



Kigelia africana Fruit Carbon as a Low Cost Adsorbent for Removal of Copper(II) Ions from Aqueous Solution

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ABSTRACT

Fruit of *Kigelia africana* tree is cylindrical and weigh approximately 2.5 kg. A mature tree produces hundreds of fruits every year but not used for any purpose, and hence a waste material in this region. Heating dried fruit powder with 1:1 sulphuric acid at 110°C for 24 h has resulted in carbonaceous material which showed marked adsorption properties. Copper(II) adsorption capacity of this *Kigelia africana* fruit powder carbon material (KAFP) was found to be 21.74 mg/L and almost 90% removal was achieved by treating 100 mg of adsorbent material in 100 mL (10 mg/L) of Cu(II) solution. Adsorption data fitted well into Langmuir adsorption isotherm equation. Metal uptake was maximum at pH 7 and almost negligible at much lower pH values.

INTRODUCTION

Effective methods available for wastewater treatment generally involve costlier adsorbents and hence not economically viable. Therefore, continuous research is going on to develop newer low cost adsorbents from agricultural waste (Sivaraj et al. 2002), domestic waste (Hameed 2009), industrial waste (Wang et al. 2005), forest trees (Babu & Gupta 2008) and many more sources. Lignin content and other functional groups present on the surface of these adsorbents are responsible for the uptake of metals and non metals from aqueous solution. In India, it is popularly known as 'Sausage tree' and locally known as 'Balam khira'. This tree can grow up to 20 m tall and widely planted for its ornamental flowers, firewood and shade. A full grown tree bears hundreds of fruits hanging in and each cylindrical fruit weighs about 2.5 kg. Bark and fruits of this tree have demonstrated medicinal properties (Owolobi et al. 2007, Olalye & Rocha 2007), but their utilization in India is negligible. Thousands of *Kigelia africana* trees grow in the forest belts of Punjab, Haryana and Himachal Pradesh. Fruits and leaf litter are thrown into wasteland as there is no known use in this region. Finding an alternate method to convert this readily available waste material into a valuable resource will certainly benefit the mankind. A variety of adsorbents were developed from leaves (Kumar et al. 2006), stem (Anirudhan et al. 2005), seeds (Gonzalez & Montoya 2009), fruits (Inbaraj & Sulochana 2004) and almost all parts of many plants and trees. However, no work has been reported on this popularly grown *Kigelia africana* tree fruits or leaves as a precursor to develop adsorbents, and therefore, the present work has been undertaken.

MATERIALS AND METHODS

Plant material: *Kigelia africana* belongs to Bignoniaceae family. Mature ripe fruits were collected from Punjab Engineering College campus, Chandigarh on 5th February, 2010. They were washed with water, cut into small pieces and air dried in the open for a few days and later further dried in an electric oven at 110°C for 72 h and powdered in a mechanical mill. 0.25 L of 1:1 conc. H₂SO₄ was added with 100g of plant material powder kept in a 0.5 L beaker. This mixture of fruit powder and sulphuric acid was heated in an electric oven at 110°C for 24 hours. It was stirred once in an hour. The slurry was washed thoroughly with water and finally with distilled water and dried. Dry carbonized *Kigelia africana* fruit powder (KAFP) material was stored in an airtight container for further use.

Chemical reagents: All chemicals used in this study were of analytical grade and a stock solution of 1000 mg/L was prepared by dissolving 3.801g of Cu(NO₃)₂·3H₂O in 1 L of deionized water. Working standards were obtained by diluting stock solution with appropriate volume of deionized water. 0.05 N NaOH and 0.05 N HNO₃ were used to maintain pH of initial metal ion solutions. Conc. H₂SO₄ was employed in the carbonization of the plant material.

Batch adsorption studies: A series of 0.1 L of metal ion solutions in the concentration range of 10 mg/L to 25 mg/L were taken in 0.25 L conical flasks. 0.1 g of KAFP adsorbent material was added to each conical flask solution and they were closed with screw corks. The suspensions were shaken in a water bath cum shaker for 2 h and thereafter, centrifuged. The clear supernatant solution was analysed in AAS (ECIL,

India) for determination of copper concentration.

Contact time studies: 0.1 L of metal ion solution (20mg/L) was taken in 5 different 0.25 L conical flasks. 0.1 g of KAFP adsorbent was added to all conical flask solutions and they were shaken for 15, 30, 60, 90 and 120 minutes respectively. Clear solution was drawn from these conical flasks after shaking and analysed for copper.

Adsorbent dose studies: 0.1, 0.15, 0.2 and 0.25g of KAFP was added to four 0.25 L conical flasks containing 0.1 L of 20 mg/L metal ion solution. All flasks were closed with screw corks and shaken in a laboratory shaker for 2 h. Clear solutions were drawn after 30 min and analysed for copper concentration.

pH studies: Batch adsorption experiments were conducted to find adsorption of copper (II) ions onto KAFP at different initial metal ion concentrations. pH of the solutions were maintained by adding either NaOH or HNO₃.

RESULTS AND DISCUSSION

Batch adsorption data obtained at different initial metal ion concentrations ranging from 10 mg/L to 25 mg/L fit well into Langmuir adsorption isotherm equation. Langmuir constants Q and b are calculated from slope and intercept of linear Langmuir plot for the adsorption of Cu(II) ions on KAFP from aqueous solution (Fig. 1). Following Langmuir equation was used.

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q}$$

Where, C_e = equilibrium concentration, q_e = amount adsorbed on to the adsorbent (mg/g), Q = sorption capacity (mg/g), b = sorption energy (L/mg).

Another dimensionless equilibrium parameter, R_L was calculated from the following relation.

$$R_L = \frac{1}{1 + bC_e}$$

R_L value gives the information regarding the nature of isotherm applied (Table 1).

Langmuir constant, Q values for Cu(II) adsorption on KAFP and other low cost adsorbents are given in Table 2. R_L values between 0 and 1 confirm applicability of Langmuir isotherm equation for the adsorption of Cu(II) from aqueous solution. Langmuir equilibrium parameter at different initial metal ion concentrations for Cu(II) adsorption on KAFP is presented in Table 3. Percent removal of Cu(II) ions decreased from 90.9 to 70.16 when initial metal ion concentration was increased from 10 mg/L to 25 mg/L. Whereas, metal ion uptake by KAFP increased from 4.56 mg/g to 8.77 mg/g. Freundlich isotherm is shown in Fig. 2. Though R^2 value is very close to 1 (0.966), $1/n$ and K_f values

Table 1: Langmuir equilibrium parameter and nature of the isotherm applied.

Value of R_L	Nature of isotherm applied
$R_L > 1.0$	Unfavourable
$R_L = 0$	Linear
$R_L < 1.0$	Favourable
$R_L = 0$	irreversible

Table 2: Langmuir constants for the adsorption of Cu(II) ions on KAFP from aqueous solution.

Adsorbent	Sorption capacity (Q)(mg/L)	Reference
KAFP	21.74	Present work
Sunflower stalk	29.3	Sun and Shi (1998)
Saw dust	13.6	Ajmal et al. (1998)
Palm oil fibre	19.8	Low et al. (1993)
Sago waste	12.42	Quek et al. (1998)

Table 3: Equilibrium parameter values for the adsorption of Cu(II) on KAFP from aqueous solution.

C_e (mg/L)	Copper(II)
10	0.556
15	0.455
20	0.385
25	0.334

Table 4: Effect of adsorbent amount on Cu(II) ions uptake by KAFP from aqueous solution.

% Cu(II) removal	Amount of adsorbent (mg)	Amount of Cu(II) adsorbed (mg/g)
87.25	100	21.3
90.35	150	19.2
89.3	200	17.9
89.85	250	15.7

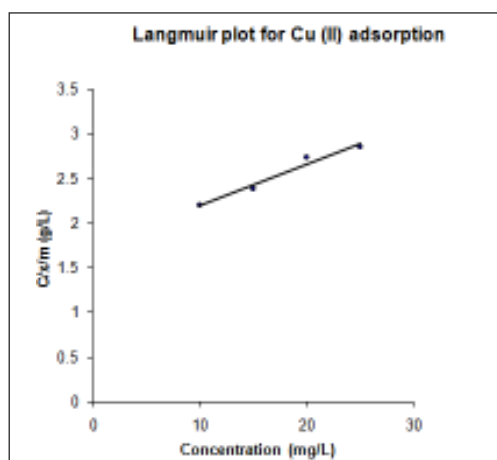


Fig. 1: Langmuir plot for the adsorption of Cu(II) ions on KAFP from aqueous solution.

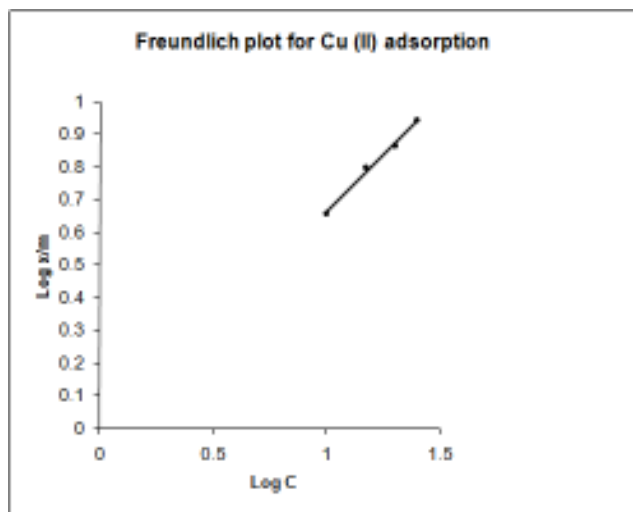


Fig. 2: Freundlich plot for the adsorption of Cu(II) ions on KAFP from aqueous solution.

confirm the applicability of Langmuir isotherm equation in this case. Contact time studies revealed that equilibrium was achieved well within 30 minutes (Fig. 3). Percent removal of Cu(II) ions increased from 20 to 92 approximately on increasing adsorbent dose from 0.1 g to 0.25 g but amount of metal ion intake by the adsorbent decreased from 21.3 mg/g to 15.7 mg/g. This is due to the increase in the available adsorbent surface (Table 4). 0.05 N HNO₃ and 0.05 N NaOH solutions were used to adjust pH of initial metal solutions. Effect of pH on copper adsorption onto KAFP was studied at different pH values of 2-8. Uptake of metal ion was minimum at lower pH (2-3) and increases at higher pH values (3-

7).

Mechanism of adsorption: FTIR peaks at 2365.5cm⁻¹ (-C=C-stretching), 1377.9cm⁻¹ and 1583.7cm⁻¹ (carboxylate ion), 2923cm⁻¹ (methylene-C-H stretching) and 3368.5cm⁻¹ (intermolecular hydrogen bond) were observed. Ion exchange may be the most predominant mechanism as acidic carboxylate groups are found on the surface of the adsorbent sample. At much lower pH, H⁺ ions compete with metal cations resulting in much less metal removal from the aqueous solution. But at higher pH values, increase in metal uptake is due to the decrease in H⁺ ions in the solution.

CONCLUSIONS

- Carbonization of KAFP was achieved by heating with conc. H₂SO₄ at 110°C for 24 h.
- Adsorption data obey Langmuir adsorption isotherm equation.
- Equilibrium was achieved within 30 minutes.
- The study reveals the effectiveness of *Kigelia africana* fruit powder carbon in removing copper from aqueous solution as it showed comparable adsorption capacity value with other known low cost adsorbents.
- Maximum adsorption capacity of KAFP was 21.74 mg/g.
- 90.7% Cu(II) removal was achieved when 0.1 g of KAFP added to 0.1 L of 10 mg/L solution.
- Presence of acidic functional groups like carboxylate ions on the surface of the adsorbent was confirmed by FTIR spectrum.

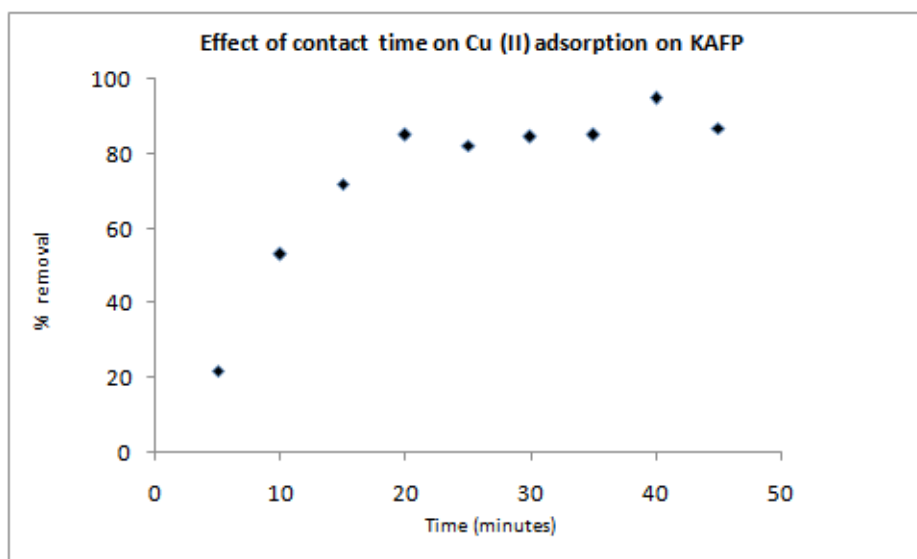


Fig. 3: Effect of contact time on Cu(II) adsorption on KAFP. Contact time revealed that equilibrium was achieved well within 30 minutes.

- Ion exchange may be one of the possible mechanisms of adsorption in this case.

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