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International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.4, pp 1854-1860, April-June 2013

The Removal Of Copper From Aqueous Solution Using Senna uniflora (Mill.)

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Abstract: In the present study, carbonized Senna uniflora (mill.) was investigated as a biosorbent for the removal of copper ions from aqueous solutions. Batch adsorption studies showed that senna uniflora(mill.) was able to adsorb Cu(II) ions from aqueous solutions in the concentration range of 100 – 200 mg L^{-1}. The adsorption was favoured with maximum adsorption at pH 5, whereas the adsorption starts at pH 1. The effects of contact time, initial concentration of metal ions, adsorbent dosage and particle size have been reported. The applicability of Langmuir and Freundlich isotherms were tried for the system to completely understand the adsorption isotherm processes. Among these two isotherm models, the adsorption of Cu(II) ions on SUC fits very well with Langmuir adsorption isotherm which indicates the monolayer adsorption process. The carbonized *senna uniflora (mill.)* was found to be cost effective and has good efficiency to remove copper ions from aqueous solution.
Keywords: Senna uniflora, Adsorption, Copper, Aqueous solution.

1.Introduction

The presence of toxic heavy metals in industrial effluents has become a matter of environmental concern. Copper(II) is known to be one of the heavy metals and widely used in many industries including metal cleaning and plating, paper board, printed circuit board, wood pulp, fertilizer, paints and pigments, etc.[1]The effluents in these industries usually contain a considerable amount of copper, which spreads into the environment through soils and water streams and accumulates along the food chain, resulting in a high risk to human health, as high concentrations of copper will cause stomach upset and ulcer, mental retardance, liver and brain damage, and so on. As copper(II) does not degrade biologically, the control of Cu(II) pollution has special importance for both organisms that live in waters and those that benefit from waters.

Different methods of treating wastewaters containing heavy metal ions have been developed over years which include coagulation, ion- exchange, membrane separation, reverse osmosis, solvent extraction, chemical precipitation, electro flotation, etc. Among these methods, adsorption is a much preferable technique for the removal of heavy metals from polluted waters compared to others due to ease of operation and cost- effective process.

In recent years, considerable attention has been focused on the removal of copper from aqueous solution using adsorbent derived from low-cost materials. Several adsorbents such as saw dust, silica and iron oxide, sewage sludge ash,anatase-type titanium dioxide, olive mill residues, inorganic colloids, blast furnace sludge and activated carbon have been used for the treatment of Cu(II) rich effluents at the solid-solution interface. The plant selected for adsorption of copper(II) ions in this study is senna uniflora(mill.). In India it was first reported from Karnataka and also in parts of Maharastra. It is a new plant record for Tamilnadu. It is probably introduced in waste places, both urban and rural seen as aggressive colonizer. Senna uniflora is used in relieving inflammatory pain, an insight into the development of new agents for treating inflammatory diseases. Carbonized senna uniflora(mill.) is a low cost adsorbent material. The present paper investigates, in detail, the adsorption of copper by carbonized senna uniflora (mill.). The paper attempts to examine the reuse of carbonized Senna uniflora(mill.) as an adsorbent for the contaminated water bodies. In this study the name of the adsorbent is abbreviated as SUC.

2.Materials and methods

2.1 Preparation of Adsorbent

The plant *Senna uniflora(mill.)* was collected , cut into small pieces and dried in the absence of sunlight. It was treated with concentrated sulphuric acid in the ratio 2:3. It was then kept in a hot air oven at 100-120 ^{0}C and washed with distilled water repeatedly to remove the free acid completely. It was then dried in a hot air oven at 120- 150^{0}C. The dried adsorbent material was sieved using nylon sieves of sizes 212, 210, 150 , 90 and 75 µm. The particle size of 75 µm was used in the present study.

2.2 Adsorbate Solution

A stock solution of Cu(II) (1000 mgL^{-1}) was prepared by dissolving $CuSO_4.5H_2O$ in distilled water. The solution was further diluted to the required concentrations before use.

2.3 Batch Adsorption Experiments

Adsorption experiments were carried out in batches of 50 ml of 200 mgL-^{1} of copper(II) solution with 0.2g of carbonized senna uniflora(mill.). pH of the solution was kept at 4 for all experiments unless otherwise mentioned. The pH values of solutions were adjusted with dilute HCl or NaOH solution by using Systronics digital pH meter 335 with combined glass electrode. The temperature of the experiments was maintained at 305 K±1. The solutions were shaken in a mechanical rotary shaker at 225 rpm for 60 minutes to study the effect of pH, carbon dosage, concentration and particle size and then filtered and copper concentration was measured by spectrophotometer.

To examine the effect of pH, adsorption experiments were conducted at different pH ranging from 1 to 5 at 200 mg L-^{1} of Cu (II) solution. The optimum pH was determined from this study. [4]The adsorption studies were also conducted in batch experiments as function of adsorbent dosage (0.1g to 0.8g), metal ion concentrations (50,100,150,200,250,300mg L^{-1}) and particle size (75, 90, 150, 210 and 212 µm) for maximum adsorption.

The percentage of Cu(II) ions adsorption by SUC was computed using the equation:

$$\% \text{ adsorption} = \{C_i – C_e/ C_i \}*100 \quad \text{------------------(1)}$$

Where C_i and C_e are the initial and equilibrium concentration of Cu(II) ions (mgL^{-1}) in solution. Adsorption capacity was calculated by using the mass balance equation for the adsorbent

$$q= (C_i – C_e) V/W \qquad \text{----------------------(2)}$$

where q is the adsorption capacity (mg/g), C_i is the initial concentration of metal in solution (mg L^{-1}), C_e is the equilibrium concentration of metal in solution (g L^{-1}), V is the volume of metal ion solution (L) and W is the weight of the adsorbent (g).

3.Results and Discussion

3.1 Effect of pH

pH of the solution is the most important parameter affecting metal ion adsorption. This is because hydrogen ion competing with the positively charged metal ions on the active sites of the adsorbent[2]. The effect of pH on the adsorption of Cu(II) ions on SUC has been studied by varying it in the ranges of 1 to 5 as shown in fig (1). As shown in fig (1), the uptake of Cu(II) ions depends on pH, it increases with the increase in pH reaching the maximum adsorption at pH 5. Above pH 5 precipitation of Cu(II) ions occured.

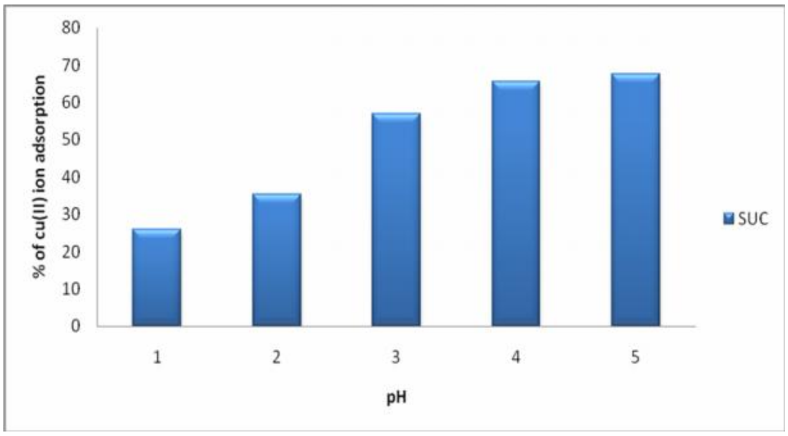

Fig. 1. Effect of pH on the adsorption of Cu(II) ions (initial concentration = 200 mg L^{-1}, temperature = 305 K, contact time = 60 min and adsorbent dosage = 4.0g/L)

3.2 Effect of Adsorbent Dosage

The adsorption studies of Cu(II) ions on SUC were done at 305 ± 1 K temperature by varying the quantity of adsorbent from 0.1 to 0.8g while keeping the volume of the metal solution constant at pH 4. The influence of adsorbent dosage in percent adsorption of Cu(II) ions is shown in fig (2).

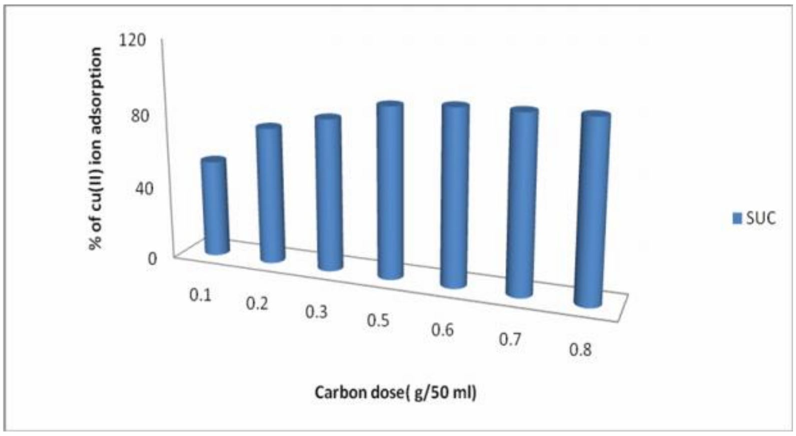

Fig. 2. Effect of adsorbent dosage on the adsorption of Cu(II) ions (initial concentration = 200 mg L^{-1}, temperature = 305 ± 1K, contact time = 60 min and pH 4.0)

The results from fig 2 indicates that the adsorption increased with the increase in the dose of the adsorbent. The increase in the adsorption percentage is due to the increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the adsorption sites.

3.3 Effect of Initial Cu(II) ion Concentration

In batch adsorption processes, the initial metal ion concentration of metal ions in the solution plays a key role as a driving force to overcome the mass transfer resistance between the solution and solid phase. The effect of initial metal ion concentration ranging from 100-300 mg/L^{-1}on SUC was studied by taking different concentrations of $CuSO_4$ solutions at pH 4, while keeping the dosage of the adsorbent 4g/L constant and temperature at 305± 1 K. This result is shown in fig (3)

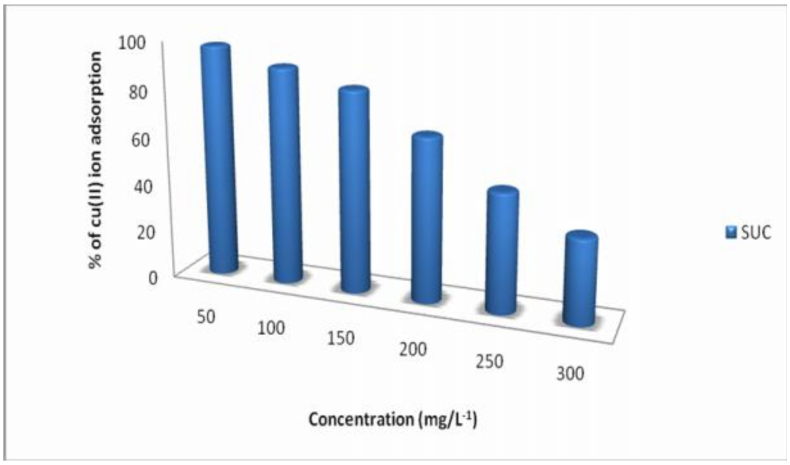

Fig. 3. Effect of initial metal concentration on the adsorption of Cu(II) ions (contact time = 60 min, pH 4.0,temperature = 305 ± 1 K, and adsorbent dosage = 4.0g/L)

It is indicated from the fig (3) that the percent adsorption decreases with the increase of initial metal ion concentration. As a result of the above observations, it is indicated that the adsorption process of Cu(II) ions on SUC has to be dependent on concentration of the metal ion solution up to some extent.

3.4 Effect of particle size

Surface area of the adsorbent is an important parameter for adsorption. Exposure of adsorbent sites for solid metal ion interaction is high if the surface area of adsorbent is high. Hence to study this parameter batch adsorption studies were done by using four different particle sizes of SUC such as 75, 90, 150, 210 and 212 µm.

The relationship between the size of the particles of the adsorbent and the corresponding metal ion removal percentage is illustrated in Fig 4 .

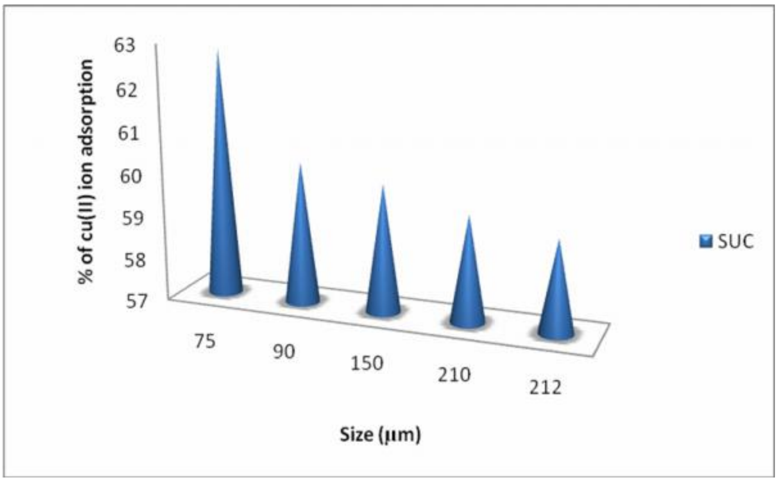

Fig. 4. Effect of particle size on the adsorption of Cu(II) ions (Initial concentration = 200 mg L^{-1}, contact time = 60 min, pH 4.0,temperature = 305 ± 1 K, and adsorbent dosage = 4.0g/L)

Fig 4 indicates that the percentage Cu(II) ion removal has increased with the decrease in particle size. As the particle size is smaller, the surface area per unit weight of adsorbent is larger and consequently the higher percentage of metal removal is noted. Hence maximum percentage of Cu(II) ions were removed by taking the adsorbent size of 75 µm. Hence for the entire study, SUC of 75 µm was used in order to produce effective adsorption process.

3.5 Adsorption Isotherm:

The equilibrium adsorption isotherms are of fundamental importance for the design of adsorption systems since they predict how metal ions will partition between adsorbent and liquid phases at equilibrium as a function of metal concentration.

The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. Langmuir and Freundlich isotherm are commonly used in batch adsorption studies. Hence these two isotherms have been analyzed for Cu(II) ion adsorption.

3.6 Langmuir Isotherm

This model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes [3]. The data of the equilibrium studies for adsorption of Cu(II) ions onto SUC may follow the following form of Langmuir model:

$$C_e/qe = (1 / Q_o) *C_e + 1/b\ Q_o \quad \text{----------(3)}$$

Where C_e is the equilibrium concentration (mg/dm^3); q_e is the amount of Cu(II) ions adsorbed at equilibrium (mg/g); Q_o and b are Langmuir constants related to adsorption capacity(mg/g) and energy of adsorption (dm^3/mg) which reflects quantitatively the affinity between the adsorbate and adsorbent. The values of Q_o and b can be obtained from the slope and intercept of a plot of C_e/qe against C_e respectively. Fig (5) shows Langmuir isotherm model for Cu(II) ions on SUC.

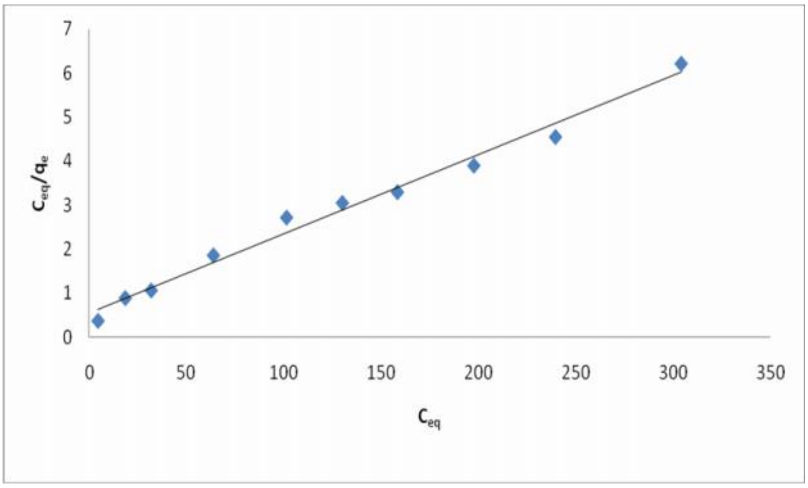

Fig. 5. Langmuir adsorption isotherm plot for the adsorption of Cu(II) ions at 305 K

Table 1: Langmuir adsorption isotherm parameters and correlation coefficients for the adsorption of Cu(II) ions on SUC at 305 K.

Langmuir Parameter	
Q_0	55.55556
b	0.032432
R^2	0.985

The high value of correlation coefficient R^2 from table 1 indicates that the adsorption of Cu(II) ion by SUC follows Langmuir isotherm model. The table 1 also gives information about the adsorption capacity (Q_0) and energy of adsorption b of SUC.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by[1], [4]

$$R_L = 1/ (1+bC_o) \quad \text{-------------(4)}$$

Where b is the Langmuir isotherm constant and C_o is the initial Cu(II) concentrations. R_L value indicate the type of isotherm. The adsorption process as function of R_L may described as [4]

$R_L > 1$ unfavourable, $R_L = 1$ Linear, $0 < R_L < 1$ favourable, $R_L = 0$ irreversible.

R_L values were calculated for SUC for the adsorption of Cu II) ion and are shown in fig (6).

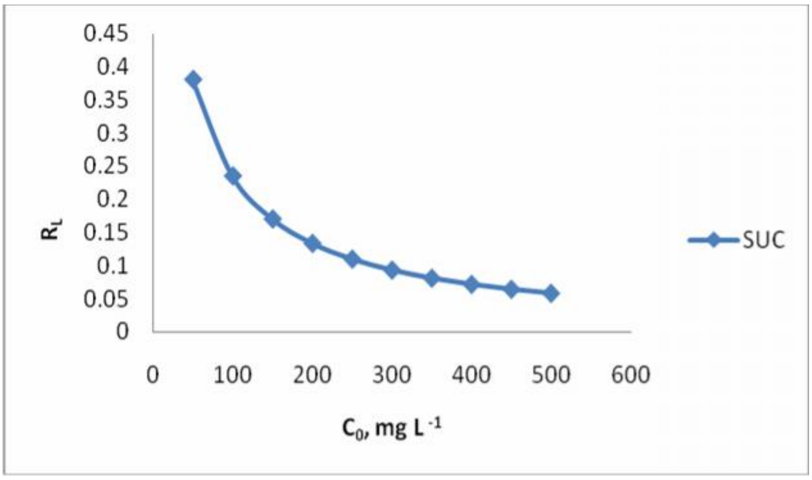

Fig. 6. Plot of R_L Vs. initial Cu(II) concentration

In the present study, the calculated R_L value for adsorption of Cu(II) ions on SUC obtained at 305 ±1 K based on Langmuir isotherm for the adsorption of Cu(II) ion onto SUC was found to be $0 < R_L < 1$ and this indicates a highly favourable adsorption within the concentration range of 50 – 500 mg L^{-1}

3.7 Freundlich model

The Freundlich model can be applied for non-ideal sorption on heterogenous surfaces and multilayer adsorption. It is expressed by the following equation

$$q_e = K_f C_e^{1/n} \quad \text{----------(5)}$$

The equation may be linerized by taking logarithms

$$\log (q_e) = 1/n \log C_e + \log(K_f) \quad \text{---------(6)}$$

The Freundlich intensity of adsorption (1/n) and adsorption capacity K_f were calculated from slope and intercept of the plot of log (q_e) against log (c_e) respectively which is shown in Fig (7).

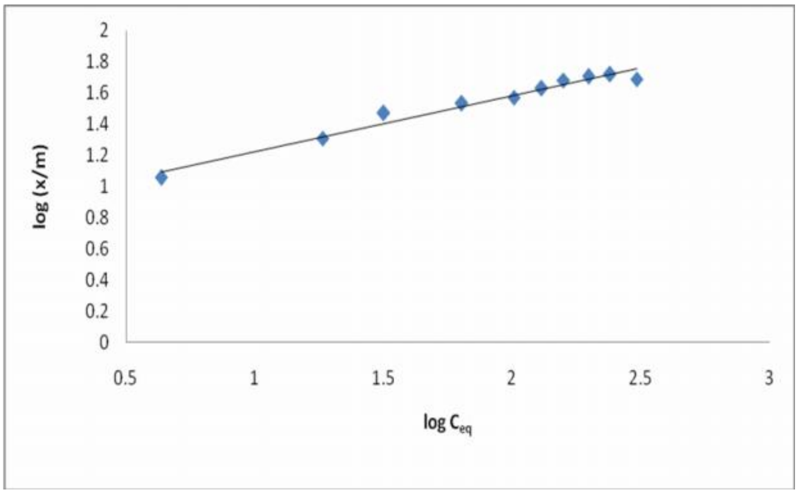

Fig. 7. Freundlich adsorption isotherm plot for the adsorption of Cu(II) ions at 305 K

Table 2: Adsorption isotherm model parameters and correlation coefficients for the adsorption of Cu(II) ions on SUC at 305 K.

Freundlich Parameters	
1/n	0.358
K_F (mg/g)	7.3621
R^2	0.970

From the table (2), the Freundlich constant, 1/n denoting the intensity of adsorption indicates a favourable adsorption since 1/n < 1, [5], [6] the adsorptions of Cu(II) ions onto SUC studied had been more favourable. The adsorption capacity (K_F) obtained for different adsorbents has been comparable, among them SUC shows highest value of adsorption capacity.

4.Conclusion

This work clearly indicates the potential of using carbonized senna uniflora(mill.) as an excellent adsorbent for the removal of Cu(II) ions from aqueous solutions. The amount of Cu(II) ions adsorbed onto the SUC increased with an increase in pH and dosage of adsorbent. The optimum pH was found as pH 5 for the removal of Cu(II) ions by SUC. The SUC of particle size 75 mμ was identified to bring about maximum adsorption percentage of Cu(II) ions. The equilibrium data was analyzed for the Langmuir and Freundlich isotherm model. Among these two isotherms, Langmuir isotherm fitted well with the experimental data than Freundlich isotherm This confirms the monolayer adsorption process. Taking into consideration of the above results, it can be concluded that the carbonized *senna uniflora(mill.)* is a suitable adsorbent for the removal of Cu(II) ions from aqueous solution in terms of low cost, natural and abundant availability.

Acknowledgement

Authors thank the Management of Bishop Heber College(Autonomous), Tiruchirappalli, Tamilnadu, India for providing laboratory facilities and also UGC for providing financial support.

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