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INFLUENCE OF ELECTROLYTES ON DECONTAMINATION OF Cu(II) IONS BY SURFACE OF COCONUT COIR

F. KAUSAR[a], N. KHALID[b] , M. L. MIRZA[a,d], M. I. DIN[c*]
[a]*Department of Chemistry, The Islamia University of Bahawalpur, Pakistan*
[b]*Chemistry Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan*
[c]*Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan.*
[d]*University of Sargodha ,Mandi Bahauddin Campus, Mandi Bahauddin, Pakistan*

The decontamination phenomenon of copper ions has been studied on surface of coconut coir in batch method. This phenomenon studied by changing the nature and concentration of electrolytes (HNO_3, H_2SO_4, HCl and $HClO_4$), weight of adsorbate and adsorbent, temperature of system and contact time. Estimation of copper in coconut coir has been done by Atomic absorption spectrometric (AAS) technique. It was observed thatthe adsorption of copper decreased with the increase in the concentrations of electrolytes and increased with increase in temperature (283-333 K) and maximum adsorption observed at 1.00×10^{-4}mol L^{-1} concentration of HNO_3, 10 mL of (3.15×10^{-4}mol L^{-1}) copper stock solution,0.25 g coconut coir with contact time of 15 minutes. The results showed that sorption process follow pseudo-second order and this process obeyed the Dubinin-Radushkevich, Langmuir ($Q = 56.88 \pm 3.16 \times 10^{-3}$ m mol g^{-1}, $b = 9.74 \pm 2.41 \times 10^{3}$ dm^3 mol^{-1}) and Freundlich isotherms ($1/n = 0.324 \pm 0.023$, $K = 0.508 \pm 0.014$ m mol g^{-1}) within the range of concentration of copper from 1.57×10^{-4} to 2.36×10^{-3} mol L^{-1}. The sorption mean free energy 13.13 ± 0.95 kJ mol^{-1} was calculated from the Dubinin-Radushkevich isotherm which indicated the ion-exchange mechanism of chemisorption. Thermodynamic quantities i.e. free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) have also been calculated for this process and the positive value of enthalpy was represented to bean endothermic process.

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Keywords: Coconut coir; copper adsorption; kinetics; sorption isotherms; thermodynamics.

1. Introduction

The environmental pollution of heavy metals is one of the critical worldwide issues due to their exponential increase in urbanization and industrization. The monitoring of hazardous metal ions in industrial wastewaters and subsequent their removal is required before safe disposal. Copper is a useful metal extensively used in pigments, in jewelry, wood preservatives, paints, metal works, pigments, petroleum refinery, motor vehicle, laboratory chemical and pharmaceutical industries. Significant amount of copper is being released from these sources that exceeds the recommended accepted limits of World Health Organization (WHO) in tab water of 1.5 mg L^{-1} [1]. Therefore, there is a need to remove the copper contents from such industrial wastes before their safe disposal.

For pre-concentration and removal of copper ions from aqueous media different conventional methods are being used which are precipitation [2], flotation [3], coagulation [4], flocculation [5], ion exchange [6-8], reverse osmosis [9], electro-dialysis [10] and adsorption method. High operational costs, relatively low efficiency especially at low concentrations and the formation of by-products are the main factors which limit the use of these processes [11]. The adsorption process

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[*] Corresponding author: imrandin2007@gmail.com

has been used frequently due to its simplicity, high efficiency and low maintenance cost.

Adsorptive removal of copper has been investigated using active carbon [12], palm fiber [13], sawdust [14], jute fibre [15], sugar beet pulp and fly ash [16], low ranked Pakistani coals [17]. However, the exploitation of rapid, more efficient and cost effective system is still desired.

The present work deals with the removal of copper ions from aqueous media with the help of coconut coir as an adsorbent. The selection of coconut coir was made since it is abundantly available as a waste byproduct in many countries. Moreover it contains cellulose, hemi-cellulose and lignin [18-20], all of which are good adsorbents for the removal of metal ions [21, 22].

2. Materials and methods

2.1 Materials

Coconut coir was collected from Rawalpindi market, washed with de-ionized water to remove dust particles, dried in an oven at 60 °C till constant weight, manually cut into minute pieces and stored in airtight jar.

0.1 gram of specpure metal (Johnson and Mathey, UK) and calculated amount of nitric acid were mixed and diluted it with distilled water for the preparation of stock solution of copper ions. For the preparation of standard solutions, stock solution was diluted with different amount of water to get different concentrations.

2.2 Equipment

The adsorbed copper metal ions on coconut coir were characterized with polarized Zeeman atomic absorption spectrophotometer (Hitachi model Z-2000) to determine the adsorbed amount of copper ions. This spectrophotometer has a strong magnetic field across the air-acetylene flame burner (having slot of 100×0.5 mm^2) and a hollow cathode copper lamp (Hitachi, radiation source). The functional group analyses were recorded with FTIR Thermo-Scientific Nicolet-6700 spectrophotometer (range 4000–400 cm^{-1}).

2.3 Adsorption measurements

Adsorption measurements were made employing a batch technique at ambient temperature (297 ± 1 K) except where otherwise specified, by shaking 0.25 g of coconut coir in a 10 mL of an aqueous solution of 3.15×10^{-4}mol L^{-1} of copper ions in 30 cm^3 Pyrex culture tubes for a specific time and the contents were filtered. The adsorption amount of copper ions in filtrate was finding by using AAS and optimized instrumental parameters. The value of copper ions adsorbed in each analysis is the average of at least two measurements.

The % age adsorption of copper ions from the solution and the adsorbed amount of copper (Q_t) were determined using the equation (1) and (2) respectively.

$$\%\,\text{age Adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \tag{1}$$

$$Q_t = \frac{(C_i - C_t)}{m} \times V \tag{2}$$

Where C_i is initial concentration, C_f is concentration after equilibrium, Ct is concentration at time "t" of copper ions in solutions (mg L^{-1}), V is the volume of copper ions solution (mL) and m is mass of the adsorbent (g).

3. Results and Discussions

The adsorption phenomenon of copper ions has been studied on coconut coir using batch method by changing the nature and concentration of electrolytes (HNO_3, H_2SO_4, HCl and $HClO_4$), weight of adsorbate and adsorbent, temperature of system and shaking time. Estimation of copper in coconut coir has been done by Atomic absorption spectrometric technique. The reason for the changing in parameters was to find the values where maximum adsorption occurred. The determined relative standard deviation was within ± 3.2 % unless otherwise specified.

The verification of the adsorption of copper ions was made by observing the variation in the absorption peaks in the FTIR spectra of the samples of coconut coir and copper loaded coconut coir. The characteristic absorption bands at 3400–3200 and 2921-2851 cm^{-1} are assigned to for the stretching of surface O–H and aliphatic C–H groups respectively [23]. The peaks at 1740 and 1367–1371 cm^{-1} are associated with COO^{-1}anions and around 1029 due to CO group. The peaks around 1593^{-1} are due to OH bending of the adsorbed H_2O [24-25]. The FTIR spectrum of copper loaded coconut coir exhibited changes in the peak positions. The shifting of peaks to 2921.7, 1589, 1365 and 1019 cm^{-1}, clearly indicate the binding of copper ions with carboxylic group in the coconut coir. Adsorption of Cr on coconut coir with similar minor shifting of FTIR peaks have been reported [26].

3.1 Optimization of concentration of electrolytes

The interaction of electrolytes with the adsorbent surfaces results the some variations in adsorption properties. So, the adsorption behavior of copper (1.574×10^{-4} mol L^{-1}) was studied by varying the acid (HNO_3, HCl, $HClO_4$ and H_2SO_4) concentration ranging from 0.0001 to 1.0 mol L^{-1}using 0.25 g of coconut coir and shaking time of 15 min and the results are shown in Fig. 1(a). From Fig. 1(a), it is observed that with an increase in concentration of electrolyte the adsorption of copper ions on coconut coir decreases and the maximum adsorption was occurred in 1.0×10^{-4} mol L^{-1} of nitric acid which is the optimized value of concentration of electrolyte. This could be explained on the basis of the competition between the positively charged copper ions and excess of H^+ ions in the medium and almost all the acids show same adsorption trend.

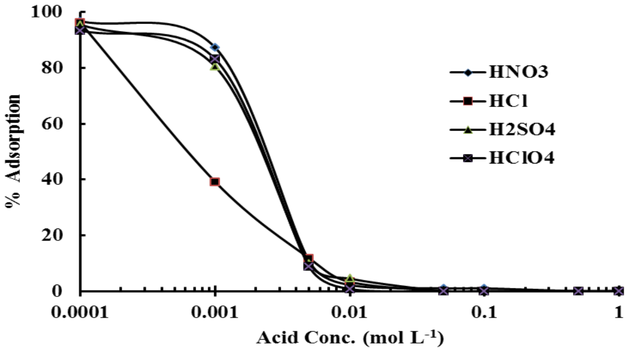

Fig.1 (a): Interaction of electrolytes with the adsorbent surfaces

When the concentration of acid increase the amount of H^+ also increased and due to the increase in amount of H^+, the attachment of copper ions on the surface of coconut coir decreased and it can be explained on the basis of the surface complex formation model. In this model the hydrolyzed coconut surface possesses negative charge i.e., [C. coir–O^-], where cations exchange reaction can occur in aqueous solutions as follows:

$$n[\text{C. coir–OH}] \rightleftharpoons n[\text{C. coir–O}^-] + nH^+ \qquad (3)$$

$$M^{a+} + n[\text{C. coir–O}^-] \rightleftharpoons M[\text{C. coir–O}]_n^{a-m} \qquad (4)$$

The overall reaction can be written as:

$$M^{a+} + n[\text{C. coir–OH}] \rightleftharpoons M[\text{C. coir–O}]_n^{a-m} + nH^+ \quad (5)$$

Where (M^{a+}) is Metal ion with a+ charge, n is number of protons released and [C. coir–OH] is hydroxyl group on the surface of coconut coir. The reaction (5) is reversible in acidic solutions.

3.2. Optimization of Adsorbent amount

The adsorbent amount was varied from 50-300 mg for 10 mL of (3.148×10^{-4} mol L^{-1}) of copper ion solution and shaking time of 15 minutes and the values of adsorption with change in the amount are shown in Fig. 1(b). This spectrum shows that when the amount of adsorbent increase from 0.05 to 0.25 g, adsorption of copper ions also increases from 37 to 97 % and with further increase in amount there was no noticeable increase in adsorption. The percentage adsorption of copper ions increases with increase in the amount of adsorbent may be explained on the basis that when the adsorbent amount increase, more sites are available for adsorbate and this process attains equilibrium between adsorbate and adsorbent. Due to this equilibrium, increase in the amount of adsorbent does not affect the adsorption.

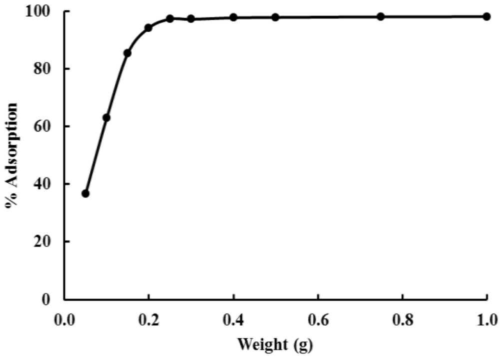

Fig.1 (b): Effect of adsorbent dose for the adsorption of copper ions on coconut coir

3.3. Optimization of contact time

By varying the contact time from 1min to 30 min with other constant parameters, it was observed that percentage adsorption was rapidly increased in contact time upto 15 minutes and with further increase in contact time the percentage adsorption of copper was almost constants shown in Fig. 1(c).

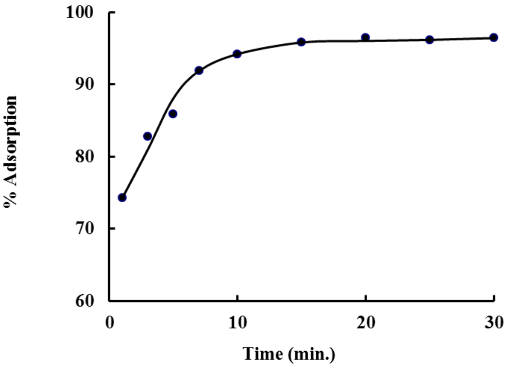

Fig.1 (c): Effect of time of contact for the adsorption of copper ions on coconut coir

The initial rapid increase in percentage adsorption of copper ions can be due to the availability of more vacant active sites on the surface of adsorbent, however, in the latter stage the adsorption process became slow due to the unavailability of active sites for binding the copper ions on coconut coir surface.

Kinetic explaination

The adsorption data was applied to the Morris-Weber equation:

$$Q_t = K_p\, t^{0.5} \tag{6}$$

Where, Q_t = Adsorbed conc. of copper (mg/g) at time "t"
K_p = Intra-particle diffusion coefficient.

The plot of $t^{0.5}$versus $Q_t$is shown in Fig. 2(a), which clearly shows that initially the adsorption was rapid up to 10 minutes which then slowed down upto 30 minutes, which were depicted from two distinct slopes of 0.093 and 0.008 for first 10 minutes and 11-30 minutes respectively.

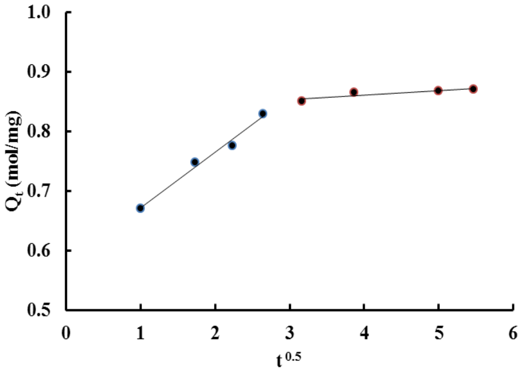

Fig.2 (a): Interpretation of kinetic data by Morris-Weber equation

By using the Reichenberg equation, nature of the adsorption either via intra-particle diffusion or film diffusion mechanism was verified:

$$X = \left(1 - \frac{6}{\pi^2}\right) e^{-B_t} \tag{7}$$

where $$X = \frac{Q_t}{Q_e} = \frac{\text{Amount of metal adsorbed at time "t"}}{\text{Amount of metal adsorbed at equilibriu m}}$$

The value of B_t is a function of X that can be calculated by using the equation:

$$B_t = -0.4977 \ln(1 - X) \tag{8}$$

The plot of B_t versus time is a straight line Fig. 2(b) with a correlation factor of 0.949 which shows that the sorption is controlled by film diffusion.

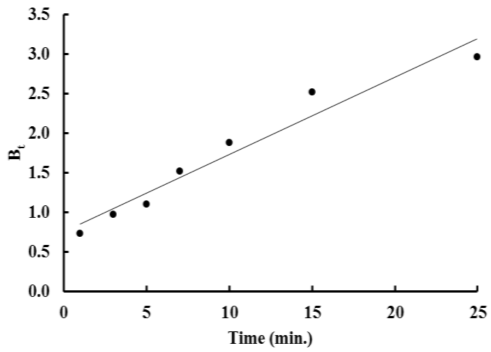

Fig.2 (b): Interpretation of kinetic data by Reichenberg equation

In order to evaluate kinetic adsorption parameters, the obtained kinetic adsorption data of copper ions on coconut coir was fitted to the pseudo-second order (Eq. 9) rate equations in the linear form and first order Lagergren (Eq. 10)as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

$$\log(q_e - q_t) = \log q_e \frac{k_1}{2.303} t \tag{10}$$

Where q_e and q_t are the adsorbed amounts (mg g^{-1}) of copperions atequilibrium andat time "t" respectively, k_1(min^{-1}) and k_2(g mg^{-1} min^{-1}) are the rate constants offirst order model andof pseudo-second order model and t is time.

The straight lines were obtained by plotting$\frac{t}{q_t}$ versus "t" and log (q_e- q_t) versus "t" with correlation coefficients (R^2) of 0.999 and 0.949 respectively, Fig. 2(c). The determined parameters of kinetic for the pseudo-second order models and first order are given in Table 1.

Table 1: Kinetic parameters for the adsorption of copper ions on coconut coir

First order			Pseudo-second order		
Q_e	k_1	R^2	Q_e	k_2	R^2
(mg g^{-1})	$(min)^{-1}$		(mg g^{-1})	(g mg^{-1} min^{-1})	
0.194	0.197	0.949	0.885 0.871*	20367	0.999

* Experimentally measured

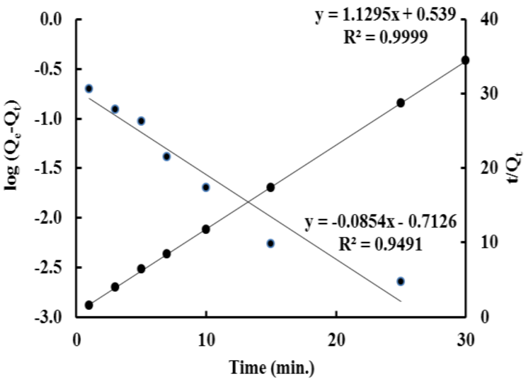

Fig.2(c): Kinetic Modeling for the adsorption of copper ions on coconut coir

It was observed that determined (0.885 mg g^{-1}) value and experimental (0.871 mg g^{-1}) values of adsorption capacity are corresponded to each other and higher R^2 value confirmed that the experimental kinetic data is in good agreement with the pseudo-second order model.

3.4. Optimization of concentration of metal ions

By varying the concentration of copper metal ions from $1.57 \times 10^{-4}$to 2.36×10^{-3}mol L^{-1} where the other parameters was constants, It was observed that with increase in the concentration of copper ions the percentage adsorption of copper ions on coconut coir was decreased as shown in Fig. 3(a). This is due to increase in concentration of copper ion can cause increased in number of metal ions which are competing with the fixed number of available binding sites at the adsorbent surface.

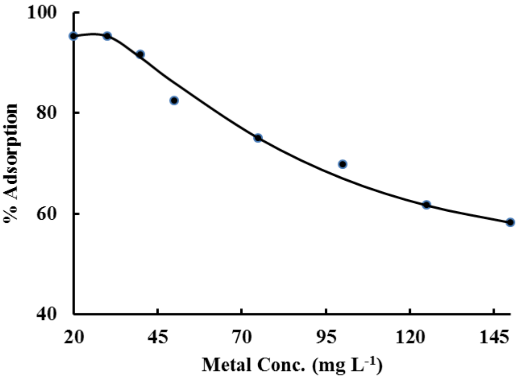

Fig.3 (a): Effect of Adsorbate concentration for the adsorption of copper ions on coconut coir

3.4.1 Adsorption Isotherms

The adsorption data of copper ions on coconut coir were applied to various adsorption isotherm models i.e., Dubinin-Radushkevich, Freundlich and Langmuir isotherms.

Langmuir isotherm

The Langmuir model represents adsorption on homogenous surfaces without any sideways interaction between adsorbed metal atoms or ions. It was found that the data obeyed Langmuir adsorption isotherm over the complete concentration range of adsorbate. The Langmuir isotherm in linearized form can be written as:

$$\frac{C_e}{C_{ad}} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (11)$$

Where C_{ad} and C_e are the concentrations (mol g^{-1}) of copper adsorbed of at equilibrium and of copper in solution, Q and b are Langmuir constants.

The plot of C_e/C_{ad} versus C_e was a straight line Fig. 3(b), which confirms the applicability of the Langmuir isotherm on the adsorption of copper. Langmuir constants Q and b were determined from the slope and intercept of the plot, and were found to be $56.88 \pm 3.16 \times 10^{-3}$ m mol g^{-1} and $9.739 \pm 2.41 \times 10^3$ dm^3 mol^{-1}, respectively.

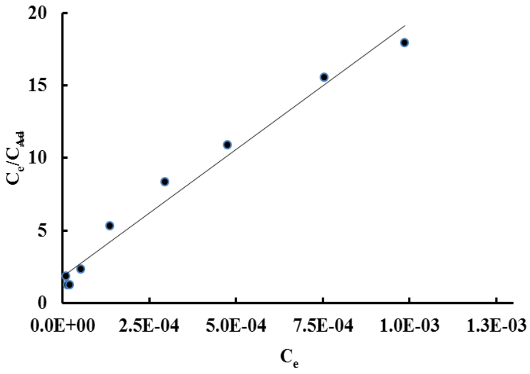

Fig.3 (b): Langmuir adsorption isotherm model for the adsorption of copper ions on coconut coir

Freundlich isotherm

Freundlich adsorption isotherm relates the adsorbed amount of copper per unit mass of the adsorbent (C_{ad}) with the concentration of copper at equilibrium (C_e), and describes the process of multilayer adsorption. Fruendlich equation in linearized form can be written as:

$$\log C_{ad} = \log K + \frac{1}{n} \log C_e \tag{12}$$

Where K and 1/n are Freundlich constants representing the intensity of adsorption and adsorbent capacity respectively,

The plot of log C_{ad} versus log C_e was a straight line Fig.3(c), and the values of K and 1/n, may be computed from the intercept and slope of the plot and were found to be 0.508 ± 0.014 m mol g^{-1} and 0.324 ± 0.023 respectively.

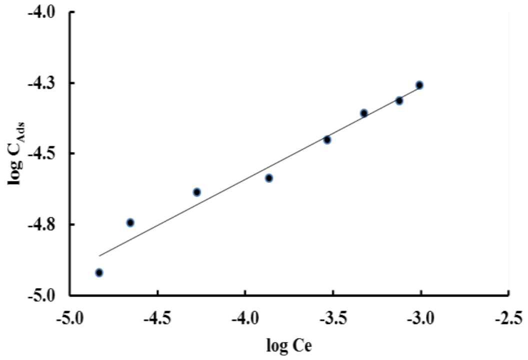

Fig.3 (c): Freundlich adsorption isotherm model for the adsorption of copper ions on coconut coir

The determined adsorption capacity of Cu^{2+} ions on coconut coir through the Freundlich isotherm (32.29 mgg-1) was compared with the reported values of adsorption capacities of different adsorbents (Table 2). Results in Table 2 revealed that the determined adsorption capacity of copper ions on coconut coir is comparable to those of activated sludge and hen egg shell, and significantly higher than Granular activated carbon, Palm fibre, Saw dust (Oak tree), Jute fibres, Sugar beet pulp, Papaya wood, Fly ash, and Pakistani coal.

Table 2: Datafor adsorption capacity of different adsorbents for the extraction of copper.

S. No.	Adsorbent	Capacity	Reference
		(mg g^{-1})	
1	Granular active carbon	3.60	[12]
2	Palm fibre	2.0	[13]
3	Saw dust (Oak tree)	3.60	[14]
4	Jute fibres	4.23	[15]
5	Sugar beet pulp	0.15	[16]
6	Hen egg shell (mg/g),	32.02	[28]
7	Pakistani Coal	4.242	[17]
8	Activated sludge	31.77	[27]
9	Fly ash	1.38	[29]
10	Coconut coir	32.29	Present work

Dubinin-Radushkevich (D-R) isotherm

To verify the chemical or physical nature of adsorption, results of copper ions adsorption on coconut coir were subjected to the Dubinin-Radushkevich isotherm using the following expression:

$$C_{ad} = C_m \exp(-\beta\epsilon^2) \tag{13}$$

Where $C_{ad}$is the adsorbed amount of copper on adsorbent, C_m is the maximum adsorbed amount of copper using the optimized experimental conditions, εis Polanyi potential and β is a constant related to the sorption energy,

$$\varepsilon = RT\ln(1+\frac{1}{C_{Eq}}) \tag{14}$$

Where R is the ideal gas constant, T is temperature in Kelvin and $C_{Eq}$is equilibrium concentration of copper in solution

D-R isotherm in linearized form of can be expressed as:

$$\ln C_{ad} = \ln C_m - \beta\varepsilon^2 \tag{15}$$

Plot of $\ln C_{ad}$ against $\varepsilon^2$was a straight line Fig.3 (d) indicating that adsorbed copper ions also obeyed the D-R equation and the value of β was determined 4×10^{-3} K J^2 mol^{-2}. The mean adsorption energy (E_s) was determined by substituting the value of βin equation (16).

$$E_S = \frac{1}{(-2\beta)^{1/2}} \tag{16}$$

The values of C_m($1.22 \pm 0.015 \times 10^{-4}$mol g^{-1}) and β ($-29.20 \pm 2.13 \times 10^{-4}$ $kj^2 mol^{-2}$) were determined from the intercept and slope of this straight line respectively. The value of the mean sorption energy “E” which is the mean free energy of one mole of solute transfer to the surface of adsorbent was determined (13.08 ± 0.95 kJ mol^{-1}), which was in the expected range of 8-14 kJ mol^{-1} for ion exchange or chemisorptions process.

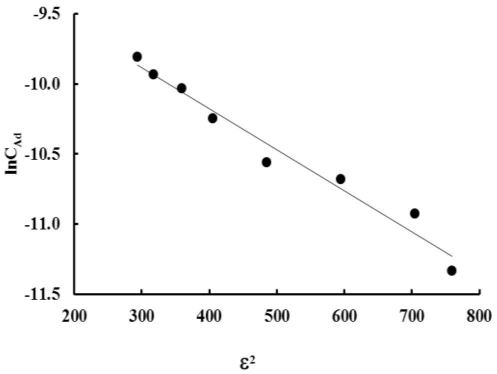

Fig.3 (d): D-R adsorption isotherm model for the adsorption of copper ions on coconut coir

3.5 Optimization of temperature

By varying the temperature from 283 to 333 K where the other parameters were constants, it was observed that with the increase in temperature the adsorption of 1.574×10^{-4} mol L^{-1} of copper ions on the surface of coconut coir increased as shown in table 3.

Table 3:Results for Adsorption of copper ions on coconut coir by varying temperature

Low-rank Pakistani coal	*0.25 g*
Contact time	*15 min.*
Volume Equilibrated	*10 cm^3*
Concentration of copper ions	*6.29×10^{-4} mol L^{-1}*

Temp.	$1/T \times 10^{-3}$	$C_{Ad} \times 10^{-4}$	$C_{Eq} \times 10^{-5}$	K_c	$\ln K_c$
(K)		(mol L^{-1})	(mol L^{-1})		
283	3.534	5.220	10.748	4.857	1.580
293	3.413	5.398	8.970	6.018	1.795
303	3.300	5.655	6.397	8.840	2.179
313	3.195	5.730	5.649	10.142	2.317
323	3.096	5.881	4.139	14.209	2.654
333	3.003	5.945	3.501	16.978	2.832

Van't Hoff plot was used to determined ΔS^0 from intercept and ΔH^0 from slope by using the equation.

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{17}$$

$$K_C = \frac{C_s}{C_e} \tag{18}$$

where K_c is equilibrium constant, ΔS^0 is the change in entropy, ΔH^0 is the enthalpy change, T is absolute temperature R is gas constant and.

When $\ln[K_c]$ was plotted against 1/T a straight line was obtained (Fig. 4) with intercept of $\Delta S/R$ and slope of $-\Delta H/R$, thus ΔH can be calculated from slope and ΔS can be calculated from intercept. The Gibb's free energy (ΔG) for the sorption system was calculated from a relationship:

$$\Delta G = -RT \ln K_c \tag{19}$$

The calculated values of ΔS, ΔH and ΔG are shown in Table 4. The negative values of ΔG represent that this process is spontaneous and increase in the value of -ΔG with the increase in temperature represents that the adsorption of copper ions is more satisfactory at higher temperatures. The positive value of enthalpy (ΔH) and (ΔS) indicates the endothermicity and randomness of the adsorption process respectively.

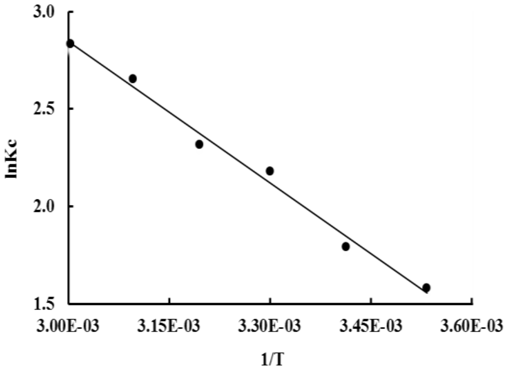

Fig.4: Thermodynamics parameters for

Table 4: Calculated thermodynamic quantities for adsorption of copper

Temperature	ΔG	ΔH	ΔS
(K)	(KJ mol^{-1})	(KJ mol^{-1})	($JK^{-1}mol^{-1}$)
283	−3.718		84.17
293	−4.372	20.102	83.53
303	−5.490		84.46
313	−6.029		83.48
323	−7.127		84.30
333	−7.841		83.91

4. Application of the procedure

Apply this developed procedure with optimized conditions for removing copper ions from ordinary tap water (T_W) to find applicability of this procedure. The results along with the determined composition of tap water sample are shown in Table 5. The data showed that the determined concentration of copper in the sample of tap water was quite low, therefore, the removal efficiency of copper was checked by spiking the sample with 20.0 mg L^{-1} of Cu^{+2} ions. The data in Table 5 indicate that concentration of copper was decreased by 94.85 % from the spiked tap water in a single step within 15 minutes indicating that coconut coir has good potential to remove copper from such matrices.

Table 5: Determined composition of tap water sample

Cations/anions	Concentration
	(mg L^{-1})
Ca	35.52
Mg	16.92
Na	18.92
K	1.23
Fe	0.01
HCO_3^{-2}	141.20
Mn	0.01
CO_3^{-2}	9.00
Zn	0.09
NO_3^{-}	1.50
Cu	0.01
SO_4^{-2}	8.30
Pb	0.01
Cl^{-}	3.80
Cu^{2+}**	1.03**
Cu^{2+}*	20.00*

* Concentration after spiking
** Concentration after decontamination

5. Conclusions

The study concluded that this cheaper coconut coir has high potential to be utilized for the extraction of copper from bulk aqueous solutions within a short shaking time of 15 min and without using any other chemical method. The maximum adsorption observed at 1.00×10^{-4}mol L^{-1} concentration of HNO_3, 10 mL of (3.15×10^{-4}mol L^{-1}) copper stock solution, 0.25 g coconut coir with contact time of 15 minutes. The sorption data of copper ions on coconut coir obeyed the Dubinin-Radushkevich, Langmuir and Freundlichisotherm models and it was occur in the presence of a variety of anions and cations. Thermodynamic quantities i.e. free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have also been calculated for this process and the positive value of enthalpy was represented to be an endothermic process.

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