Removal of copper from aqueous solution using newspaper pulp as an adsorbent

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A B S T R A C T

Newspaper pulp was found to be a potential adsorbent for removal of copper from aqueous medium. Detail adsorption study of Cu on newspaper pulp was investigated. Batch adsorption study was carried out as a function of contact time, adsorbent dose, temperature (303–323 K). The experimental data was analyzed using Freundlich, Langmuir, Dubinin–Radushkevich (D–R) and Redlich-Peterson (R–P) isotherm models. It was found that Freundlich, Langmuir and R–P models fitted well. pH variation study revealed that the adsorption increased with increase in pH of the solution. Maximum loading capacity was found to be 30 mg g^{-1} at 20 mg L^{-1} of initial Cu concentration. Adsorption data were analyzed using two kinetic models, Lagergren first order and pseudo second order. It was observed that pseudo second order represented the best correlation. Langmuir isotherm was used to obtain the thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption. The negative value of free energy and positive value of enthalpy change indicate that the adsorption of Cu on newspaper pulp is a spontaneous process and endothermic. The results of activation energy also confirmed that the adsorption of Cu on newspaper pulp is physical in nature. Present investigation emphasized that newspaper pulp may be utilized as a low cost adsorbent for copper removal.

1. Introduction

Release of heavy metals such as Cr, Ni, Cd, Pb and Cu from industrial wastewater into the aquatic system is a major environmental concern. These heavy metals enter into the urban water system causing health problems. Soils irrigated by wastewater results in accumulation of heavy metals in the surface soils which further releases these contaminants upon saturation into groundwater and soil solution for plant uptake. Waste water irrigation further enhances the heavy metal content of the soils [1].

Copper is one of the major contaminants emanating from electrical, electroplating, and metal finishing industries. It is often found in high concentrations near mines, landfills and waste disposal sites. In human copper toxicity causes itching and dermatization, keratinization of the hands and soles of feet [2,3]. Severe gastro-intestinal irritation and possible changes in the liver and kidney occur due to intake of excessively large doses of copper [4]. Inhalation of copper spray increases the risk of lung cancer among exposed workers [5]. Maximum permissible concentrations of copper in drinking water by World Health Organization (WHO), United State Environmental Protection Agency (USEPA) are 1–2, and 1.3 mg L^{-1}, respectively [6]. The permissible level of copper

for industrial waste water to be discharged to the surface water is 3 mg/L [7]. Hence the removal of copper from wastewater before its discharge into the aquatic system is extremely important and deserves immediate attention.

Coagulation, chemical precipitation, ion exchange, membrane filtration, electrochemical techniques are some of the most widely used techniques for the removal of heavy metals including copper [8]. Adsorption process is a simple cost effective method which has been extensively adopted. According to Babel and Kurniawan [8] low cost adsorbents having high adsorption capacity for heavy metals include chitosan, zeolites, waste slurry, clay, peat moss, fly ash, coal, blast furnace slag, lignin, etc. Of these only chitosan, zeolite, fly ash peat moss and waste slurry show mentionable adsorption of Cu(II). Maximum adsorption capacity of chitosan for Cu(II) was 222 mg g^{-1}, chabazite (zeoliote) 5.10 mg g^{-1}, fly ash-wollastonite 1.18 mg g^{-1}, eutrophic peat moss 19.56 mg g^{-1} and waste slurry was 20.96 mg g^{-1}. Excepting chitosan none of the low cost adsorbents reviewed were effective for copper removal from industrial effluents. Of late biosorption has proven to be an effective technology for the removal of heavy metals. Bio-materials used to remove heavy metals include carrot residues [9], *Sargassum wighiti* [10], lentil, wheat, rice [5], tea industry waste [11], biomass of *Cladonia rangiformis hoffm* [12] and *Neorospora crassa* [13].

Cellulose is the most abundantly available natural biopolymer. Sorptive properties of cellulose towards metal are well documented [14,15]. Cellulose has better environmental acceptability in

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Nomenclature

A	Arrhenius factor
b	Langmuir constant $(L\,mg^{-1})$
C_0	initial Cu concentration of the solution $(mg\,L^{-1})$
C_e	equilibrium Cu concentration $(mg\,L^{-1})$ after adsorption
C'_e	equilibrium Cu concentration $(mg\,L^{-1})$ after desorption
E	mean free energy of adsorption $(KJ\,mol^{-1})$
E_a	Arrhenius activation energy $(KJ\,mol^{-1})$
f	Redlich–Peterson constant
ΔG°	free energy of adsorption
ΔH°	standard enthalpy
k	specific rate constant
k_1	first order rate constant
k_2	second order rate constant of adsorption $(g\,mg^{-1}\,min^{-1})$
k_d	D–R constant related to adsorption energy $(mol^2\,KJ^{-2})$
k_f	Freundlich constant
k_r	Redlich–Peterson constant
K_L	equilibrium constant corresponding to the Langmuir constant b $(L\,mol^{-1})$
m	mass of the adsorbent
n	Freundlich constant
N	Redlich–Peterson constant
q_e	amount of Cu(II) adsorbed at equilibrium $(mg\,g^{-1})$
q_t	amount of Cu adsorbed at time (t)
Q_m	theoretical saturation capacity for D–R isotherm $(mg\,g^{-1})$
R	gas constant $(kJ\,mol^{-1}\,K^{-1})$
R^2	statistical linear coefficient of determination (the square of correlation coefficient)
ΔS°	standard entropy
T	temperature (K)
V_m	saturated monolayer adsorption capacity $(mg\,g^{-1})$
X	$C_0 - C_e$
X/m	loading capacity

Greek letter

ε	Polyani potential

comparison to synthetic polymers with regard to biological compatibility and bio-decomposition. Waste newspaper pulp is a low cost cellulosic material. The present paper investigates, in detail, the adsorption of copper by processed newspaper pulp. Kinetics and thermodynamics of the adsorption process has been studied along with the conventional treatments of adsorption envelope, loading capacity and adsorption isotherm studies. The paper attempts to examine the reuse of newspaper as an adsorbent for the contaminated water bodies.

2. Experimental

2.1. Preparation of processed newspaper pulp

Old newspaper was treated with concentrated sodium bicarbonate solution for removing the foreign materials like, grease, black ink and the bleaching material (chlorine dioxide) which are usually present in the newspapers. The newspaper pulp was washed several times with distilled water till the pH of the supernatant water layer of the pulp was around 6.5–7. The pulp was gravity filtered through Whatman 40 filter paper, air dried and finely ground by mixer grinder to make it feathery. Characterization of the newspaper pulp has been detailed elsewhere [16].

2.2. Reagents

Analytical grade $CuSO_4 \cdot 7H_2O$ was dehydrated at $110\,^\circ C$ and was used for making stock solution of Cu(II) $(1000\,mg\,L^{-1})$ in $18\,M\Omega$ ASTM grade water. The stock solution was diluted by serial dilution method as per requirement.

2.3. Batch adsorption experiments

Adsorption experiments were carried out in batches of 50 mL of $7.02\,mg\,L^{-1}$ of Cu(II) solution with known weights of newspaper pulp. pH of the solution was kept at 5.8 ± 0.05 for all experiments unless otherwise mentioned. The solutions were shaken in a mechanical shaker for a definite period of time. It was then filtered and Cu concentration was measured before and after adsorption by atomic absorption spectrophotometer (GBC AVANTA). Adsorption parameters such as adsorbent dose, shaking time were optimized by the method of continuous variation. The optimized parameters were found to be 0.1 g adsorbent dose and 30 min contact time to reach equilibrium for $7.02\,mg\,L^{-1}$ Cu(II) concentration.

2.4. pH variation study

To study the influence of pH on adsorption, the batch experiments were carried out in the pH range of 2.0–7.0. pH of the solution was adjusted using dilute NaOH and HCl. For desorption study, initially Cu(II) was adsorbed over the newspaper pulp at pH 5.8. The pH was then adjusted in the range of 2–7 using dilute NaOH and HCl and were shaken for half an hour. The percentage of desorption was calculated as follows.

$$\%\text{Desorption} = \left(\frac{C'_e - C_e}{C_0 - C_e} \right) \times 100$$

where C_0 is the initial Cu concentration of the solution $(mg\,L^{-1})$, C_e is the equilibrium Cu concentration $(mg\,L^{-1})$ at a particular pH, C_e' is the equilibrium Cu concentration $(mg\,L^{-1})$ at a particular pH after desorption.

2.5. Kinetic and thermodynamic study

Kinetic and thermodynamic studies were carried out for three different Cu(II) concentrations at temperature of 30, 40 and $50\,^\circ C$.

2.6. Instrumentation

Cu(II) was analyzed using atomic absorption spectrophotometer, GBC AVANTA, chloride, fluoride, phosphate and nitrate was measured using ion chromatography (Metrohm Ion Chromatograph).

3. Results and discussion

3.1. Effect of adsorbent dose

Fig. 1 shows the adsorption of Cu(II) with varying weight of the adsorbent at pH 5.8 ± 0.05.

It indicates that the uptake of Cu(II) increases as the adsorbent dose increases from 0.01 to 0.2 g in 50 mL of Cu(II) solution. Beyond 0.2 g of the adsorbent the Cu(II) removal becomes more or less constant over the concentration range of $7.02–24.39\,mg\,L^{-1}$. The adsorbent dose of 0.2 g was able to adsorb 94.2% Cu(II) from 50 mL of $7.02\,mg\,L^{-1}$ Cu(II) solution. This increase of Cu(II) removal may be attributed to the active site of the adsorbent surface.
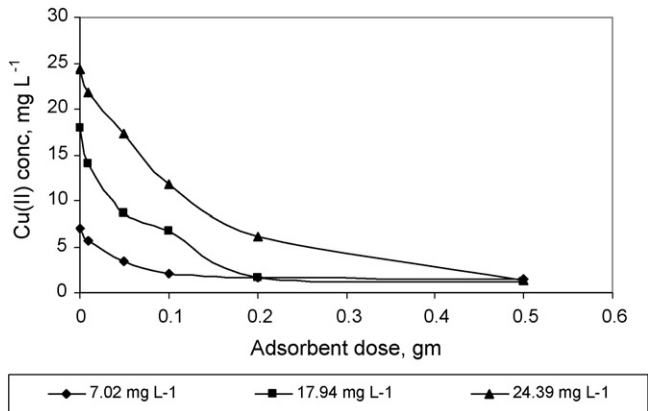
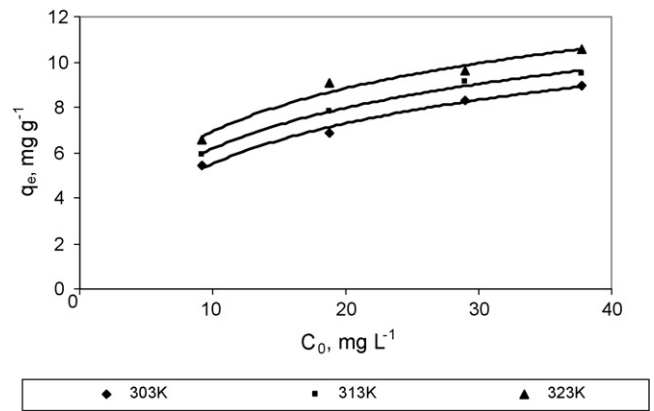Fig. 1. Effect of adsorbent dose at three different Cu(II) concentrations.
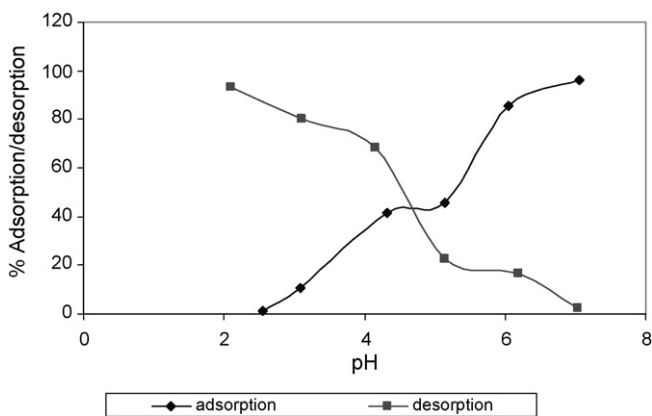

Fig. 2. Adsorption/desorption profile of Cu(II) as a function of varying pH.

3.2. Effect of pH

Fig. 2 depicts the effect of Cu(II) removal at various pH levels (2.0–7.0) for an initial Cu(II) concentration of 18.27 mg L^{-1}. It is evident from Fig. 2 that Cu adsorption increases with increase in pH of the solution and reaches maximum at pH 7. Further increase in pH (beyond pH 7) may be attributed to the precipitation of Cu as Cu(OH)$_2$ [17]. Fig. 2 also represents the desorption profile of Cu(II)

Fig. 4. Adsorption profile of Cu(II) as a function of varying temperature.

from the adsorbent surface. Experimental results show that the percentage of desorption decreases with increase in pH of the solution and reaches minimum at pH 7.0. As the newspaper pulp consists of cellulosic matrix, the adsorbent surface contains a large number of active site [−OH] which is associated with intramolecular hydrogen bonding as visible in Fig. 3.

The metal uptake depends on these active sites as well as the nature of the metal ions of solution. This is further explained in relation to the competitive effect between the H$_3$O$^+$ and the Cu(II) ions. At the low pH the H$_3$O$^+$ predominates and occupies the binding sites of the adsorbent whereas on increase in pH the concentration of H$_3$O$^+$ decreases and that of OH$^-$ increases on the surface of the adsorbent. The surface charge of the adsorbent thus changes to negatively charged sites which results in higher attraction of cations [17].

3.3. Effect of temperature

The adsorption of Cu(II) was carried out at three different temperatures 303, 313, and 323 K using newspaper pulp as an adsorbent. The experimental results are shown in Fig. 4. The isotherm constants of Freundlich and Langmuir isotherms on varying temperature are reported in Table 1. The adsorption capacity increases with increase of solution temperature. This indicates that the adsorption of Cu(II) on newspaper pulp is an endothermic process.
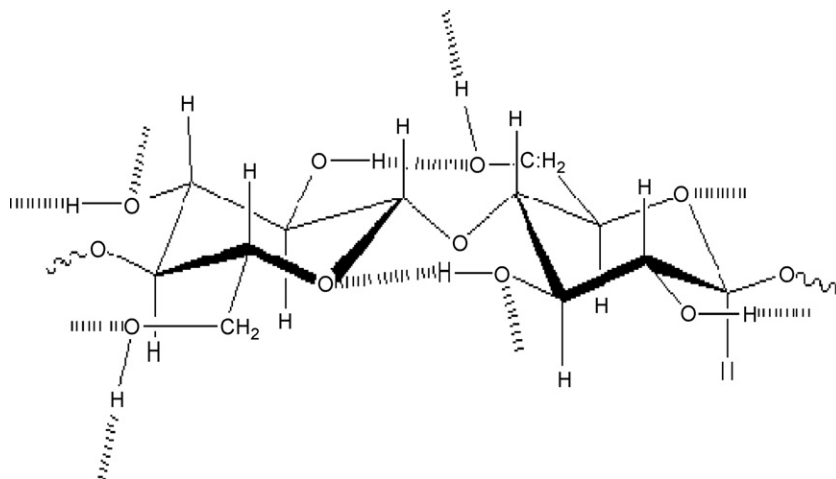

Fig. 3. Structure of cellulose matrix.

Temperature (K)	Freundlich			Langmuir		
	k_f	n	R^2	k_L (L mol^{-1})	V_m (mg g^{-1})	R^2
303	2.38	2.73	0.99	6590	10.94	0.98
313	2.8	2.90	0.98	6890	11.83	0.99
323	3.03	3.03	0.95	7074	13.0	0.98

3.4. Adsorption Isotherms

Adsorption of Cu(II) on newspaper pulp was studied in the concentration range of 0–24.39 mg L^{-1} with varying weights of adsorbent (Fig. 1). The adsorption data were applied to the four adsorption isotherm models. The adsorption parameters of four different isotherms namely Langmuir, Freundlich, D–R and R–P were studied for three different initial Cu(II) concentrations. Langmuir model represents the monolayer adsorption onto a homogeneous surface with a finite number of active sites whereas D–R model does not assume homogeneous surface The Freundlich and R–P models are empirical in nature. Freundlich isotherm considers the heterogeneous adsorption surface and the possibility of multilayer adsorption. The isotherm constants of Freundlich and Langmuir were calculated using normal linearisation method whereas for D–R and R–P models constants were obtained by Robust fit using SOLVER. Constants values of all four isotherms are presented in Table 2.

The isotherms used to explain the experimental data are explained below.

Langmuir model

$$\frac{1}{q_e} = \frac{1}{bV_mC_e} + \frac{1}{V_m} \tag{1}$$

where V_m represents saturated monolayer adsorption capacity (mg g^{-1}) and b is the Langmuir constant (L mg^{-1}) related to bond energy of adsorption system, respectively, C_e is the equilibrium concentration of the solute (mg L^{-1}) and q_e is the amount of Cu(II) adsorbed at equilibrium (mg g^{-1}). The Langmuir constant b and V_m can be calculated from the slope and intercept of linear equation of $1/q_e$ versus $1/C_e$.

Freundlich isotherm

The well-known Freundlich equation can be written as

$$\text{Log } q_e = \text{Log } k_f + \frac{1}{n}\text{Log } C_e \tag{2}$$

where n and k are the Freundlich constant. The calculated value of n and k are shown in Table 2.

Dubinin–Radushkevich (D–R) isotherm

$$\ln q_e = \ln Q_m - k_d\varepsilon^2 \tag{3}$$

where ε (Polyani potential) is $[RT\ln(1+1/C_e)]$, Q_m the theoretical saturation capacity (mg g^{-1}), k_d a constant related to adsorption energy (mol^2 KJ^{-2}), R is the gas constant (kJ mol^{-1} K^{-1}) and T is the temperature (K).

The slope of the plot $\ln q_e$ versus ε^2 gives the K_d and Q_m values.

Redlich–Peterson (R–P) isotherm

The R–P isotherm is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{k_r} + \frac{1}{fC_e^N} \tag{4}$$

where k_r, f and N are the R–P constants C_e is the equilibrium concentration of Cu.

It is evident from Table 2 that adsorption data fit reasonably well in Langmuir, Freundlich as well as R–P isotherm as reflected in the correlation coefficients (R^2). The Freundlich constant n increases with increasing initial Cu concentration. D–R isotherm shows a definite trend for k_d value. However, the correlation coefficient (R^2) in D–R isotherm decreases with the increase in initial concentration of Cu. No definite trend was observed for Langmuir constant b and V_m.

The affinity between Cu(II) and newspaper pulp adsorbent can be predicted using the Langmuir parameter b from the dimensionless separation factor R_L [18].

$$R_L = \frac{1}{(1+bC_0)} \tag{5}$$

where C_0 is the initial Cu(II) concentration and b is Langmuir isotherm constant. The adsorption process as a function of R_L may be described as

$R_L > 1$ unfavorable
$R_L = 1$ linear
$0 < R_L < 1$ favorable
$R_L = 0$ irreversible

In the present study, the calculated R_L value for adsorption of Cu(II) on the newspaper pulp adsorbent were found to be 0.66, 0.46 and 0.14 as shown in Fig. 5 which indicates a highly favorable adsorption within the concentration range of 7.02–24.39 mg L^{-1}. R_L in the range of 0–1 at all initial Cu(II) concentrations confirms the favorable uptake of Cu(II) in the sorption process [19].

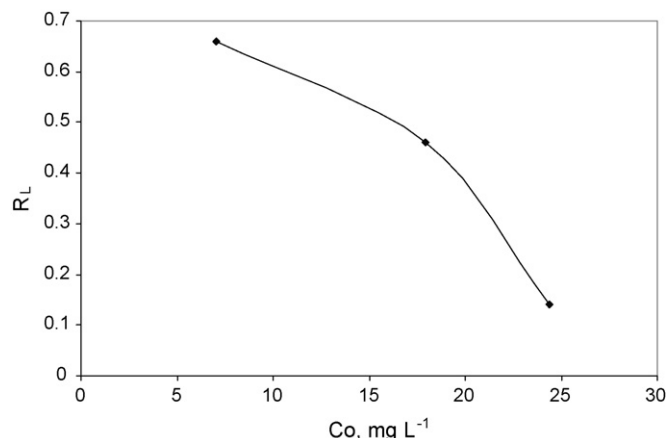| Isotherm	Constants	Initial concentration (mg L^{-1})		
		7.02	17.94	24.39
Freundlich	n	0.86	1.28	1.84
	k_f	1.13	1.86	1.83
	R^2	0.95	0.85	0.90
Langmuir	b (L mg^{-1})	0.073	0.065	0.24
	V_m (mg g^{-1})	10.92	27.77	9.20
	R^2	0.92	0.82	0.93
D–R	K_d (mol^2/KJ^2)	1.39	14.98	8.93
	Q_m (mg g^{-1})	7.67	29.73	11.38
	R^2	0.95	0.96	0.69
	Errsq	0.99	19.98	25.78
R–P	k_r	1.12	1424.6	207.15
	f	12399	2936.75	261.58
	n	−21.45	−0.38	0.13
	R^2	0.99	0.95	0.84
	Errsq	0.07	13.04	11.40

Fig. 5. Plot of R_L vs. initial Cu(II) concentration.

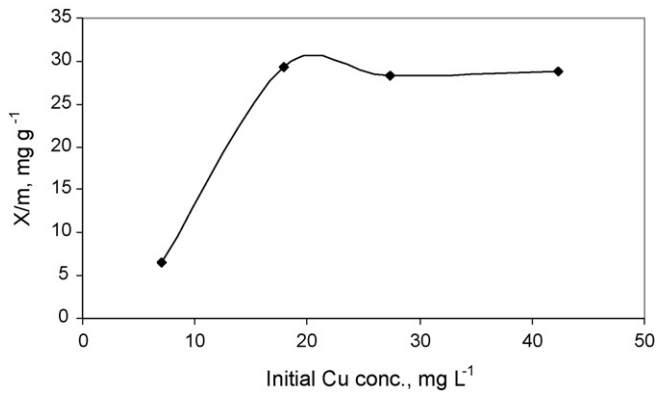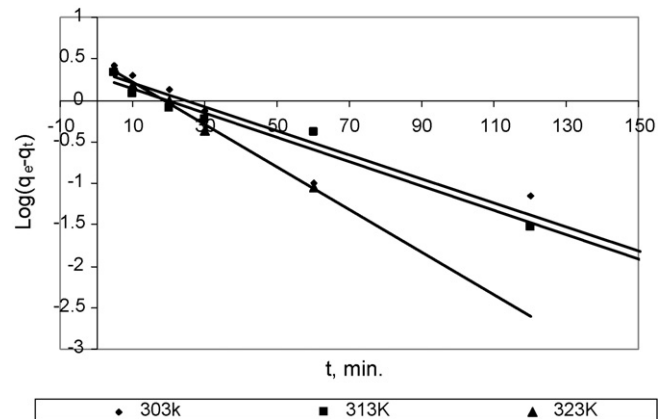Fig. 6. Plot of loading capacity vs. initial Cu(II) concentration.

Fig. 7. Plot of $\text{Log}(q_e - q_t)$ vs. t.

The constant k_d gives an idea about the mean free energy E (kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the D–R isotherm constant K_d using following equations [20]:

$$E = \frac{1}{\sqrt{2k_d}} \tag{6}$$

The calculated E value was found to be 0.66, 0.18 and 0.23 KJ mol^{-1} for three different initial concentration of Cu(II) (7.02, 17.94 and 24.39 mg L^{-1}) on the newspaper pulp adsorbent medium. It is evident from the results that E value is less than 8 KJ mol^{-1} which indicates that the adsorption process of Cu(II) on newspaper pulp follows physical adsorption [21].

Isotherm constants in each equation were determined through robust fitting using SOLVER programme. A generalized error function, as shown below was defined

$$\text{Err} = \sum_{i=1...n} \left[\left(\frac{X}{m} \right)_{\text{exp.}} - \left(\frac{X}{m} \right)_{\text{cal.}} \right]^2 \tag{7}$$

where, n = number of adsorption experiments carried out with a particular Cu(II) concentration $(X/m)_{\text{exp.}}$ = experimental value of adsorbate per g of adsorbent, $(X/m)_{\text{cal.}}$ = calculated value of adsorbate per gm of adsorbent using a set of isotherm constants for a particular isotherm model.

3.5. Loading capacity

Loading capacity of an adsorbent at a particular level of adsorption may be defined as the amount of adsorbate adsorbed per unit weight of the adsorbent. Loading capacity (X/m) of the processed newspaper pulp was determined at different initial concentrations with varying adsorbent dose at a solution pH 5.8. Maximum loading capacity was found to be 30 mg g^{-1} at 20 mg L^{-1} of initial Cu concentration. Fig. 6 represents the plot of loading capacity (X/m) versus initial Cu concentration C_0 (mg L^{-1}). It is evident from Fig. 6 that the loading capacity of newspaper pulp is dependent on the

initial concentration of Cu. The comparative study of the monolayer adsorption capacity, V_m (mg g^{-1}) of Langmuir constant under similar conditions (pH and temperature) has been made with other available cellulosic adsorbent as shown in Table 3. Cellulosic waste materials such as oil shale waste, tea waste, tobacco dust, oil shell waste, etc. have been used for Cu removal from wastewater by various researchers. Comparing the loading capacity of these waste materials under similar condition, newspaper pulp was found to be a potential adsorbent with higher loading capacity for Cu. Thus, it can be utilized effectively for removing Cu from wastewater.

3.6. Adsorption kinetics and thermodynamic study

Two kinetic models, Lagergren's first order rate equation [22] and pseudo second order equation [23] were successfully employed for explaining the kinetic data of an adsorption process.

Lagergren's first order model

$$\text{Log}(q_e - q_t) = \text{Log}\, q_e - \frac{k_1 t}{2.303} \tag{8}$$

where q_e is the amount of adsorbed Cu onto the newspaper pulp at equilibrium (mg g^{-1}), q_t is the amount of Cu adsorbed at time t, k_1 is the first order rate constant. The plot of $\text{Log}(q_e - q_t)$ versus t in Fig. 7 reveals that the kinetic data of adsorption of Cu on newspaper pulp follows Lagergren first order model with high correlation coefficient (R^2). The rate constant k_1 for three different temperature calculated from the slope of the linear plot is listed in Table 4.

Pseudo second order rate equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

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

Table 3
Comparative study of the monolayer adsorption capacity with other cellulosic adsorbent under similar conditions

Cellulosic material	pH	Initial concentration of Cu (mg L^{-1})	Loading capacity (mg g^{-1})	References
Oil shale waste	5.5	400	18.82	[31]
Tobacco dust	4–5	15	36	[32]
Tea industry waste	5.5	5	5.5	[11]
Rice husk	5–6	100	29	[33]
Chitosan-cellulose bead	4–10	50	14–16	[34]
Newspaper pulp	5.5	20	30	Present study

Table 4
Kinetic parameters of Cu(II) by newspaper pulp with varying temperature

Temperature (K)	Lagergren 1st order				Ho 2nd order			
	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	E_a (KJ mol^{-1})	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	E_a (KJ mol^{-1})
303	0.0334	2.24	0.86	22.97	0.042	6.00	0.99	20.12
313	0.0336	1.96	0.96		0.062	6.99	0.99	
323	0.0591	2.96	0.99		0.069	8.98	0.99	

Integrating Eq. (9) for boundary condition $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{10}$$

Eq. (10) can be rearranged to obtain

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

which is the linearised form of Ho second order model. The plot of t/q_t against t in Fig. 8 represents the kinetic data of adsorption of Cu on newspaper pulp. The good fit of kinetic data in second order rate expression shows excellent linearity with high correlation coefficient ($R^2 = 0.99$) over the temperature range of 303–323 K. The value of q_e and k_2 obtained from the slope and intercept of the straight line is shown in Table 3. The increasing trend of adsorption capacity q_e at time t and second order rate constant k_2 in Table 4 favors the adsorption of Cu on newspaper pulp at higher temperature.

The pseudo second order rate equation of Cu(II) adsorption on newspaper pulp is expressed as a function of temperature by Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{12}$$

where E_a is the Arrhenius activation energy (KJ mol^{-1}), A the Arrhenius factor, R the gas constant (8.314 J mol^{-1} K^{-1}), k is the specific rate constant and T is the solution temperature. The ln k versus $1/T$ gives a straight line with slope $-E_a/R$ and intercept ln A as shown in Fig. 9. The k value of Arrhenius equation was obtained from the rate constant (k_1) of Lagergren first order and pseudo second order (k_2). The Arrhenius activation energy calculated from the slope was found to be 22.97 KJ mol^{-1} for Lagergren kinetic model and 20.31 KJ mol^{-1} for pseudo second order kinetic model as mentioned in Table 2. The results of activation energy confirm that the nature of adsorption process is physical adsorption onto the newspaper pulp. The physisorption process usually have energies in the range of 5–40 KJ mol^{-1} while higher activation energy (40–800 KJ mol^{-1}) suggest chemisorption [24,25].
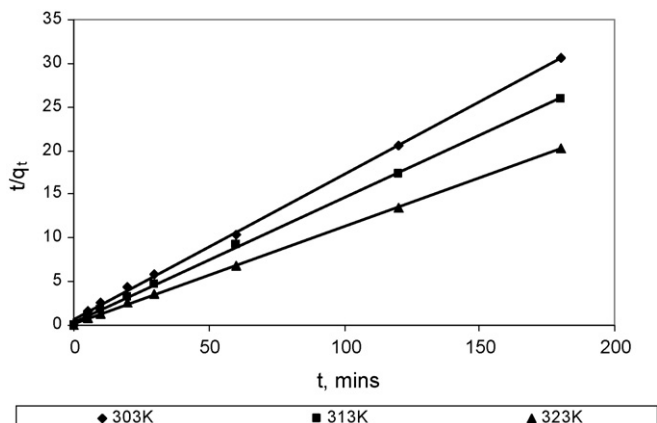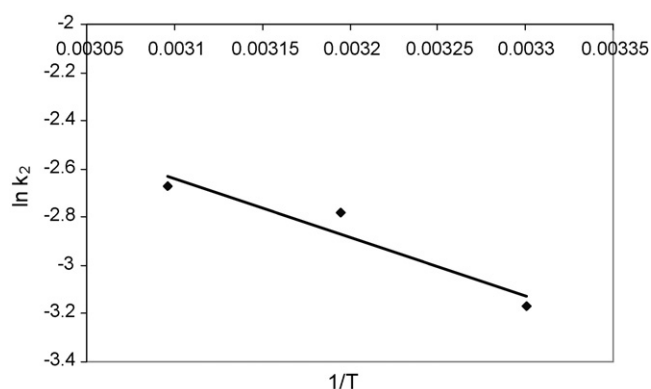

Fig. 9. Plot of $\ln k_2$ vs. $1/T$.

The free energy of adsorption (ΔG°) can be related with the equilibrium constant K_L (L mol^{-1}) corresponding the Langmuir constant, b, as mentioned in Table 4 by the following equation [26,27]:

$$\Delta G^\circ = -RT \ln k_L \tag{13}$$

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using the following equation:

$$\ln k_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{14}$$

where R is the gas constant and T is the absolute temperature as mentioned in Arrhenius equation. The constant b is the Langmuir constant corresponding to the temperatures of 303, 313 and 323 K (Table 4). The plot of $\ln k_L$ versus $1/T$ (Fig. 9) gives the straight line from which ΔH° and ΔS° was calculated from the slope and intercept of the linearised form. Table 5 shows the values of thermodynamic parameters of Cu adsorption on newspaper pulp. The negative value of ΔG° confirms the spontaneity of the adsorption process with increasing temperature and the positive value of ΔH° suggests that the adsorption is endothermic in nature. The positive ΔS° interprets the increased randomness at the solid/solution interface. The positive values of E_a and ΔH° indicate the presence of an energy barriers in the adsorption process and endothermic.

3.7. Adsorption mechanism

Newspaper pulp, comprising cellulosic matrix, is regarded as the most abundant biopolymer in nature. Cellulose is a linear homopolymer of (β1–4) linked β-D-glycopyranose unit (Glc) aggregated to form a highly ordered structure due to its chemical constitution and spatial conformation [28]. Three hydroxyl groups in each Glc are able to interact with one another forming intra

Fig. 8. Plot of t/q_t vs. t.

Table 5
Thermodynamic parameters of Cu(II) on newspaper pulp

Temperature (K)	ΔG° (KJ mol^{-1})	ΔH° (KJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
303	−22.15	2.89	82.67
313	−22.98		
323	−23.81		

and intermolecular hydrogen bonds [29]. At low pH the hydroxyl groups in Glc interact more with H$^+$ ions. The repulsive electrostatic interaction at low pH (acidic range) may hinder Cu(II) for approaching the surface of the adsorbent. However, the electrostatic repulsion decreases with increase in solution pH and Cu would favor to approach the surface of the adsorbent. At pH 6, there are three species present in solution as suggested by Elliot and Huang [30].
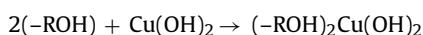
(i) Cu^{2+} in small quantity
(ii) CuOH$^+$ and Cu(OH)$_2$ in large quantity

These species are adsorbed on the surface of the newspaper pulp either by ion exchange or by hydrogen bonding as shown below:

Ion exchange

$$2(-ROH) + Cu^{2+} \rightarrow 2(-RO)Cu + H^+$$

$$-ROH + CuOH^+ \rightarrow (RO)CuOH + H^+$$

Hydrogen bonding

$$2(-ROH) + Cu(OH)_2 \rightarrow (-ROH)_2Cu(OH)_2$$
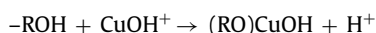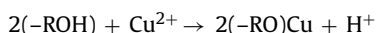
where R represents the cellulosic matrix of newspaper pulp.

In the present study, pH of the solution remains same before and after adsorption. Therefore, the possibility of ion exchange between Cu(II) and cellulose may be lower whereas the probability of hydrogen bonding would be comparatively higher. This is further established from the calculated value of activation energy, E_a, which indicates the adsorption process to be physisorption.

3.8. Residual elemental concentrations

Residual elemental concentrations after adsorption are very important factor for any water treatment study. In present study the cations and anions were measured after Cu adsorption to see the possibility of leaching any undesirable elements from newspaper pulp. The experiment was carried out for 18.5 mg L^{-1} of initial Cu(II) concentration with an adsorbent dose of 1 g per liter. The results are shown in Table 6. It was found that the leaching of cations and anions from newspaper pulp was well within the limit of WHO guideline.

3.9. Recovery study

The recovery of Cu from the adsorbent was performed using 0.01, 0.1 and 1.0 M HCl solution to remove the bound Cu from the newspaper pulp. For each above-mentioned concentration, three replicates of 0.05 g of adsorbents were loaded with 50 mL of 17.65 mg L^{-1} Cu

Table 6
Residual elemental concentration after adsorption

Cations (mg L^{-1})		Anions (mg L^{-1})	
Ca^{2+}	2.46	F$^-$	0.031
Mg^{2+}	0.49	Cl$^-$	4.26
Mn^{2+}	0.16	NO$_3^-$	0.166
Fe^{3+}	0.058	PO$_4^{3-}$	n.f.
Zn^{2+}	0.022	Br$^-$	n.f.
Pb^{2+}	n.f.		

Weight of pulp = 0.05 g, volume of water = 50 mL, shaking time = 30 min. n.f. = not found.
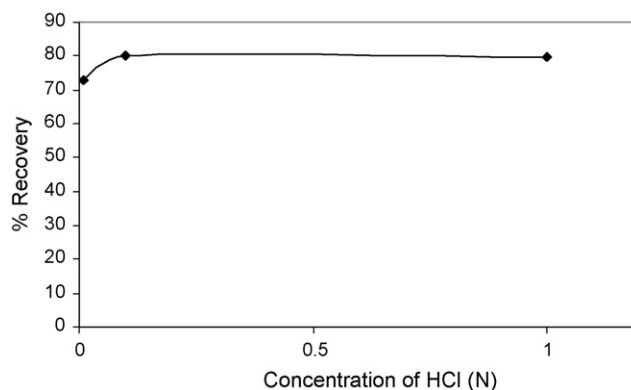
Fig. 10. Recovery of Cu(II) from newspaper pulp after adsorption.

solution. The Cu was adsorbed onto newspaper pulp and the adsorbent with loaded Cu was stripped using 0.01, 0.1 and 1.0 M HCl solution. Fig. 10 shows 80% of Cu bound by newspaper pulp was recovered from the adsorbent using 0.1 M HCl. Higher concentration of HCl did not increase the Cu recovery. After stripping of Cu from the newspaper pulp, it was reused for Cu(II) removal from Cu loaded aqueous medium. Adsorption efficiency of the newspaper pulp was found to decrease by 5%.

4. Conclusion

The newspaper pulp, an unavoidable waste material, is a potential adsorbent for Cu. The maximum loading capacity, X/m of newspaper pulp was found to be 30 mg g^{-1} for initial concentration of 20 mg L^{-1} of Cu at pH 5.5.

pH study revealed that maximum Cu removal could be achieved at pH 7. The experimental data was found to fit better with the pseudo second order kinetic model for entire temperature range. The value of activation energy, E_a confirms that the nature of adsorption is physisorption of Cu onto the newspaper pulp. The negative value of ΔG° and positive ΔH° obtained confirms that Cu adsorption is a spontaneous and an endothermic process.

Recovery of Cu from newspaper pulp was found to be 80% using 0.1N HCl. Adsorption efficiency of newspaper pulp was decreased by 5% for removing Cu from aqueous medium.

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