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**KINETICS AND THERMODYNAMIC STUDIES ON REMOVAL OF
COPPER METAL ION FROM AQUEOUS SOLUTION USING RICE STRAW**

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Abstract

The adsorption percentage of Cu(II) ions from aqueous solution in the absence and in the presence of different concentration of hydrochloric acid on rice straw (SIII) and its ash (R400) were studied in a modified batch adsorption technique. The kinetic data was analyzed using various kinetic models particularly pseudo-first-order, pseudo-second-order and intra-particle diffusion. The pseudo-second-order kinetic model was found to agree well with the experimental data. Thermodynamic parameters such as enthalpy (ΔH°), free energy (ΔG°) and entropy (ΔS°) changes towards calculated and adsorption process was spontaneous at R400 in the absence and in the presence of 0.005 M HCl and exothermic in nature.

Keywords: Copper; rice straw; removal

Introduction

Heavy metal ions can be released into wastewater from various industries such as metal finishing, electroplating, battery manufacturing, steel industries, tannery, paint manufacturing, electronic industries, etc. [1]. Copper is known to be one of the most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment [2–6].

Copper can be removed by precipitation as copper hydroxide but this method is only efficient in alkaline media. One of the interesting methods which have been employed to remove copper from wastewater are membrane separation, electrochemical treatment, reverse osmosis and solvent extraction [7]. All these methods are generally expensive; therefore it is important to search for a low-cost method which is effective and economic. Recently, the adsorbents based on natural products and their derivatives have gained particular attention, e.g. sawdust [8–10], sugar beet pulp [11, 12], rice husk [9, 13–18], treated rice husk [19], orange waste [20], bamboo charcoal [21], and treated orange waste [22].

Many researchers have been investigated agriculture bi-product as adsorbents for removal of copper metal ion [5, 12, 23–32]. The main objective of this study is to assess the effectiveness of rice straw and its ash in the removal of copper by

determining the efficiency of adsorption in the absence and in the presence of different concentration of HCl solutions.

Our research:

Materials and methods

Instrumentation

AAS Vario 6 Analytik Jena atomic adsorption spectrometer operating with an air acetylene flame was used to determine the concentration of Cu(II). Five standard solutions with concentrations of copper metal ions in the linear range of the instrument were used to construct each calibration curve. During analysis of the samples for copper metal ions concentration, those samples in which the concentration of copper ions is observed beyond the linear range of the references were diluted to appropriate concentrations.

The pH of the solution was measured with a microprocessor pH Meter (PH 211) using HANNA electrode (HI1230) calibrated with standard buffer solutions of pH values: 4, 7 and 10.

Adsorbate Solution

Stock solution of copper metal ions was freshly prepared by dissolving required quantity of Analar grade salts in the distilled water. The salts used are copper sulfate for the preparation of stock solution. The stock solution was further diluted with distilled water to desired concentration for obtaining the test solutions.

Adsorbent: adjustment of adsorber

To prepare the rice straws, they were initially ground and homogenized using a food blender with steel blades for 10 min. Particle sizes \leq 212 mesh (SIII), were obtained by passing the milled material through a steel sieve. Also SIII of rice straws was burn-off at 400 °C (R400).

Mechanism adsorption studies

Batch process was employed for adsorption studies. A 0.5 g adsorbent was placed in a polypropylene bottle having 100 ml of Cu (II) solution. The mixture was then filtered at predetermined time interval and the final concentration of metal ions was determined in the filtrate by Atomic Absorption Spectrophotometer. Amount of Cu (II) adsorbed was then calculated by subtracting final concentration from initial

concentration. Adsorption studies were carried out by varying the adsorbate concentration (10 mg l^{-1}), the agitation time (3–180 min), and adsorbent amount (0.5 g).

The amount of copper adsorbed, q_e (mg g^{-1}) was computed by using the following equation:

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

Where C_0 and C_e are copper ion concentrations (mg L^{-1}) before and after adsorption, V is the volume of adsorbate (L) and m is the mass of the adsorbent (g). The percent removal of copper ion is calculated by the following equation:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Effect of temperature

Equilibrium adsorption of Cu(II) ions was performed at five different temperatures such as 25, 30, 35, 40, 45 °C in absence and presence of 0.005M hydrochloric acid solution. Dose of 0.5 g of SIII, or R400 of rice was firstly weighed accurately and introduced directly into 250 ml polypropylene bottle. Then, 100ml of aqueous solutions containing metal ions with 10 mg/l concentration were added to each bottle and shaken till 3 hrs. to attain the equilibrium. The concentration of the residual aqueous phase was determined using an atomic absorption spectrophotometer.

Results and discussion:

Efficiency of adsorbent

Effect of acid concentration

Table. 1 shows the effect of pH on the adsorption efficiency of SIII and R400 for copper metal ion. The amount of adsorption is calculated after three hours as batch techniques. It is seen from table that amount of adsorption of copper ions by SIII in aqueous solution in absence of acid is 72.9 %, whereas the adsorption in presence of 0.01M HCl reaches to (43.3%), and reaches to (11.98%) with increasing of 0.05M HCl. The decreasing in uptake at higher concentration of acid may be due to the affect of anionic group to H^+ ions on the surface of adsorbent, due to restricting the number of binding sites for metal ions [33].

The adsorption amount of Cu (II) with samples R400 and R400 + HCl , is higher than that in the raw sample, this may be attributed to appearance of silanol group (Si–OH) on the surface of adsorber after ignition, this group may act as Lewis basis in deprotonated form (Si–O–) to bind with Lewis metal ions such as Cu(II) and Cd(II), Hence, this metal ions can form more monodentate or bidentate complexes with Si–O– group[34].

Effect of temperature

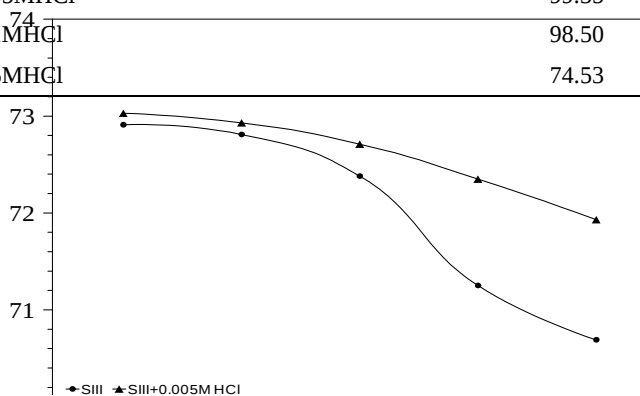
Fig.1. shows the effect of the increasing temperature on the adsorption of copper ions on SIII, R400 in the absence and in the presence of hydrochloric acid (0.005M) were studied by employs the adsorption experiments in a temperature range of 25–45 °C with agitating through time of 3 hours.

An increase in the temperature from 35 to 45 °C leads to an decrease in the efficiency of adsorption of copper ions onto SIII. The decrease in adsorption capacity of SIII with temperature indicates an exothermic process. The effect of temperature on Cu(II) adsorption on SIII+0.005M HCl can be inferred from figure 1. From the figure it can be observed that, when the temperature of the solution is changed from 25 to 45 °C, the amount of Cu(II) ions adsorbed slightly decreased,

The equilibrium adsorption capacity of Cu(II) ions onto R400 and R400+ 0.005M HCl were favored at low temperatures.

Table 1:Efficiency of copper ions adsorption on SIII, R400 in the absence and in the presence of deferent concentration of HCl at 25 °C.

Adsorbent and adsorption media	Adsorption efficiency
SIII	72.91
SIII+ 0.005MHCl	73.03
SIII+ 0.01MHCl	43.29
SIII+ 0.05MHCl	11.98
R400	96.51
R400+ 0.005MHCl	99.35
R400+ 0.01MHCl	98.50
R400+ 0.05MHCl	74.53



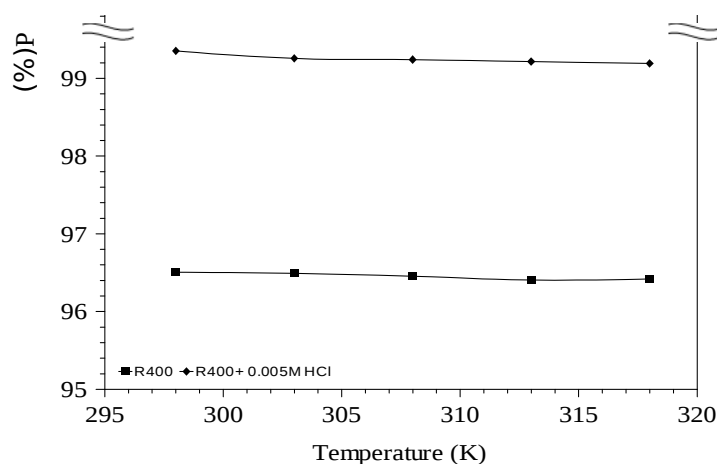


Fig.1. Effect of temperature on efficiency of copper ions

Data Evaluation

Pseudo-first-order and pseudo-second-order reaction rate model [35 - 38] were employed to study the copper adsorption onto SIII, R400 in absence and presence of 0.005M hydrochloric acid solution at 25 °C. The mathematical representations of models are given in Eqs. (3) and (4).

Pseudo first-order adsorption kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The adsorption rate constant (k_1) were calculated from the slope of the linear plot of $\ln(q_e - q_t)$ versus time.

Pseudo second-order adsorption kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Kinetic data were plotted between t/q_t against t .

The pseudo-first-order adsorption rate constant k_1 from the slopes and q_e can be calculated from the intercept from Figs. 2,3. The corresponding values of k_1 , q_e and r^2 are presented in Table 2 at tested temperature. As can be seen from the results, the correlation coefficients were low ($r^2 < 0.90$). Also q_e values calculated from the plots were lower than the experimental data. Therefore, it may conclude that copper adsorption system did not follow pseudo-first-order equation perfectly and higher orders rate equations should be applied to test the applicability.

The pseudo-second-order adsorption rate constant k_2 and q_e were determined from the slope and intercept of the plot. The values k_2 , calculated q_e values and the correlation coefficients r^2 are given in Table 2 and Figs. 4,5 shows the plots with initial copper concentration 10 mg/L at tested temperatures. As can be seen from the results that the correlation coefficients r^2 were high (>0.99). The well fitting by the data suggested that pseudo-second-order model can be considered in the present adsorption system.

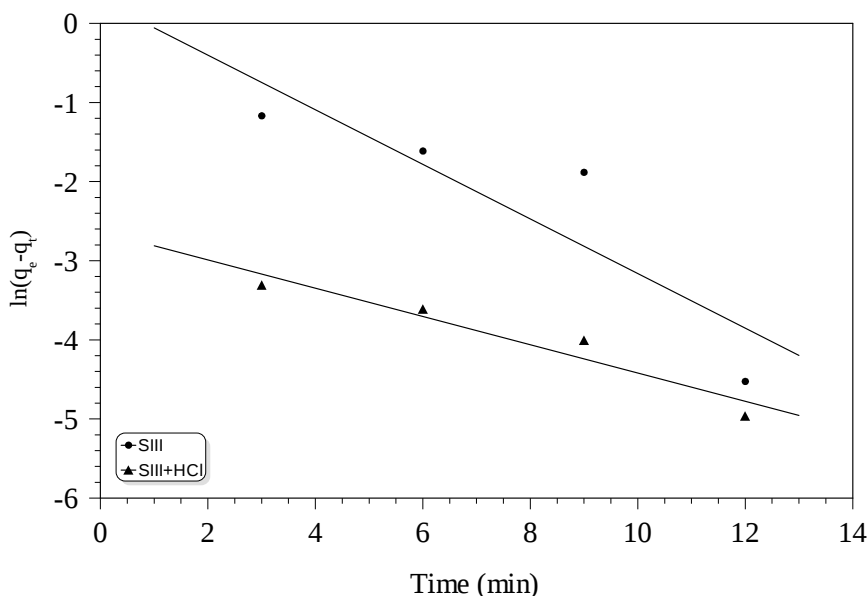


Fig. 2. Linear fitting curves of $\ln(q_e - q)$ versus t for the copper ions adsorption onto SIII Rice in the absence and in the presence of 0.005 M HCl at 25 °C.

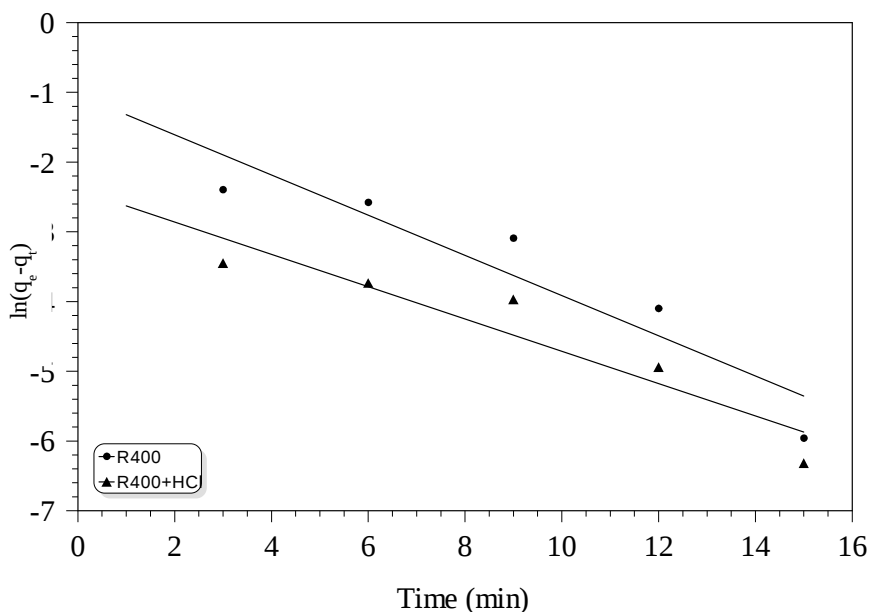


Fig. 3. Linear fitting curves of $\ln(q_e - q)$ versus t for the copper ions adsorption onto ignited rice at 400°C in the absence and in the presence of 0.005 M HCl at 25°C

Table 2. Comparison of the pseudo-first-order, and pseudo-second-order calculated and experimental q_e values at 25°C .

	Pseudo-first order					Pseudo-second order			
	$q_{e, \text{exp}}$ (mg g^{-1})	$q_{e, \text{cal}}$ (mg g^{-1})	k_1 (min^{-1})	$t_{1/2}$ (min)	r^2	$q_{e, \text{cal}}$ (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$t_{1/2}$ (min)	r^2
SIII	1.76	1.33	0.3448	2.01	0.7771	1.86	0.0515	1.0453	0.99416
HClSIII+ 0.005N	1.79	0.07	0.1786	3.88	0.9245	1.80	0.6552	0.0850	0.99997
R400	1.94	0.36	0.2882	2.40	0.8733	1.97	0.1896	0.2678	0.99981
HClR400+ 0.005N	1.99	0.09	0.2318	2.99	0.8820	2.00	0.6011	0.0833	0.99998

$\ln(q_e - q_t)$

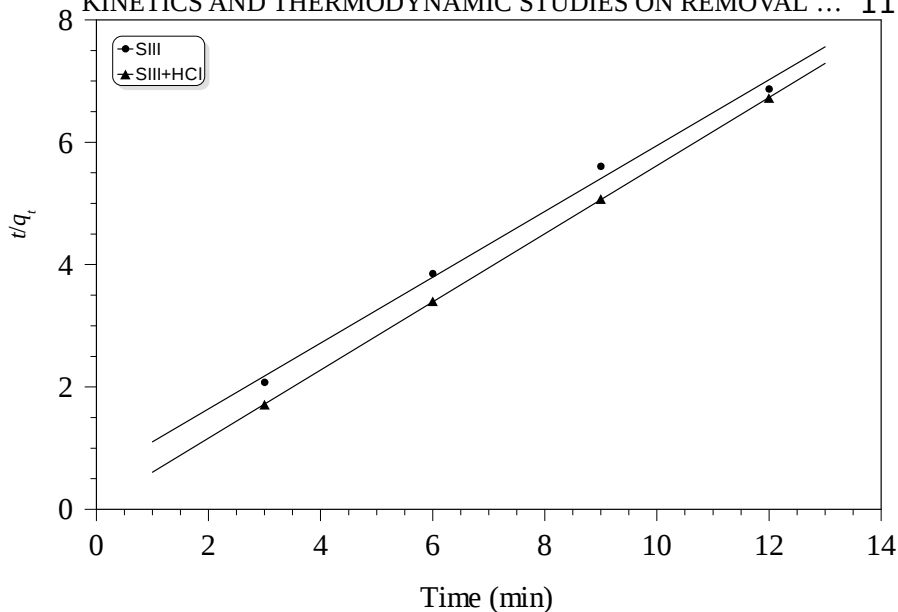


Fig. 4. Linear fitting curves of t/q_t versus t for the copper ions adsorption onto SIII rice in the absence and in the presence of 0.005 M HCl at 25 °C.

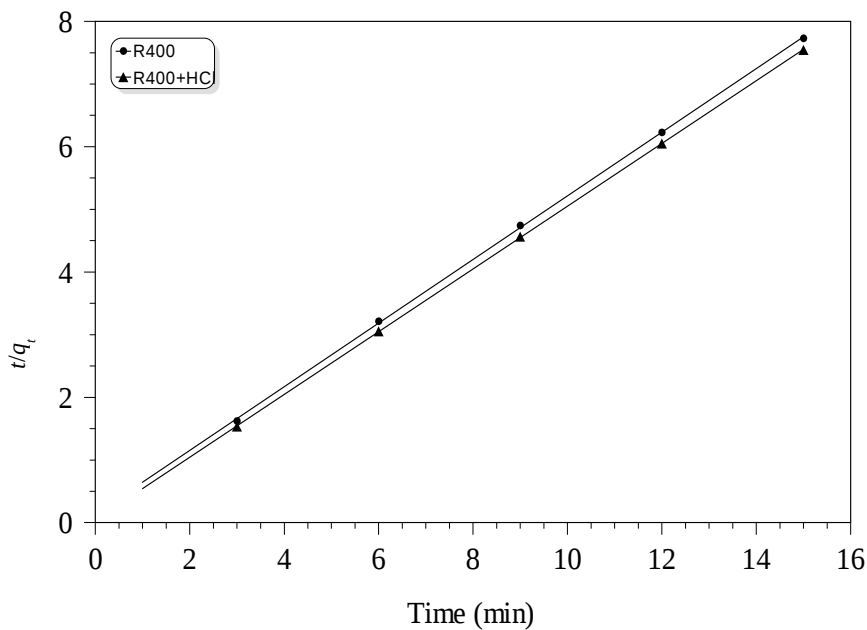


Fig. 5. Linear fitting curves of t/q_t versus t for the copper ions adsorption onto ignited wood at 400 °C in the absence and in the presence of 0.005 M HCl at 25 °C.

Adsorption mechanisms

The first-order and pseudo-second-order models cannot identify the diffusion mechanism. For this reason, the kinetic results were then subjected to analyze by the intraparticle diffusion model. Mathematical model described by Weber and Morris [39] was used to provide the definite adsorption mechanism. According to this model, the plot of uptake, q_t , versus the square root of time ($t^{1/2}$) should be linear if the intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. The initial curved portion of the plots seems to be due to boundary layer adsorption and the linear portion to intraparticle diffusion, with the plateau corresponding to equilibrium [40–43].

Intraparticle diffusion model is of major concern because it is rate-determining step in the liquid adsorption systems. During the batch mode of operation, there was a possibility of transport of sorbate species into the pores of sorbent, which is often the rate controlling step.

The rate constants of intraparticle diffusion (k_{id}) were determined using the following equation:

$$q_t = k_{id} t^{1/2} \quad (5)$$

where q_t is the amount sorbed at time t and $t^{1/2}$ is the square root of the time.

The plot of q_t against $t^{1/2}$ would result in a straight line if the rate limiting is the intra-particle diffusion. Moreover, the line would pass through the origin if the intra-particle diffusion is the only rate controlling step. The result of linearity test of q_t against $t^{1/2}$ is shown in Figs. 6,7. In the present study, the plots of q_t against $t^{1/2}$ obtained from copper removal onto SIII and R400 in absence and presence of 0.005 M hydrochloric acid did not pass through the origin and were not linear over the whole time range. The linearity was evaluated separately. For the first proportion, diffusion model was that mass of copper ions transferred across the bulk solution to the solution around adsorbent surface and the second linearity showed copper ions diffusion into adsorbent surface pores. The higher slopes for the first proportion implied that copper ions transferred from bulk solution to biochar surface were faster. The lower slopes of the second proportion suggested intra-particle diffusion was rate-controlling step after a long contact time.

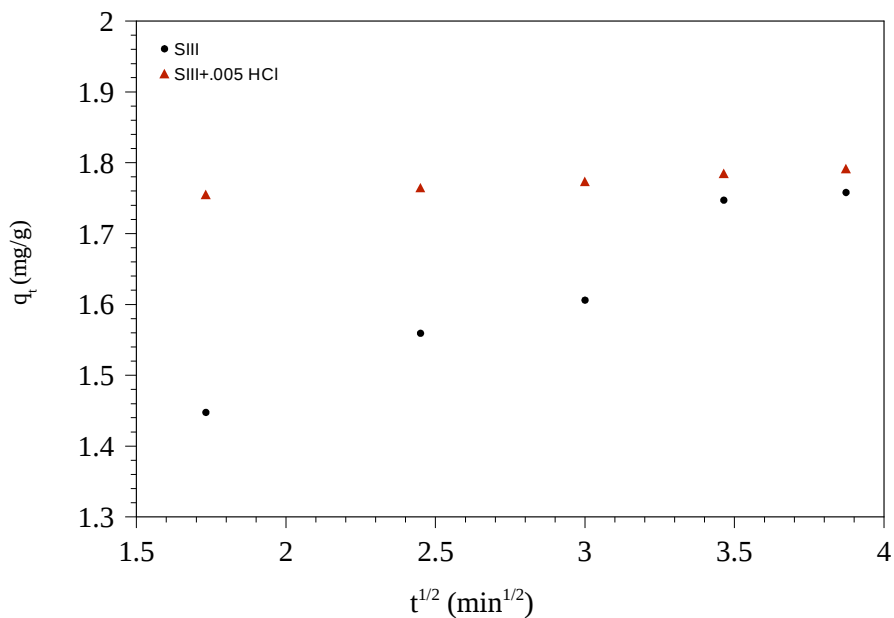


Fig. 6. Weber and Morris (intraparticle diffusion) plot for the adsorption of Cu(II) by SIII in the absence and in the presence of 0.005M HCl at 25 °C.

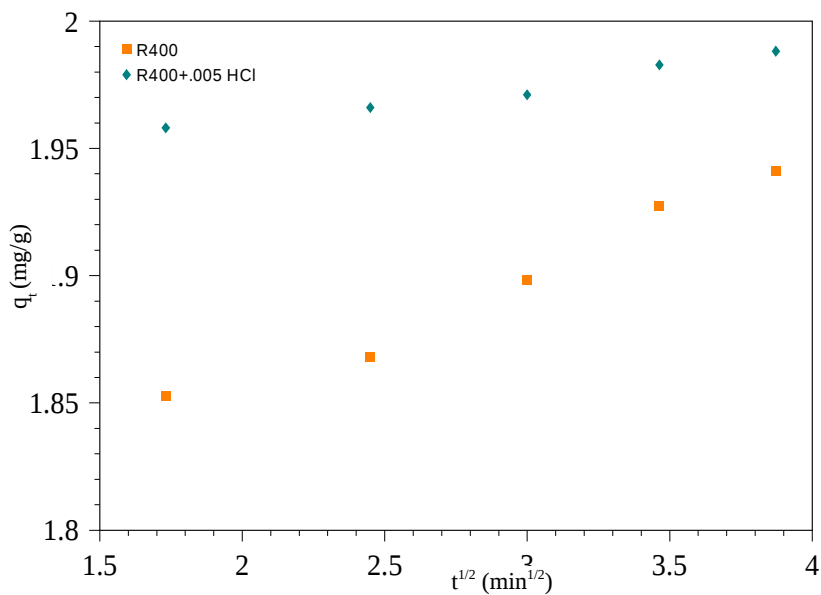


Fig. 7. Weber and Morris (intraparticle diffusion) plot for the adsorption of Cu(II) by R400 in the absence and in the presence of 0.005M HCl at 25 °C.

Adsorption Thermodynamics

Thermodynamic parameters, including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were used to decide whether the adsorption process is spontaneous or not. ΔG° were calculated from the following equation;

$$\Delta G^\circ = -RT \ln K_D \quad (6)$$

Where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), and K_D is the distribution coefficient. The K_D value was calculated using following equation [44];

$$K_D = \frac{q_e}{C_e} \quad (7)$$

Where q_e and C_e are the equilibrium concentration of metal ions on adsorbent (mg L^{-1}) and in the solution (mg L^{-1}), respectively. Relation between ΔG° , ΔH° and ΔS° can be expressed by the following equation;

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

This equation can be written as;

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Thermodynamic parameters, ΔH° and ΔS° , were calculated from the slope and intercept of the plot of $\ln K_D$ versus $1/T$, respectively.

The effect of temperature on the adsorption of copper metal ions onto SIII, R400 in absence and presence of 0.005M hydrochloric acid solution are given from the plots and curves of the distribution coefficient values K_D versus temperatures in Figs.8,9. It can be found that K_D slightly decreased with temperature increasing, a certification of the exothermic adsorption nature.

As the temperature increases, the mobility of copper ions increases causing the ions to escape from the solid phase to the liquid phase. Therefore, the amount of copper that can be adsorbed will decrease.

The results were further substantiated by the various thermodynamic parameters evaluated of adsorption, such as free energy, ΔG° , enthalpy change, ΔH° , and entropy change, ΔS° .

For significant adsorption to occur, the free energy change of adsorption, ΔG° , must be negative. The adsorption of Cu(II) onto all adsorbate is exothermic in

nature, giving a negative values of ΔH° . Hence, ΔS° has to be positive in R400 in absence

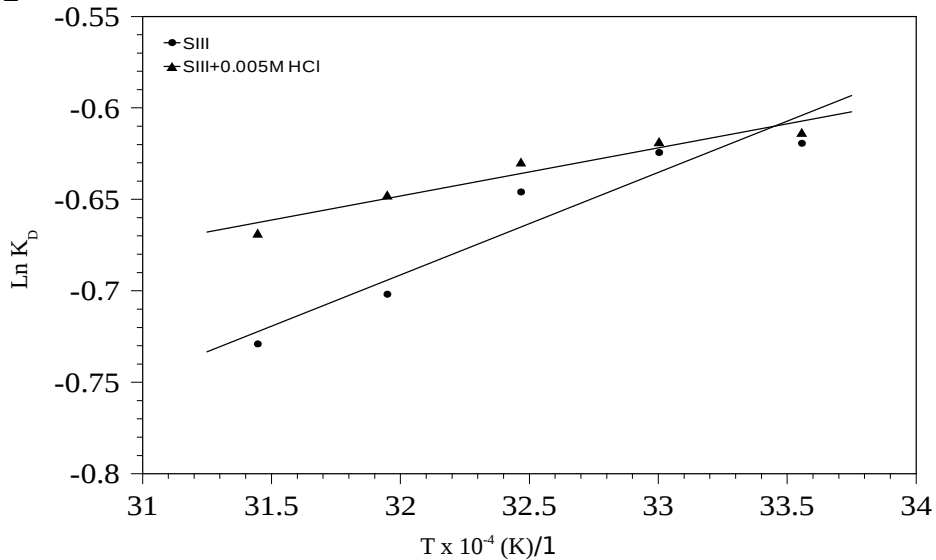


Fig. 8. Van't Hoff plot of adsorption equilibrium constant K_D of copper metal ion on SIII in the absence and in the presence of 0.005M HCl.

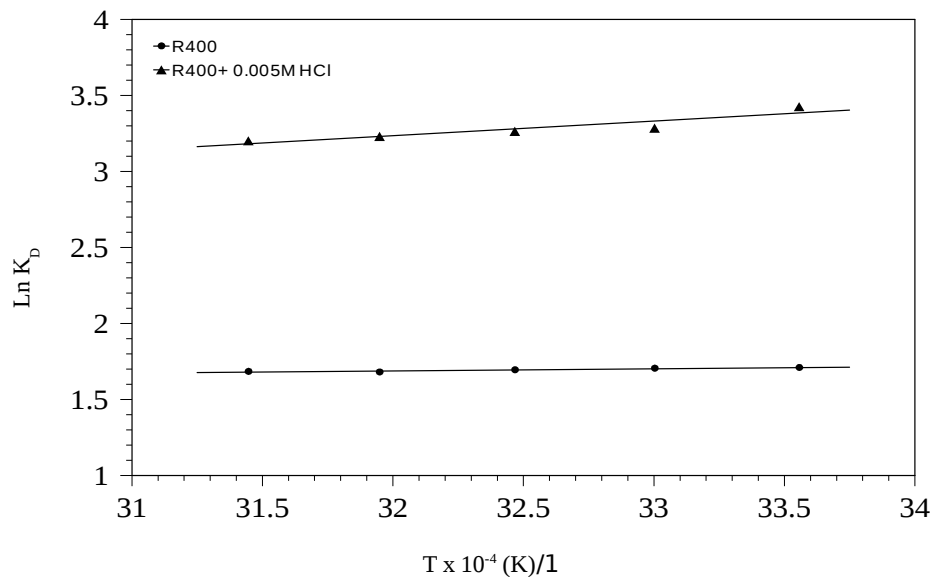


Fig. 9. Van't Hoff plot of adsorption equilibrium constant K_D of copper metal ion on .R400 in the absence and in the presence of 0.005M HCl

and present of 0.005 M HCl, and that the positive value of $T\Delta S^\circ$ has to be larger than ΔH° . The positive value of ΔS° in R400 in absence and presence of HCl suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbents towards Cu(II) ions. The positive ΔS° value also corresponds to an increase in the degree of freedom of the adsorbed species [45].

The negative value of ΔH° for Cu(II) ions onto all adsorbates as shown in Table 3 indicates exothermic nature of adsorption. According to Alkan et al. [48], enthalpy change due to chemisorption takes value between 40 and 120 kJ mol⁻¹, which is larger than that due to physisorption. Therefore, the low value of heat of adsorption obtained in this study indicates that adsorption is likely due to physisorption. The negative value of entropy change, ΔS° , of SIII, and SIII+HCl, shows a decreased disorder at the solid/liquid interface during copper adsorption.

The negative value of free energy change, ΔG° , is an indication of a spontaneous process whereby no energy input from outside of the system is required.

Table 3. Thermodynamic parameters of the adsorption of copper metal ions by SIII and R400 in the absence and in the presence of 0.005M HCl.

	Temp (K)	K_D	ΔH° (kJ/mole)	ΔS° (J/mole)	ΔG° (kJ/mole)
SIII	298	0.538	-4.66	-20.77	1.54
	303	0.536		-20.56	1.57
	308	0.524		-20.49	1.65
	313	0.496		-20.71	1.83
	318	0.482		-20.70	1.93
SIII + 0.005M HCl	298	0.542	-2.19	-12.44	1.52
	303	0.539		-12.36	1.56
	308	0.533		-12.34	1.61
	313	0.523		-12.37	1.69
	318	0.513		-12.44	1.77
R400	298	5.526	-1.19	10.21	-4.24
	303	5.500		10.24	-4.29
	308	5.443		10.21	-4.34
	313	5.366		10.16	-4.37
	318	5.387		10.25	-4.45
R400 + 0.005 M HCl	298	30.755	-8.00	1.62	-8.49
	303	26.711		0.90	-8.28
	308	26.154		1.15	-8.36
	313	25.284		1.28	-8.41

Conclusion

The present study has demonstrated that rice straw and its ash possess the adsorption capacity for removal of copper metal ions in absence and presence of different concentration of hydrochloric acid solution. The following are the conclusions arrived from this study.

1. Copper showed higher adsorption capacity and rate in absence and low concentration of hydrochloric acid solutions.
2. Experimental data were better described by pseudo-second order model as evident from correlation coefficient values (r^2)
3. Thermodynamic parameters such as standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated for predicting the nature of adsorption. The negative value of ΔH° for Cu(II) ions onto all adsorbates indicates exothermic nature of adsorption.
4. Rice straw and its ash can be used as an effective natural biosorbent for the economic treatment of wastewater containing Cu(II).

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