Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(3):732-740

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Equilibrium and kinetics study for the removal of copper from aqueous solution by activated carbon derived from *Annona squmosa* seed

Renukadevi C.[1], Santhi T.[2*]and Makeswari[2]

[1]*Department of Chemistry, Excel College of Engineering and Technology,Komarapalayam, Namakkal, Tamil Nadu, India*
[2]*Department of Chemistry Karpagam University, Coimbatore, India*

ABSTRACT

Activated carbon prepared from Annona squmosa seed for the removal of copper from aqueous solutions has been studied. Parameters such as equilibrium time, effect of pH, effect of metal ion concentration and adsorbent dose on removal were studied. The adsorbent exhibited good sorption potential for copper at pH 6.0. The adsorption followed the pseudo-second-order rate equation and fits the Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Tempkin equations well. The maximum adsorption capacity of copper was calculated from Langmuir isotherm and found to be 19.5 mg/g. The desorption studies were carried out using dilute hydrochloric acid solution and maximum desorption of 90% for copper occurred at solution pH.

INTRODUCTION

Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms [1]. Copper pollution arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu-based agri-chemicals.Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic [2] and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [3]. Copper sulphate is used widely as an algicide in ornamental ponds and even in water supply reservoirs, which are affected by blooms of blue-green alge [4]. Maximum acceptable copper concentration in drinking water is less than 3000_g/dm3 [5,6].The conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. Among all the methods adsorption is highly effective and economical.Though the use of commercial activated carbon is a well known adsorbent for the removal of heavy metals from water and wastewater, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence, it is a growing need to derive the activated carbon from cheaper and locally available waste materials. Several research workers used different low-cost adsorbents from agriculture wastes such as coconut coirpith [8], sawdust [3], rice husk [9], banana pith [10], cottonseed hulls [11], apple wastes [12], sugarcane bagasse pith[13], peanut hull carbon [14], activated carbons obtained from agricultural by-products [15] and Mn-oxide coated granular activated carbon [16] for the removal of copper and cadmium from water and wastewater. In spite of several researchers adopted various low-cost adsorbents there is still a need to develop suitable adsorbents for the removal of copper and cadmium from.

Our research labs are also making efforts in this aspect of pollution control methods and some successful procedures have been developed for some polluting ions and they have been reported to the Literature [17-25].

In the present work, sorption abilities of chemically activated bio-adsorbents derived from Annona*squmosa* seed have been explored with an object of controlling the concentration of Cu $^{2+}$ in the wastewater by optimizing various physicochemical parameters such as pH, time of equilibration and sorbet concentrations.

EXPERIMENTAL SECTION

2.1Batch adsorption studies

The adsorption experiments were carried out in order to evaluate the effect of pH, contact time, adsorbent dose, metal ion concentration, adsorption kinetics, adsorption isotherm and desorption studies of sulphuric acid activated carbon (HAS).

2.2. Experimental procedure

Adsorption experiments were carried out by batch method using a series of flasks which were prepared with 50 mL of metal solution(25–200 mg/L, respectively) and the pH was adjusted from2 to 9 using a digital pH meter (cyber scan, EUTECHINSTRUMENTS). About 0.2 g of the adsorbent was added,and the flasks were agitated at room temperature and different optimized parameters such as agitation speed of 120 rpm, contact time of 2 h, metal ion concentration of 100 mg/L of copper(II)until equilibrium was reached. The suspensions were filtered and metal concentrations in the supernatant solutions were measured using a UV–visible spectrophotometer.The amount of copper(II) ion adsorbed and % removal of copper(II) ion in the equilibrium (qe) was computed by the following mass–balance relationship:

$$q_e = (C_o - C_e)V/W \qquad (1)$$

where Co and Ce are the concentrations (mg L^{-1}) of Cu(II)at initial and equilibrium respectively. V is the volume (L) of the solution and W is the weight (g) of the adsorbent used.

2.3.Preparation of activated carbon *Annona Squmosa* (HAS)

The dried *Annona Squmosa* 1.0 kg was added in a small portion to 1000 mL of 98% sulphuric acid for 12 hrs and washed thoroughly in a distilled water until it pH attained neutral pH and soaked in two percent $NaHCO_3$ overnight. Then the material was washed with distilled water and dried 110±20C. Then preserved in desiccators for use.

2.4. Characterization of prepared adsorbents

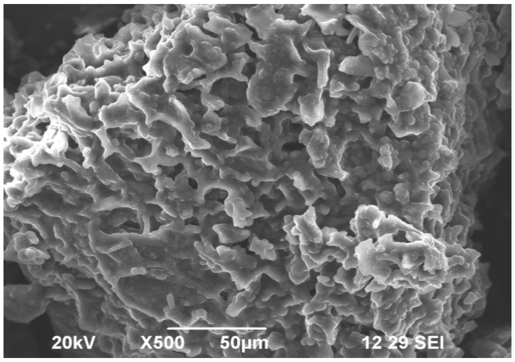
Determination of zero point charge (pHzpc) was done to investigate the surface charge of activated adsorbent at different solution pH.FTIR (JASCO-60 plus) of the adsorbent was recorded using KBr pellets in the range of 400–4000 cm^{-1}. SEM (VEGA3 TESCAN) was used to characterize the surface morphology of the composite before and after the adsorption of Cu(II) ions. Elemental analysis of the composite was evaluated using EDX. XRD (X'per PRO model-PNalytical make) measurements were obtained.

RESULTS AND DISCUSSION

3.1. Surface characteristics of the adsorbent

The surface structure of adsorbent such as HAS before and after adsorption was analyzed by scanning electron microscopy (SEM). SEM images of HAS before metal ion adsorptions are shown in Fig. 1a. As shown in Fig. 1a, It is clear that the adsorbent has considerable number of heterogeneous pores where there is a good possibility for metal to be trapped and adsorbed.Fig.1b shows the adsorbent is covered with Cu (II) ion, which proves adsorption of Cu(II) ions by the HAS surface. This is confirmed by the EDX results.

Further confirmation of the adsorption of Cu (II) on HAS was done by (EDX) analysis. Fig. 2a and 2b shows EDX pattern for HAS before and after adsorption. The EDX pattern (Fig. 2a) for the unloaded HAS, did not show any characteristic signal for the adsorption of Cu (II) ions. Fig. 2b shows signals of presence of Cu (II) ions were observed. Furthermore the adsorption was confirmed by the amplified intensity of the Cu (II) signal (Fig. 2b) from diffusion or accumulation of metal ions onto the surface of HAS.



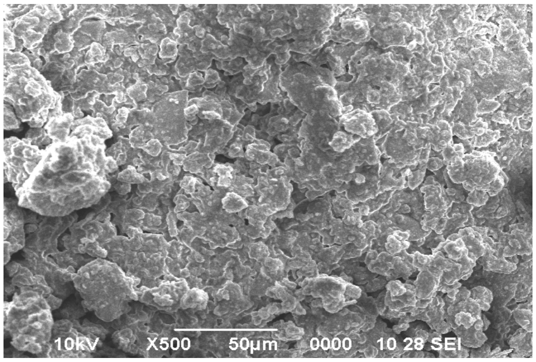
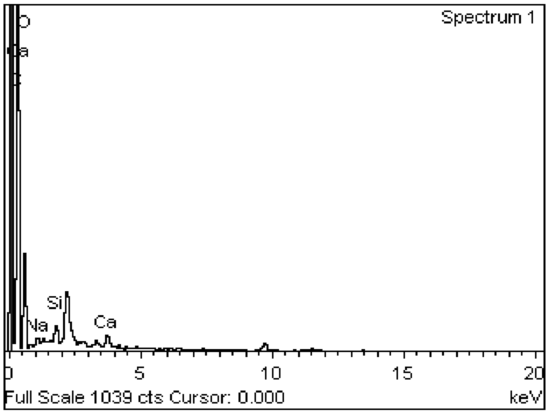


Fig.1a. SEM image of HAS-BFig.1b. SEM image of HAS-Cu



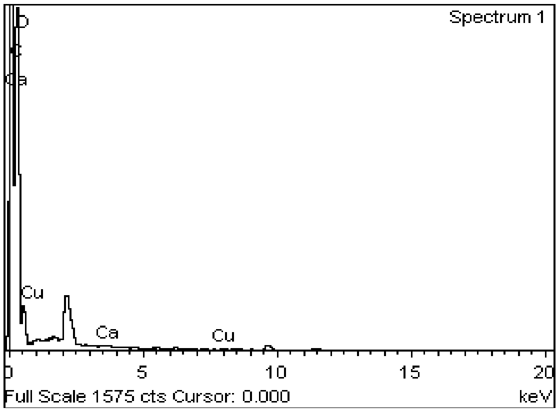


Fig.2a. EDAX result of HAS-B **Fig. 2b. EDAX result of HAS-Cu**

The FT-IR results of the absorbent precursor and the carbon are shown in Fig. 3a and 3b.These spectra contain a peaks at 3421 and 3462 cm^{-1}. This indicates the presence of hydrogen-bonded OH groups. It may be phenyl hydroxyl groups. The intense bent at about region 2852-2854 cm^{-1} for the precursor was attributed to the asymmetric and symmetric vibration modes of methyl and methylene group (C-H group). The peak around 1647 cm^{-1} can be assigned to aromatic ring vibrations. The peak at 1022-1047 cm^{-1} is related to lignin. Therefore it is possible that cellulose, hemicelluloses as well as lignin, having many OH groups in their structure, make up most of the absorbing layer.

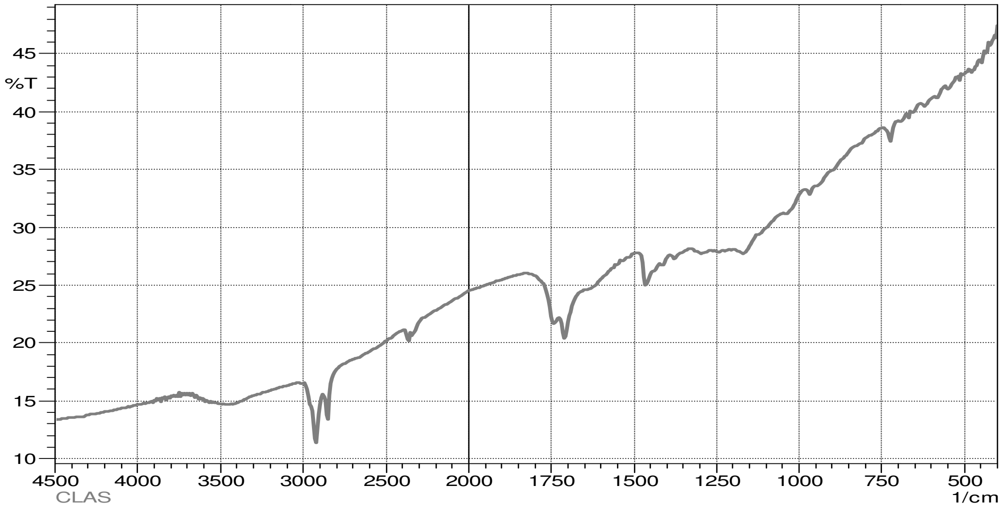


Fig. 3a. FTIR result for HAS-Before adsorption of Cu(II) ions

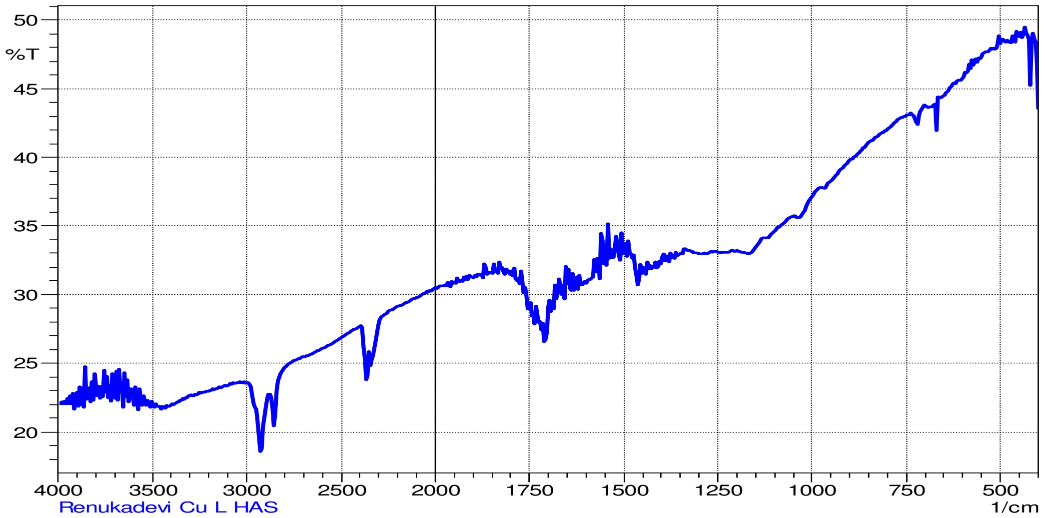


Fig. 3b. FTIR result for HAS-After adsorption of Cu

The zero point charges (pH_{ZPC}) of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. The point of zero charge for HAS is found to be 3.65. This result indicated that the pH_{ZPC} of HAS was depended on the raw material and the activated agency. The zero point charge ($pH_{ZPC} = 3.65$ for HAS) is below the solution pH (pH = 5) and hence the negative charge density on the surface of HAS increased which favours the adsorption of Cu (II) ions [26].

3.2. Batch adsorption experiments

3.2.1. Effect of solution pH

One of the most important factors that affect the adsorption of metal ions is the pH of the solution. The pH affects both the adsorbent and adsorbate chemistry in solution. The experiments carried out at different pH shows that there was a change in the percent removal of copper ion over the entire pH range of 2 to 10 shown in the Figure 4; PH is one of the most important parameters controlling the adsorption process. When the pH was lower than 3, the uptake went up sharply with the increase of pH. The maximum copper ion uptake was obtained at 5 pH, removal efficiency was 68 %. It appears that a change in pH of the solution results in the formation of different ionic species, and different carbon surface charge.

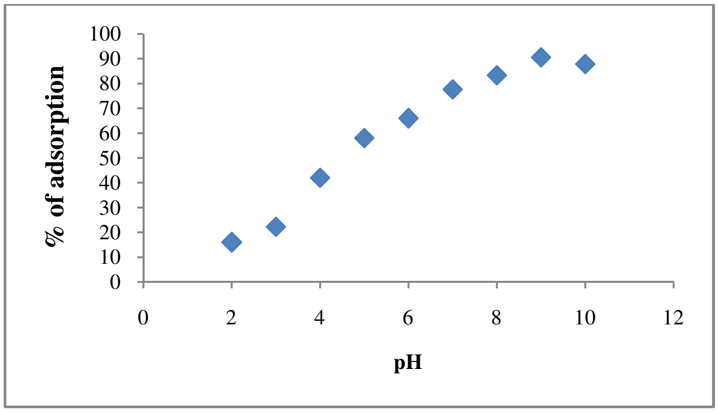


Fig. 4. Effect of solution pH on the adsorption of Cu (II) ion

3.2.2. Effect of adsorbent dose

The effect of adsorbent dose on the percentage removal of Cu (II) ion was studied. The results are presented in Fig. 5. It is showed that the percentage removal of Cu (II) ion increased with increase in adsorbent dose from 0.2g/50mL to1.0g/50mL. This increase in Cu (II) ion removal is due to the availability of higher number of Cu (II) ions per unit mass of adsorbent (HAS), i.e., higher Cu (II)/ adsorbent ratio. Thus, further experiments were carried out using 0.2g of adsorbent per 50 ml of Cu (II) ion solution, as it exhibits appreciable removal capacity, for the optimization of adsorption parameters.

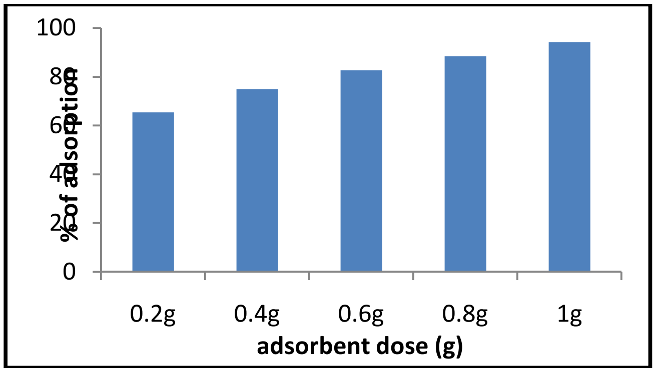


Fig. 5. Effect of adsorbent dose on the adsorption of Cu (II) ion

3.2.3. Effect of metal ion concentration and contact time

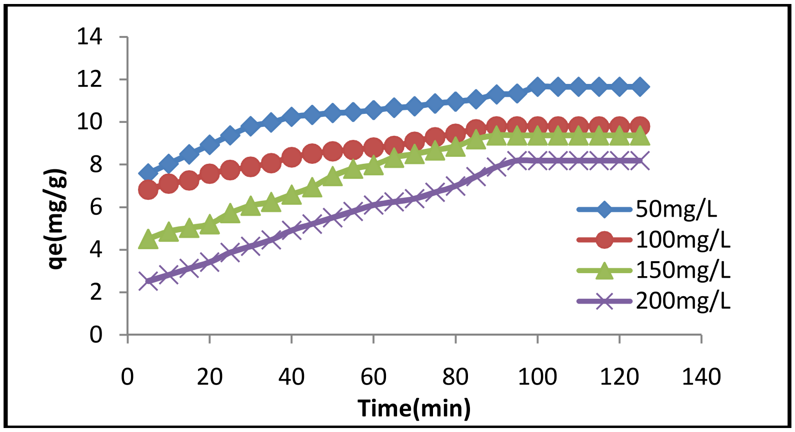


Fig. 6. Effect of metal ion concentration on the adsorption of Cu (II) ion

The adsorption capacity is dependent on the initial metal ion concentration. The dependence of adsorption capacity of HAS on initial concentration of Cu (II) is shown in Fig. 6. As seen from Fig. 6, equilibrium uptake has been increased with increase in the initial metal ion concentration and the contact time but the percentage of adsorption decreased with increasing the metal ion concentration in the range of concentrations studied. The increase in adsorption capacity with an increase in initial metal ion concentration is a result of the increase in driving force due to concentration gradient developed between the bulk solution and surface of the adsorbent. At higher concentration of metal ions, the active sites of HAS were surrounded by much more metal ions and the process of adsorption continues, leading to an increased uptake of metal ions from the solution.

3.3. Adsorption isotherm

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. The equation parameters of these equilibrium models often provide some insight into the sorption mechanism, the surface properties and the affinity of the adsorbent [27]. The results obtained for adsorption of Cu (II) ions were analyzed by use of well-known models given by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. For the adsorption isotherms, initial metal ion concentration was varied whereas solution pH and amount of adsorbent were held constant.

Langmuir adsorption isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. Therefore, the Langmuir isotherm model was chosen for the fitting of a monolayer and/or chemical adsorption on the adsorbent surface. It is represented as follows [28]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \qquad (2)$$

whereq_e (mg/g) is the amount of adsobate adsorbed at equilibrium, C_e (mg/L) is the liquid-phase adsorbate concentration at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity of the adsorbent, and b (L/mg) is the Langmuir adsorption constant, respectively.

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on a heterogeneous surface through a multilayer adsorption mechanism and adsorption capacity is related to the concentration of metal at equilibrium. This model describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich model is expressed as follows [29]:

$$\log q_e = \frac{1}{n}\log(C_e) + \log K \qquad (3)$$

where Ce (mg/L) is the liquid-phase adsorbate concentration at equilibrium, K is the Freundlich isotherm constant, and 1/n (dimensionless) is the heterogeneity factor, respectively.

Temkin and Pyzhev considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms, and suggest that the heat of adsorption of all the molecules in the layer would decrease linearly due to these interactions [30]. The Temkin isotherm has been used in the following form:

$$q_e = B\ln A + B\ln C_e \qquad (4)$$

where*A* is Temkin constant representing adsorbent–adsorbate interactions and *B* is another constant related with adsorption heat [31]. Temkin isotherm takes into account the adsorbing species–adsorbent interactions. Isotherm constants *A* and *B* can be determined from plot of *q*e versus ln *C*e. The constant b is related to the heat of adsorption. To determine the adsorption occurred is physical or chemical in nature, the equilibrium data were applied to D–R model [32]. Polanyi potential [33] can be calculated by using the following equation:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \qquad (6)$$

The mean adsorption energy, *E* (kJ/mol) is calculated with the help of following equation:

$$E = \frac{1}{\sqrt{-2'Y}} \qquad (7)$$

The results obtained from the Langmuir, Freundlich, Tempkin and D-R model for the removal of Cu (II) onto HAS are shown in Table 1. The correlation coefficients reported in Table 1showed strong positive evidence on the adsorption of Cu (II) onto HAS follows the Langmuir isotherm. The applicability of the linear form of Langmuir model to HAS was proved by the high correlation coefficients R^2 = 0.9842. This suggests that the Langmuir isotherm provides a good model of the sorption system. The maximum monolayer capacity Qm obtained from the Langmuir is 30.03mg/g. Therefore, the equilibrium adsorption of Cu (II) ions on HAS can be represented appropriately by the Langmuir model in the concentration range studied.The correlation coefficients (0.8693) showed that the Freundlich model is comparable to the Langmuir model. The 1/n is (0.3627) lower than 1.0, indicating that Cu (II) is favorably adsorbed by HAS. The heat of Cu (II) ion adsorption onto HAS was found to be 392.08.The correlation coefficients R^2 obtained from Tempkin model were comparable to that obtained for Langmuir and Freundlich equations, which explain the applicability of Tempkin model to the adsorption of Cu (II) onto HAS.The values of E calculated using D-R model is 0.3521 kJ/ mol, which indicating that the physico-sorption process plays the significant role in the adsorption of Cu (II) onto HAS.

From the isotherm models tested for the adsorption of Cu(II) ions HAS is fitted by the Langmuir model is confirmed. It should be a monolayer homogeneous adsorption.

Table 1. Ccoefficients of isotherm parameters for Cu (II) adsorption onto HAS

Isotherm Model	Constants and correlations	Cu (II) (g/50mL) (0.2g/50mL)
Langmuir	Q_m(mg.g⁻¹)	30.030
	Ka(Lmg⁻¹)	0.00505
	R^2	0.9842
Freundlich	1/n	0.3627
	$K_{F(}$mgg⁻¹)	1.0573
	R^2	0.8693
Temkin	α(Lg⁻¹)	3.0000
	ß(mgL⁻¹)	0.152
	R^2	0.8233
Dubinin-Radushkevich	Qm (mg.g⁻¹)	190.89
	K (x 10- 5mol2 KJ⁻²)	4.0332
	E=(KJ mol⁻¹)	0.3521
	R^2	0.8758

Adsorption kinetics

The kinetics of adsorbate uptake is important for choosing optimum operating conditions for design purposes. In order to investigate the mechanism of adsorption and potential rate controlling steps such as chemical reaction, diffusion control and mass transport process, kinetic models have been used to test experimental data from the adsorption of Cu (II) ions onto HAS. These kinetic models were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion models, which were respectively presented as follows in Eqs. (11)– (14) [39 – 41]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (12)$$

$$q_t = k_{ip} t^{\frac{1}{2}} + C \qquad (13)$$

$$q_t = \frac{1}{\beta \ln(\alpha\beta)} + \frac{1}{\beta \ln t} \qquad (14)$$

where t is the contact time of adsorption experiment (min); q_e (mg/g) and q_t (mg/g) are respectively the adsorption capacity at equilibrium and at any time t; k_1 (1/min), k_2 (g/mg min), α (mg/g min), β (g/mg), k_{id} (mg/g min$^{1/2}$) are the rate constants for these models, respectively. The correlation coefficients for all the four kinetic models were calculated and the results are shown in *Table 2.*

The adsorption process of Cu (II) ions can be well fitted by use of the pseudo-second order rate constant for HAS. The linear regression coefficient value $R^2 = 0.9977$ obtained for pseudo-second-order kinetics was closer to unity than the R^2 value (0.969) for first-order kinetics. This indicates that adsorption of Cu (II) ions by HAS follows pseudo-second-order kinetics.

In the intra particle diffusion model, the values of q_t were found to be linearly correlated with the values of $t^{1/2}$. The linear regression coefficient value $R^2 = 0.962$ for Cu (II) obtained for Intra particle diffusion model was closer to unity. The k_{dif} values were calculated by use of correlation analysis. $k_{dif} = 2.1424$ for the removal of Cu (II) ions.

Among these kinetic models we conclude that the adsorption of Cu (II) ions onto HAS follows pseudo second order kinetic model and it is a chemisorptions process.

Table 2. Ccoefficients of Kinetic parameters for Cu (II) adsorption onto HAS

Kinetic models	
1.First -order kinetic model	
K_1(mg min^{-1})	0.0084
q_e(mg g^{-1})	4.717
R²	0.9692
2.Second-order kinetic model	
K_2(mg min^{-1})	0.004
q_e(mg g^{-1})	12.25
R²	0.9977
Experimental value	
q_e(mg g^{-1})	12.14
3. Elovich	
A_E	1.4211
B_E	0.7463
R²	0.9836
4. Intra particle Diffusion	
K_{diff}	2.1424
C	14.713
R²	0.962

CONCLUSION

The result of this investigation shows that activated carbon was prepared from *Annona squmosa* seed has a suitable adsorption capacity for removal of Cu (II) from aqueous solutions. The equilibrium adsorption is achieved in 120 min. The isotherms like Langmuir, Freundlich, and Tempkin and DubininRadushkevich isotherm equations are well fitted. Monolayer adsorption behaviour was explained using Langmuir-type isotherm. The kinetic study was well fitted with Pseudo-second-order kinetic study, shows the chemisorptions mechanism.

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