing mass of adsorbent. The partial aggregation among the available active binding sites could have been responsible for less removal of copper at high doses. Also, due to lack of active binding sites, the lower removal was obtained at low adsorbent doses.

3.5. Effect of Temperature

Since the adsorption process depends on temperature, the effect of temperature on adsorption of copper on laterite, the adsorption studies were carried out at three temperatures 200°C, 300°C and 400°C. For this, at each temperature, set of 50 ml of Cu solutions of different concentrations ranging from 10 mg/L to 200 mg/L and 0.5 g of laterite was taken separately, adjusted the pH to around 5.0 and agitated for 2.0 hours. A portion of solution was immediately centrifuged and diluted properly and analysed for copper. The adsorption scenario was shown in the Fig.5. From the plots it was observed that amount of copper adsorbed per gm. increases with increasing in concentration at particular temperature as like effect of concentration. Further, the extent of adsorption of copper is decreasing with increasing temperature. This is because the copper may adsorb on the adsorbent laterite due to physical forces arising between the adsorbate copper ions and the adsorbent and they decrease with increasing temperature. So, lower temperatures are favourable for removal of copper.

3.6. Adsorption kinetics

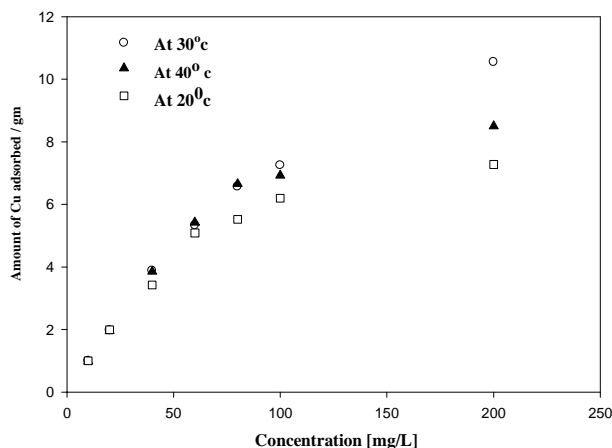


Fig.5. Effect of Temperature

For this study, 200 ml of 100 mg/L Cu solution and 1.0g of laterite was taken in a conical flask and agitated at room

temperature (28oC) for required time (4 hours). About 1.0 mL portion of contents was withdrawn at regular time intervals (15 min), centrifuged, filtered and the filtrate was analysed for copper and the amount of Copper was adsorbed on one unit mass of adsorbent pulp was calculated by using the formula:

$$q_e = \frac{(C_i - C_e)}{m} \times V \dots(2)$$

Where C_i is the initial concentration (mg/L) of Copper, C_e is the concentration of Copper (mg/L) in solution at equilibrium, V is the volume of solution in litres and m is the mass of the adsorbent (g). The adsorption date for kinetics is analyzed by using two different kinetic models such as pseudo first-order and pseudo-second-order kinetic models.

3.6.1. Pseudo-first order model

The pseudo-first order model is represented mathematically by following equation (3)

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \dots(3)$$

Where q_e and q_t are the amount of Cu adsorbed on the unit amount of adsorbent at equilibrium and at given time (t) in (mg/g) respectively. K_1 is the rate constant for pseudo-first-order adsorption in $(\text{min})^{-1}$ and the kinetic results were shown in Fig.6.

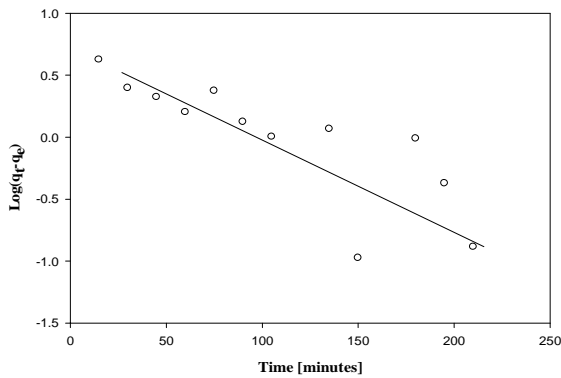


Fig.6. Kinetic studies (psuedo first order)

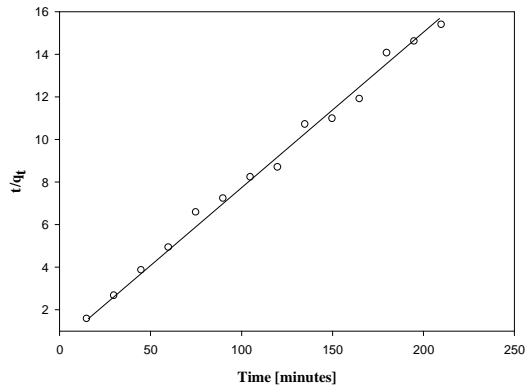


Fig.7. Kinetic studies (psuedo Second order)

3.6.2. Pseudo-second order model

The pseudo-second order model is represented by the following equation (4).

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} t \dots\dots\dots (4)$$

Where q_e and q_t are the amount of Cu adsorbed on the unit amount of adsorbent at equilibrium and at given time in (mg/g) respectively. K_2 is the rate constant for pseudo-second-order adsorption in $(\text{mg/g})^{-1} \cdot (\text{min})^{-1}$. The kinetic results were shown in Fig.7. The rate constants and the correlation coefficient values for the two models were calculated from the plots of $\log(q_e - q_t)$ vs. t and (t/q_t) vs. t , respectively and represented in Table.1. The correlation coefficient values infer that the kinetics is well predicted by pseudo second order with correlation coefficient 0.9994.

Table.1. Kinetic parameters for adsorption of Copper on laterite

Parameter	Value
Initial Copper concentration	100 mg/L
Experimental q_e value	15.4966
Pseudo first order	
Rate constant (K_1)	-0.003 min^{-1}
Correlation coefficient (r_2)	-0.8501
Pseudo Second order	
Rate constant (K_2)	0.06839 $(\text{mg/g})^{-1} \text{min}^{-1}$
Correlation coefficient (r_2)	0.9994

3.7. Adsorption Isotherms

Different isotherms are available in literature to understand the effects of various factors on adsorption. The distribution of metal ions between the liquid phase and adsorbent is a measure of the position of equilibrium in the adsorption and can be expressed by one or more series of isotherms. The shape of the isotherms can predict whether the adsorption is favourable or unfavourable. For this study, Langmuir adsorption and Freundlich isotherms were tested to fit the experimental data. The adsorption isotherm studies were conducted at room temperature and at pH 5.0 by taking various initial concentrations of copper solutions ranging from 5.0 mg/L to 1000 mg/L. 50 mL of copper solution was added to 0.5 g of laterite and agitated for 120 minutes to attain equilibrium. A known volume of Cu solution was centrifuged and filtered and then analysed for copper. The adsorption isotherm studies were represented in Figs.8 and 9 for Langmuir and Freundlich adsorption isotherms respectively. The parameters of both the studies are tabulated in Table.2.

3.7.1. Langmuir adsorption isotherm

Langmuir adsorption isotherm was used to describe the observed sorption of Copper ions and is as shown by the following equation.

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad \dots(5)$$

Rewriting as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \cdot K_L} \cdot \frac{1}{C_e} \quad \dots(6)$$

Where q_m and K_L are the Langmuir constants, q_e is the amount of Copper adsorbed at equilibrium (mg/g), and C_e is the equilibrium concentration of Cu ions in solution (mg/L). The values of q_m and K_L are determined by plotting $(1/q_e)$ vs. $(1/C_e)$ which is shown in fig 8.

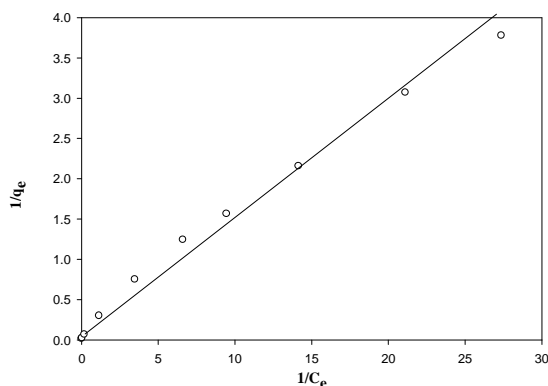


Fig.8. Langmuir Adsorption Isotherm

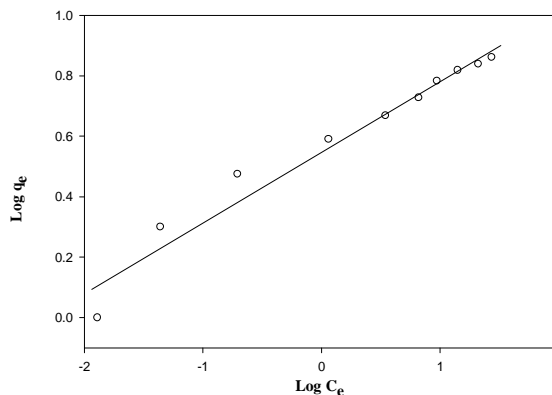


Fig.9. Freundlich Adsorption Isotherm

3.7.2. Freundlich adsorption isotherm

Freundlich adsorption isotherm model is purely empirical model used to describe the adsorption in aqueous systems and to explain the adsorption of copper ions on to adsorbent. The Freundlich isotherm is shown by the following equation.

$$q_e = K_f C_e^{1/n} \quad \dots (7)$$

Rewriting as

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad \dots (8)$$

Where K_f and n are the Freundlich constants which indicate the adsorption capacity and adsorption intensity. These values were determined by plotting the $\log(q_e)$ vs. $\log(C_e)$.

Table.2. Parameters of adsorption isotherm models

Langmuir model			Freundlich model		
q_m (mg/g)	K_L (L/mg)	r_2	K_f (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	r_2
7.249184	0.973509	0.9959	3.552232	4.31565199	0.9807

The experimental data fitted reasonable well to the linearized equation of the Langmuir adsorption isotherm over the range of concentration of Copper ion. The correlation coefficient was 0.9959. The adsorption parameters q_m and K_L were found to be 7.2491 and 0.9735 respectively. The essential characteristics of the Langmuir isotherm can be used to predict the affinity between the sorbate and sorbent using the dimensionless equilibrium parameter R_L can be calculated by using the formula [16-18]

$$R_L = \frac{1}{1 + K_L C_0} \quad \dots (9)$$

Where K_L is the Langmuir constant and C_0 is the initial concentration of Cu ions. The value of separation parameter R_L provides important information about the nature of adsorption process. The value of R_L indicates the type of Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavourable ($R_L > 1$). The R_L value varies from 0.093 to 0.01 in the concentration range 10 mg/L to 100 mg/L indicating that the adsorption of Copper ions on laterite is favourable.

4. Conclusions

Based on above discussion the following conclusion can be drawn. Laterite adsorbent is cheaper and can be preferred for removal of copper. Optimum contact time is found to be 120 minutes at room temperature. Optimum pH is found to be around 5.0. Optimum initial copper solution concentration is 200 mg/L. The adsorption kinetics obeyed pseudo-second-order reaction and Langmuir model was followed.

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