ABSTRACT

Industrialization and urbanization often lead to an increase in the discharge of toxic metals into the environment, which results in damage to ecosystems and human health. A recent focus on the removal of metal ions from solution is the use of agricultural and vegetable materials through adsorption. In the present study, the sportive potential of Morinda Citrifolia barks for Cu (II) ions has been investigated in a batch system. Equilibrium studies were performed to address various experimental parameters like pH, adsorbent dose and initial concentration for the removal of copper (II) ions. The adsorption data was described by Langmuir model. The values showed that acid treated Morinda Citrifolia has a better sorptive potential than base treated Morinda Citrifolia and both the adsorbents can be used for the economic treatment of wastewaters containing Copper (II) ions.


INTRODUCTION

Water pollution is the introduction of chemical, biological and physical matter into water bodies that degrade the quality of life that lives in it. Water is polluted in many ways like effluent of leather and chemical industries, electroplating industries and dye industries.\textsuperscript{[1]} Several industrial and agricultural processes and mining activities have increased the concentration of toxic contamination in water and waste water around the world. The presence of heavy metals in the environment has led to a number of environmental
The metal ions such as copper, chromium, lead, mercury pose severe problem to living things. They do not undergo biodegradation and many of them are soluble in aqueous solutions, therefore become more available for living systems and accumulate in the environment. Copper is absorbed in the human body, if too much of is ingested, an excess condition can lead to tissue injury and metabolic disorders. Developing countries mainly suffer from water pollution; the expensive method of treatment is the main problems in these countries. Bio sorption, a biological method of environmental control, can be an alternative to conventional treatment facilities. In this work, the adsorption of copper (II) ions was studied using low cost adsorbents by a batch mode process with respect to the pH, initial concentration and adsorbent dose. The adsorbents used in the present study were carbon obtained from barks of morinda citrifolia (AMC&BMC).

MATERIALS AND METHODS

Preparation of carbon
Carbon (AMC) was prepared by treating air-dried barks of morinda citrifolia, with concentrated sulphuric acid a weight ratio of 1:1. The resulting black product was kept in a furnace, maintained at 500°C 12 h followed by washing with water until free from excess acid and dried at 150 °C±5 °C. The carbon product was ground and was used as adsorbents for all the experiments. The (BMC) carbon was prepared by keeping the barks of morinda citrifolia in muffel furnace at 300°C then treated with saturated sodium bicarbonate solution. The adsorbents made into 0.75μm—150 μm size and it was allowed into the mechanical sieving machine manufactured by Jayanth scientific industries, Mumbai.

Adsorbate
100 ppm of copper (II) solutions was prepared by dissolving 0.393g of copper sulphate pentahydrate in double-distilled water and making up to 1000 ml. The stock solution was diluted to obtain required standard solutions.

Analysis
The concentrations of copper in the solutions after equilibrium were determined by Solar A2 Solaram Atomic Absorption spectrophotometer. The pH of the solution adjusted by 1M HCl and the Ph was measured with a systronics digital pH meter using a combined glass electrode. The shaking was carried out in a mechanical shaker with rpm of 225, manufactured by Macro scientific works, JawaharlalNagar.Delhi-7.
Adsorption experiment

Batch mode experiments were conducted using 250mL Erlenmeyer flasks by contacting 50mL of the aqueous Cu (II) solution of different initial concentrations. The initial pH of the solution was adjusted before starting each experiment. The experiments were performed in a mechanical shaker for a period of 90 minutes at room temperature. The remaining concentration of Cu (II) ions in each sample after adsorption at different time intervals was determined by atomic absorption spectroscopy after filtering the adsorbent with Whatmann filter paper No.40 to make it adsorbent free. The Cu (II) concentration retained in the adsorbent phase was calculated. \[ q_e = \frac{(C_i - C_e) \cdot V}{W} \] Equation 1. Where \( q_e \) Cu (II) concentration, \( C_i \) and \( C_e \) are the initial and equilibrium concentrations (mg/L) of Cu (II) solution respectively. \( V \) is the volume (L), and \( W \) is the mass (g) of the adsorbent.

RESULTS AND DISCUSSION

Effect of pH

The most important single parameter influencing the sorption capacity is the pH of adsorption medium. The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and rejects. The nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbent.\(^\text{[15]}\) The pH of feed solution is an important controlling parameter in the heavy metal adsorption process and thus the role of hydrogen ion. To study the effect of pH on Cu (II) adsorption onto AMC&BMC, the experiments were carried out using 2mg/L to 15mg/L Cu (II) concentration with 0.25g/50ml adsorbent mass at room temperature for 90 minutes equilibrium time. The experiments (Fig. 1) showed that the optimum pH for the adsorption of Cu (II) ions by AMC&BMC occur at 4&5.
Effect of concentration

The copper (II) removal on AMC&BMC was studied as a function of initial concentrations (2ppm, 4ppm, 6ppm, 8ppm, 10ppm). The increasing of initial metal ion concentration from aqueous solution (Fig. 2). At the same time, the percent of copper (II) removal (Fig. 2) sharply decrease with the increasing of the initial concentration.\textsuperscript{[16]} This opposite trend is determined by the fact that at higher concentrations, the diffusion of copper (II) ions to the un-reacted functional groups is inhibited. Hence an optimum concentration of 2 ppm was chosen for subsequent studies.

\begin{center}
\includegraphics[width=0.5\textwidth]{fig2.png}
\end{center}

\textbf{Fig.2 Effect of concentration}

Effect of adsorbent dose

The adsorption of copper (II) was studied by changing the quantity of adsorbents (0.1, 0.2, 0.3, 0.4, 0.5, TO 1g/50mL) in the test solution while keeping the initial concentration (2mg/L), temperature and pH (4) constant for 90 minutes for AMC. The solutions were agitated in a shaker, filtered and the metal ion concentrations in the filtrate were measured. Fig. (3) Shows that the adsorption of Cu (II) increases rapidly with increase in amount of adsorbent and reaches an equilibrium after a point.\textsuperscript{[17]} The maximum removal was obtained in the dosage of 0.5 mg/50 ml for AMC and 0.7 mg/50 ml for BMC. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles.
Effect of equilibration time:
The time dependent behavior of copper (II) ions uptake adsorption was measured by varying the equilibrium contact time in the range of 20-180 minutes. The copper (II) concentration was kept at 2mg/L, the amount of carbon added was 0.1 mg ---1g/the adsorption efficiency of copper (II) ions attained the equilibrium on both the carbons within 80 minutes.\(^{[18-20]}\) Thereafter it becomes constant. Figure 4 showed the adsorption constant with contact time.

Equilibrium isotherm
The analysis and study of equilibrium data is very important in view to develop a model equation which can accurately represent the results and could be used for the design purposes. Langmuir isotherm model was used to describe the equilibrium characteristics of adsorption of metal onto AMC&BMC respectively. The model developed by Langmuir is given by the following linearized equation--- (2)Where \( q_e \) is the equilibrium metal ion
concentration on the adsorbent (mg/g), Ce is the equilibrium metal ion concentration in the solution (mg/g) and KL is the Langmuir adsorption constant (L/mg). It can be seen from fig. 4 that the Langmuir equation fitted well for both the adsorbents with R2 values 9998 & 0.9224. The values of the different Langmuir parameters are calculated. The values show that AMC has a better sorptive potential than BMC and both the adsorbents can be used for the economic treatment of wastewaters containing copper (II).[21-25]

\[1/q_e = 1/q_m + (1/q_m K_L) (1/C_e) \] ------equ-2

![Fig.5 Equilibrium isotherm](image)

**CONCLUSION**

The efficiency of the adsorbents carbon obtained from morinda citrifolia bark for the removal of Cu (II) ions from aqueous solution was investigated. Parameters such as pH, dose and initial concentration were studied. The optimum pH for the removal of copper ions was found to be 4 at an initial concentration of 2 ppm for both the adsorbents. The removal was found to be increase with time and attains equilibrium at 80 minutes. The equilibrium data fitted well with Langmuir adsorption isotherm. The results of the study showed that acid
treated morinda citrifolia bark can be efficiently used as compared to base treated morinda citrifolia as a low-cost adsorbent on the removal of Cu (II) from aqueous solutions.

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