Research Article

Experimental Optimization of an Agricultural Waste in the Uptake of Cu(II) Ions

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Abstract

The potential of tamarind hull, a low cost agricultural waste, to remove copper ions from aqueous solutions is evaluated in a batch process. The tamarind hulls are crushed, powdered and modified using 0.5 N sulfuric acid and formaldehyde. The experiments were performed to assess sorption capacity of the sorbent. The influences of variable parameters viz., particle sizes and doses of the sorbent material, agitation time and the pH are studied for Cu(II)-MTHP system. The optimum conditions form the maximum removal of Cu(II) ions by modified tamarind hull powder is established, from the experimental results and is presented in this paper.

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Introduction

Water bodies are extremely polluted by heavy metal ions released from diverse industries such as metal plating, mining, painting, wire drawing, batteries and printed circuit board manufacturing, as well as agricultural sources. Heavy metals, such as Cu, Zn, Pb and Cd, are prior toxic pollutants leached out by industrial wastewater [1]-[2]. Heavy metals are indispensable for many organisms in small amounts, but their enhanced doses induce acute or chronic poisoning. Dosage of heavy metal ions exceeding the tolerance limits, may disrupt the normal function of the central nervous system, cause changes in the blood content and adversely affect the functions of lungs, kidneys, liver and other organs. The long-term action of heavy metals may cause the development of cancer, allergy, dystrophy, physical, neurological degenerative processes, Alzheimer's and Parkinson's diseases. [3]

Copper ions (Cu^{2+}) are water-soluble. They are employed in industries like mining, metallurgical, electrical, electroplating, paints, pigments and electronics. The maximum permissible limit of Cu(II) in effluent discharges into water bodies is 0.25 mg/ L^2 [4]. The excess Cu(II) in aqueous waste discharges has become one of the prior pollutants. These excess Cu(II) accumulates in liver and brain. Copper toxicity is afundamental cause of Wilson's disease [5]. Many conventional techniques such as chemical precipitation, membrane filtration, electrolysis, ion exchange, co-precipitation and adsorption have been employed for the removal of heavy metals in wastewater treatment [6]. Among all this, the adsorption technique has gained momentum and popularity in recent times. Agricultural wastes are natural abundant in the environment, economic and readily available for the sorption of heavy metal ions from aqueous solutions. Agricultural wastes may therefore serve as an excellent alternative to activated carbon, which is quite unaffordable especially in developing countries [7].Adsorbent materials derived from Biomass can be used for the effective removal and recovery of heavy metal ions from wastewater: from algae, bacteria, sea-weeds, some higher plants, and agricultural wastes [8]. In view of abundant availability of these naturally occurring materials, a systematic study to assess the potential use of modified tamarind hull powder for the removal of Cu(II) from aqueous solutions is carried out in this paper.

In India, tamarind (*Tamarindus indica L.*) is an economically important tree which grows abundantly in the dry tracts of Central and South Indian states. Indian production of tamarind is about 3 lakh (0.3 million) tonnes per year. The hard pod shell is removed (deshelled) when the fruit is ripe and the fruit is the chief acidulate used in the preparation of foods. The shells (hulls) are discarded as waste and pose greater disposable problem [9]. These hills are available at no cost and so far, no studies have been reported for the removal of Cu(II) ions using TH powder. Hence, the present study aims at the exploitation and utilization of Tamarind Hull Powder (THP) for the sorption of Cu(II) ions.

Materials and Methods

Chemicals

All the chemicals used were of analytical reagent grade. Doubly Distilled (DD) water was used to carry out the experimental studies. Stock solution of 1000ppm copper solutions were prepared by dissolving 2.6826g of $CuCl_2 \cdot 2H_2O$ in 1000 ml water. Aliquots of the adsorbate solutions of varying Cu(II) ions concentrations (2-14 ppm: 2ppm) were prepared by progressive dilutions of stock copper solution. 0.1 N HCl and NaOH solutions were employed to adjust the pH of the aliquots.

Procedure of adsorbent preparation and modification

Tamarind hulls were collected from various localities in Coimbatore, washed well with distilled water and sun dried. Then the dried hulls (Fig. 1) were ground in a laboratory blender and sorted into different particle sizes using standard test molecular sieves. The varied sizes of the THP were treated with formaldehyde followed by H_2SO_4 to modify the nature of the sorbent materials. After modification, the material was washed well, dried and kept it in air tight container, there after called as Modified Tamarind Hull Powder (MTHP).

Figure 1 Image of Tamarind Hull

Batch Equilibration Studies

Batch Equilibration experiments were carried out at room temperature, in order to investigate the nature of metal – adsorbent interaction. The influence of various parameters viz., particle sizes and dosages of MTHP, agitation time between MTHP and sorbate solution, pH of the medium were investigated. An optimum initial concentration of Cu(II) ions was fixed for all the studies. The flasks with the contents (50ml of sorbate solution with varying particle size, dosage and pH values) were agitated at preset time intervals with 140 rpm using a Kemi Orbital mechanical shaker. The agitated samples were filtered and the residual concentrations of the Cu(II) ions were analyzed using AAS (AA-6200, Shimadzu make). The percentage removal was calculated from the recorded values. The quantity of Cu(II) ions adsorbed onto the adsorbent at the time of equilibrium (q_e) was calculated using the following expression:

$$q_e = (C_o – C_e) V/m \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations (mg/L) of Co(II) ions in solution. V is volume (L) of solution and m is weight of adsorbent (g) taken for experiment.

The percentage of adsorption of metal from aqueous solution was estimated by using the following equation [10].

$$\% \text{ adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

Results and Discussions
Effect of Particle Sizes

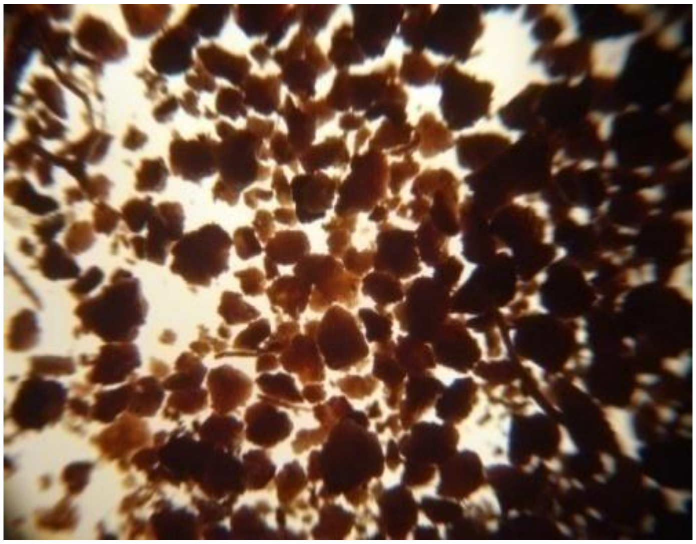

Figure 2: Microscopic Structure of MTHP

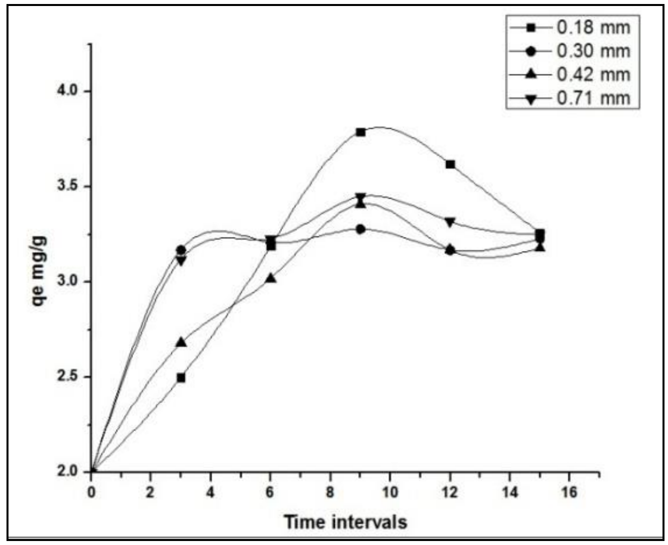

Figure 3: Effect of particle size

Adsorbent particle size has a significant influence on the kinetics of sorption due to change in number of adsorption sites. The sorption experiments of Cu(II) carried out for five different particle sizes of MTHP viz., 0.18, 0.21, 0.30, 0.42, 0.71 mm are shown in Fig. 3.The steep rise in the curve indicate that the smaller 0.18 mm particle size of MTHP exhibited maximum percentage removal of 93% for Cu(II) ions. The number of binding sites for adsorption increases with surface area. This is due to higher surface area of unit weight for lesser particle size and thence greater percentage removal [11,12]. In view of these experimental results, it was decided to limit the discussion of further experiments using 0.18mm particle size for Cu(II)-MTHP system. The MTHP microscopic structure of 0.18mm particle size is depicted in Fig. 2

Effect of Agitation Time

The amount of adsorption of Cu(II) increased with the contact time. However, the adsorption tends towards attaining equilibrium at 9 min. The gradation in the amount adsorbed is represented by the continuous smooth rise in the curve (Fig.4) plotted against the preset time intervals (3-15 minutes: 3 minutes interval). After 9 minutes, the semi parabolic curve indicates that the system tend towards saturation and had attained equilibrium at 9 minutes. The rapid initial adsorption is probably due to the abundant availability of active sites on the sorbent surface for the adsorption of these metal ions. As the surface sorption sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior sites of adsorbent particles which may be responsible for the slower stage [13]. Further, increase in contact time did not register an increase in adsorption. Thus, 9 minutes agitation time was considered to be the optimum contact time for the present system.

Effect of Dosage

Adsorbent dose seems to have a great influence on sorption process. Dose of adsorbent added into the solution determine the number of binding sites available for adsorption. The adsorption density decreased from 3.79 to 1.8 mg/g when the adsorbent dose was increased from 50mg to 200mg at 50mg intervals as evident from Fig. 5. It is obvious from the figure that 50mg of MTHP had maximum adsorption of Cu(II), the corresponding curve being atop in the graph. The decrease in adsorbent density is basically due to the adsorption sites remaining unsaturated during the adsorption process. This may be due to the overlapping and aggregation of adsorption sites which occurs as a result of overcrowding of adsorbent particles due to increase in the dose [14].

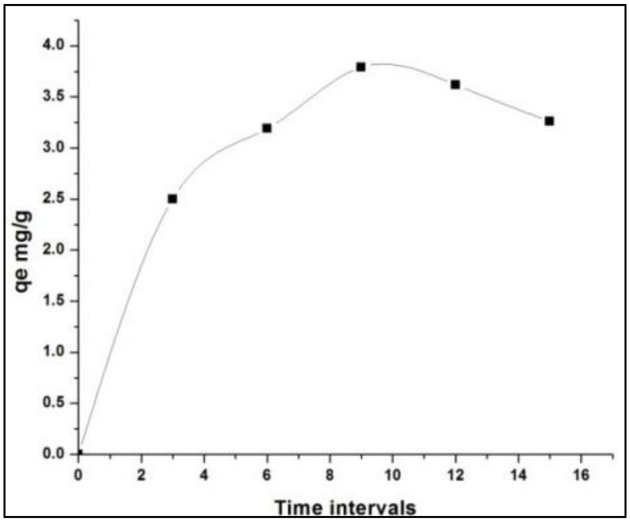

Figure 4 Effect of agitation time

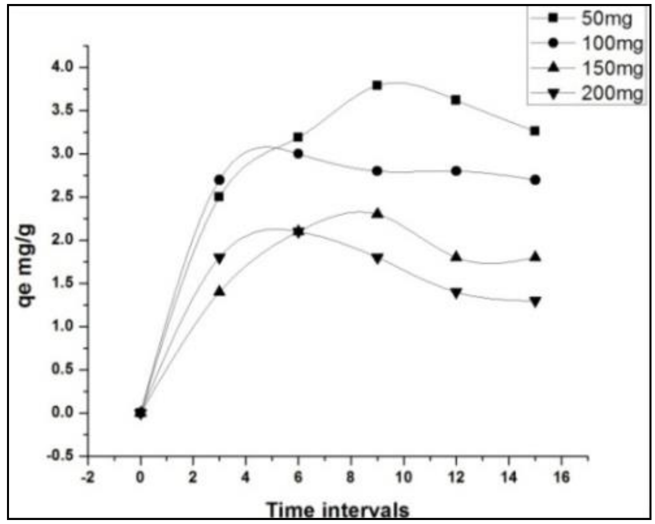

Figure 5 Effect of adsorbent dosage

Effect of pH

The pH dependence for maximum removal of Cu(II) ions onto MTHP was studied at varying pH environments viz., 3-11. It was observed that the ability of trapping Cu(II) ions by MTHP is pH dependent as evident from the Fig. 6 wherein the maxima had occurred at pH 5.6 in the inverted parabolic curve. Binding sites are generally protonated orpositively charged (by the hydronium ions) at low pH values. This leads to repulsion between the metal cation and the adsorbent at a higher pH value [15]. The precipitation of insoluble copper hydroxide might have occurred at pH values greater than 6.

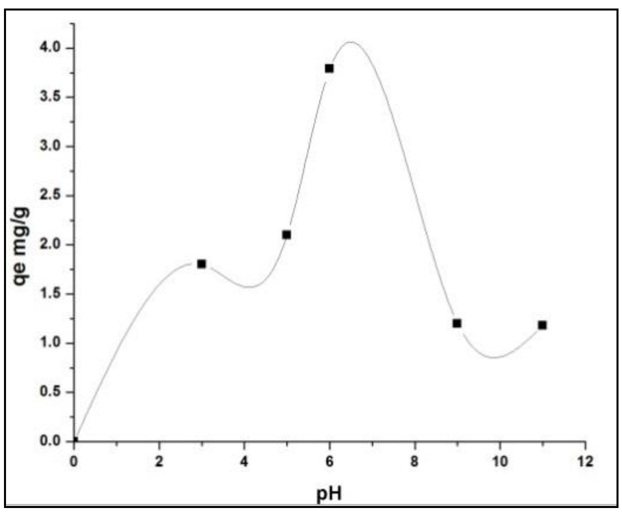

Figure 6 Effect of pH

Conclusion

The experimental results have led to the conclusion that the modified tamarind hull powder, has 93% efficiency to adsorb Cu(II) ions from the aqueous solutions. The modification has enhanced the sorption capacity of the chosen material. 0.18mm particle size, 50 mg dosage, 9 minutes agitation time, 4ppm initial concentration of Cu(II) ions, pH 5.6 of the solution medium, were optimized for the significant removal of divalent ion by MTHP.

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