Removal of Cu(II) ions from aqueous solution using tree leaves

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ABSTRACT

The presence of toxic heavy metal ions discharged into the water bodies from different industries pose serious threat to living beings. Copper is one of the hazardous heavy metal used in different industries such as mining and smelting, plating, brass manufacture, petroleum refining, electroplating industries and Cu-based agrichemicals. It is released from these industries with various concentrations. Although copper is an essential metal for living beings at lower concentration but it is also potentially toxic at higher concentration.

Present study reported the effect of various physico-chemical parameters for the removal of Cu(II) ions using neem leaves. The optimum pH for adsorption was found to be 6. Kinetics data were best described by the pseudo-2nd-order model. The experimental data were fitted well with Freundlich and Halsey isotherm models. The mean sorption energy was calculated using Dubinin-Radushkevich isotherm model and it confirmed that the sorption process was chemical in nature. Different active functional groups were identified by FTIR studies which were responsible for Cu(II) ion adsorption process. Application study using electroplating industrial waste water and regeneration experiment of the adsorbent were also investigated.

1. INTRODUCTION

The increasing concentration of heavy metals such as Cr(VII), Pb(II), Cu(II), Zn(II), Cd(II) etc in water bodies is mainly due to effluent discharges from different process industries. Pollution of natural waters by metal ions has become a major issue all over the world because metal concentrations in waters often exceed the admissible values. Consequently, industries are required to diminish the contents of heavy metals in their effluents to acceptable levels. The increasing waste products are forcing scientist to study new and alternative technologies to remove trace metals from polluted waters and one of the main goals regarding heavy metals removal from waste waters consists in the reduction of these pollutants at very low levels.

The excessive intake of the copper in human accumulates in the liver and produces gastrointestinal problems, kidney damage and anemia. Inhalation of copper containing sprays is responsible with an increasing lung cancer among the exposed industrial workers (Bhattacharyya and Gupta, 2011). According to USEPA the maximum acceptable concentration of Cu(II) in drinking water is 1.3 mg L^{-1} (ATSDR 2004) and U.S. Environmental Protection Agency (EPA) standards, the permissible limit of copper discharge in industrial effluents into water bodies is limited to 0.25 mgL^{-1} (Zhu et al. 2008).

In order to reduce the environmental risks arising from the Cu(II) ions pollution in waste water, it is necessary to develop low-cost remedial adsorption technique using various natural/agricultural wastes. The aim of this article is to investigate the effects of pH, contact time and initial concentration on the Cu(II) removal from aqueous solution by neem laves. Application study using industrial waste and desorption study were also carried out at optimum batch conditions.

2. MATERIALS AND METHODS

2.1 Preparation of Adsorbent and Cu(II) Solution

Neem leaves are used as adsorbent & collected from local area near Kolkota, West Bengal, India. It was treated with 0.1 N NaOH to remove lignin based color materials followed by 0.1 N

H_2SO_4. Finally it was sieved to obtain particle size of 250-350 µm prior to use for the present studies.

1000 mg/L of Cu(II) solution was prepared by dissolving 3.929 g of Copper(II) sulfate pentahydrate in 1000 ml double distilled water. This stock solution was finally diluted to obtain required standard solutions.

2.2 Reagents and Instruments

All the chemicals used in the adsorption process were of analytical grade and supplied by E. Merck Limited, Mumbai, India. WTW make pH meter (Multi 340i/SET, Germany), atomic absorption spectrophotometer (AA 240 VARIAN, Australia), FTIR (Jasco FT/IR-670 Plus) and scanning electron microscope (S-3400N, Hitachi, Japan) were used for the process. Fig. 1 shows the scanning electron micrographs of the neem leaves and it clearly indicated the irregular and porous surface of the adsorbents.

2.3 Batch Experiment

The removal experiments were conducted by batch technique. The solution pH of the solution was changed by adding 0.1 N HCl or 0.1 N NaOH solutions. Fixed amount of leaves was added in the stoppered conical flask containing 100 mL of Cu(II) ions solution of desired concentration then the content was shaken in an electrical shaker at the rate of 110-125 strokes/minute. At the regular interval of time the conical flask from the shaker was withdrawn and then the adsorbent was separated from the Cu(II) ions solution by filter paper and filtrate was analyzed using Atomic Absorption Spectrophotometer (APHA 1998)**.** The percentage of removed Cu(II) ions in solution was calculated using following equation (Eq. 1),

$$\text{Percentage removal of Cu(II) ions} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

Where C_0 is the initial Cu(II) ions concentration (mg/L) and C_t is Cu(II) ions concentration at time t (mg/L).

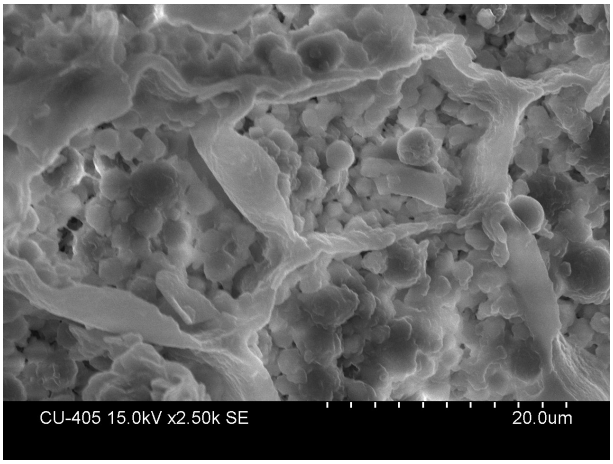

Figure 1. Scanning Electron Micrographs (SEM) of neem leaves (500 X)

3. RESULTS AND DISCUSSION

3.1 Optimum Condition for Batch Experiment

Solution pH is one of the important factors for adsorption process. The effect of initial pH of the solution on Cu(II) ions adsorption is shown in Fig. 2. The adsorption experiments were conducted in the pH range 2-6 to avoid the precipitation of $Cu(OH)_2$ at above the pH 6. At pH>6, the

percentage removal increases rapidly may be due to combination of adsorption and precipitation. So pH 6 was considered as optimum pH for the adsorption process.

The effect of contact time, initial Cu(II) ions concentration and adsorbent dosage on the removal of Cu(II) ions were also studied. Percentage removal of Cu(II) ions increases with the increase of contact time, adsorbent dosage and it is reverse for initial metal ions concentration.

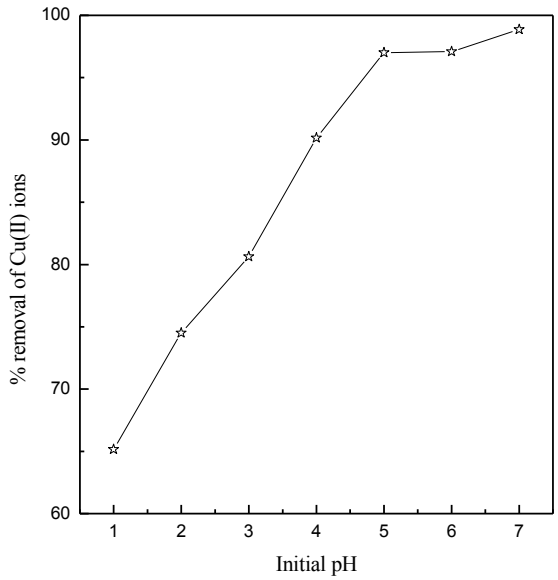

Figure 2. Effect of initial pH for the adsorption process

3.2 Kinetics Study

Data obtained in the contact time variation experiment were analyzed using different rate equations. These equations are

i) Pseudo 1st -order model (Lagergren, 1898) (Eq. 2)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2)$$

where K_1 is the Pseudo first-order rate constant (min^{-1}), q_e is the amount of Cu(II) adsorb per gram of the sorbent at equilibrium, q_t *is a*mount (mg) adsorb per gram of sorbent at any time t.

ii) Pseudo 2nd -order model (Ho et al., 2000) (Eq. 3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \qquad (3)$$

K_2 is the pseudo second-order rate constant (mg/g/min).

iii) Pore diffusion or intra-particle diffusion model (Weber and Morris, 1963) (Eq. 4)

$$q_t = k_i t^{0.5} + C \qquad (4)$$

Where K_i is the Intra-particle rate constant ($mg/g/min^{1/2}$)

The adsorption process depends on the several factors including structure of the adsorbent, physical and chemical characteristics of solute and adsorbent. Pseudo first-order and pseudo second-order kinetic model were based on the assumption of physisorption control adsorption process. Intraparticle diffusion in liquid-porous solid systems may be described by surface diffusion, pore-volume diffusion or both the process. The conformity between experimental data and the kinetic model predicted values were expressed by correlation coefficient (r^2) and chi square (χ^2) which can be defined as Eq. 5

$$\chi^2 = \Sigma \frac{(q_t - q_{tm})^2}{q_{tm}}) \tag{5}$$

The values of rate constants and statistical parameters for each model are shown in Table 1. Pseudo-2nd-order model is more applicable for the adsorption process as evidence from the statistical parameters.

Table 1 Different kinetic model parameter

Pseudo 1st –order model		
K_1 (min^{-1})	r^2	χ_t^2
0.03224	0.7921	1.4566
Pseudo 2nd-order model		
K_2 (mg/g/min)	r^2	χ_t^2
0.0191	0.9934	0.0234
Intra particle diffusion		
K_i ($mg/g/min^{1/2}$)	r^2	χ_t^2
0.1042	0.9661	0.0054

3.3 Isotherm study

Adsorption isotherm study were conducted using Cu(II) ion concentration variation data. The equations for isotherm studies are as follows

i) Langmuir isotherm model (Langmuir, 1918) (Eq. 6)

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{6}$$

Where b is Langmuir constant (L/mg), C_e, Cu(II) ions concentration in solution at equilibrium (mg/L), q_e, amount adsorb per gram of the sorbent at equilibrium, q_{max} is maximum sorption capacity (mg/g).

ii) Freundlich isotherm model (Freundlich, 1906) (Eq. 7)

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

where K_f Measure of adsorption capacity (mg/g) and *n* Freundlich constants, intensity of sorption $(mg/g)/(mg/L)^{1/n}$.

iii) Halsey isotherm model (Murthy et al., 2010) (Eq. 8)

$$\ln q_e = \left[\left(\frac{1}{n_H} \right) \ln K_H \right] - \left(\frac{1}{n_H} \right) \ln \left(\frac{1}{C_e} \right) \tag{8}$$

Where K_H is the adsorption capacity as in Halsey isotherm model and n_H is Halsey isotherm model constant.

iv) Harkins-Jura isotherm model (Murthy et al., 2010) (Eq. 9)

$$\frac{1}{q_e^2} = \left[\frac{B}{A}\right] - \left[\frac{1}{A}\right]\log C_e \tag{9}$$

Where A and B are Harkins-Jura isotherm constants.

Table 2 Different isotherm model parameter

Langmuir isotherm model			
q_{max}(mg/g)	b (L/mg)	r^2	χ_e^2
17.4886	0.0617	0.8572	4.5375
Freundlich isotherm model			
K_f	n	r^2	χ_e^2
1.8840	2.1693	0.9690	0.4122
Harkins-Jura isotherm model			
A	B	r^2	χ_e^2
32.3102	1.7382	0.9471	1.9723
Halsey isotherm model			
K_H	n_H	r^2	χ_e^2
0.2531	2.1692	0.9691	0.4120

The Langmuir adsorption isotherm model was applied for the estimation of maximum adsorption capacity. The Freundlich isotherm is an empirical equation based on the adsorption on the heterogeneous surface. Halsey isotherm model was also used to explain the multilayer adsorption system for Cu(II) ions. Harkins-Jura isotherm model suggested the multilayer adsorption as well as heterogeneous pore distribution in the adsorbents surface. From the statistical parameter (Table 2), it can be concluded that the Freundlich isotherm model and Halsey isotherm model were more applicable than other three isotherm model studied.

3.4 Sorption Energy Calculation

Sorption energy was calculated by Dubinin-Radushkevich (Dubinin et al., 1947) isotherm model. The linear from of the model was described as in Eq. 10.

$$\ln C_{abs} = \ln X_m - \lambda\varepsilon^2 \tag{10}$$

Where C_{abs} is the amount of Cu(II) ions adsorbed onto sorbent surface (mol/g), X_m, maximum sorption capacity of sorbent (mmol/g), λ Constant related to sorption energy (mol^2/kJ^2) and ε Polanyi potential (KJ^2/mol^2).

The Polanyi potential (Polanyi, 1932) which is equal to (Eq. 11)

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \tag{11}$$

From the plot $\ln C_{abs}$ vs. ε^2 gave a straight line from which the values of λ and X_m were calculated. Using the value of λ, the mean sorption energy, E, was evaluated as in Eq. 12.

$$E = \frac{1}{\sqrt{-2\lambda}} \tag{12}$$

If E < 8 kJ/mol, the adsorption process was physical in nature and in it the ranges from 8 to 16 kJ/mol, it was chemical in nature (Naiya et al., 2009). The estimated value of E was 11.5934 kJ/mol, suggested that the adsorption process was chemical in nature.

3.5 FTIR Study

The Fourier Transform Infrared spectra (FTIR) study of fresh and metal loaded neem leaves at optimized batch condition were carried out to identify the function groups responsible for the adsorption process. Aliphatic acid C=O stretching were observed as the wave number shifting from 1715.83 cm^{-1} to 1730.30 cm^{-1}. FTIR spectrum of neem leaves also showed the intense bands at 1455.88 cm^{-1} which shifted to 1435.25 cm^{-1} that indicated the responsibility of alkane group for the adsorption process.

3.6 Desorption Study

Desorption experiments were conducted to estimate the Cu(II) releasing efficiency from loaded leaves. This experiment was conducted using different concentration of HCl solution (1N - 6N) at optimum batch condition. Table 3 indicated the percentage of regeneration increases with increasing strength of HCl solution.

3.7 Treatment of Cu(II) Ions Containing Wastewater Collected from Electroplating Industry

Suitability of neem leaves for the treatment of Cu(II) ions containing waste was conducted using electroplating industrial waste collected from Kolkata. The waste water composition is mentioned in Table 4. Experiments were carried out under optimum batch condition, i.e., at optimum pH, contact time and adsorbent dosage.

Table 3 Desorption of Cu(II) from loaded neem leaves

Percentage regenerated Cu(II) ions from Cu(II) ions loaded neem leaves					
Strength of HCl					
0. 1 (N)	0.2 (N)	0.3(N)	0.4 (N)	0.5 (N)	0.6 (N)
60.12 %	65.85 %	71.78 %	76.88 %	80.43 %	82.18 %

Table 4 Analysis of electroplating wastewater using natural adsorbents

Parameters	Untreated effluent	Treated effluent
pH	5.89	6.07
Cu(II) (mg/L)	6.25	0.36
Cr(VI) (mg/L)	54.50	24.36
Ca(II) (mg/L)	26.40	16.34
Na(I) (mg/L)	173.26	120.56
K(I) (mg/L)	2.52	1.39
Zn(II) (mg/L)	1.45	0.94
TDS (mg/L)	829.00	789.18

4. Conclusions

Maximum Cu(II) ions adsorption is occurred at pH 6. Pseudo-2^{nd}-order model was more applicable for the adsorption process as evidence from the statistical parameter. Freundlich isotherm model and Halsey isotherm model were more applicable than other three isotherm model studied in the adsorption experiment. Active functional group for the Cu(II) ions adsorption process were identified by FTIR studies. Regeneration of used adsorbents was carried out using different concentration of HCl solutions. Neem leaves are suitable for Cu(II) ions removal from aqueous solutions as well as industrial waste water.

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