Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(12):654-664

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Mechanistic studies of copper (II) ion adsorption on activated *Hibiscus sabdariffa* stem nano carbon

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ABSTRACT

An adsorbent prepared from Hibiscus Sabdariffa Stem, by acid treatment was tested for its efficiency in removing copper ion. The process parameters studied include agitation time, initial copper (II) ion concentration, adsorbent dose, pH and temperature. The adsorption followed second order reaction equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from the Langmuir isotherm plot at an initial pH of 6.5 and at 30, 40, 50, 60 ± 0.5 ^{0}C. The influence of pH on metal ion removal was significant and the adsorption was increased with increase in temperature. A portion of the Copper (II) ion was recovered from the spent AHSNC using 0.1M HCl.

Key words: Acid Activated Hibiscus Sabdariffa Stem Nano Carbon (AHSNC), Copper (II) ion, Adsorption isotherm, Equilibrium, Thermodynamic parameters, Intra-particle diffusion.

INTRODUCTION

Heavy metal pollution of water and water bodies is a serious environmental problem that affects the quality of water. The consequences are decreasing water supply, increase in cost of purification, eutrophication of water bodies and decrease in aquatic production [1]. In order to tackle the menace poise by heavy metal pollution of water, several options have been adopted. These include oxidation and reduction, chemical precipitation, filtration, electrochemical treatment, ion exchange, membrane separation, reverse osmosis, adsorption, evaporation and electrolysis [2]. However, adsorption has been proven to be one of the best options available for the removal of heavy metals from aqueous solution [3, 4]. In view of the above, several researches have been conducted using various materials as adsorbents [5]. However, some of these adsorbents also contain other toxicants; some are expensive and are characterized with limited surface area for adsorption.

A search of literature revealed that fruit stone has been used for adsorption of some heavy metals from aqueous solution but literature is scanty on the use of activated carbon produced from fruit stone for the adsorption of Pb (II) and Cu (II) ions from aqueous solution. Therefore, the objective of the present study is to investigate the possibility of using AHSNC as an adsorbent for the removal of Cu (II) ions from aqueous solution.

EXPERIMENTAL SECTION

Adsorbent

The *Hibiscus Sabdariffa Stem* collected from nearby Thiruvarur district was carbonized with concentrated Sulphuric acid and washed with water and activated around 1100°C in a muffle furnace for 5 hrs then it was taken out, ground well to fine powder and stored in a vacuum desiccators.

Chemicals

All chemicals used of high purity commercially available Analar grade. 1000 mg/L of stock solution of Copper (II) was prepared by dissolving accurately weighed 3.9296 gram of Copper (II) sulphatepentahydrate in 1000 ml distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentration. The pH of each experimental solution was adjusted to the required initial pH value using dilute HCl (or) NaOH before mixing the adsorbent. The concentration of residual Copper (II) ion was determined with UV-visible spectrophotometer (Systronics 2203).

Batch Experiments

The effect of various parameters on the removal of Copper (II) ion onto AHSNC was studied batch adsorption experiments were conducted at (30-60°C). For each experimental run, 50 ml of Copper (II) solution of known initial concentration and pH were taken in a 250 ml plugged conical flask. A 25 mg adsorbent dose is added to the solution and mixture was shaken at constant agitation speed (150 rpm) sample were withdrawn at appropriate time intervals (10-60 min) and the adsorbent was separated by filtration. The residual solutions were analyzed to determine the Copper (II) ion concentration.

The effect of dosage of adsorbent on the removal of Copper (II) ion was measured by contacting 50 ml of 50 mg/L of Copper (II) ion solution with 25 mg to 250 mg of AHSNC till equilibrium was attained. Adsorption equilibrium isotherm is studied using 25 mg of AHSNC dosage per 50 ml of Copper (II) ion solution. The initial concentration were ranged from (25 to 125 mg/L) in all sets of experiments. The plugged conical flask was shaken at a speed of 150 rpm for 60 minutes. Then the solution was separated from the mixture and analyzed for Copper (II) ion concentration. The adsorption capacity was calculated by using a mass equilibrium equation as follows:

$$q_e = (C_0 - C_e)\, V/M \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, C_0 and C_e being the initial Copper (II) ion concentration (mg/L) and equilibrium concentration, respectively V is the experimental volume of Copper (II) ion solution expressed in liters [L] and M is the adsorbent mass expressed in grams [g]. The Copper (II) ion percentage can be calculated as follows:

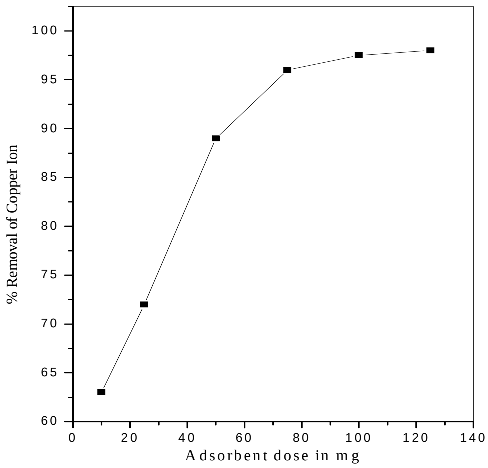
$$\%R = (C_0 - C_t) \times 100/C_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The effect of pH on the rate of adsorption was investigated using Copper (II) concentration of 25 mg/L constant AHSNC dosage. The pH values were adjusted with dilute HCl and NaOH solution. The adsorbent – adsorbate mixture was shaken at room temperature using agitation speed (150 rpm) for 60 minutes. Then the concentration of Copper (II) ion solution was determined.

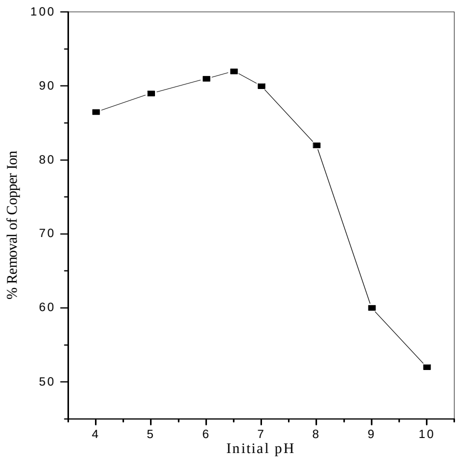
RESULTS AND DISCUSSION

Effect of agitation time and initial Copper (II) ion concentration:
The kinetics of adsorption of Copper (II) ion by AHSNC is shown in **Figure.1** with smooth and single plots indicating monolayer adsorption of metal ion on the AHSNC. The removal of metal ion increased with the lapse time and attains equilibrium in 60 min for 50 mg/ L. With increase in metal ion concentration from 25 to 125 mg/L, the amount of metal ion adsorbed increased while the percent removal decreased, The experimental results of adsorptions at different concentrations collected in **Table 1** observed that percent adsorption decreased with increase in initial indicating that the metal ion removal by adsorption on AHSNC concentration dependent[6].

Effect of AHSNC mass:
The amount of Copper (II) ion adsorption increased with the increase in AHSNC dose and reached a maximum value after a particular dose (**Fig.2)**. Taken an initial metal ion concentration of 50 mg/L, complete metal ion removal was obtained at a maximum AHSNC dose of 125 mg. The increase in the adsorption of metal ion with AHSNC dose was due to the introduction of more binding sites for adsorption and the availability more surface area[7].



Fig;2- Effect of Adsorbent dose on the removal of Copper Ion
[Cu]=50mg/L;Contact Time 60min;Temprature 30^{0}C



Fig;3- Effect of Initial pH on the removal of Copper Ion
[Cu]=50 mg/L;Temprature 30^{o}C;Adsorbent dose=25mg/50ml

Effect of pH:
The experience carried out at different pH show that there was a change in the percent removal of metal ion over the entire pH range shown in **Fig. 3**. This indicates the strong force of interaction between the metal ion and AHSNC that either H^+ or OH^- ions could influence the adsorption capacity. In other words, the adsorption of metal ion on AHSNC does involve ion exchange mechanism that have been an influence on the metal ion adsorption while varying the pH. This observation is in line with the type I and II isotherm and positive $\triangle H^0$ value obtained, which indicates irreversible adsorption probably due to polar interactions[8].

Effect of other ions:
The effect of other ions like Ca^{2+} and Cl^- on the adsorption process studied at different concentrations. The ions added to 50mg/L of metal ion solutions and the contents were agitated for 60 min at 30^0C. The results had shown in the **Fig. 4** reveals that low concentration of Cl^- does not affect the percentage of adsorption of metal ion on AHSNC, because the interaction of Cl^- at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion Ca^{2+} increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases that, decreases the percentage adsorption. The interference was more in the presence of Ca^{2+} compared with Cl^- ion. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbentand increase the affinity of the sorbent for such ions[9].

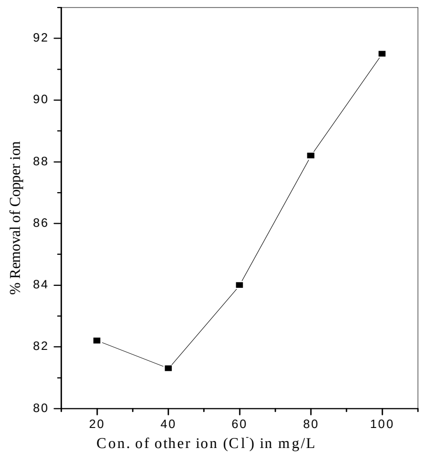


Fig.4-Effect of ionic strength on the adsorption of Copper ion
[Cu]=50 mg/L;pH=6.5;Dose=25mg/50 ml

Effect of temperature:
The adsorption capacity of AHSNC increased with increase in the temperature of the system from 30 to 60^0 C. Thermodynamic parameters such as change in free energy ($\triangle G^0$), enthalpy ($\triangle H^0$) and entropy ($\triangle S^0$) were determined using the following equations.

$$K_0 = C_{solid}/C_{liquid} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$
$$\triangle G^0 = -RT \ In \ K_0 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$
$$\log K_0 = \triangle S^0/(2.303R) - \triangle H^0/(2.303RT) \ldots (5)$$

Where K_0 is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. $\triangle H^0$ and $\triangle S^0$ were obtained from the slope and intercept of van't Hoff plot and are presented in Table 4. Positive value of $\triangle H^0$ shows the endothermic nature of adsorption. This rules the possibility of both physical as well as chemical adsorption. Because in the case of physical adsorption alone, while increasing the temperature of the system the extent of metal ion adsorption decreases, as desorption increases with temperature[5]. As chemisorptions is mainly an irreversible process, the low positive $\triangle H^0$ value depicts that Copper (II) ion is both physically as well as chemically adsorbed onto AHSNC. This is in agreement with the type I and II isotherm obtained, which is close to irreversible adsorption [10].

The negative values of $\triangle G^0$ (Table 4) indicate that the metal ion adsorption is spontaneous. The positive value of $\triangle S^0$ shows increased randomness at the solid-solution interface during the adsorption of metal ion on AHSNC. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules thus allowing the prevalence of randomness in the system. Enhancement of adsorption capacity of AHSNC at higher temperatures may be attributed the enlargement of pore size and/or activation of the adsorbent surface [11].

Adsorption Isotherms

Freundlich isotherm

The linear form of Freundlich isotherm [12] is represented by the equation

$$\log q_e = \log K_f + (1/n)\log C_e \quad \ldots\ldots\ldots\ldots(6)$$

Where q_e is the amount of Cu (II) ions adsorbed per unit weight of the sorbent (mg/L), K_f is a measure of adsorption capacity and 1/n is the adsorption intensity. The value of K_f and n are calculated from the intercept and slope of the plot of log q_e vs log C_e respectively. The constant K_f and n values are given in the**Table-2.** In general K_f value increases the adsorption capacity for a given adsorbate increase.

The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The value of n>1 represents favorable adsorption condition(or) the value of 1/n are lying in the range of 1 to 10 confirms the favorable condition for adsorption. The adsorption co-efficient K_f of Copper (II) on AHSNC was found to be around 5.6 L/g. The K_f values indicates that the saturation time for adsorption of metal ion is attained quickly slue to high affinity of AHSNC towards adsorbate, while low K_f values indicates low adsorption rate of copper ion [13]. The values of 1/n were around 3.0 (mg/L) for Copper (II) ions. The high values of 1/n signifies that the forces which are exerted on the surface of AHSNC during metal ion adsorption are strong rate from the values K_f and 1/n it is reveals that AHSNC is more efficient for removal of Copper (II) ions.

Langmuir isotherm

The Langmuir isotherm model [14] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

$$C_e/q_e = (1/Q_m b) + (C_e/Q_m) \quad \ldots\ldots\ldots\ldots(7)$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate per unit mass of adsorbent, Q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. Q_m is the amount of adsorbate at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption (or rate of adsorption). The linear plot of specific adsorption capacity C_e/q_e against the equilibrium concentration (C_e). The Langmuir constant Q_m and b were determined from the slope and intercept of the plot and are presented in table 2. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L [15]. By the equation

$$R_L = (1/(1+bC_o)) \quad \ldots\ldots\ldots\ldots(8)$$

Where, C_o (mg/L) is the highest initial concentration of adsorbent and b (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

$R_L > 1$	Unfavorable adsorption
$0 < R_L < 1$	Favorable adsorption
$R_L = 0$	Irreversible adsorption
$R_L = 1$	Linear adsorption

The R_L values between 0 to 1 indicate favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L values are given in the **Table 3.** The values of b were increased with increasing the concentration of Copper (II) ion.High b values indicate high adsorption affinity the monolayer saturation capacity Q_m were around 185 mg/L for AHSNC**.**

Thermodynamic treatment of the adsorption process
Thermodynamic parameters associated with the adsorption, via standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant, K_0 is given by the equation

$$\Delta G° = -RT \ln K_0 \ldots\ldots\ldots\ldots (9)$$

Where, ΔG° is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant(8.314 J mol/K).The adsorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot of $\ln(q_e/C_e)$ against C_e at different temperature and extrapolating to zero C_e according to the method suggested by Khan and Singh [16] The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature,

$$\ln K_0 = (\Delta H^o/RT)+(\Delta S^o/R) \ldots\ldots\ldots\ldots(10)$$

Where, ΔH° is the standard heat change of sorption (kJ/mol) and ΔS° is standard entropy change (kJ/mol). The value of ΔH° and ΔS° can be obtained from the slope and intercept of plot of $\ln K_0$ against 1/T. The value of thermodynamic parameter calculated from equation 9 and 10 are shown in table 4. The thermodynamic treatment of the sorption data indicates that ΔG° values were negative at all temperature. The results point out that physisorption is much more favorable for the adsorption of Cu (II) ions. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption [17]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of metal ion adsorption increases, this rules out the possibility of chemisorptions. The low ΔH° value depicts metal ion is physisorbed onto adsorbent AHSNC.

The negative $\Delta G^°$ values table 4 were conform the spontaneous nature of adsorption Cu (II) ions onto AHSNC**.** The lesser values of $\Delta G^°$ suggest that adsorption is physical adsorption process. The positive value of $\Delta H^°$ further confirms the endothermic nature of adsorption process. The positive values of $\Delta S^°$ in **Table 4,** showed increased randomness of the solid solution interface during the adsorption of Copper (II) ion onto AHSNC.

Adsorption kinetics
The study of adsorption dynamics describes the solute up take rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface [18] .The kinetics of Cu (II) ions adsorption on the AHSNC were analyzed using pseudo second-order, Elovich and intra-particle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation co- efficient (γ) and the values are close or equal to 1. A relatively high correlation coefficient (γ) value indicates that the pseudo second-order model successfully describes the kinetics of Cu (II) ions adsorption.

The pseudo second- order equation
The pseudo second-order adsorption kinetic rate equation is expressed as

$$dq_t/d_t = k_2(q_e-q_t)^2 \ldots\ldots\ldots\ldots(11)$$

Where, K_2 is the rate constant of pseudo second- order adsorption (g mg/min). For the boundary conditions t = 0 to t= t and $q_t = 0$ to $q_t = q_t$ the integrated form of Eq. (9) becomes:

$$1/(q_e - q_t) = 1/q_e + K_2 t \ldots\ldots\ldots\ldots (12)$$

This is the integrated rate law for a pseudo second-order reaction. Equation (12) can be rearranged to obtain Eq.(13),which has a linear form:

$$t/q_t=(1/k_2 q_e^2)+ ((1/q_e)t \ldots\ldots\ldots\ldots(13)$$

If the initial adsorption rate (h)(mg $g^{-1}min^{-1}$) is :

$$h=k_2q_e^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Equation (11) and (12) becomes,

$$t / q_t = 1 / h + 1 / q_e\, t \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

The plot of (t/q_t) and t of Eq. (15) gives a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The pseudo-second order rate constants k_2, the calculated h values, and the correlation coefficients (γ) are summarized in Table 5. At all studied initial Copper (II) ion concentrations, the straight lines with extremely high correlation co-efficient (>0.99) were obtained. From table 5, the values of the rate constant k decrease with in increasing initial Copper (II) ion concentration for AHSNC. This is shows that the sorption of Cu (II) ions on AHSNCfollows pseudo second order kinetic model.

The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t / d_t = \alpha \exp(-\beta q_t) \ldots\ldots\ldots(16)$$

Where, α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation. Chien and Clayton [19] assumed αβt>>t and by applying boundary conditions $q_t = 0$ at t= 0 and $q_t = q_t$ at t = t Eq.(12) becomes:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \ldots\ldots\ldots\ldots\ldots (17)$$

Since Cu (II) ions adsorption fits with the Elovich model, a plot of q_t vs. ln(t) yields a linear relationship with a slope of (1/β)and an intercept of (1/β)ln (αβ). The Elovich model parameters α, β, and correlation coefficient (γ) are summarized in table 5. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second–order kinetics models. This may be due to increase the pore or active site on the AHSNC adsorbent.

The intra particle diffusion model

The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris[20] based on the following equation for the rate constant:

$$q_t = k_{id}\, t^{(1/2)} + C \ldots\ldots\ldots\ldots\ldots\ldots(18)$$

Where, k_{id} is the intra-particle diffusion rate constant (mg/g/min) and C is the constant. Since the rate limiting step is intra-particle diffusion, the graph drawn between (q_t) (mg/g) verses square root of the contact time ($t^{1/2}$) yields a straight line passing through the origin. The slope gives the value of the intra-particle diffusion coefficient (k_{id}) and correlation coefficient (γ) indicate the fitness of this model. The value of C gives an idea about the thickness of the boundary layer. The intercept value indicate that the line were not passing through origin, there are some other process affect the adsorption. But the correlation coefficient (γ) value is very high, so that the intra-particle diffusion takes place along with other process that may affect the adsorption. The values are given in **Table 5**.

Desorption studies:

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. If the adsorbed metal ions can be desorbed using neutral pH water, then the attachment of the metal ion of the adsorbent is by weak bonds. The effect of various reagents used for desorption studies. The results indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed metal ion. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the AHSNC through physisorption as well as by chemisorptions mechanisms.

TABLE1. EQUILIBRIUM PARAMETERS FOR THE ADSORPTION OF COPPER (II) ION ONTO AHSNC

M_0	Ce (mg / L)				Qe (mg / L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	0.5647	0.4907	0.4274	0.3882	48.8706	49.0187	49.1452	49.2236	97.741	98.037	98.290	98.447
50	2.6732	2.3598	1.9375	1.6349	94.6536	95.2804	96.1249	96.7302	94.654	95.280	96.125	96.730
75	5.981	5.283	4.612	4.019	138.038	139.435	140.776	141.961	92.025	92.957	93.851	94.641
100	11.635	10.750	4.612	8.896	176.730	178.501	190.776	182.209	88.365	89.250	95.388	91.104
125	18.156	17.035	9.819	14.886	213.689	215.930	230.362	220.228	85.475	86.372	92.145	88.091

TABLE 2.LANGMUIR AND FREUNDLICH ISOTHERM PARAMETER FOR THE ADSORPTION OF COPPER (II) ION ONTO AHSNC

Temp. (°C)	Langmuir Parameters		Freundlich Parameters	
	Q_m	B	K_f	n
30°C	247.24	0.2656	62.627	2.3457
40°C	247.38	0.3036	66.705	2.3843
50°C	294.31	0.3052	73.779	1.9873
60°C	247.12	0.4144	75.790	2.4425

TABLE 3. DIMENSIONLESS SEPERATION FACTOR (R_L) FOR THE ADSORPTION OF COPPER (II) ION ONTO AHSNC

(C_i)	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.0700	0.0618	0.0615	0.0460
50	0.0363	0.0319	0.0317	0.0236
75	0.0245	0.0215	0.0214	0.0158
100	0.0185	0.0162	0.0161	0.0119
125	0.0148	0.0130	0.0129	0.0096

TABLE 4. THERMODYNAMIC PARAMETER FOR THE ADSORPTION OF COPPER (II) ION ONTO AHSNC

(C_0)	ΔG°				ΔH°	ΔS°
	30°C	40°C	50°C	60°C		
25	-9490.9	-10177.7	-10880.3	-11488.0	10.807	67.035
50	-7239.5	-7820.1	-8623.1	-9377.6	14.615	71.951
75	-6161.3	-6714.0	-7318.8	-7949.2	11.914	59.589
100	-5107.46	-5507.9	-8135.0	-6440.9	15.578	68.793
125	-4464.90	-4805.2	-6611.9	-5540.13	11.188	52.024

TABLE 5. THE KINETIC PARAMETERS FOR THE ADSORPTION OF COPPER (II) ION ONTO AHSNC

C_0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
25	**30**	50.344	0.0091	0.9908	23.1081	2211324	0.3641	0.9791	0.0587	0.9884	1.8833
	40	50.415	0.0094	0.9929	23.9904	5052320	0.3812	0.9812	0.0558	0.9905	1.8895
	50	50.469	0.0099	0.9900	25.1652	12043615	0.3990	0.9783	0.0531	0.9876	1.8954
	60	50.572	0.0098	0.9911	24.9794	9204893	0.3924	0.9794	0.0539	0.9887	1.8947
50	**30**	97.362	0.0049	0.9902	46.0252	6954177	0.1936	0.9785	0.0570	0.9878	1.8722
	40	97.987	0.0048	0.9913	46.3642	9416204	0.1957	0.9796	0.0559	0.9889	1.8767
	50	98.758	0.0050	0.9904	48.9173	16360127	0.1998	0.9787	0.0542	0.9880	1.8839
	60	99.454	0.0050	0.9925	49.0114	11820181	0.1948	0.9808	0.0553	0.9901	1.8851
75	**30**	142.162	0.0032	0.9906	64.9030	7023515	0.1299	0.9789	0.0582	0.9882	1.8577
	40	143.434	0.0033	0.9899	67.9524	11075470	0.1320	0.9782	0.0567	0.9875	1.8649
	50	144.867	0.0034	0.9899	70.648	13999204	0.1322	0.9782	0.0560	0.9875	1.8711
	60	145.713	0.0028	0.9918	59.2016	40289310	0.1411	0.9801	0.0521	0.9894	1.8749
100	**30**	182.230	0.0024	0.9901	79.8875	4881656	0.0978	0.9784	0.0605	0.9877	1.8359
	40	183.972	0.0024	0.9912	81.4203	5976928	0.0980	0.9795	0.0598	0.9888	1.8414
	50	185.818	0.0024	0.9923	83.4851	7269610	0.0981	0.9806	0.0591	0.9899	1.8473
	60	187.562	0.0025	0.9914	89.324	12537090	0.1000	0.9797	0.0572	0.9890	1.8557
125	**30**	220.503	0.0019	0.9938	94.6630	4275167	0.0793	0.9821	0.0618	0.9914	1.8191
	40	222.818	0.0019	0.9939	94.5267	3870831	0.0780	0.9822	0.0622	0.9915	1.8227
	50	225.430	0.0018	0.9925	91.2575	2331382	0.0747	0.9808	0.0644	0.9901	1.8230
	60	227.167	0.0019	0.9932	97.4180	3965584	0.0764	0.9815	0.0622	0.9908	1.8313

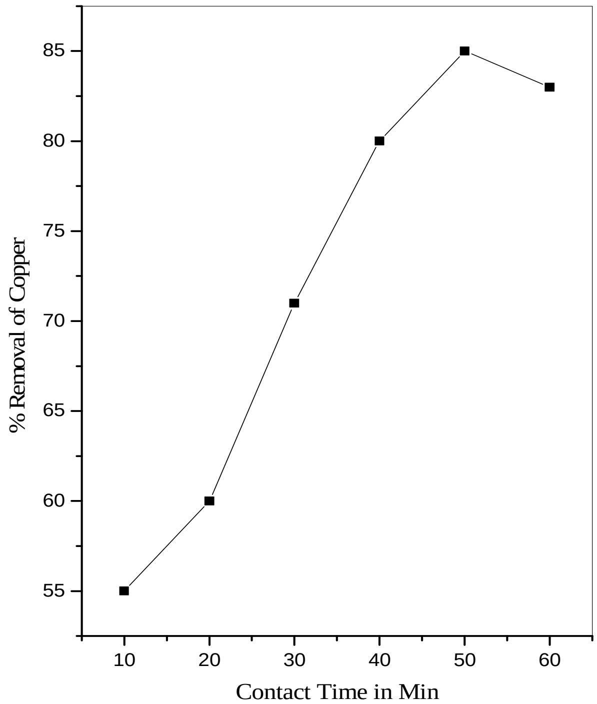
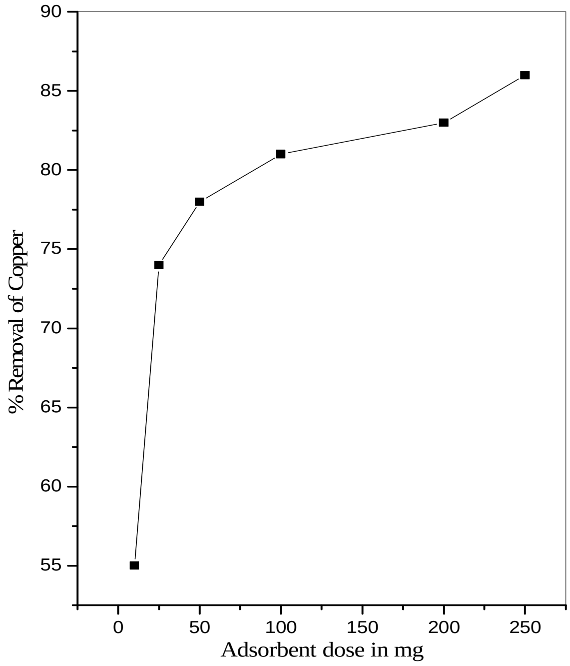
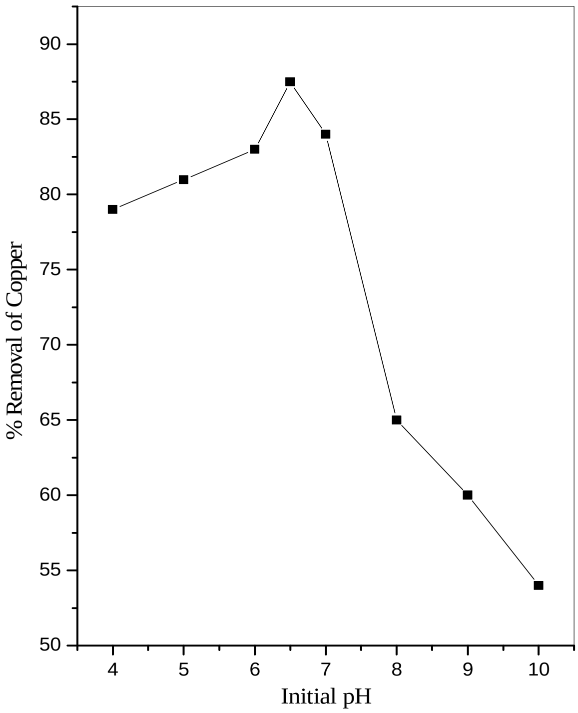


Fig:1- Effect of Contact Time on the Removal of Copper Ion
[Cu]=50 mg/L;Temprature 30^{o}C;Adsorbent dose=25mg/50ml



Fig;2- Effect of Adsorbent dose on the removal of Copper Ion
[Cu]=50mg/L;Contact Time 60min;Temprature 30^{0}C



Fig;3- Effect of Initial pH on the removal of Copper Ion
[Cu]=50 mg/L;Temprature 30^{o}C;Adsorbent dose=25mg/50ml

CONCLUSION

AHSNC prepared from *Hibiscus Sabdariffa Stem* was found to be effective in removing Copper (II) ion from aqueous solution. The adsorption is faster and the rate is mainly controlled by intra-particle diffusion. Using the sorption equation obtained from the Langmuir and Freundlich isotherms, it was found that AHSNC is an effective one for the removal of metal ion. The equilibrium data conformed well to the Langmuir and Freundlich isotherm models. The temperature variation study showed that the metal ion adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the metal ion solution. pH dependent results and desorption of metal ion in mineral acid suggest that the adsorption of metal ion on AHSNC involves chemisorptions as well as physisorption mechanism.

Acknowledgement:
The authors express sincere thanks to the Principal, Thiru. Vika. Govt. Arts College, Kidarankondan, Thiruvarur, Tamilnadu, India for the successful completion of this research work.

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