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Effect of Powdered Commercial and Activated Charcoal on Removal of Copper and Nickel from Wastewater of Electroplating Industry

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Batch adsorption kinetic studies were carried out on electroplating wastewater with powdered commercial charcoal (specific surface area 5401.69 cm^2/g) and powdered activated charcoal (specific surface area 5802.35 cm^2/g) as adsorbents. The effect of concentration of adsorbent and contact duration were studied on copper and nickel removal efficiency. Higher efficiency (x/m value) of adsorption is obtained at lower dose of powdered activated charcoal (PAC), which removes 61.28% copper and 50.35% nickel at a maximum dose of 25 g/L, whereas similar dose of powdered commercial charcoal (PCC) removes 28.74% copper and 24.80% nickel respectively. From the results it can be concluded that PAC may be most effective than PCC in the removal of copper and nickel at very low dose. Their efficiencies are moderately affected by the pH and COD of the wastewater.

Key Words: Absorption, Powdered commercial and activated charcoal, Copper and nickel removal, Adsorption isotherms.

INTRODUCTION

Electroplating industries are one of the oldest industries concentrating on surface finishing and metal deposition for higher life of articles and for decorative purposes. Depending upon the specific requirements, various metals or their alloys may be electroplated on a surface. These metals include Cu, Ni, Cr, Cd, Fe, Pb and their alloys. When the plated articles are removed from the electroplating tank, some of the solution sticks with the articles which goes into the effluent during rinsing. The excessive presence of metallic concentration in the effluent causes harmful effects on human beings, animals, aquatic life and vegetation. Although wastes from the plating industry do not approach the volume of wastes produced by some other industries, they are nevertheless an important source of pollution because of the extremely toxic nature of the constituents[1, 2].

Adsorption process has proved to be the most significant and economically feasible alternative method. Adsorption of heavy metals on activated carbon, carbonaceous materials and synthetic inorganic adsorbents has been studied[3–7]. Copper adsorption capacity from plating operation on to peanut hull carbon has been found to be 18 times larger than commercial coal-based activated carbon

and peat using the simple metal sorption model[8]. Holl and Horst[9] modelled the sorption of ions on to activated carbon using the surface complexation theory; two commercial activated carbons were investigated and the surface complexation model satisfactorily predicted carbon loading. The present communication describes studies on the use of the two adsorbents, *viz.*, powdered commercial charcoal (PCC) and powdered activated charcoal (PAC) for the removal of copper and nickel from the wastewater of electroplating industry.

EXPERIMENTAL

A number of combined wastewater samples under investigation were collected from M/s. Excel Shine Private Ltd. and were analyzed according to standard procedures for various physico-chemical characteristics. The wastewater samples were treated with different dosages of PAC and PCC (*viz.*, 5, 10, 15, 20 and 25 mg/L) at room temperature for two different contact durations; the resultant mixtures were then filtered and analyzed for the metal content by colorimetry as well as AAS method.

The analysis of the metal was done by flame atomic absorption spectrophotometer (Shimadzu) model UV (1601) and colorimetric procedure for copper with sodium diethyl thiocarbamate and nickel with dimethyl glyoxime using UV (1201) spectrophotometer (Shimadzu Corporation).

RESULTS AND DISCUSSION

Results presented in Table-1 indicate the effect of different dosages of adsorbent (PAC and PCC) on various physico-chemical characteristics of the wastewater. It can be seen that there is a reduction in the Cu and Ni content when the dosages of PAC and PCC vary from 5.0 to 25 g/L at 60 and 240 min of contact duration. The observed gradual increase in pH with increase in adsorbent dosages can be linked with removal of components contributing to the acidic character of the wastewater sample. There is a higher reduction in the Cu^{2+} content from the initial value of 152.7 ppm to 59.10 ppm and Ni^{2+} from 293.5 ppm to 145.7 ppm for maximum dose of 25 gm/L of PAC at 240 min of contact duration. Similarly, lower reduction in the Cu^{2+} content up to 123.0 ppm and Ni^{2+} up to 245.5 ppm has been observed for PCC. With increase in the concentration of adsorbents lesser reduction in the COD due to adsorption of organic matter present in the wastewater is observed.

Table-2 (A, B, C and D) represents the data for the model of Freundlich and Langmuir adsorption isotherm for removal of copper and nickel at 60 and 240 min of contact duration for PAC and PCC. For Freundlich adsorption isotherm the values of equilibrium concentration (C_{eq}) and per gram removal (x/m) of copper and nickel are given. For Langmuir isotherm model, the inverse value of equilibrium concentration, *i.e.*, $1/C_{eq} \times 10^3$ and removal per gram per litre, *i.e.*, $1/q_e \times 10^2$ are considered. It can be seen that the removal of Cu^{2+} and Ni^{2+} increases with increase in dosages of adsorbent as well as contact time. A decrease in adsorption per gram of adsorbent was observed on increasing the amount of adsorbent. The logarithmic value of equilibrium concentration and removal per

TABLE-1
INFLUENCE OF DIFFERENT DOSES OF PAC AND PCC ON VARIOUS PHYSICO-CHEMICAL CHARACTERISTICS OF COMBINED WASTEWATER OF ELECTROPLATING INDUSTRY

Adsorbents : (1) Powdered activated charcoal (Specific surface area: 5802.35 cm^2/g), (2) Powdered commercial charcoal (Specific surface area 5401.69 cm^2/g)
Temperature: 300 K

Treatment dose (g/L)	Powdered activated charcoal								Powdered commercial charcoal							
	Contact duration: 60 min				Contact duration: 240 min				Contact duration: 60 min				Contact duration: 240 min			
	pH	Cu^{2+} ppm	Ni^{2+} ppm	COD ppm	pH	Cu^{2+} ppm	Ni^{2+} ppm	COD ppm	pH	Cu^{2+} ppm	Ni^{2+} ppm	COD ppm	pH	Cu^{2+} ppm	Ni^{2+} ppm	COD ppm
Untreated	4.48	152.7	293.5	174.2	4.48	152.7	293.5	174.2	4.48	152.7	293.5	174.2	4.48	152.7	293.5	174.2
5.0	4.80	125.6	245.3	138.5	4.80	116.2	229.4	138.0	4.75	145.0	284.0	152.9	4.75	144.0	282.4	150.0
10.0	5.15	104.2	221.7	136.0	5.16	95.5	198.7	136.0	5.10	139.2	275.5	145.0	5.12	136.9	272.5	145.0
15.0	5.38	95.5	205.9	136.0	5.38	69.7	165.4	136.0	5.38	134.0	267.9	145.0	5.38	129.8	265.9	145.0
20.0	5.77	87.7	185.6	136.0	5.80	59.1	145.7	136.0	5.70	129.5	260.5	145.0	5.70	125.9	254.9	145.0
25.0	5.95	78.2	175.8	136.0	5.95	59.1	145.7	136.0	5.89	127.4	254.0	145.0	5.90	123.0	245.5	145.0

unit weight gives the linear plot for Cu^{2+} and Ni^{2+} by PAC and PCC, which confirms the applicability of Freundlich adsorption isotherm.

Figs. 1 and 2 show the plots of log x/m *vs.* log C_{eq} for the adsorption of Cu^{2+} and Ni^{2+} from wastewater by PAC and PCC. The nature of the curve is a straight line and slope corresponding to 1/n and intercept K are observed.

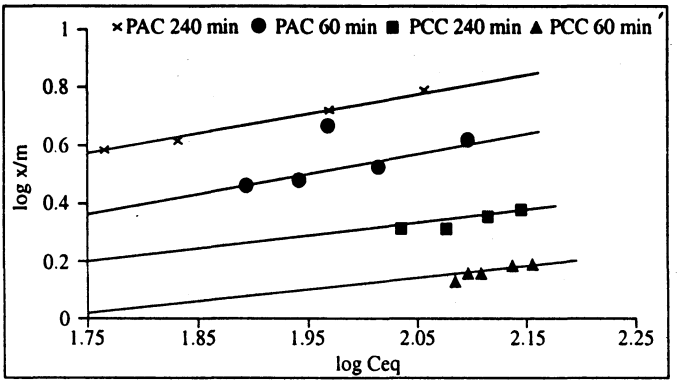

Fig. 1. Freundlich adsorption isotherm for removal of Cu^{2+} by PAC and PCC

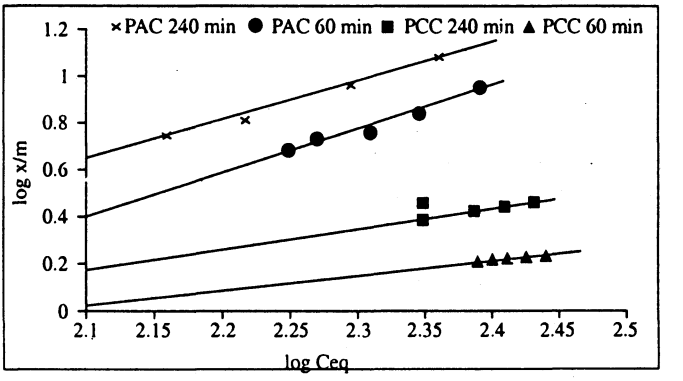

Fig. 2. Freundlich adsorption isotherm for removal of Ni^{2+} by PAC and PCC

The straight line confirms the applicability of the Freundlich isotherm model in both cases and indicates monolayer coverage of the adsorbent on the outer surface of the adsorbent. The value of 1/n related to adsorption intensity is close to one, which indicates high adsorptive intensity at higher equilibrium concentrations that rapidly diminishes at lower equilibrium concentration covered by the isotherm. The values of K. related to adsorption capacity and the values of 1/n related to adsorption intensity for Cu^{2+} and Ni^{2+} for PAC and PCC have been found for 60 and 240 min of contact duration.

Figs. 3 and 4 show the Langmuir adsorption isotherm for adsorption of Cu^{2+} and Ni^{2+} on to PAC and FCC. Plots of Langmuir parameters, *viz.*, $1/C_{eq} \times 10^3$ and $1/q_e \times 10^2$ give the nature of the curve for both cases as linear.

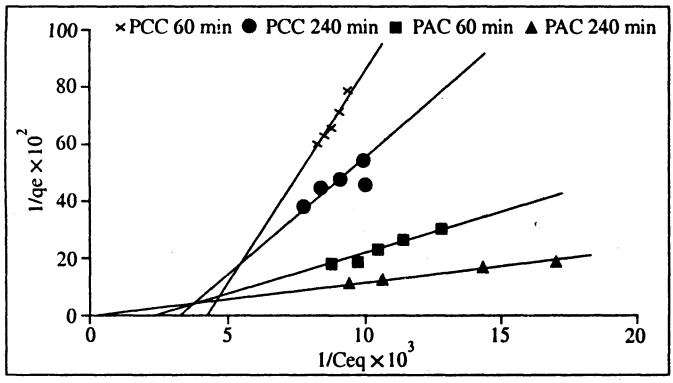

Fig. 3. Langmuir adsorption isotherm for removal of Cu^{2+} by PAC and PCC

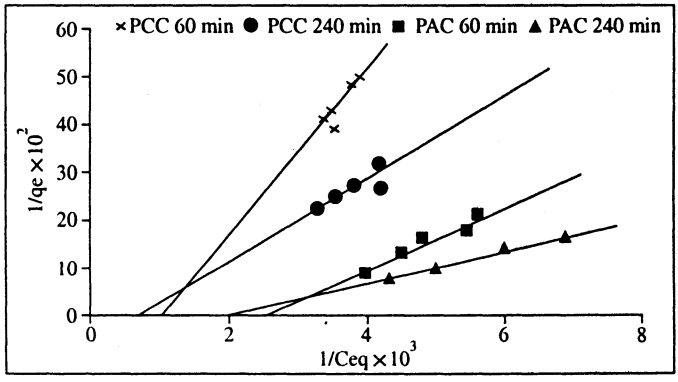

Fig. 4. Langmuir adsorption isotherm for removal of Ni^{2+} by PAC and PCC

The data indicated in Table-2 (A, B, C and D) give the linear nature of the plots presented in Figs. 3 and 4, confirming the applicability of Langmuir model also, which is governed by the mathematical expression

$$\frac{1}{q_e} = \frac{1}{\theta_0} \cdot b \times \frac{1}{C_{eq}} + \frac{1}{\theta_0}$$

where q_e = amount of Cu and Ni adsorbed per unit weight of adsorbent (mg/g), C_{eq} = equilibrium concentration of Cu and Ni (mg/L), x = amount of Cu and Ni adsorbed (mg/L), m = weight of adsorbent (g/L), θ_0 = Langmuir constant related to the capacity of adsorption (mg/g), b = Langmuir constant related to the energy of adsorption (dm^3/mg).

Figs. 3 and 4 show the Langmuir isotherm parameter for removal of Cu and Ni using PAC and PCC. The observed linearity suggests the applicability of this isotherm model in both the cases as well as further confirms the monolayer formation. The Langmuir constant related to adsorption capacity (θ_0) (mg/g) has higher values indicating availability of more surface active region on to adsorbent sites. The value of $b \times 10^3$ (L/mg) in terms of x/m is related to adsorption energy.

This 'b' value is a characteristic of the system, it is not dependent on concentration of adsorbent.

Table-3 represents the Freundlich and Langmuir adsorption isotherm parameters for Cu and Ni in the electroplating industry wastewater. An adsorption capacity value of PAC is found higher than that of PCC when contact period is

TABLE-2 (A)
FREUNDLICH AND LANGMUIR PARAMETERS FOR REMOVAL OF COPPER AND NICKEL FROM WASTEWATER BY ADSORPTION ON TO PAC

Adsorbent: Powdered activated charcoal — Temperature: 300 K
Specific surface area: 5802.35 cm^2/g — Contact duration: 60 min

Treatment dose (g/L)	Parameters									
	Eq. conc. C_{eq} (mg/L)		x/m = q_e (mg/g)		% removal		$1/q_e \times 10^2$		$1/C_{eq} \times 10^3$	
	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
Untreated	152.7	293.5	—	—	—	—	—	—	6.5487	3.4071
5.0	125.0	245.3	5.54	9.64	18.13	16.42	18.0505	10.3734	8.0000	4.0766
10.0	104.2	221.7	3.81	7.18	31.75	24.46	20.6185	13.9275	9.5969	4.5105
15.0	95.5	205.4	4.85	5.87	37.45	30.01	26.2467	17.0357	10.4710	4.8685
20.0	87.7	185.6	3.25	5.39	42.56	36.76	30.7692	18.5528	11.4020	5.3879
25.0	78.2	175.8	2.98	4.70	48.78	40.13	35.5570	21.2765	12.7870	5.6882

TABLE-2 (B)
FREUNDLICH AND LANGMUIR PARAMETERS FOR REMOVAL OF COPPER AND NICKEL FROM WASTEWATER BY ADSORPTION ON TO PCC

Adsorbent: Powdered commercial charcoal — Temperature: 300 K
Specific surface area: 5401.69 cm^2/g — Contact duration: 60 min

Treatment dose (g/L)	Parameters									
	Eq. conc. C_{eq} (mg/L)		x/m = q_e (mg/g)		% removal		$1/q_e \times 10^2$		$1/C_{eq} \times 10^3$	
	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
Untreated	152.7	293.5	—	—	—	—	—	—	6.5487	3.4071
5.0	144.0	282.4	1.74	2.22	5.69	3.98	57.4712	45.0436	6.9444	3.5410
10.0	136.9	272.3	1.58	2.12	10.34	7.22	63.2956	47.1645	7.3046	3.6729
15.0	129.8	262.9	1.52	2.04	14.99	10.42	65.7886	43.0141	7.7041	3.8037
20.0	125.9	254.9	1.34	1.99	17.54	13.42	74.6245	50.7664	7.9428	3.9354
25.0	123.0	245.5	1.18	1.92	19.04	16.35	84.1705	52 0852	8.1300	4.0735

Eq. conc. = equilibrium concentration — x/m = removal (mg/L)/weight of adsorbent (g/L)
(1) For Freundlich plot, *i.e.*, x/m. — (2) For Langmuir plot, *i.e.*, q_e.

TABLE-2 (C)
FREUNDLICH AND LANGMUIR PARAMETERS FOR REMOVAL OF COPPER AND NICKEL FROM WASTEWATER BY ADSORPTION ON TO PAC

Adsorbent: Powdered activated charcoal Temperature: 300 K
Specific surface area: 5802.35 cm^2/g Contact duration: 240 min

Treatment dose (g/L)	Parameters									
	Eq. conc. C_{eq} (mg/L)		x/m = q_e (mg/g)		% removal		$1/q_e \times 10^2$		$1/C_{eq} \times 10^3$	
	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
Untreated	152.7	293.5	—	—	—	—	—	—	6.5487	3.4071
5.0	116.2	229.4	7.30	12.82	23.90	21.83	13.6986	7.8003	8.6058	4.3591
10.0	95.5	198.7	5.72	9.48	37.45	32.29	17.4825	10.5485	10.4712	5.0327
15.0	69.7	165.4	4.15	6.40	54.34	43.64	24.0163	15.6128	14.3472	6.0459
20.0	59.1	145.7	3.74	5.91	61.28	50.35	26.7379	16.9204	16.9204	6.8634
25.0	59.1	145.7	3.74	5.9	161.28	50.35	26.7379	16.9204	16.9204	6.8634

TABLE-2 (D)
FREUNDLICH AND LANGMUIR PARAMETERS FOR REMOVAL OF COPPER AND NICKEL FROM WASTEWATER BY ADSORPTION ON TO PCC

Adsorbent: Powdered commercial charcoal Temperature: 300 K
Specific surface area: 5401.69 cm^2/g Contact duration: 240 min

Treatment dose (g/L)	Parameters									
	Eq. conc. C_{eq} (mg/L)		x/m = q_e (mg/g)		% removal		$1/q_e \times 10^2$		$1/C_{eq} \times 10^3$	
	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
Untreated	152.7	293.5	—	—	—	—	—	—	6.5487	3.4071
5.0	140.3	275.0	2.54	3.70	8.31	6.30	39.3725	27.0212	7.1275	3.6363
10.0	131.4	258.7	2.13	3.48	13.94	11.85	46.9458	28.7374	7.6103	3.8654
15.0	121.0	244.8	2.11	3.24	20.78	16.59	47.3924	30.8636	8.2690	4.0849
20.0	108.8	222.8	2.19	3.53	28.74	24.08	45.6685	28.3208	9.1900	4.4900
25.0	108.8	222.8	2.19	2.82	28.74	24.08	57.1432	35.4664	9.1900	4.4900

TABLE-3
FREUNDLICH AND LANGMUIR PARAMETERS OF Cu AND Ni FOR POWDERED ACTIVATED CHARCOAL AND POWDERED COMMERCIAL CHARCOAL

Time (min)	Freundlich isotherm				Langmuir isotherm			
	1/n		K	θ_0 (mg/g)	$b \times 10^3$ (dm^3/mg)	1/n	K	θ_0 (mg/g)	$b \times 10^3$ (dm^3/mg)
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Powdered activated charcoal								
60	1.78	2.37	1.062	1.295	19.01	19.38	2.85	2.50
240	1.04	1.87	3.239	4.531	69.69	31.67	1.00	2.00
Powdered commercial charcoal								
60	1.50	1.61	1.023	1.244	4.40	8.65	3.81	1.18
240	1.45	1.14	1.659	2.749	13.84	40.41	1.59	0.37

increased nearly four times. The 1/n value of Freundlich isotherm is found higher at 60 min contact duration; this indicates higher intensity of the adsorption process in comparison to that when contact time is increased four times. Higher value of K indicates higher surface coverage or higher adsorption capacity of PAC at 240 min of contact duration.

Conclusion

Activated charcoal may be more effective than commercial charcoal in the removal of Cu^{2+} and Ni^{2+} at very low dose. Their efficiencies moderately affect the pH and COD of wastewater. Higher efficiency (x/m value) of adsorption is obtained at lower dose of activated charcoal, which removes 61.28% Cu and 50.35% Ni at the maximum dose of 25 g/L, whereas similar dose of commercial powdered charcoal removes 28.74% Cu^{2+} and 24.80% Ni^{2+} respectively. At room temperature both charcoals, *viz.*, PAC and PCC, work as adsorbents and follow Freundlich and Langmuir adsorption isotherm models for the removal of Cu^{2+} and Ni^{2+} from the combined wastewater of electroplating industry.

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