International Journal of Theoretical & Applied Sciences, **1**(1): 25-31(2009)

Chemical modified bark for Cu (II) sorption from aqueous solution

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ABSTRACT

In present study the removal of Copper ions from aqueous solution containing 100-800 mg/lit, using chemically modified Acacia bark was performed on laboratory scale. The chemical modification was done by treating grinded bark with formaldehyde in acidic medium. The Cu (II) is exchanged against protons on the modified bark that contain carboxyl groups in both pectin and tannin compounds. The effects of different parameters such as effect of pH, effect of bark doses, effect of temperature, effect of time and effect of metal ion concentration have been investigated. The efficiency of copper removal increases to maximum to about 45% at around pH 5 with only 0.2 gram material. The study also revealed that the rate of sorption increase with increase in the quantity of material. The sorption copper ions are more in initial time of sorption process but the rate decreases with contact time increase. It is noted that with increasing temperature the absorption capacity of copper ions also increases indicating endothermic nature of adsorption. The equilibrium data for copper ion follow the Langmuir and Freundlich isotherms. It has been observed that interaction of copper ion on bark material follow a cation exchange mechanism which is supported by elution process in which recovery of about 90% of copper take place with 0.1N HCl solution.

Key words: *Acacia catechu*, sorption, heavy metal, copper (II), Langmuir and Freundlich isotherms

INTRODUCTION

The removal of heavy metal ions from aqueous solution is important for controlling pollution or also for the raw material recovery. Heavy metals have been excessively released into the environment due to rapid industrializations. Heavy metal ions such as Cd, Zn, Cu, Ni, Pb, Hg and Cr are often detected in industrial waste water and they originate from mining activities, smelting, battery manufacture, petroleum refining etc [1,2]. The presence of heavy metal ion such as copper in waters system is a potential health hazard to aquatic, animal and human life. There are several methods used for removing heavy metal ions from aqueous solution such as chemical precipitation, membrane filtrations, ion exchange and adsorption, reverse osmosis, solvent extraction etc [3-6]. The excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems [7]. Copper ion is a serious hazard in industrial and mining effluents and antifouling paints of oil tankers and ships. Because its presence in water causes rich growth of ichthyoplanktons. The presence of copper metal ions in water produces various problems for agriculture and human health. Heavy metal ions are non biodegradable and if they can be accumulated in living tissues causing various diseases and disorders [8]. Adsorption is one of the physicochemical treatment process found to be effective in removing heavy metal ions from aqueous solution. Now a days plant wastes are most commonly used as adsorbents. Because they are inexpensive as they have no or very low economic value [9]. Most of the adsorption studies have focused earlier on untreated plant wastes, but the application of untreated plant wastes as adsorbents can cause several problems such as low adsorption capacity, High BOD and COD as well as TOC due to release soluble organic compounds contained in plant materials. The increase in content of these can threaten the aquatic life as well as human life. Therefore plant wastes needs to be modified or treated before being applied for the decontamination of heavy metal ions [10, 11].

Bark is a common waste produced in forestry and was used selectively for the removal of cations especially toxic heavy metal ions. The metal ions are exchanged against protons on the bark substances that contains carboxyl group in both pectin and tannin compounds. The ion exchange is the only region for the removal of metal ions on modified barks [12]. Retention capacity of copper in case of bark and wood varies from 18.5 – 115 mg Cu/g of dry bark of wood [12-15]. The mechanism of copper binding with the bark was earlier reported as reaction between copper and COOH groups of polysaccharides [15, 16]. Hydrogen bonding of copper with cellulose as hydrated ion, Cu $(H_2O)_6^{2+}$ [16] and the formation of complexes with phenolic group of lignin [10,17]. Removal of metal ions depends upon the nature of the bark used, grain size and predominant the heavy metal ions present in the solution [18].Acacia catechu is a moderate size deciduous tree with rough dark gray brown bark. It belongs to family Leguminoseae mimoseae. The bark of this plant is used in treating sore mouth, body pains, gravel, bronchial asthma and indigestion. The objective of study was focused on the use of modified Acacia Catechu bark for the removal of copper metal ions from aqueous solution. More over the effect of important factors affecting the adsorption such as effect of sorbent quantity, effect of pH, effect of contact time, effect of temperature, effect of initial metal ion concentration, sorption–desorption behavior and isotherm for both Langmuir and Freundlich were investigated.

MATERIAL AND METHODS

Bark material

Acacia Catechu tree bark was gathered from plant into clean plastic bag, washed with distilled water and dry on clean table for 4 days. The dried bark was grounded and sieved to 60-80 mesh size, stored in plastic bags ready to use.

Apparatus and chemicals

Spectrophotometer model ME 802, AEMAX made was used for determination of copper (II). The weights of the samples were calculated on electronic balance Lakshmi Samson made. All the chemicals used in the study were of analytical grade. The pH values of the solution were adjusted by 0.1N HNO_3 and 0.1 N NaOH. The stock solutions of Cu (II) were prepared by dissolving approximate quantities of Cu $(NO_3)_2$ salts in HNO_3. Fresh solutions were made for each study.

Preparation of sorbent material

Sorbent material was prepared by treating 10 grams dried fraction with 100 ml of 0.1 H_2SO_4 and 6.5 ml of 39% HCHO. The mixture was stirred at 50^0C for 2 hour and filtered through a glass funnel. The product material so formed was then washed with distilled water till the pH of the filtrate reached between 4-6. The treatment with formaldehyde under temperature and acidic condition polymerizes and insolubilizes the tannin and pectin compounds [12] . The resin phenol or formaldehyde was so formed which make the possible interaction with divalent metal ions and OH groups [18].

Adsorption procedure

Dried sorbent material (0.2 g each) were added into 50 ml Erlenmeyer containing volume of 20 ml of each Cu(II) and was adjusted to desired pH. The mixture solutions were stirred at room temperature for 30 minutes to attain equilibrium. After filteration, Cu (II) solutions of filtrate were analyzed by spectrophotometer. The amount of copper ions adsorbed were calculated as

$$\% \text{ Adsorption} = \frac{C_o - C_e}{C_c} \times 100$$

Where C_0 and Ce are the initial and final concentration of the adsorbate respectively.

Effect of sorbent quantity

Batch studies have been carried out with four modified bark material powder fraction such as 0.2 g, 0.4 g, 0.6 g, and 0.8 g. These samples of different weight were added in 20 ml of Cu

(II) to the flask solutions of initial metal ion concentration 800 mg/lit. The mixtures were shaken for 30-40 minutes. Then the samples were analyzed for Cu (II) sorption after filtration (Table 1and Fig. 1).

Effect of pH

The effect of pH on the sorption capacity of modified bark sample was investigated using solution of different pH 3, 5, and 8 at room temperature as shown in Table 2 and Fig. 2. Metal solution at this pH was adjusted using 0.1N HNO_3 and 0.1 NaOH. 20 ml of metal ion solutions taken in a flask were shaken with 0.2g of modified bark materials in each one for 40 minutes. The sorbent was removed from the solution by filtration and residual copper ion concentration in the solution was analyzed by spectrophotometer.

Effect of contact time

The effect of contact time on the adsorption capacity of modified bark material was investigated using solution of 800 mg/lit concentration of copper metal. 0.2g of bark was added to 20 ml of copper solution in three different flasks. The samples were withdrawn at periodic time interval of 30, 60, 90 and 120 minutes with after continuous shaking. The filtrates were analyzed for Cu (II) concentration after sorption. The results of the study are shown in Table 3 and Fig. 3.

Effect of temperature

Effect of temperature was studied by placing 20 ml of copper solution with a concentration 800 mg/lit was placed in a 100 ml of conical flasks. 0.2 g of bark material was added to it and then shaken with a constant speed at temperature 30^0C and 40^0C for 30, 45, 60, and 75 minutes. Then the mixture were filtered and analyzed. The results of effect of temperature are shown in Table 4 and Fig. 4.

Effect of initial Cu (II) concentration

The metal ion sorption capacities of bark is presented as a function of equilibrium concentration 125-343 mg/lit in aqueous solution in Table 5 and Fig. 5. To prevent precipitation of metal ions as hydroxides at high concentration, the solution pH was adjusted to 4-5. All other parameter such as contact time 25 minutes, volume of solution (20 ml) and quantity of sorbents (0.2 g) were kept constant.

Sorption-desorption

Bark material on which desorption of Cu (II) have been done was added to 0.1 N HCl solution. Cu (II) was almost removed from the bark samples and dissolved in eluant. The regenerated sample has been washed with water several times and after that its utilization is possible.

Adsorption model

The Freundlich equation [7,19] is in the linearised form,

$$\log \frac{x}{m} = \log k + n \log C_e$$

where x/m is the amount of metal ions adsorbed at equilibrium, Ce are the equilibrium concentration, K and n are Freundlich constants concerning the multilayer adsorption intensity respectably [20,21]. The Langmuir equation [22] in the linear forms,

$$\frac{C_e}{x/m} = \frac{1}{KX_m} + \frac{1}{X_m} C_e$$

Where x/m represents the amount of metal ions adsorbed at equilibrium, C_e are the equilibrium concentrations, Xm and K are Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively [21]. Lanmuir and Freundlich isotherm were obtained from the experiments (shown in Fig. 6 and 7).

RESULTS AND DISCUSSION

Effect of sorbent quantity

The dependence of adsorption of Cu (II) on the amount of modified bark was studied at room temperature 21^0C at pH 5 by varying the sorbent quantity in 20 ml volume at constant Cu (II) concentration. It has been observed that the percentage of Cu (II) ions removal increases with increase in sorbent quantity (Table 1 and Fig. 1). The percentage removal of Cu (II) ions increased from 50 to 72 for adsorbent quantity of 0.2 g to 0.8 g, respectively. Provably this was due to high number of unsaturated adsorption sites [23].

Effect of pH

The results of effect of pH on sorption are represented in Table 2 and Fig. 2. pH is one of the main factor which influences surface change of the sorbent, degree of ionization and speciation of adsorbate [24]. In the low pH there is a occupation of the negative sites by the H^+ and H_3O^+ and leads to the reduction of the vacancies for metal ions and consequently cause decreases in metal ions sorption [25] that is 28%. It has been observed that the percentage of adsorption of Cu (II) increased with increasing pH and maximum adsorption of Cu (II) was obtained at pH 5 (45%). Above pH 5, the precipitation of copper in aqueous solution was observed. The effect of pH shows that sorption of Cu (II) is more favorable in acidic medium.

Effect of contact time

The effect of contact time on sorption of Cu (II) are shown in Table 3 and Fig. 3. The study shows that the equilibrium was attain after shaking for 30-4- minutes for Cu (II) ion. Therefore in each experiment the shaking period was selected 30 minutes. The adsorption rate initially increased and the equilibrium was attained at 40 minutes at adsorption efficiency of 56%. The removal efficiency decrease by about 2% with further increase in contact time after equilibrium. This was probably resulted from saturation of adsorbent surface with Cu (II) followed by adsorption and desorption processes that occur after saturation. The time interval studies on the sorption of copper metal showed a fast rate of removal initially due to large unoccupied sites on the biosorbent [26].

Effect of temperature

The effect of temperature on the sorption of copper ions onto the modified bark material was studied within range 30-40^{0}C at different time as shown in Table 4 and Fig. 4. It was observed that with increase in temperature increase in adsorption capacity (56-65%) was investigated. The increase in copper adsorption with temperature was due to change in pore size, desolvation of the Cu (II) ions and increase in intraparticle diffusion [27].

Effect of initial metal ion concentration

The effect of initial concentration on percentage removal of Cu (II) ions by modified material are shown in Table 5 and Fig. 5. The metal uptake mechanism is particularly dependent upon initial metal concentration. It has been observed that the adsorption of Cu (II) decreased from 80% to 7% by increasing the concentration from 20 mg/lit to 320 mg/lit respectively. This is because the sufficient adsorption sites are available at low initial concentration, but at higher concentration copper ions are greater than adsorption sites available [28]. This effect may also be due to an increase in electrostatic interactions which involves sites of progressively lower affinity for metal ions [29].

Sorption-desorption

Elution of copper ion from lowded modified bark was carried out by using 0.1 N HCl solutions. Elution of Cu (II) was done by adding 0.2 g bark material sorbed Cu (II) material in flask containing 50 ml of 0.1 N HCl solutions. This mixture solution after filtration and analysis contain 90% of adsorbed Cu (II) ion. These results indicate the possibility of regenerating the bark material for its reuse.

Adsorption model

The linearized Langmuir and Freundlich isotherm are obtained for copper ions and represented in Figs 6 and 7. Both the isotherms show the relationship between C_e and C/x/m (mg/g) According to Langmuir model sorption occurs uniformly on active sites once adsorbate occupies the sites, no further adsorption take place at that site. The study revealed that Cu (II) ion adsorption on modified material perfect according to isotherm equation.

CONCLUSIONS

The chemically modified acacia bark has been converted into useful adsorbent. This material exhibit very good adsorption of Cu (II) ions from aqueous solution. The adsorption of Cu (II) ions increase with increase in sorbent quantity and the maximum adsorption occur in case of 0.8 g modified bark material. The removal of Cu (II) ions increases with increase in pH and maximum uptake of metal ions obtained at pH 5. The time contact studies study shows maximum adsorption 56% occur with in 40 minutes. The effect of temperature on the sorption of copper ions onto the modified bark material was studied within range 30-40^{0}C at different time and it was observed that with increase in temperature the adsorption capacity increases. The effect of initial metal ions concentration on the adsorption capacity indicates that with increase in metal ion concentration there is decrease in adsorption capacity. This material can be easily synthesized at relatively rate and could be used for removal of copper ions from waste water.

ACKNOWLEDGEMENT

The authors thank the Eternal University, Baru Sahib for the financial support.

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Table 1. Effect of biosorbent doses on % adsorption of copper ion

S.No.	Bark fraction (g)	% Adsorption
1.	0.2	50
2.	0.4	60
3.	0.6	68
4	0.8	72

Table 2. Effect of pH on adsorption of copper ion

S.No.	Bark fraction (g)	pH value	% Adsorption
1.	0.2	3	28
2.	0.2	5	45
3.	0.2	8	34

Table 3. Effect of contact time on % removal of copper ion

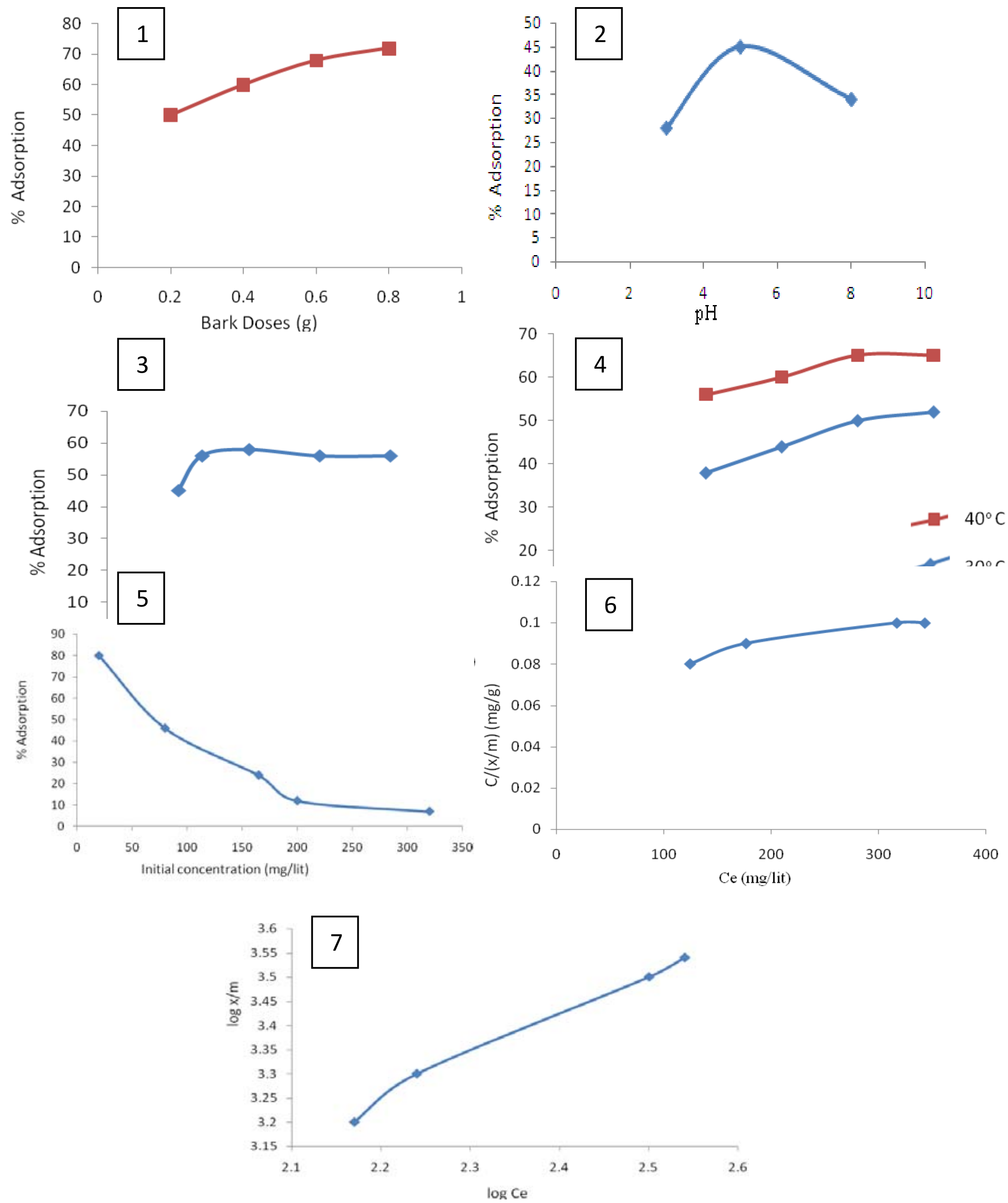
S.No.	Bark fraction(g)	Room temperature	Time Interval (minutes)	% Adsorption
1.	0.2	18^0C	30	45
2.	0.2	18^0C	40	56
3.	0.2	18^0C	60	58
4.	0.2	18^0C	90	56
5.	0.2	18^0C	120	56

Table 4. Effect of temperatures on % removal of copper ion

S.No.	Bark fraction (g)	Time interval (minutes)	% Adsorption at temperature (30^0C)	% Adsorption at temperature (40^0C)
1.	0.2	30	38	56
2.	0.2	45	44	60
3.	0.2	60	50	65
4.	0.2	75	52	65

Table 5. Effect of initial metal ion concentration

S.No.	Bark fraction (g)	Initial concentration (mg/lit)	% Adsorption
1.	0.2	20	80
2.	0.2	80	46
3.	0.2	165	24
4.	0.2	200	12
5.	0.2	320	07



Figurs. 1. Effect of increasing sorbent quantity on removal of Cu (II) from metal solution; 2. Effect of pH on removal of Cu (II) ; 3. Effect of Contact time on removal of Cu (II); 4. Effect of temperatures (^{0}C) at different times on Cu (II) Removal; 5. Effect of initial metal ion concentration on sorption by modified bark; 6. Langmuir adsorption isotherm for Cu(II) sorption by modified bark; 7. Freundlich adsorption isotherm for Cu (II) sorption by modified bark.