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Research Article

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Kinetic and thermodynamic study of removal of copper from aqueous solution using *Senna uniflora (mill.)*

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ABSTRACT

The application of carbonized senna uniflora (mill.) as a biosorbent for the removal of copper ions from aqueous solutions was investigated. 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 kinetics tested with pseudo-first-order and pseudo- second- order models yielded high R^2 values. The thermodynamic parameters such as standard Gibb's free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were evaluated by applying the Van't Hoff equation. The thermodynamics of Cu(II) adsorption onto SUC indicates its spontaneous and endothermic nature. Desorption studies were done using various concentrations of HCl solution. HCl solution of higher concentration shows maximum desorption percentage. 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, Kinetics, Aqueous solution

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INTRODUCTION

Heavy metal pollution is an environmental problem of worldwide concern. The heavy metals, such as lead, copper, cadmium, zinc and nickel are among the most common pollutants found in industrial effluents. Even at low concentrations, these metals can be toxic to organism including humans[1]. 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.[2] 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 Cu(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.

EXPERIMENTAL SECTION

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 washed with distilled water repeatedly to remove the free acid completely. It was then kept in a hot air oven at 120 ^{0}C. The dried adsorbent material was sieved using nylon sieves of sizes <75 , 75-95, 95-150 and 150-210 µm . The particle size of <75µm 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.

RESULTS AND DISCUSSION

3.1 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 2.37 for all experiments.. The temperature of the experiments was maintained at 305 K±1 except for thermodynamic study. The solutions were shaken in a mechanical rotary shaker at 225 rpm for predetermined time.

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

$$\% \text{ adsorption} = \{C_i - C_e/ C_i \}*100 \qquad \text{-------------1}$$

Where C_i and C_e are the initial and equilibrium concentration of Cu(II) ions (mgL^{-1}) in solution. Adsorption capacity q_t, at specific time, t, was calculated by the following equation

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

where q_t 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).

3.2 Kinetic study

Kinetics of the adsorption process have been evaluated for this work. This study describes solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid liquid interface[3]. Kinetic experiments were conducted to assess the time taken for the equilibrium to be obtained. The adsorption plot reveals that the rate of percent adsorption of Cu(II) ions is initially high which is probably due to the availability of larger surface area of SUC for the adsorption of Cu(II) ions. As the surface adsorption sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior site of the adsorbent particles. In all subsequent experiments the equilibrium time is maintained at 240 min, which was considered sufficient for the removal of Cu(II) by SUC. The rate of kinetics on SUC was analyzed using pseudo-first-order, pseudo-second-order. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2)

3.3 Pseudo-first-order model

The pseudo-first order model was proposed by Lagergren in 1898 for the adsorption of solutes from a liquid. The rate equation is

$$dq/dt = k_1(q_e-q_1) \qquad \text{---------- (3)}$$

Integrating equation (1) and applying boundary conditions t=o to t= t and q=0 to q=q, the integrated form of equation (1) becomes

$$\text{Log}\ (q_e-q_t) = \log\ (q_e) - k_1 {*} t/2.303 \qquad \text{-------(4)}$$

where q_e is the amount of metal ion adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of metal ion adsorbent at a given time(mg/g) and k_1 is the rate constant (min^{-1}) of first order adsorption. This is the most popular form of pseudo-first order kinetic model equation. In order to obtain the rate constant, the straight line plots of log (q_e-q_t) against t, for different initial concentrations of Cu(II) ions have been analyzed (fig1 & 2). The rate constant (k_1), adsorption capacity (q_e) and correlation coefficient (R^2) values have been calculated from these plots and presented in table 1.

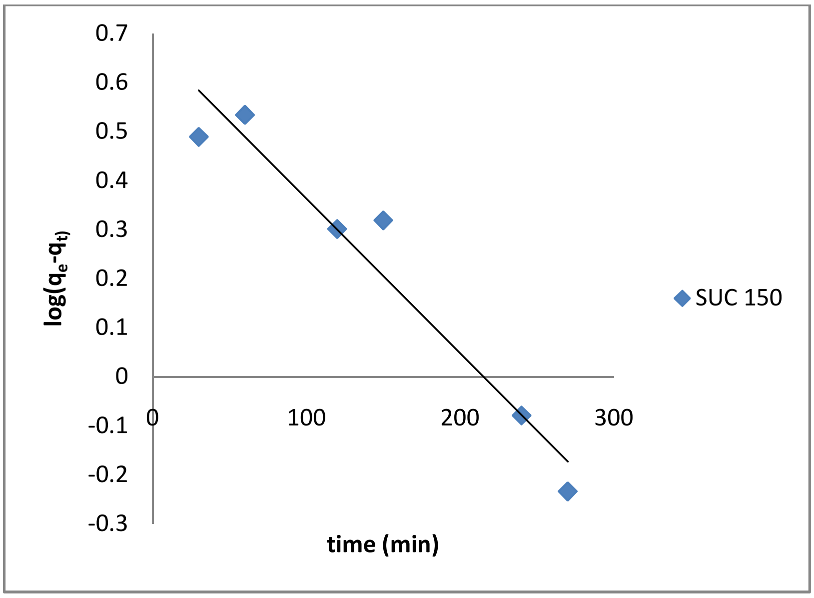

Fig. 1. Pseudo-first-order kinetic plots for the adsorption of Cu(II) ions at 305 K using 150 mg L^{-1} of copper solution

Table 1 Pseudo-first-order kinetic model for the adsorption of Cu(II) ions on SUC at 305 ±1 K.

Adsorbent	Cu (II) Conc(mg L^{-1})	q_e (mg/g)	K_1 X 10^{-2}	R^2
	150	4.7643	0.6909	0.943
	175	8.5901	1.3818	0.913

The table 1 indicates that the correlation coefficient R^2 in this model lies between 0.913 and 0.943.The equilibrium adsorption capacity q_e and rate constant K_1 increases with increase in concentration of copper solution. Therefore, it is predicted that pseudo-first-order kinetic model could be applied to the present study.

3.4 Pseudo-second order model

The rate constant for the adsorption of metal ion on SUC was determined by Lagergren equation. This equation modified by Ho and McKay and the differential equation for this reaction is

$$dq_t/dt = k_2\,(q_e - q_t)^2 \qquad \text{--------------(5)}$$

where k_2 is the second order rate constant of adsorption($gmg^{-1}min^{-1}$)

Integrating Equation(5) for the boundary conditions t=0 to t=t and q_t=0 to q_t= q_t,

$1/(q_e - q_{t)} = 1/ q_e + k_2t$ ---------------(6)

Equation (6) can be rearranged to obtain

$t/ q_t =1/ k_2q_e^2 +1*t/ q_e$ ---------------(7)

$h=k_2q_e^2$ -------------(8)

where, q_t and q_e are milligrams of solute adsorbed per gram of adsorbent at time t and at equilibrium respectively. k_2 is the rate constant of the second order adsorption. h is the initial sorption rate(mg/g min). It pseudo-second order kinetics is applicable, the plot of t/ q_t vs t of equation (7) should give a linear relationship and q_e and k_2 can be determined from the slope and intercept of the plot respectively. Figures (3) shows Pseudo-second order model for the adsorption of Cu (II) ions of concentrations 150 and 175 mg/L^{-1} on SUC at 305 K

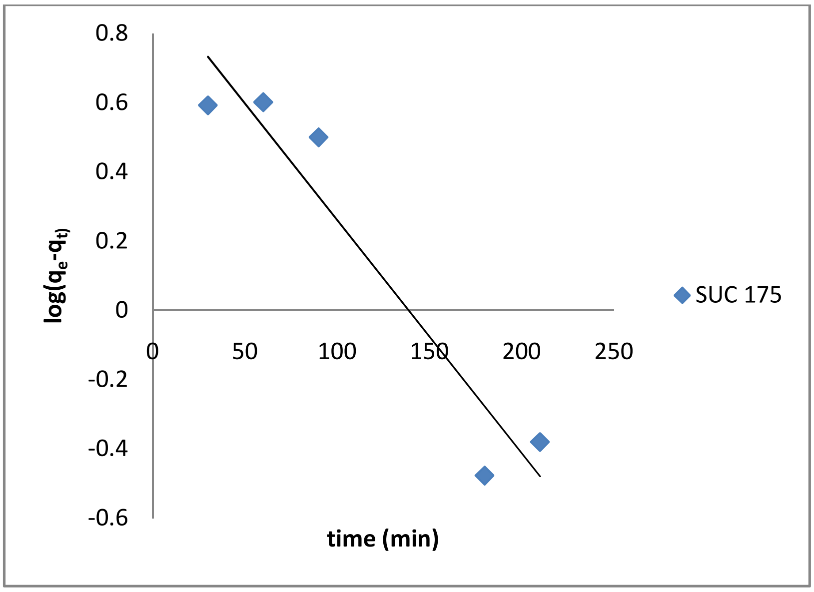

Fig. 2. Pseudo-first-order kinetic plots for the adsorption of Cu(II) ions at 305 K using 175 mg L^{-1} of copper solution

The values $K_{2,}$ h were calculated from the pseudo-second-order model and reported in table 2

Table 2 Pseudo-second-order kinetic model for the adsorption of Cu(II) ions on SUC at 305 K.

Adsorbent	Cu (II) Conc. (mg L^{-1})	q_e (mg/g)	K_2 (g/mg min) X 10^{-2}	h (mg/g min)	R^2
SUC	150	31.25	0.726241	7.092199	0.997
	175	32.25806	0.280994	2.923977	0.997

The correlation coefficient (R^2) values for this model is very high found i.e. R^2 = 0.997 which is very ideal correlation coefficient value to be a perfect model. Hence it can be established that the adsorption of Cu(II) ions onto SUC perfectly follow the pseudo-second-order kinetic model.

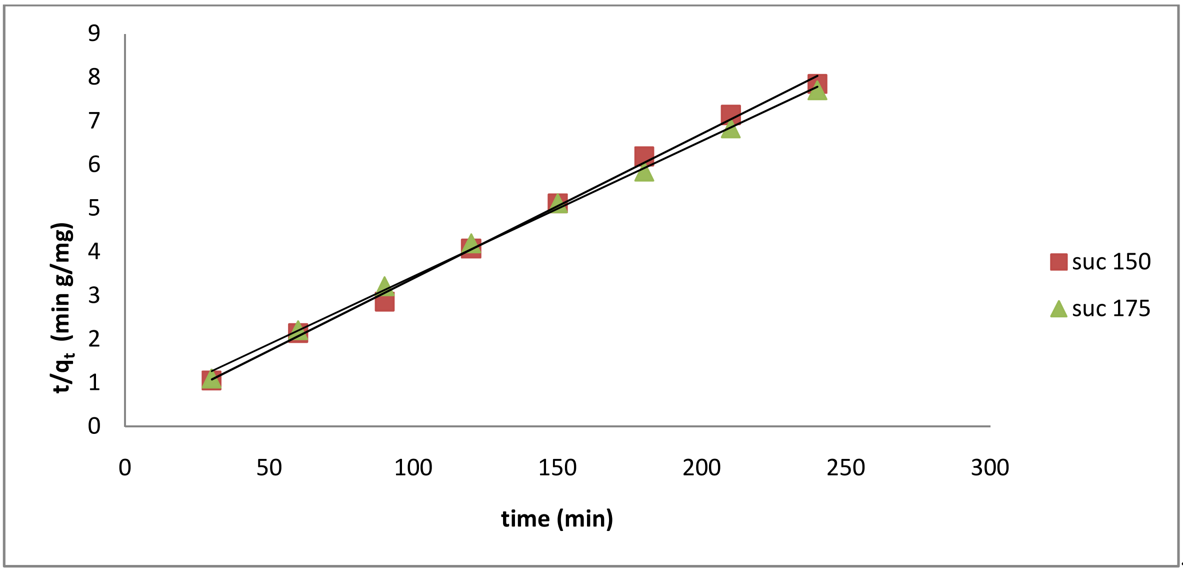

Fig. 3. Pseudo-second-order kinetic plots for the adsorption of Cu(II) ions at 305 K

3.5 Thermodynamic Parameters

According to the values of thermodynamic parameters, then spontaneity of adsorption process will be determined. ΔG^0 can be calculated using the reaction [2]:

$$\Delta G^0 = -RT \ln b \qquad \text{--------(9)}$$

ΔH^0 and ΔS^0 were calculated from the slope and intercept of the linear plot of ln b versus 1/T fig 4 according to the Van't Hoff equation. Obtained thermodynamic parameters are listed in table 3.

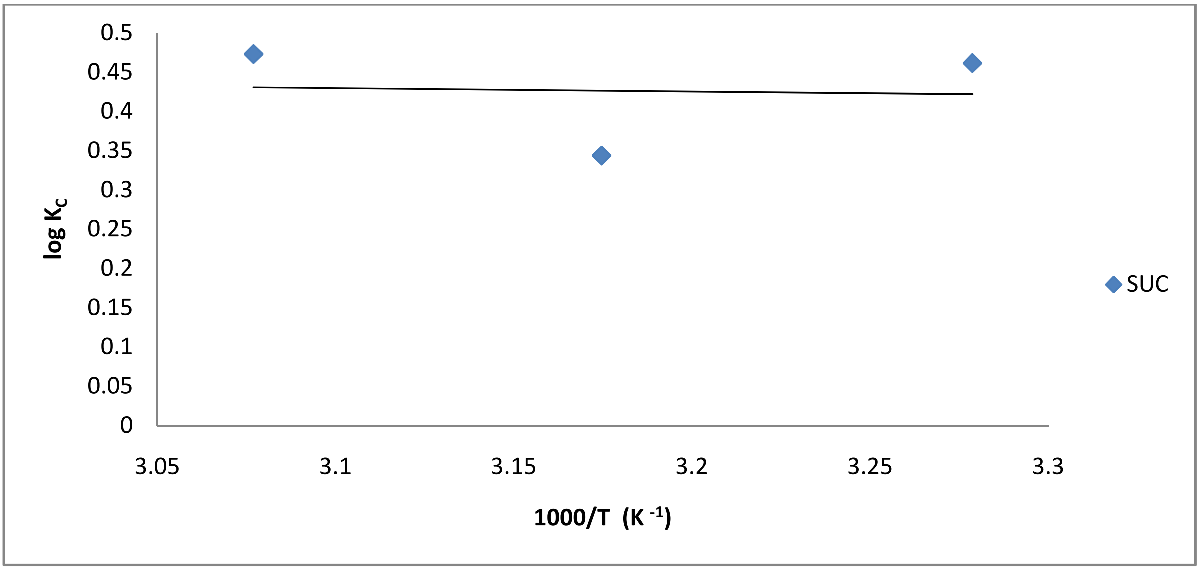

Fig. 4. Van't Hoff plot for the adsorption of Cu(II) ions by SUC

Table 3 Thermodynamic parameters for the adsorption of Cu(II) ions on SUC.

Adsorbent	T (Kelvin)	ΔG^O	ΔH^O	ΔS^O
SUC	305 ± 1	-2.69645	0.823327	10.81814
	315 ± 1	-2.00919		
	325 ± 1	-2.76334		

ΔH^0 was positive value, suggesting endothermic reaction. The positive value of ΔS^0 suggests the increased randomness at the solid/solution interface during the adsorption of Cu(II) onto SUC. The negative values ΔG^0 imply the spontaneous nature of the adsorption process. Further the decrease in the values of ΔG^0 with the increasing temperature indicates the adsorption was more spontaneous at higher temperatures. This indicates that a better adsorption is actually obtained at higher temperatures.

3.6 Desorption study

Desorption study help to elucidate the mechanism of adsorption and recover precious metals from wastewater and adsorbents[4]. The desorption of Cu(II) ions from SUC was performed using various solvents such as HCl, HNO_3, NaCl and EDTA to remove the bound Cu(II) ions[5]. The Cu (II) ion loaded adsorbent SUC after adsorption process was collected and gently washed with distilled water to remove any un-adsorbed Cu(II) ions. Then these adsorbents were dried and reused for batchmode desorption process. The result of the desorption studies is shown in fig (5)

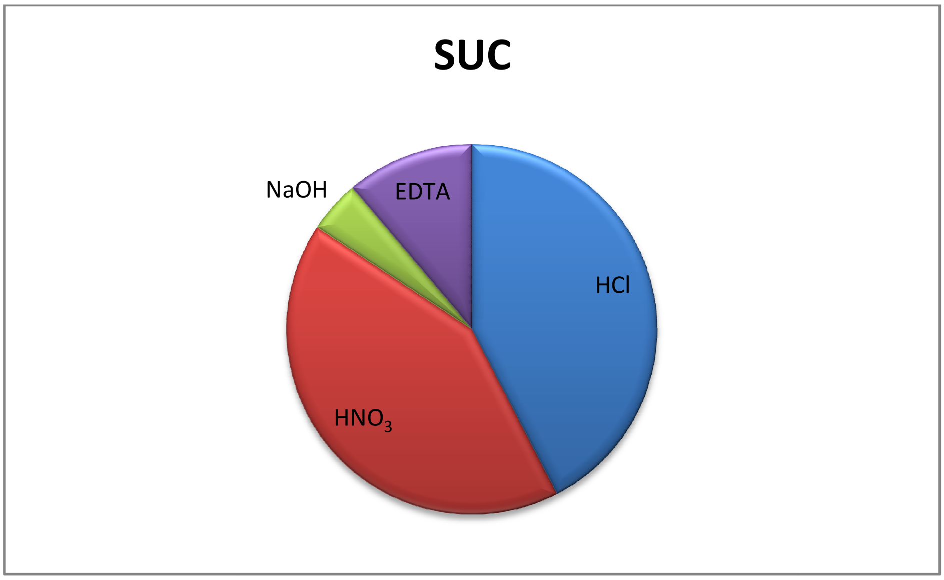

Fig. 5. Desorption efficiencies of Cu(II) ions from SUC by various solvents (HCl, HNO_3, NaOH and EDTA of 0.1M concentration)

From fig 5, it can be seen that NaOH and EDTA had the least percentage of desorption as compared with other solvents such as HCl and HNO_3. This is because NaOH and EDTA Can desorb Cu(II) ions that are weakly bonded to the surface of SUC. Therefore, only a small fraction of the Cu(II) ions held to the adsorbent are attached by weak bonds to sorption sites. The inorganic acids HCl and HNO_3 were found to desorb quite a high percentage of Cu(II) ions from SUC. This indicates that the adsorption of Cu(II) ions onto SUC is by ion exchange mechanism. This is confirmed by repeating the desorption test with different concentrations of HCl solutions. HCl of concentration 0.025M, 0.05 M and 0.1M were used as solvents for this test[6]. The result of this desorption analysis is shown in fig 6 and table 4.

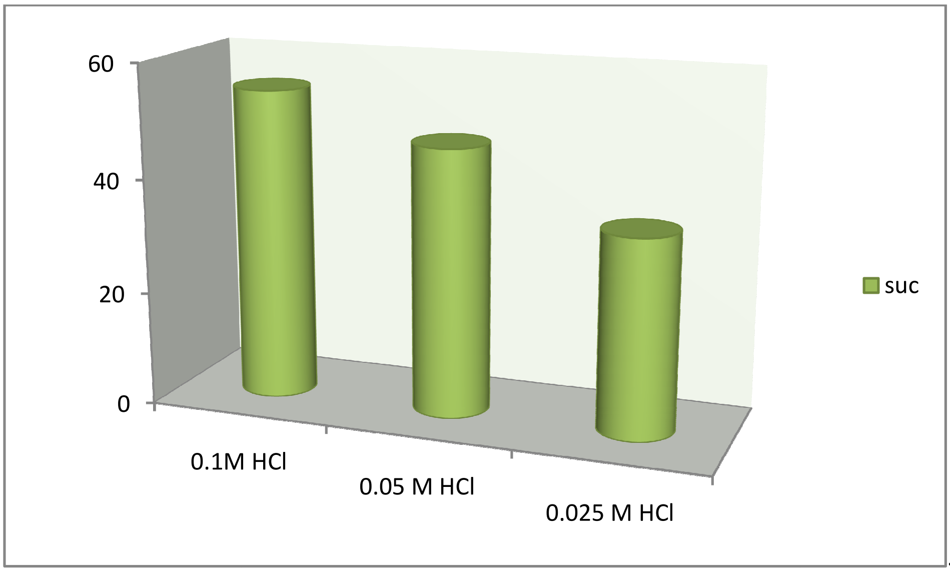

Fig. 6. Desorption efficiencies of Cu(II) ions from SUC by various concentrations of HCl (0.1M, 0.05 M and 0.025 M)

Table 4 Desorption of Cu(II) ions from SUC by various concentrations of HCl

% of desorption		
0.025M HCl	**0.05M HCl**	**0.1M HCl**
34.66981	46.93396	54.71698

From table 4 it is observed that the desorption percentage increased with increasing concentrations of HCl solution from 0.025M to 0.1M. The maximum desorption of Cu(II) ions took place using 0.1 M HCl. On increasing the concentration of HCl solution, the hydrogen ion concentration also increases which leads to increase in the exchange of hydrogen ion for Cu(II) ions in solution[5]. This confirms that the adsorption of Cu(II) ions onto SUC is by ion-exchange mechanism.

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 reaction rate increased with an increase in temperature. The kinetic studies indicated that the adsorption of Cu(II) ions on SUC followed both pseudo- first and pseudo-second-order models. Among these two models ,the best fit data was observed in pseudo-second-order model than first-order model. The adsorption dynamic studies indicated that the negative value of ΔG^0 and positive value of ΔH^0 obtained confirms that Cu adsorption is a spontaneous and an endothermic process. From this study, recovery of Cu(II) from used SUC was efficient using various concentrations of HCl. On increasing the concentration of HCl , the desorption percentage also increases. The overall results indicated 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.

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