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Adsorption of Ni(II), Cu(II) and Fe(III) from Aqueous Solutions Using Activated Carbon

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Abstract: An activated carbon was tested for its ability to remove transition metal ions from aqueous solutions. Physical, chemical and liquid-phase adsorption characterizations of the carbon were done following standard procedures. Studies on the removal of Ni(II), Cu(II) and Fe(III) ions were attempted by varying adsorbate dose, pH of the metal ion solution and time in batch mode. The equilibrium adsorption data were fitted with Freundlich, Langmuir and Redlich-Peterson isotherms and the isotherm constants were evaluated. Time variation studies indicate that adsorptions follow pseudo-second order kinetics. pH was found to have a significant role to play in the adsorption. The processes were endothermic and the thermodynamic parameters were evaluated. Desorption studies indicate that ion-exchange mechanism is operating.

Keywords: Activated carbon, Adsorption, pH, Desorption, Metal ions removal

Introduction

Wastewater containing heavy metal pollutants cause direct toxicity, both to human and other living organisms due to their presence beyond specified limits. The main goal today is to adopt appropriate methods and to develop suitable techniques either to prevent metal pollution or to reduce it to very low levels.

Nickel is largely present in the wastewaters of electroplating, motor vehicle and aircraft industries¹. Acute nickel(II) poisoning causes dizziness, head ache, nausea and vomiting, chest pain, dry cough and shortness of breathe, rapid respiration, cyanosis and extreme weakness². World Health Organization, WHO has suggested that the maximum amount of nickel in drinking water should be 0.1 mg/L³. But in many electroplating effluent water it is as high⁴ as 50 mg/L.

Human body requires about 2 mg/L of copper but prolonged oral administration of excessive quantities of copper may result in liver damage and chronic poisoning and gastro-intestinal catarrh⁵. Copper is also toxic to aquatic organisms even at very small concentrations⁶. It is found in sizeable amounts in the liquid effluent streams of printed circuit board plants⁷ and other effluents. Iron(III) is also toxic at higher concentrations. It is desirable, therefore, to undertake investigations on the removal of these metal ions from water.

Among the various cleanup methods available for metal ions removal, namely, electrolytic reduction, precipitation, oxidation, ultra filtration, ion exchange, adsorption, *etc.*, adsorption (especially, activated carbon adsorption) appears to have the least adverse effects. It includes a broad range of carbonaceous materials at a high degree of porosity and large surface area⁸ and finds use for the removal of toxic, biodegradable and non-biodegradable substances from wastewaters. It is attractive as it can treat wastewater to acceptable quality suitable for reuse.

The removal efficiency of a commercial activated carbon (M/s. Loba Company, Mumbai) towards nickel(II), copper(II) and iron(III) was attempted in the present study. The effects of adsorbate dose, pH, time and temperature were studied.

Experimental

Adsorbent

The granular activated carbon was ground and the portion retained between 150 and 250 μ m sieves was used for study. The adsorbent was named as CC.

Characterization of CC

Physicochemical characteristics such as, moisture content, density, volatile matter content, total ash content, water solubles, acid extractable content and pH were determined following standard procedures⁹. Boehm titrations were performed to find out the amounts of surface functional groups¹⁰. Liquid phase adsorption characterizations were done following the method of Maria J. Martin *et al.*¹¹ The infrared spectrum was recorded in an Impart – 420, Nicolet spectrometer. BET surface area of the sample was measured using nitrogen adsorption isotherms.

Analysis of metal ions

All the metals were estimated following a suitable colorimetric method. Nickel(II) was estimated by the dimethylglyoxime method¹², copper(II) and iron(III) by the thiocyanate methods^{13, 14}.

Isotherm procedure

Prior to isotherm studies, minimum contact times for adsorption equilibria to become established were estimated. Each experiment comprised three replicate 100mL glass-stoppered bottles containing appropriate amount of adsorbent and 50mL of adsorbate solutions of selected concentrations. Control flasks without the adsorbents are also prepared simultaneously. Mixtures were maintained in a rotary shaker (orbitek) at constant temperature (30, 45 or 60 °C). After the attainment of equilibrium the contents of each flask were filtered through Whatmann No.41 filter paper, with the first 10mL discarded. The filtered samples were then analyzed for unadsorbed metal ions. The equilibrium adsorption data were then fitted to Freundlich, Langmuir and Redlich-Peterson isotherm equations:

$$\begin{aligned}
 \text{Freundlich} \quad q_e &= K_F C_e^{(1/n)} \\
 \text{Langmuir} \quad q_e &= K_L C_e / (1 + b C_e) = q_m b C_e / (1 + b C_e) \\
 \text{Redlich-Peterson} \quad q_e &= K_R C_e / (1 + b_R C_e^\beta)
 \end{aligned}$$

where q_e is the adsorption capacity in mg/g; C_e is the equilibrium concentration of adsorbate (mg/L); K_F and n are Freundlich constants; K_L and b are Langmuir constants; q_m is the Langmuir monolayer adsorption capacity and K_R , b_R and β are Redlich-Peterson isotherm constants.

pH variation studies

In order to find out the optimum pH for maximum removal of adsorbate, experiments were carried out with solutions of same metal ion concentration but adjusted to different initial pH values (with HNO₃ or NaOH). Measurements were carried out below which chemical precipitation of metal hydroxides do not occur. These values have been estimated to be 7.8 for Ni(OH)₂; 2.5 for Fe(OH)₃; and 7.5 for Cu(OH)₂.

Desorption Studies

Some desorption experiments were also conducted in order to explore the feasibility of recovering both the adsorbed species and the adsorbent and to elucidate the nature of adsorption processes. They were carried out as follows. After adsorption experiments using the selected adsorbent and adsorbate doses, the adsorbate loaded adsorbents were separated and washed gently with several portions of distilled water to remove any unadsorbed species. The samples were then air-dried and agitated with 0.1M solutions of HCl, AcOH or water for a period of 10 hours and the amounts of desorbed species were determined in the usual way.

Results and Discussion

Characterization of the adsorbent

The parameters evaluated are listed in Table 1.

Table 1. Characteristics of Activated Carbon

Characteristics	Result	Characteristics	Result
Proximate Analysis, %		Iodine Number, mg/g	482.299
Moisture	1.6454	Phenol Value, g/L	46.610
Ash	16.7338		
Volatile matter	3.9360	Methylen Blue Number, mg/g	9.482
Fixed carbon	77.6848		
Particle size, μm	150-250	Tannin Value, mg/L	955.690
Surface area (N ₂ -BET), m ² /g	503.1523	Carboxyl groups, mequiv/g	0.052
Apparent density, g/mL	0.7421	Phenolic groups, mequiv/g	0.205
Water solubles, %	1.8239	Lactonic groups, mequiv/g	0.163
Acid-extractable content, %	10.1276	Acidic groups, mequiv/g	0.420
pH	9.42	Basic groups, mequiv/g	0.452

Table 1 reveals that the carbon under study is of high surface area and that it has quite good amounts of micro and mesopores as well. Apart from having the desired textural characteristics of a good adsorbent, the carbon was also found to have quite good amounts

of surface groups like carboxyl, phenolic, lactonic and basic groups. The presence of these groups is also evident from the FT-IR spectrum of the carbon (Figure 1).

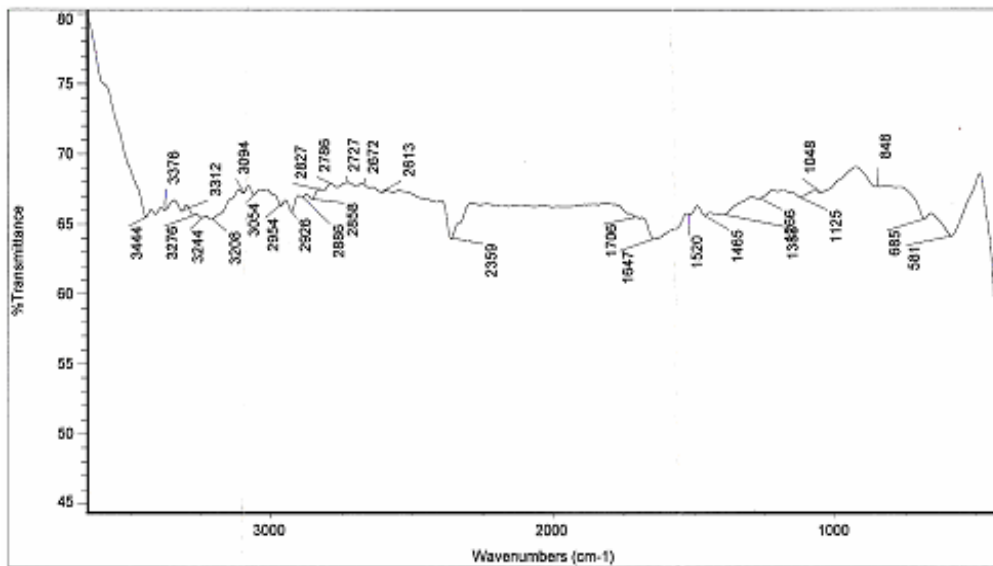


Figure 1. FT-IR spectrum of CC

Adsorption Isotherms: Adsorption Models

The assumptions associated with the Langmuir isotherm are well known¹⁵; Adsorption can not proceed beyond a monolayer coverage and all adsorption sites are equivalent. The Freundlich model, on the other hand, assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The Redlich-Peterson model is described as a combination of both the other models and is often used to describe equilibrium data over a wide range of concentration. For each and every individual adsorption system, the data were fitted to the three isotherm equations and the results are given in Table 2 [Conditions: adsorbent dose 0.1g/50mL of adsorbate solution; initial concentration of metal ion solutions, $C_i = 15\text{-}100\text{mg/L}$ for Ni; $20\text{-}100\text{mg/L}$ for Cu and $15\text{-}80\text{mg/L}$ for Fe(III)]. All the curves were of L type under Giles classification¹⁶.

According to Treybal¹⁷ it has been shown using mathematical equations that n values between 0 and 1 represent beneficial adsorption. Indeed, the n values found for all the adsorption systems fall in this range. The Langmuir constant b is a measure of adsorption intensity and the parameter q_m is a measure of adsorption capacity. Adsorption capacity of the adsorbents toward metal ions decrease in the order Ni(II), Cu(II), Fe(III) [values in Table 2], whereas the adsorption intensity decrease in the opposite order. The b values found indicate stronger interaction forces between carbon surface and Fe(III) ions compared to Ni(II) and Cu(II), in agreement with the higher ionic potential of Fe(III). The b values determined are further used to calculate the dimensionless separation factor, R_L ^{18, 19}, defined as

$$R_L = 1/(1 + bC_i)$$

where C_i is the initial solute concentration. The magnitude of R_L value gives an idea about the nature of adsorption equilibrium: the process is non-spontaneous when R_L is greater than one; favourable when R_L lies between 0 and 1; and irreversible when R_L is zero.

In all the systems studied, R_L values were comprised between 0 and 1 (values not listed) indicating favourable adsorption of all the metal ions on the activated carbon.

Table 2. Isotherm parameters for the adsorption of metal ions on CC

Metal ion	Model	Model parameters				r^2
		K_F		$1/n$	n	
		mmol/g	mg/g			
Ni (II)	Freundlich	0.3869	1.4173	0.5065	1.9743	0.9589
Cu(II)		0.4977	4.2362	0.2285	4.3764	0.9918
Fe(III)		0.2171	6.6024	0.1517	6.5920	0.9715
		Model parameters				
		K_L	b	q_m	r^2	
Ni (II)	Langmuir	0.5272	0.4110	1.2827	0.9849	
Cu(II)		1.8132	2.4509	0.7398	0.9876	
Fe(III)		5.6017	26.2230	0.2136	0.9260	
		Model parameters				
		K_R	b_R	β	r^2	
Ni (II)	Redlich-Peterson	0.3852	0.0907	1.6397	0.9948	
Cu(II)		3.5824	6.0319	0.8682	0.9975	
Fe(III)		83.1143	382.8209	0.8561	0.9716	

Effect of pH

The effects of pH in external solutions on adsorption extent are presented in Figure 2 (adsorbent doses: 0.1g/50mL, $C_i= 50\text{mg/L}$).

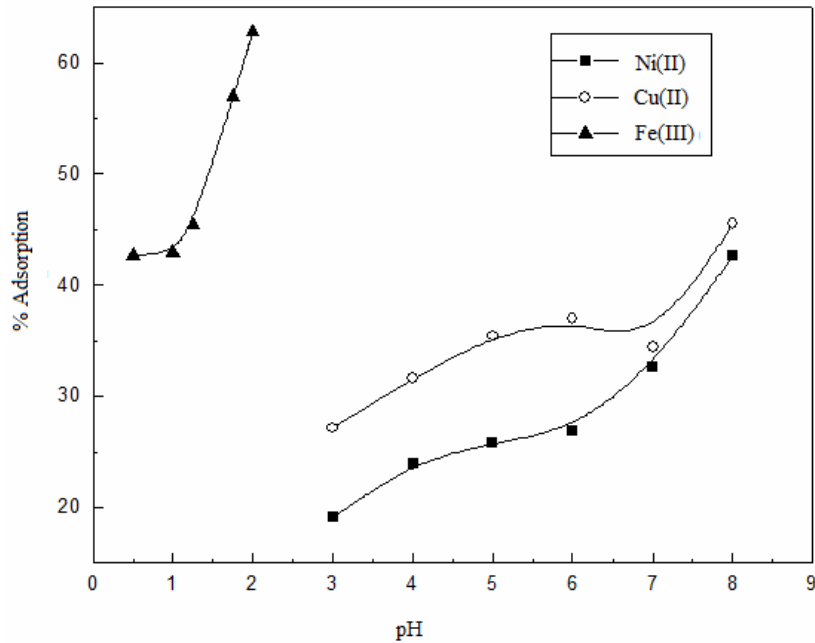


Figure 2. Adsorption of metals on CC: Effect of pH

For the three metal cations (Ni^{2+} , Cu^{2+} and Fe^{3+}) increase in solution pH throughout the range studied resulted in increased adsorption. This trend is in agreement with the fact that the metal ions are adsorbed by ion-exchange mechanism. 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, thereby reducing the available sites for metal cations.

Kinetics

To describe the adsorption kinetics, a pseudo-second order rate model reported in the literature was applied²⁰⁻²² in the following form

$$t/q_t = (1/h) + (1/q_{e(2)})t$$

where, h is the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$); k_2 is the over all rate constant for the sorption process ($\text{g mg}^{-1} \text{min}^{-1}$); $q_{e(2)}$ is the amount of metal ion adsorbed at equilibrium (mg/g); and q_t is the adsorbed at time t (mg/g).

The second order kinetic parameters evaluated are presented in Table 3. Good agreement between the predicted and experimental results was found. Hence, the applied pseudo-second order rate model succeeded in representing properly the experimental data for the adsorption of metal ions with high correlation coefficients ($r^2 > 0.99$). It is also to be noted that the experimental adsorption capacities [$q_{e(\text{exp})}$] are very close to the adsorption capacities predicted by the second order kinetic model [$q_{e(2)}$], these values are also furnished in Table 3.

Table 3. Pseudo-second order parameters for CC–metal ion systems

Metal ion	C_i mg/L	Equilibrium uptake mg/g		Pseudo- second order rate constant, $k_2 \text{ gmg}^{-1} \text{min}^{-1}$	Initial sorption rate, $h \text{ mgg}^{-1} \text{min}^{-1}$	r^2
		$q_{e(2)}$	$q_{e(\text{exp})}$			
Ni(II)	25	5.84	5.48	2.054×10^{-2}	0.7001	0.9994
	50	13.04	11.21	3.130×10^{-3}	0.5321	0.9984
Cu(II)	20	7.59	6.44	6.511×10^{-3}	0.3754	0.9979
	40	9.90	8.93	7.665×10^{-3}	0.7504	0.9992
Fe(III)	50	11.76	11.36	4.668×10^{-3}	0.6461	0.9982
	100	13.04	12.07	4.834×10^{-3}	0.7884	0.9984

Effect of Temperature

The equilibrium studies for all the systems were conducted at two more temperatures in addition to room temperature (30 °C), namely 45 and 60 °C. For all the systems increase in temperature resulted in greater adsorption. A representative graph for showing the effect of temperature is shown in Figure 3 for the Ni (II)-CC system.

The increased adsorption at higher temperatures can be due to one or more of the following reasons. Acceleration of some originally slow step(s);²³ creation of some new activation sites on the adsorbent surface²⁴ and decrease in the size of the adsorbing species.²⁵ This could well occur due to progressive desolvation of the adsorbing ion as the solution temperature increases.

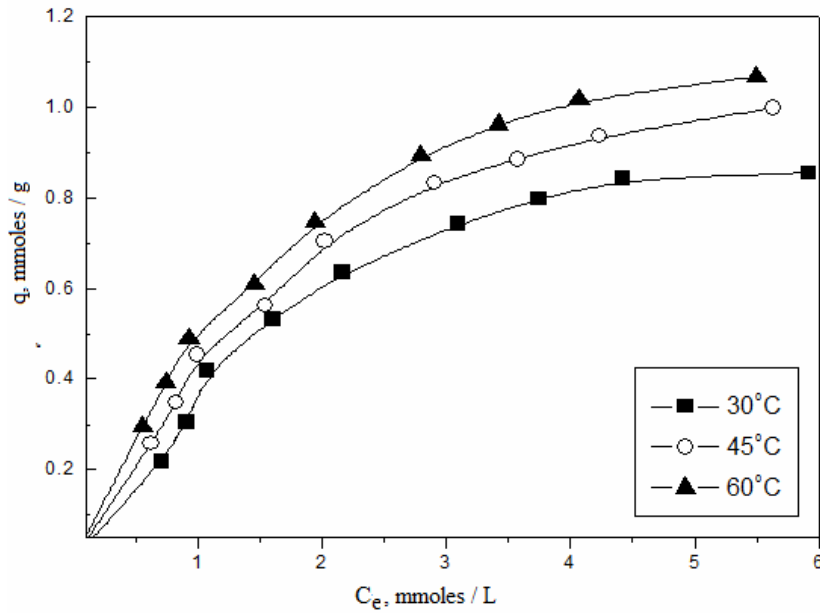


Figure 3. Effect of temperature: Adsorption of Ni(II) on CC

Thermodynamic parameters such as Gibbs's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated using the following expressions:

$$K_C = \frac{C_{ae}}{C_e}$$

$$\Delta G = -RT \ln K_C$$

$$\log K_C = \left[\frac{\Delta S}{2.303R} \right] - \left[\frac{\Delta H}{2.303RT} \right] \quad (1)$$

Where K_C is the equilibrium constant for the distribution of metal ions between the liquid and solid phases; C_{ae} is the solid phase metal ion concentration, mg/L; C_e is the liquid phase metal ion concentration, mg/L; T is absolute temperature, °K and R the gas constant. Equation (1) was used to construct Van't Hoff plots and ΔH and ΔS were calculated from the slope and intercept of the Van't Hoff plot, respectively. Thermodynamic parameters evaluated for varied metal ion concentrations are listed in Table 4.

The ΔG values obtained for most CC–metal ion systems were positive indicating that CC is less effective in removing metal ions from aqueous solutions. The positive values of ΔH obtained for all the processes are further confirmations that they are endothermic, which is an indication of strong interaction between the adsorbate and the adsorbent. The positive values of ΔS suggest increased randomness at the solid-liquid interface during the adsorption of metal ions. The adsorbed solvent (water) molecules, which are displaced by the adsorbated species, gain more translational entropy than is lost by the adsorbate ions. Furthermore, before the adsorption process takes place the adsorbate ions are heavily solvated (the system is more ordered) and this order is lost when the ions are adsorbed on the surface, due to the release of solvated water molecules.

Table 4. Thermodynamic parameters for the adsorption of metal ions on CC

Metal ion	C_i mg/L	ΔG , kJ mol ⁻¹			ΔH kJ mol ⁻¹	ΔS JK ⁻¹ mol ⁻¹
		30°C	45°C	60°C		
Ni(II)	15	1.2332	0.4290	-0.1344	1.5192	46.0948
	25	0.6259	0.2501	-0.1250	8.3305	25.4083
	35	1.0334	0.8013	0.4532	6.4164	17.6900
	45	1.3395	0.9146	0.6598	7.5700	20.6349
	60	1.8508	1.4022	1.1286	8.0422	20.5066
	70	2.1516	1.7710	1.4510	7.7833	18.5995
	80	2.4279	2.0570	1.7471	7.5631	16.9625
	100	3.1272	2.6101	2.3842	8.2926	17.1807
Cu(II)	20	-1.4933	-1.8412	-2.1525	-	-
	40	0.5437	0.2723	0.0857	5.0964	15.0573
	60	1.7783	1.3624	1.0723	7.8549	20.1026
	80	2.4484	2.0748	1.8570	6.5878	13.7266
	100	3.1185	2.6670	2.4018	7.9800	16.1123
Fe(III)	20	-3.6507	-3.9855	-4.0034	-	-
	30	-1.3317	-1.4240	-1.7235	40.3057	148.6469
	40	0.0063	-0.3659	-0.6050	39.6068	148.8901
	50	0.4643	0.2764	-0.1250	39.1781	149.5028
	60	1.1151	0.8407	0.5514	-	-
	80	2.1857	2.0171	1.6457	-	-

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 5.

Table 5. Results of desorption

Metal ion	% Desorption with		
	Water	0.1 M AcOH	0.1M HCl
Ni(II)	24.4	50.1	77.9
Cu(II)	29.6	49.4	85.5
Fe(III)	31.5	43.3	78.4

These results indicate that the metal ions are adsorbed by ion-exchange mechanism by the surface groups present on the carbon surface.

Conclusion

The work described has shown that the activated carbon under study can be successfully used for the adsorptive removal of metal ions from solution. The carbon possessed good textural and chemical properties. The three parameter Redlich-Peterson model can be used to represent the equilibrium adsorption of Ni(II), Cu(II) and Fe(III) and was found to be superior than Freundlich and Langmuir models. Adsorptions followed pseudo second order kinetics. Increase in solution pH result in greater retention of metal ions on CC.

The adsorption processes were found to be endothermic and the thermodynamic parameters were evaluated. Dilute hydrochloric acid can be used for desorption of these metal ions.

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