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Clerodendrum serratum Stem Activated Nano Porous Carbon by Adsorption Characteristics for Removing Cu(ii) Ions from Wastewater

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ABSTRACT

A series of batch research studies were carried out utilizing Activated *Clerodendrum serratum* Carbon (ACSC) for the adsorption removal of copper (II) ions from an aqueous solution. The investigation was carried out by looking into the effects of beginning pH, contact time, adsorbent dosage, and initial copper concentration. All of the batch experiments were conducted at a steady temperature using a wrist-action shaker set to 200 rpm. Langmuir and Freundlich's isotherms were used to examine the single-component equilibrium data. Maximum copper ion adsorption, i.e. >90%, was attained in aqueous solutions employing 0.025g of ACSC at a pH of 6.6. The copper ACSC kinetic process was modeled using a pseudo-second-order equation, the Elovich model, and intra-particle diffusion. This study found that activated ACSC has a great capability for removing Cu(II) ions from aqueous solution. The nature of adsorption was observed by analyzing various thermodynamic factors such as ΔG^o, ΔH^o, and ΔS^o.

Key words: *Activated Clerodendrum serratum Carbon, Cu (II) ion, Batch method, Adsorption isotherm, Kinetics, Thermodynamic parameters*

Introduction

The most often utilized methods for removing metals and organic compounds from industrial effluents are biological treatments, membrane processes, advanced oxidation processes, chemical and electrochemical approaches, and adsorption procedures. Sorbent adsorption constitutes a single of the most popular treatments because excellent adsorption process design results in high-quality treated effluents. Adsorption is now recognized as a reliable, efficient, and cost-effective method of water purification and separation analysis. Adsorbents that are mineral, organic, or physiological are examples, as are activated carbon molecules, zeolites, clays, silica beads, low-cost adsorbents (industrial byproducts, agricultural wastes, and biomass), and polymeric materials.

The adsorption of Cu(II) ion on activated carbon produced from *Clerodendrum serratum* used by carbonization with sulphuric acid was studied in this study. The collected kinetic and equilibrium adsorption data were used to depict the sample systematized. The amounts and rates of Cu(II)ion adsorp-

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tion from an aqueous solution utilizing above-activated carbon were then determined. According to the literature review, no study has been done to elevate the *Clerodendrum serratum* used as an adsorbent.

Experimental Methods

The substances utilized are of high purity Analar grade readily accessible.1000 mg/l of stock solution of copper ($CuSO_4$, $5H_2O$) was prepared by dissolving accurately weighed 1g of copper sulphate in 1000 ml distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentration. Before mixing the adsorbent, the pH for each research solution was adjusted to the desired initial pH value with dilute HCl (or) NaOH. The lingering copper (II) proportion was evaluated using a spectrophotometer with atomic absorption.

Preparation of adsorbent

The natural plant material of *Clerodendrum serratum* used in the present investigations was collected from a nearby Poompuhar. The stem was washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110 °C. The stem was then carbonized by adding w/v ratio conc. H_2SO_4 to obtain the main carbon. To obtain activated carbon, the primary carbon was activated at >900 °C for 6 hours under optimum circumstances.

Experimental Procedure of Batch Method

Batch adsorption methods were conducted to study the influence of effective parameters such as contact time, activated carbon dosage, initial pH, and other ion concentrations on the removal of Cu (II) ions using activated ACSC. In this experiment, different concentrations of Cu(II) ion solution (10–50 mg/l) and at different temperatures (30–60 °C) with known pH and a known amount of adsorbent (0.025 g/l) were agitated at 120 rpm until equilibrium was reached, then the solution was kept to settle down, and the residual concentration of Cu(II) ion was analyzed by a UV-visible spectrophotometer at 540 nm. All experiments were carried out at normal pH for the removal of Cu(II) ions from the aqueous solution. The effect of pH on Cu (II) ion removal was studied over a pH range of 3.0-9.0. The initial pH of the solution was adjusted by the addition of dil. HCl or dil. NaOH. The effect of activated carbon dosage on adsorption rate was investigated using the procedures described above, except that different dosages (25–125mg/50ml) were used. The amount of adsorption at time t, q_t(mg/g), can be determined, and the percentage removal of Cu (II)ion can be calculated using the formula in that order.

$$q_t = V \times \frac{(C_0 - Ct)}{w} \quad .. (1)$$

$$\% \text{ Removal} = \left(\frac{(C_0 - C_t)}{C_0}\right) \times 100 \quad .. (2)$$

Where q_t is the mass of adsorbed Cu(II) ion per unit mass of adsorbent (mg g-1) (C_0) and (C_t) are the initial and actual concentration (g dm^{-3}) of Cu (II) ion at time, respectively, V is the volume of the treated solution (ml), and w is the mass of adsorbent (g).

Results and Discussion

Influence of contact time

The Cu(II)ion adsorption in the ACSC adsorbent was evaluated as a function of contact time to determine the equilibrium time for maximal removal and to understand the kinetics of the adsorption process. The results are presented in Figure 1 and the equilibrium values are given. The figure demonstrates that the absorption rate was initially brisk, with a maximum of adsorption completed in 30 minutes and equilibrium established in 50 minutes, hence a 60-minute equilibration duration was used for all subsequent tests.

Influence of activated carbon dosage

The adsorption of the Cu(II) ion on ACSC was studied by varying the adsorbent dose to 50 mg/l of Cu(II) ion concentration. The percentage removal of Cu(II) ions in Cu(II)-eased with Cu(II)-eases in the ACSC dose is attributed to the Cu(II)-eased carbon surface area and the availability of more adsorption sites. As a result, all experiments were conducted with 0.025g of adsorbent and 50 ml of different adsorbate solutions of 10, 25, 50, 100, 200, and 250 mg/L. The findings of this investigation are depicted in Figure 2. The amount of Cu(II) ions adsorbed per gram was reduced with Cu(II) enzyme in the dosage of ACSC. This reveals that the direct and equilibrium capacities of Cu(II)ions are functions of the activated ACSC dosage.

Influence of initial pH

The adsorption process is extremely pH sensitive because the adsorbent surface includes different functional groups that are responsible for the interaction between Cu(II) ion and the adsorbent and can be protonated or deprotonated to produce different surface charges in solution at different pH values. As a result, the impacts of starting solution pH were investigated in the pH range of 3-9 for the elimination of Cu(II) ions from aqueous solutions. The percentage elimination in Cu(II) eased from 60% to 93%, whereas it in Cu(II)eased slowly after pH 6.8, as indicated in Figure 4. The pH_{zpc} of any adsorbent is a critical property that determines the pH at which the surface possesses net electrical neutrality. It is widely understood that negatively charged groups on the adsorbent's surface are required for cationic Cu(II) ion adsorption. At lower pH values (pH_{zpc}), the surface charge of the ACSC surface may become positively charged as a result of being surrounded by H_3O^+ ions, and thus the competitive effects of H_3O^+ ions, as well as the electrostatic repulsion between the Cu(II) ion and the positively charged active adsorption sites on the surface of the ACSC, cause a Cu(II) enzyme in Cu(II) ion uptake. At higher pH levels (pH > pH_{zpc}), the surface of ACSC may acquire a negative charge, resulting in an increase in Cu(II) ion uptake due to electrostatic attraction. On the other hand, the neutral surface of the adsorbent provides support for the maximal removal of Cu(II) ions from aqueous solutions, resulting in an initial pH value of 6.8.

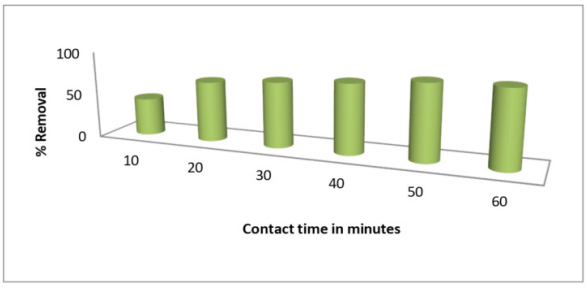

Fig. 2. Effect of Contact Time on the Removal of Cu (II)

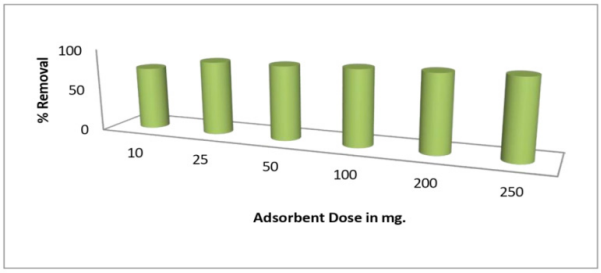

Fig. 3. Effect of Adsorbent dose on the Removal of Cu

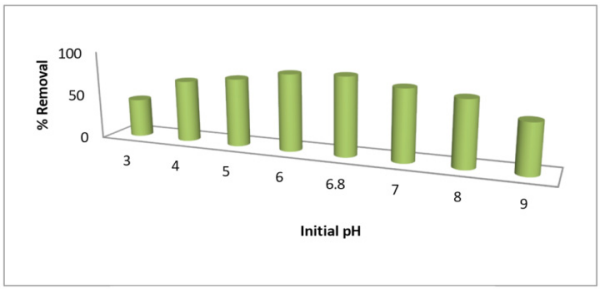

Fig. 4. Effect of Initial pH on the Removal of Cu (II)

Influence of other ions

The influence of chlorine ions on the adsorption process was investigated at various concentrations. Ions were added to 50 mg/l Cu (II) ion solutions and the mixture was agitated for 60 minutes at 30°C. Figure 5 shows that a low concentration of Cl^- has no influence on the percentage of adsorption of Cu(II) ion on ABCC because the interaction of Cl^- at accessible sites of adsorbent via competitive adsorption is ineffective. While the concentration of other ions in Cu(II)eases, the interference of these ions at available surface sites of the sorbent via competitive adsorption in Cu(II) eases the percentage adsorption. This is because ions with smaller hydrated radii Cu(II) reduce swelling pressure within the sorbent and increase the sorbent's affinity for such ions.

Thermodynamic treatment of the adsorption process

Thermodynamic parameters related with adsorption were computed using standard free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o). The following equation gives the free energy of the adsorption process when the adsorption equilibrium constant K_0 is taken into account:

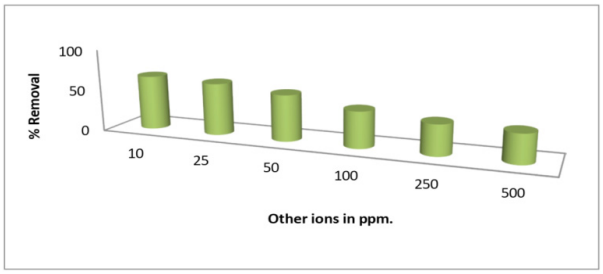

Fig. 5. Effect of other ionic strength on the removal of Cu (II)

$$\Delta G^0 = -RTlnK_0 \quad .. (6)$$

Where ΔG_0 is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin, and R is the universal gas constant (8.314 J mol/K). The slope of the plot of $\ln(q_e/C_e)$ against C_e at different temperatures was used to calculate the sorption distribution coefficient K_0. The adsorption distribution coefficient can be stated in terms of enthalpy change (ΔH^o) and entropy change (ΔS^o) as a function of temperature.

$$\mathbf{lnK_o = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}} \quad .. (7)$$

Where ΔH° is the standard sorption heat change (kJ/mol) and ΔS° is the standard entropy change (kJ/mol). The slope and intercept of the plot of $\ln K_0$ against 1/T can be used to calculate ΔH° and ΔS°. Table 1 shows the value of the thermodynamic parameter determined from equations 6 and 7.

The thermodynamic examination of the sorption data revealed that ΔG° values were always negative. The results show that physisorption is substantially more favorable for Cu(II) ion adsorption. Positive values of ΔH° indicate that adsorption is endothermic, and it governs the possibility of physical adsorption. Because, in the case of physical adsorption, while Cu(II) easing the temperature of the system, the extent of Cu(II) ion adsorption in Cu(II) eases, chemisorptions are ruled out. The low ΔH° value indicates that the Cu(II) ion is physisorbed onto the adsorbent ACSC. The negative ΔG° values confirmed the spontaneous nature of Cu(II) ion adsorption onto ACSC. The lower value of ΔG°, the more physical the adsorption process. The fact that ΔH° is positive supports the endothermic character of the adsorption process. The positive values of ΔS° in Table 4 indicated that the unpredictability of the solid solution interface was reduced following the adsorption of Cu(II) ion onto ACSC.

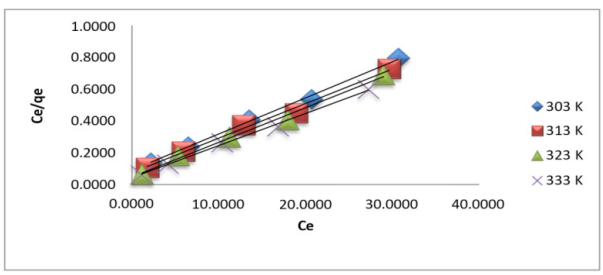

Fig. 6. Freundlich adsorption isotherm for the removal of Cu (II)

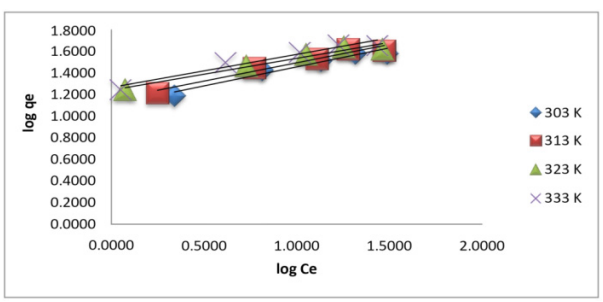

Fig. 7. Langmuir adsorption isotherm for the removal of Cu (II)

Kinetic models

Pseudo-second-order

Kinetic models are commonly used to test experimental data while investigating the mechanism of adsorption. Pseudo-second-order equations can be employed if the observed concentrations are equivalent to the surface concentrations. The linearized form of the pseudo second order equation is.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad .. (8)$$

Where q_t (mgg^{-1}) is the quantity of adsorbed Cu(II) ion on the adsorbent at time t, q_e is the equilibrium sorption uptake, and k_2, (min^{-1}) is the pseudo-second-order adsorption rate constant. The fact that the plot t/q_t vs t yields a straight line indicates that the second order kinetic model is appropriate, and q_e and k_2 are calculated from the slope and intercept of the plot, respectively. The presence of a pseudo-second-order adsorption reaction is indicated by a high regression value, as illustrated in Table 5.

The Elovich equation

The Elovich model equation is generally expressed as

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta} lnt \quad .. (9)$$

Where is the starting adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g/mg) for each experiment. If the Elovich model fits the Cu(II) ion adsorption, a plot of q^t Vs ln(t) yields a linear relationship with a slope of (1/â) and an intercept of (1/β)ln(αβ). The Elovich model parameters α, β, and correlation coefficient (R^2). According to this model, the initial adsorption (á) in Cu(II) decreases with temperature in a manner comparable to the initial adsorption rate (h) in pseudo-second-order kinetics models. This could be attributed to an increase in Cu(II) ease in the pore or active site on the ACSC adsorbent.

Intra-particle diffusion model

Kinetic data was further evaluated using the intra-particle diffusion model, which is based on the equation below.

$$log\ R = log\ K_{id} + a\ log\ t \quad .. (10)$$

Where K_{id} is the intra-particle diffusion rate constant and its relationship to boundary layer thickness. A plot of log R vs logt yields a straight line, indicating that the adsorption mechanism follows the intra-particle diffusion process and that the evidence of correlation coefficient values is close to unity, according to the preceding equation.

Conclusion

This study indicated that the new alternative adsorbents for heavy metal ion removal in industrial wastewater are effective at removing Cu(II) ions from aqueous solutions. The adsorption of Cu (II) ions onto ACSC was expected to be significantly dependent on contact time, pH, adsorbent dosage, and other ionic strengths. The adsorption data was well fitted by pseudo-second-order, Elovich, and intra-particle diffusion models, demonstrating that a chemical reaction is involved in the adsorption process. Three stages of diffusion mechanisms were discovered to control the adsorption process. The data from the isotherm equilibrium fitted well with the Langmuir isotherm model, and the monolayer adsorption capacity was determined to be 68.616 mg/g. Negative values of ΔG^o indicated the spontaneity of the Cu(II) ion adsorption process, whereas positive values of ΔH^o and ΔS^o suggested the endothermic character. This work demonstrated that *Clerodendrum serratumstem* carbon may be used to extract Cu(II) ions from aqueous solutions.

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