DOI:10.7598/cst2016.1217
ISSN:2278-3458

Chemical Science Transactions
2016, **5(2),** 361-370

RESEARCH ARTICLE

Removal of Cu(II) and Ni(II) from Aqueous Solutions by Adsorption

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Received 21 January 2016 / Accepted 13 February 2016

Abstract: Adsorptive removal of copper(II) and nickel(II) ions from aqueous solutions were attempted in this study using activated carbons prepared from waste wood shavings. Batch equilibrium adsorption experiments were carried out at room temperature to test the applicability of Freundlich, Langmuir and Redlich-Peterson isotherm equations and the isotherm parameters were evaluated. Kinetic studies performed indicate that the pseudo-second order model fits the data better than first order model and the processes were controlled by particle diffusion of metal ions. Increasing solution pH resulted in increased adsorption and dilute hydrochloric acid was found to be the better desorbing medium.

Keywords: Copper(II), Nickel(II), Adsorption, Adsorption isotherm, Adsorption kinetics

Introduction

Copper is an essential trace element found in all organs and cells and is involved in numerous biological processes like respiration, antioxidant defense, connective tissue formation and others[1]. Though it is an essential element, it is toxic when present beyond the permissible limits. The Wilson's disease and hemochromatiosis are examples of genetic overload diseases of copper. It is reported that trace amounts of copper in drinking water one-tenth of that allowed by the USEPA greatly enhanced an Alzheimer's disease in an animal model[2].

While nickel is essential in certain bacteria, plants and some domestic animals, it is harmful for humans. Nickel toxicity reports from dates well before the element itself is discovered[3]. Nickel(II) is reported to disturb biochemical processes by interacting with amino acids, peptides, sugar residues and nucleotides in biomolecules. Acute nickel poisoning in electroplating workers who drank water contaminated with $NiCl_2$ and $NiSO_4$ developed nausea, vomiting, abdominal discomfort, diarrhea, giddiness, lassitude, headache, cough and shortness of breath which lasted even for a couple of days[4]. Even microorganisms[5]. plants[6, 7] and marine organisms[8] are proven to be adversely affected by nickel exposure.

Industries that release significant quantities of these metal ions include: metal manufacturing, forming, coating and finishing industries, electroplating industries, copper wire mills, printed circuit board industries, battery manufacturing units, food preservation, and many other process industries[9-12]. Although methods like coagulation/flocculation, ion-exchange, precipitation and advanced oxidation process are frequently used for the removal of metal ions from waste streams, adsorption – especially onto activated carbon – is the most preferred one because it is non-destructive, no chemicals are used, economic and it is also a green process that uses only water and a carbon adsorbent.

Experimental

The basic carbon (C1) was prepared from waste wood shavings and wet chemical modifications with concentrated nitric acid, hydrogen peroxide and potassium persulphate were done to yield, respectively, C2, C3 and C4. The methods of their preparation and characterization can be found elsewhere[13].

Analysis of metal ions

Copper(II) was estimated by monitoring the absorption of the thiocyanate complex[14] at 380 nm and Ni(II) by that of its DMG complex[15] at 470 nm.

Procedure for batch adsorption experiments

Briefly, 50 mL of metal ion solutions were equilibrated with carbons in a mechanical shaker, filtered through Whatmann No. 41 filter paper and the filtrates were analyzed. Concentrations of metal ions are varied in isotherm studies; contact time in kinetic studies and pH of the metal ion solutions (adjusted with dilute HCl or NaOH solutions) in pH variation studies. The amounts adsorbed at equilibrium and at time *t* are calculated using the following equations:

$$\mathrm{q_e} = \frac{(C_i - C_e)v}{w} \qquad \mathrm{q_t} = \frac{(C_i - C_t)v}{w} \tag{1}$$

where, C_i, C_e and C_t are amounts of metal ions at initial, equilibrium and at time *t* (mg/L), *V* is the volume of solution (L), *W* is the amount of adsorbent (mg) and q_e and q_t are amounts adsorbed at equilibrium and at time *t* (mg/g). Dilute HCl, dilute acetic acid and water were used as the desorbing media.

Results and Discussion

Properties of the adsorbents

The physical and chemical characteristics of the carbons were reported already[13] and a brief summary is presented in Table 1.

Table 1. Some properties of activated carbons

Property	C1	C2	C3	C4
BET surface area, m^2/g	544.05	548.10	586.65	856.98
Surface acidic groups, mequiv/g	0.423	2.394	1.884	1.117
Surface basic groups, mequiv/g	0.682	0.158	0.177	0.424
pH_{ZPC}	8.57	4.21	4.51	5.02

The equilibrium adsorption isotherms obtained for Cu(II) and Ni(II) are given in Figure 1 and three isotherm equations reported in the literature[16], Freundlich, Langmuir and Redlich-Peterson are used to fit these experimental data in the following forms:

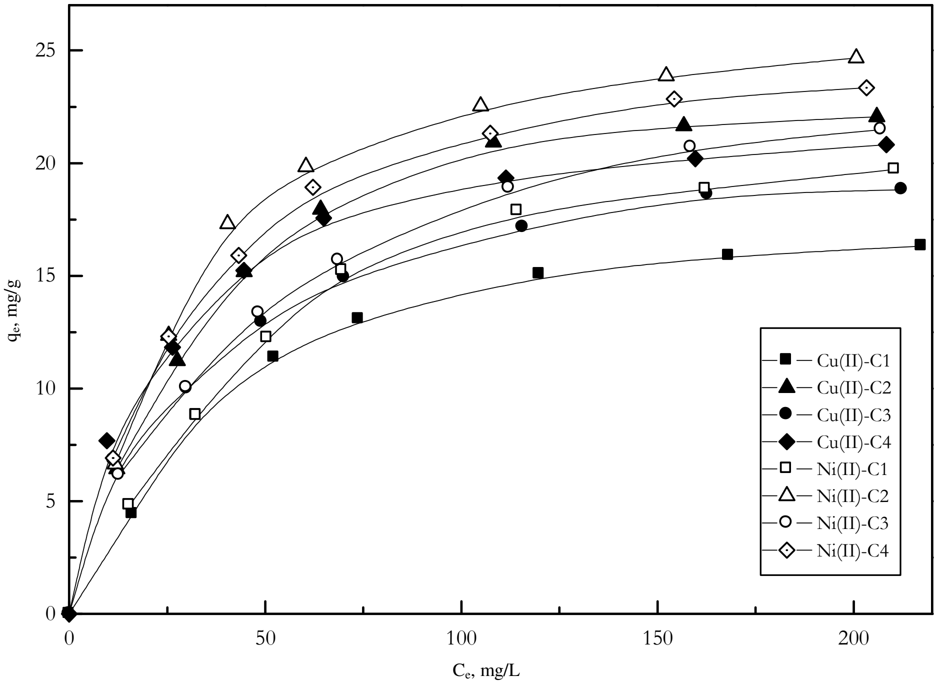

Figure 1. Adsorption isotherms for Cu(II) and Ni(II) on activated carbons

$$\text{Freundlich}\, q_e = K_F C_e^{(1/n)} \tag{2}$$

$$\text{Langmuir}\, q_e = \frac{K_L C_e}{(1 + bC_e)} = \frac{q_m b C_e}{(1 + bC_e)} \tag{3}$$

$$\text{Redlich - Peterson}\, q_e = \frac{K_R C_e}{(1 + b_R C_e^{\beta})} \tag{4}$$

Where, K_F and n are Freundlich constants; K_L and b are Langmuir constants; q_m is the Langmuir monolayer capacity; K_R, b_R and β are Redlich-Peterson constants. Each experimental data is fitted with these equations separately and the results are summarized in Tables 2 and 3. The correlation coefficient values obtained indicate that of the three models used, the three-parameter Redlich-Peterson isotherm is the best in describing the adsorptions.

The Freundlich constant K_F is a measure of adsorption intensity; $(1/n)$ represents the heterogeneity of the sorbents' surface and it decides the curvature of the isotherm[17]. The Langmuir equation assumes that all the adsorption sites are equivalent and only monolayer coverage is possible. The parameter b is a measure of adsorption intensity. The Redlich-Peterson model, on the other hand, is described as a combination of Freundlich and Langmuir models. It reduces to the Langmuir equation when β=1 and to the Freundlich when both K_R and b_R are much greater than unity[18]. For the adsorption of both Cu(II) and Ni(II), the Langmuir capacities, q_m, fall in the order: C1< C3< C4<C2 and this is due to the densities of surface groups on the carbons. Even though C3 and C4 are of higher surface area than C2; the surface groups (especially acidic, which could interact with metal cations) on them are less.

Table 2. Isotherm parameters for the adsorptions of Cu(II)

Isotherm	Carbon	Isotherm parameters			
		K_F	n	$1/n$	r^2
Freundlich	C1	2.4049	2.7046	0.3697	0.9684
	C2	3.7667	2.8782	0.3474	0.9543
	C3	3.5182	3.0842	0.3242	0.9823
	C4	4.9226	3.5575	0.2811	0.9684
	Carbon	K_L	b	q_m	r^2
Langmuir	C1	0.4656	0.0232	20.0690	0.9959
	C2	0.7680	0.0288	26.6667	0.9948
	C3	0.6962	0.0321	21.6885	0.9927
	C4	1.0483	0.0455	23.0396	0.9959
	Carbon	K_R	b_R	β	r^2
Redlich-Peterson	C1	0.3896	0.0090	1.1392	0.9962
	C2	0.6165	0.0101	1.1538	0.9992
	C3	0.9555	0.0819	0.8876	0.9950
	C4	1.1426	0.0586	0.9692	0.9962

Table 3. Isotherm parameters for the adsorptions of Ni(II)

Isotherm	Carbon	Isotherm parameters			
		K_F	n	$1/n$	r^2
Freundlich	C1	2.1909	2.3553	0.42457	0.9614
	C2	4.2940	2.9109	0.3435	0.9489
	C3	2.7418	2.5195	0.3969	0.9838
	C4	4.2531	2.9964	0.3337	0.9630
	Carbon	K_L	b	q_m	r^2
Langmuir	C1	0.4586	0.0179	25.6201	0.9928
	C2	0.9108	0.0312	29.1923	0.9930
	C3	0.5664	0.0213	26.5916	0.9988
	C4	0.8933	0.0327	27.3180	0.9984
	Carbon	K_R	b_R	β	r^2
Redlich-Peterson	C1	0.3882	0.0062	1.1635	0.9971
	C2	0.6929	0.0081	1.2017	0.9979
	C3	0.6395	0.0349	0.9328	0.9987
	C4	0.7667	0.0173	1.0896	0.9995

It is also seen from Tables 2 and 3 that the q_m values are always higher for Ni(II) than Cu(II). The high affinities of the carbons toward Ni(II) could be due to the higher ionic potential (2.8986 for Ni^{2+} *versus* 2.7778 for Cu^{2+}). Even though the radius of hydrated Cu^{2+} (5.3 A°) is lower[19] than that of Ni^{2+} (5.4 A°) which could point the higher adsorption of the former on the porous carbons studied, it appears that high concentration gradients exist at the operating conditions and the strength of the Carbon– metal ion interactions decide the overall retentivity. The Langmuir parameter, *b* is used to calculate the R_L value[20] which is given by the equation: $R_L = [1/(1+bC_i)]$. The R_L values for all the systems (Table. 4) lie between 0 and 1 indicating that the adsorptions are all favourable.

Table 4. R_L values for the adsorptions of metal ions

C_i, mg/L	Cu(II)				Ni(II)			
	R_L Value				R_L Value			
	C1	C2	C3	C4	C1	C2	C3	C4
25	0.6329	0.5814	0.5548	0.4678	0.6908	0.5618	0.6525	0.5502
50	0.4630	0.4098	0.3839	0.3053	0.5277	0.3906	0.4843	0.3795
75	0.3650	0.3165	0.2935	0.2266	0.4269	0.2994	0.3850	0.2896
100	0.3012	0.2577	0.2375	0.1802	0.3584	0.2427	0.3195	0.2342
150	0.2232	0.1880	0.1720	0.1278	0.2714	0.1761	0.2384	0.1693
200	0.1773	0.1479	0.1348	0.0990	0.2183	0.1381	0.1901	0.1326
250	0.1471	0.1220	0.1108	0.0808	0.1826	0.1136	0.1581	0.1090

Kinetic studies

The kinetic curves obtained for the adsorptions of metal ions at initial metal ion concentrations of 100 mg/L are shown in Figure 2.

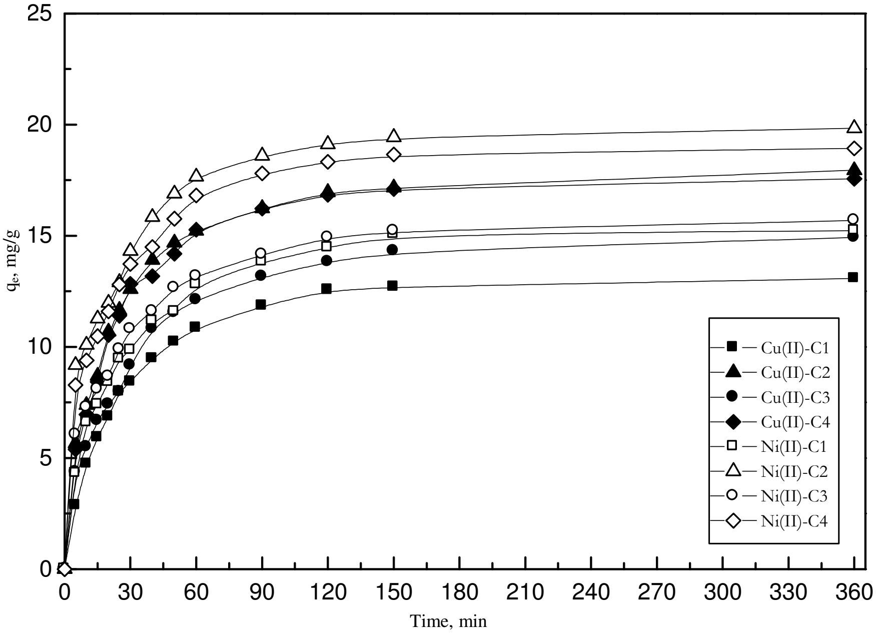

Figure 2. Kinetic curves for the adsorption of Cu(II) and Ni(II)

The kinetic data were fitted using the Lagergren's pseudo-first order model and pseudo-second order kinetic model in the following linear forms[21]:

First order : $\log (q_{e(1)} - q_t) = \log q_{e(1)} - k_1 t$
Second order : $t/q_t = (1/h) + (1/q_{e(2)})t$

where k_1 refers to the pseudo-first order rate constant (min^{-1}); $q_{e(1)}$ is the amount adsorbed predicted by the first order model; $q_{e(2)}$ is the amount adsorbed predicted by the second order model and h is the initial sorption rate (mg.g^{-1}min^{-1}) which is given by $h=k_2 q_{e(2)}^2$ with k_2 being the second-order rate constant (g.mg^{-1}min^{-1}). The kinetic data were fitted separately to these two model equations and the results (Tables 5 and 6) indicate that the sorptions are better represented by the pseudo-second order model than the first order model.

Table 5. First order kinetic parameters for the adsorptions of metal ions

Metal ion	Carbon	Equilibrium uptake, mg/g		k_1 min^{-1}	r^2
		$q_{e(1)}$	$q_{e(exp)}$		
Cu(II)	C1	9.7118	13.0760	0.0010	0.9947
	C2	10.5852	17.9462	0.0084	0.9806
	C3	10.5245	14.9220	0.0085	0.9935
	C4	11.3188	17.5655	0.0099	0.9910
Ni(II)	C1	11.9922	15.2300	0.0113	0.9883
	C2	11.2590	19.8430	0.0101	0.9929
	C3	9.8969	15.6830	0.0092	0.9970
	C4	11.7112	18.9300	0.0110	0.9980

Table 6. Second order kinetic parameters for the adsorptions of metal ions

Metal ion	Carbon	Equilibrium uptake, mg/g		k_2 g.mg^{-1} min^{-1}	h mg.g^{-1} min^{-1}	r^2
		$q_{e(2)}$	$q_{e(exp)}$			
Cu(II)	C1	13.8696	13.0760	0.0040	0.7707	0.9960
	C2	18.6916	17.9462	0.0038	1.3168	0.9999
	C3	15.7978	14.9220	0.0033	0.8284	0.9995
	C4	18.4502	17.5655	0.0038	1.3084	0.9997
Ni(II)	C1	16.0256	15.2300	0.0039	1.0041	0.9996
	C2	20.5339	19.8430	0.0044	1.8671	0.9997
	C3	14.4718	15.6830	0.0055	1.1593	0.9996
	C4	19.6464	18.9300	0.0045	1.7416	0.9997

Three main processes influence the adsorption kinetics: diffusion of adsorbate through the thin film surrounding adsorbent particle (film diffusion); diffusion of adsorbate through the porous structure of adsorbent particle (pore diffusion or particle diffusion) and binding of adsorbate at the adsorption site. The last process is rapid and normally does not represent the rate-limiting step. The methodology of Boyd[22] and Reichenberg[23] was followed to decide whether film- or particle-diffusion controls the rate of adsorption assuming that the adsorptions are primarily ion-exchange in nature. The following equations are used to represent the dynamics:

$$F = \frac{q_t}{q_e} \tag{5}$$

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\alpha}\frac{1}{n^2}e[(D_i t\pi^2 n^2)/r^2] = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\alpha}\frac{1}{n^2}e[-n^2 Bt] \tag{6}$$

Where, B is a time constant, F is the fractional attainment of equilibrium at time t, D_i is the effective diffusion coefficient, r is the particle radius and n is an integer whose value can be 1, 2, 3, …… *etc*. Bt values were derived for each F value by the use of Reichenberg's table[23]. It is suggested that if in an adsorption process the t *versus* Bt plot passes near the origin particle diffusion control the overall rate though there may be some contributions from film diffusion and the reverse is true when the intercept of the t *versus* Bt plots markedly deviate from zero. An examination over Figures 3 and 4 reveals that all the plots are all linear and pass near the origin indicating that the rate-limiting step for these processes are predominately governed by particle diffusion. The effective particle diffusion coefficient values (D_i's) are calculated by the equation $B=D_i\pi^2/r^2$ where B is the slope of the t *versus* Bt plots. The B and D_i values calculated are listed in Table 7.

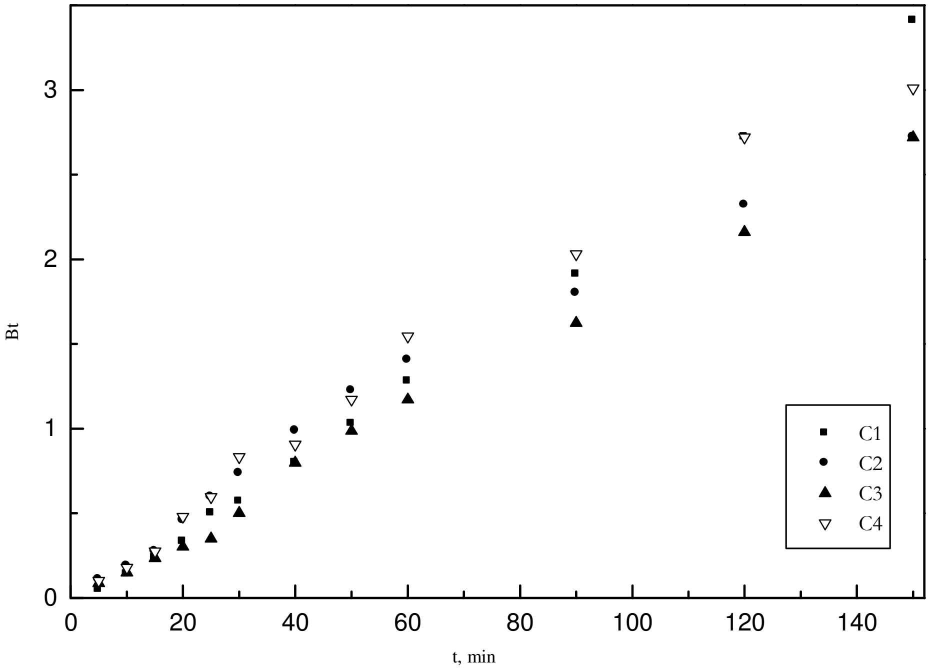

Figure 3. *t versus Bt* plots for the adsorptions of Cu(II)

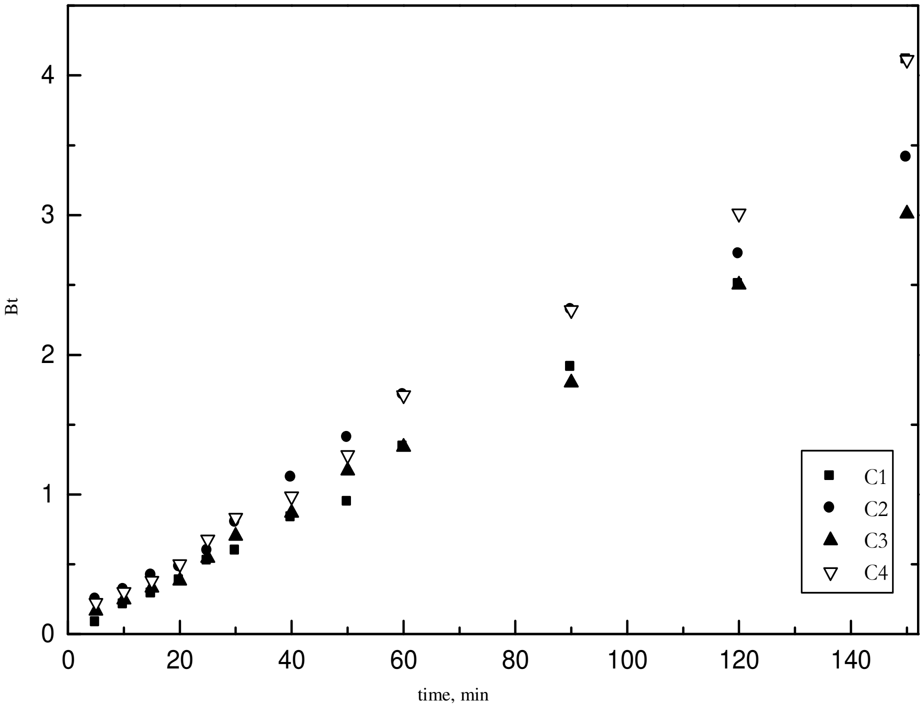

Figure 4. *t versus Bt* plots for the adsorptions of Ni(II)

Table 7. Pore diffusion coefficients for the adsorption of metal ions

Metal ion	Carbon	*B* min^{-1}	$D_i \times 10^{-7}$ $cm^2\,min^{-1}$	r^2
Cu(II)	C1	0.0233	2.3632	0.9995
	C2	0.0183	1.8561	0.9904
	C3	0.0184	1.8662	0.9978
	C4	0.0211	2.1401	0.9924
Ni(II)	C1	0.0252	2.5559	0.9846
	C2	0.0225	2.2820	0.9936
	C3	0.0200	2.0285	0.9981
	C4	0.0263	2.6675	0.9974

pH variation studies

The effect of pH on the adsorption of metal ions are presented in Figures 5 and 6 (adsorbent doses: 0.1 g/50 mL and C_i=100 mg/L). Increase in solution pH resulted in increased adsorption for both Cu^{2+} and Ni^{2+}. As the solution pH is lowered, concentration of H^+ ions will increase proportionally which will effectively compete with metal cations for active adsorption sites on carbon surface. For the parent carbon C1 whose pH_{ZPC} is 8.57 and whose surface groups' density is the poorest, the increase in adsorption percentage is smooth and low throughout the pH range studied. For all other carbons, the increase in adsorption percentage with increase in solution pH is very little up to pH ~ 4.0 and increase very sharply in the pH range 4-6. Above pH 6, the increase is again less marked and reaches a maximum around pH 8.0. The sharp increase that is centered at pH ~ 5 is in line with the pH_{ZPC} of the carbons (4.21 for C2, 4.51 for C3 and 5.02 for C4). Below this pH the carbon surfaces are positively charged, having lesser affinity towards the similarly charged Cu^{2+} and Ni^{2+}. Above this pH, the surfaces become negatively charged and their capacity for cations is tremendous. Further increase in pH result only in a small increase in the amount of adsorption[24].

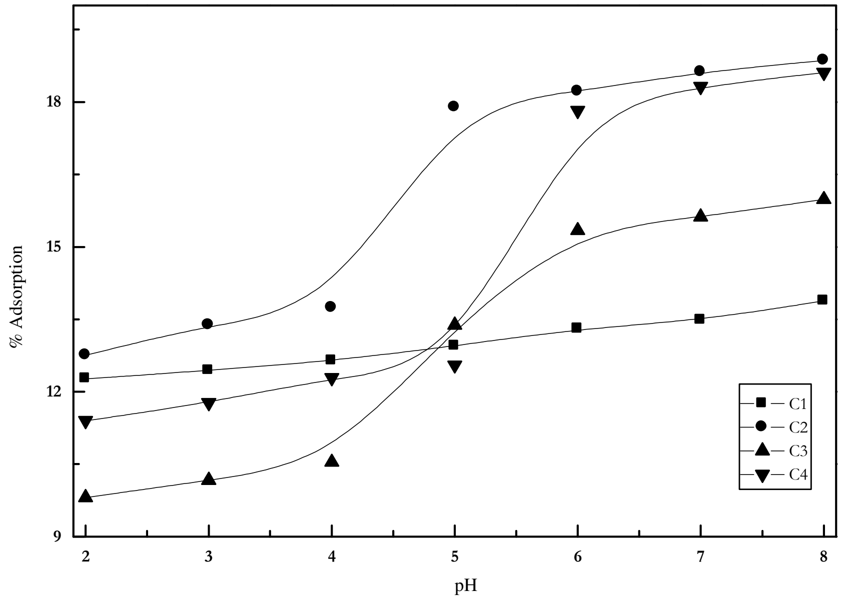

Figure 5. Adsorption of Cu(II) on activated carbons – Effect of pH

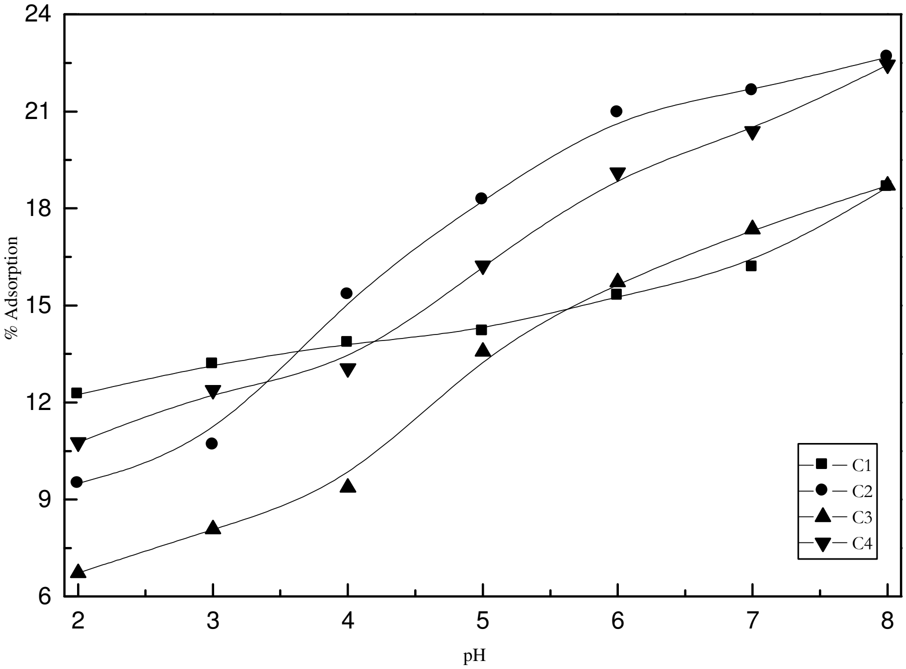

Figure 6. Adsorption of Ni(II) on activated carbons – Effect of pH

Desorption Studies

Attempts were made to regenerate the adsorbed metal ions with water, 0.1 M acetic acid and 0.1 M hydrochloric acid as regenerating agents. The results are presented in Table 8. It is evident from Table 8 that the amount of metal ions desorbed increases with the acidity of the desorbing medium. In general, the stronger HCl was able to desorb most of the metal ions adsorbed. These results also support the ion-exchange nature of the adsorption processes.

Table 8. Results of desorption studies of metal ions

Desorbing Medium	% Desorption of Cu(II)				% Desorption of Ni(II)			
	C1	C2	C3	C4	C1	C2	C3	C4
Water	11.52	10.18	10.29	10.28	15.67	12.33	12.11	11.63
Dil. AcOH	35.41	32.52	34.08	33.66	38.19	36.46	35.61	32.22
Dil. HCl	77.54	88.67	87.37	85.24	75.25	86.72	86.84	85.05

Conclusion

The work reported in this paper reveals that the carbons prepared from waste wood shavings can be successfully used for the removal of Cu(II) and Ni(II) from water. Adsorption isotherms are better represented by the Redlich-Peterson isotherm model and the kinetics were better predicted by the pseudo-second order model. Further kinetic analyses showed that the sorptions are mainly controlled by particle diffusion. The adsorptions of both Cu(II) and Ni(II) increased with increase in pH and dilute HCl is found to desorb most of the adsorbed ions.

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