Bull. Environ. Contam. Toxicol. (2002) 69:195–202

DOI: 10.1007/s00128-002-0047-0

Bulletin of Environmental Contamination and Toxicology

Treatment of Electroplating Industry Effluent Using Maize Cob Carbon

G. Selvakumari,[1] M. Murugesan,[2] S. Pattabi,[3] M. Sathishkumar[4]

[1] Department of Chemistry, Coimbatore Institute of Technology, Coimbatore 14, TN, India
[2] Department of Chemistry, PSG CAS, Coimbatore 14, TN, India
[3] Department of Environmental Sciences, PSG CAS, Coimbatore 14, TN, India
[4] Department of Biotechnology, Bharathiar University, Coimbatore 46, TN, India

Received: 10 July 2001/Accepted: 4 March 2002

Certain industries like electroplating industries release a very high amount of metals to the environment. The metals include Cr, Ni, Fe, Hg and Zn. But their concentration and presence highly depends upon the type of method used for plating. As the electroplating industries are in small scale, advanced treatments like ion-exchange, reverse osmosis, electrodialysis are costly and at the same time, methods like chemical precipitation, coagulation, flocculation etc. are less effective and has a disadvantage, of sludge formation (Namasivayam and Ranganathan, 1995). Adsorption is a sludge free process and had undergone many improvements. Activated carbon prepared from various sources has been used in the adsorption based wastewater treatment units (Sureshkumar, 2000). In the present study, carbon prepared from the maize cob, which is an agricultural waste available in plenty in tropical country like India, is used for the removal of metal ions from electroplating industry effluents.

MATERIALS AND METHODS

Maize (= corn) cob used in the present study, was collected from the field, chopped and sun dried for 24 h. One part of pulverized cob was mixed with 1.8 parts of concentrated H_2SO_4, in an airtight container and carbonized in a hot air oven at 80° ± 5°C for 12 h. The carbonized material was washed under tap water to remove free acid. The resultant was soaked in 1% (w/v) sodium bicarbonate solution overnight to remove any residual acid. The material was washed with distilled water and dried at 80°C for 6 h. It was then ground and sieved at 125 – 250 μ particle size.

The electroplating industry effluent used in the present study was collected from a local small scale electroplating plant in pre cleaned 5 litre plastic containers. The metal contents, Fe, Ni and Cr were estimated by standard methods (APHA, 1995).

Batch mode adsorption studies were carried out to determine the adsorption of metals present in the effluent on to maize (=corn) cob carbon. The effluent was diluted to different concentrations and to each 50 ml, 100 mg of adsorbent was added, agitated in a rotary shaker at 150rpm for predetermined time intervals at

Correspondence to: M. Sathishkumar

30°C. The adsorbate and adsorbent were separated by centrifugation at 10,000 rpm for 20 min. Remaining metals were analysed spectrometrically (APHA, 1995). Langmuir plot from the data was drawn and adsorption constant (Q_o) was calculated from the slope of the curve. For pH studies, the effluent was adjusted to pH ranging from 2 - 10 using dilute HNO_3 or NaOH. The fixed dosage of adsorbent was taken with the pH adjusted effluent and agitated for an equilibrium time.

In column studies the adsorbent (3g) was packed in a glass column (45 X 2.2 cm) and effluent was passed through the column. Flow rate was fixed as 10 ml/ min. Fractions were collected at regular intervals and analysed for metal contents. Data were used to plot of BDST curves and adsorption rate constant (N_o) was calculated from the plot.

Toxicity of treated and untreated effluents was studied against *Zea mays* seeds. Seeds were placed in Petri dishes lined with germination sheets soaked in different concentrations of treated and untreated effluents. Plates were incubated in a BOD incubator at $27^O \pm 2^OC$ (ISTA,1966). Percent germination and vigour index were calculated from germinating seeds (Abdul - Baki and Anderson, 1973). To determine phytotoxicity of effluents, *Z. mays* seedlings were raised in sand trays irrigated with different concentrations of treated and untreated effluents. After ten days, growth parameters, viz., root length, shoot length, root biomass, shoot biomass and total biomass were calculated. From the data, effluent tolerant index and phytotoxicity were calculated (Turner and Marshal, 1972). Data were analysed using Duncan's multiple range test (Duncan, 1955).

RESULTS AND DISCUSSION

Increase in contact time increased the metal uptake but remained constant after an equilibrium time. Equilibrium time varied with metals due to the difference in initial metal concentration and affinity of adsorbent for a particular metal ion. In diluted effluents, iron adsorption reached a maximum at 90 minutes; whereas, for Ni and Cr and undiluted effluent it was 105 min (Fig. 1).

The experiment was carried out with different adsorbent dosage up to equilibrium time. It was noted that after the adsorbent dosage level of 300mg/50ml, adsorption remained constant (Fig. 2). Consequently, this adsorbent dosage level was selected for further studies.

Results revealed that adsorption varied with pH with different metals. Maximum adsorption of Fe was observed at pH 6 to 7, Ni at > 9 and Cr between 3 to 4 (Fig 3). Based on data obtained, the optimum conditions for removal of metals from the effluent were standardized.

Langmuir isotherm was applied for the present study to estimate the adsorption capacity of the prepared carbon. Langmuir isotherm is valid for monolayer

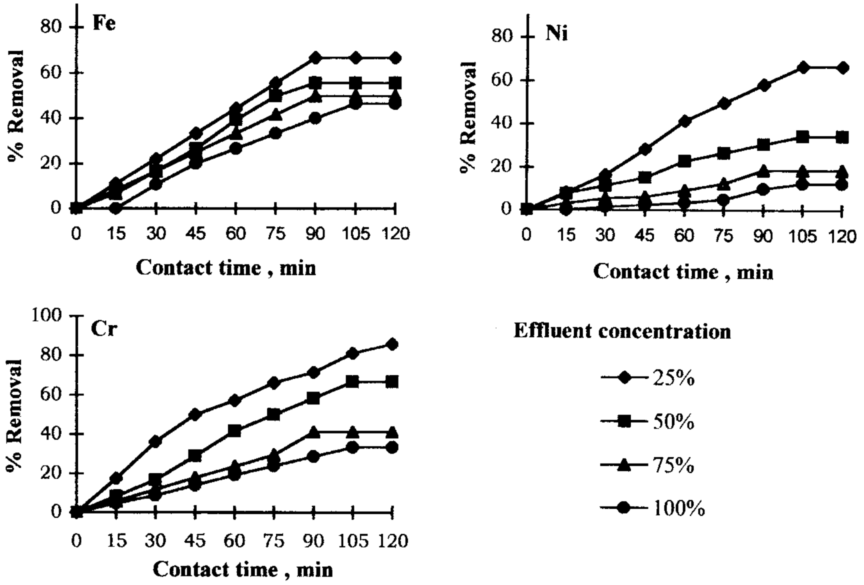

Figure 1. Effect of contact time on removal of metal ions from electroplating industry effluent (Adsorbent dosage: 100mg / 50 mL ; pH : 1.5)

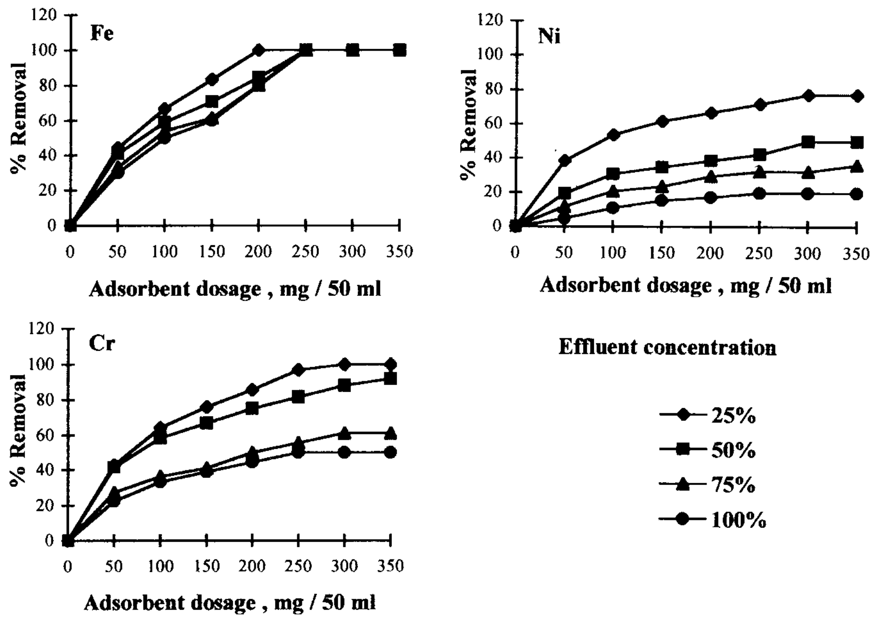

Figure 2. Effect of adsorbent dosage on removal of metal ions from electroplating industry effluent (Contact time: 105 min ; pH: 1.5)

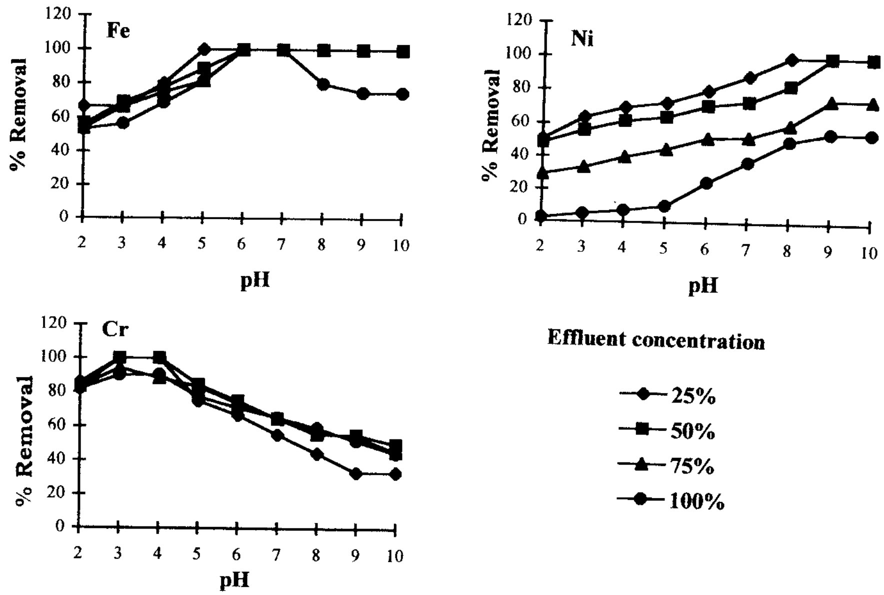

Figure 3. Effect of pH on removal of metal ions from electroplating industry effluent (Contact time:105 min ; Adsorbent dosage: 300mg/50mL)

adsorption onto a surface containing a finite number of identical sites (Langmuir, 1918). It is represented by the following equation.

$$C_e / q_e = 1 / Q_o b + C_e / Q_o \text{----------------} (1)$$

Where, C_e, is the equilibrium concentration (mg / L)

q_e, is the amount adsorbed at equilibrium time (mg / g) and

Q_o & b are Langmuir constants related to adsorption capacity and energy of adsorption respectively.

The plots of C_e/q_e Vs C_e are linear showing that adsorption of metals follows Langmuir isotherm model (Fig .4). The adsorption capacity (Q_o) was calculated to be 57.53 and 66.67 mg / g for Ni and Cr respectively; Fe was removed completely by the carbon. This shows that maize cob carbon is most effective than other adsorbents including, Peanut hull carbon (Q_o = 53.68), Granular activated carbon (Q_o = 1.49), Red mud (Q_o = 15.00), Fe(III) / Cr(III) hydroxide (Q_o = 22.94), Blast furnace slag (Q_o = 55.75), Bituminas coal (Q_o = 6.47), Manganese oxide treated Bituminas coal (Q_o = 7.29), H_2O_2 treated bituminas coal (Q_o = 8.12), Clay treated with NaCl (Q_o = 14.54), Clay treated with HCl (Q_o = 10.93), Rice hull (Q_o = 5.58) and Rice hull treated with dye stuff (Q_o = 6.16) in removing Ni (II) (Periasamy and Namasivayam, 1995; Zouboulis and Kydros,

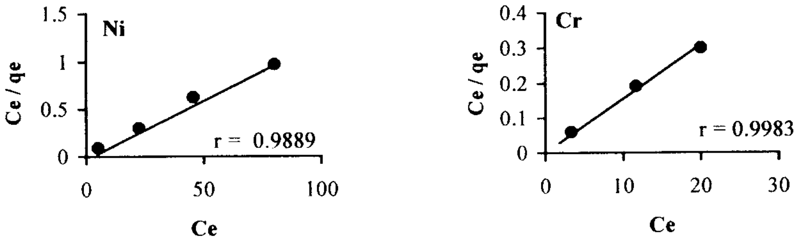

Figure 4. Langmuir plot for metal removal

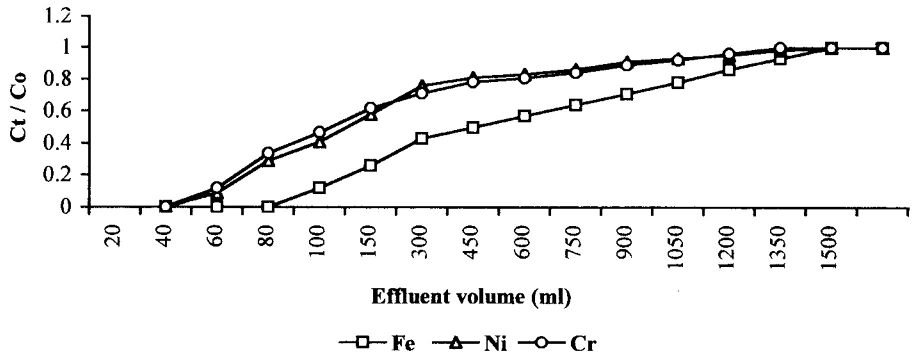

Figure 5. Break through curve for metal ions

1993; Namasivayam and Ranganathan, 1994; Dimitrova, 1996; Suemitsu *et.al.*, 1986; Hawash *et.al.*, 1994; Singh and Rawat, 1997). In case of Cr(VI) adsorption also, maize cob carbon proves to be effective when compared to Fe(III) / Cr(III) hydroxide (Q_o= 1.43) (Ranganathan, 1993).

Data in figure 5 revealed that there is a 100% removal of Cr and Ni upto 30 ml and for Fe up to 70 ml of inflow of the effluent into the column. Up to 300 ml of inflow there is a steady removal after which there is a slight decline. The Bed – Depth - Service - Time model (BDST), proposed by Hutchins (1975) is a simpler method to correlate the service time, t with process variables in fixed bed adsorber. Figure 6 shows a linear plot, fixed bed removal of metals obey the BDST model. Adsorption rate constant (N_o) was calculated from the slope of the BDST curves. N_o values were 10.62, 31.05 and 58.83 for Ni, Cr and Fe respectively. The comparison of overall adsorption capacity of batch mode data

Table 1. Effect of electroplating industry effluent on seed germination and seedling development of *Zea mays*

Treatment / Effluent concentration (%)	Percent germination	Embryonic axis length (mm)	Shoot length (mm)	Root length (mm)	Shoot biomass (mg)	Root biomass (mg)	Total biomass (mg)	Vigour index	DMRT ranking	Phyto toxicity	Effluent tolerant index	DMRT ranking
Control	100	180.00	27.13	14.80	41.40	32.90	74.30	18.00	a,1	0.00	1.000	a,1
Untreated effluent												
25	100	96.32	19.10	8.50	38.50	24.30	62.80	9.63	c,3	42.57	0.574	d,4
50	100	53.42	10.30	5.20	15.00	8.00	23.00	5.34	f,6	64.86	0.351	f,6
75	100	31.44	0.00	0.00	0.00	0.00	0.00	3.14	h,8	100.00	0.000	h,8
100	100	12.00	0.00	0.00	0.00	0.00	0.00	1.20	i,9	100.00	0.000	h,8
Treated effluent												
25	100	126.42	24.10	12.00	41.10	29.10	70.20	12.64	b,2	18.62	0.811	b,2
50	100	83.92	21.20	10.60	27.80	19.70	47.50	8.39	d,4	28.38	0.716	c,3
75	100	56.14	12.90	7.60	18.90	10.60	29.50	5.61	e,5	48.65	0.514	e,5
100	100	41.20	4.70	1.30	10.90	2.60	13.50	4.12	g,7	91.22	0.088	g,7
CV :		0.1%	0.5%	0.2%	0.1%	0.2%		0.0%			0.3%	
p :		0.01	0.010	0.010	0.010	0.010		0.010			0.0100	
SED :		0.008	0.029	0.030	0.008	0.011		0.009			0.0012	
LSD(1%) :		0.022	0.082	0.087	0.022	0.030		0.026			0.0035	

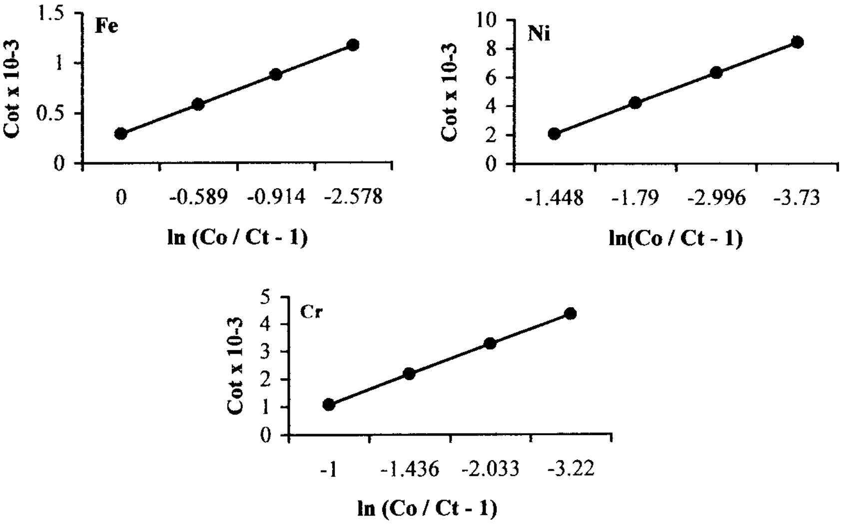

Figure 6. BDST curve for metal ions

(Q_o) with those column (N_o), revealed batch mode treatment to be more effective than column treatment. Hence the effluent was treated in batch mode in large scale at optimum conditions and the toxicity of treated effluent was tested against a plant system.

Results obtained in the effluent toxicity studies revealed that even the undiluted, raw effluent was not acutely toxic to seed germination, but affected the length of embryonic axis. Heale and O'rmrod have found retarded growth of maple, dog wood, honey suckle and pine by application of Ni at 20 mg/L. Seed germination, plant growth, root nodulation and productivity of lentil plants were adversely affected by Ni(II) particularly at high concentrations (Khan *et.al.,* 1987). Similarly, development of root and shoot were also greatly inhibited. Total biomass production was adversely affected (100%) by 75% diluted effluent. However, treatment with maize cob carbon reduced the effluent toxicity to biomass production by 50 per cent (Table. 1). The plant toxicity parameters, vigour index, phytotoxicity and effluent tolerant index also revealed that toxicity was reduced by 50 per cent by maize cob carbon treated effluent diluted to 75 per cent (Table). The study implies that maize cob carbon may be used to treat electroplating industry effluent after proper dilution.

REFERENCES

Abdul-Baki AA, Anderson JD (1973) Vigour determination in soyabean seed by multiple criteria. Crop Sci 13:630-633

APHA (1995) Standard methods for the examination of water and waste water. 19th edition. American Public Health Association, Water Pollution Control Federation, Washington, DC.
Dimitrova SV (1996) Metal sorption on blast furnace slag. Wat Res 30:228-232
Duncan DB (1955) Multiple range 'F' tests. Biometrics 11:1-42
Hawash S, Farash JY, El-Geundi MS (1994) Investigation of Nickel ion removal by means of activated clay. Adv Sci Technol 9:244-257
Heale EL, Ormrod DP (1982) Effect of nickel and copper on acer rubrum, cornus stolenifera, lonicera tatarica and pinus resinosa. Canadian J Bot 60:2674-2681
Hutchins RA (1975) New method simplifies design of activated carbon. Chem Eng 80:133
ISTA (1966) International rules for seed testing. Proc International Seed Testing Association 31:1-152
Khan MR, Singh SK, Khan MW (1987) Effect of nickel on growth of lentil plants. Indian Assoc Wat Pollut Control Tech Ann 14:57-60.
Langmuir I (1918) The adsorption of gases on plane surfaces on glass, mica and platinum. J American Chem Soc 40:1361
Namasivayam C, Ranganathan K (1994) Recycling of Fe(III)/Cr(III) hydroxide for the removal of nickel from wastewater - Adsorption and equilibrium studies. Waste Man 14:709-716
Namasivayam C, Ranganathan K (1995) Removal of Cd(II) from wastewater by adsorption on "waste" Fe(III)/Cr(III) hydroxide. Wat Res 29:1737 - 1744
Periasamy K, Namasivayam C (1995) Removal of Ni(II) from aqueous solution and nickel plating industry waste water using an agricultural waste : Peanut hull. Waste Man 15:63 - 68
Ranganathan K (1993) Adsorption studies of Heavy metals on "Waste" Fe(III) / Cr(III) Hydroxide from aqueous solutions and its application to the treatment of metal bearing wastewaters. In: Ph.D thesis, Dept. of Environmental Sciences, Bharathiar University, Coimbatore, India.
Singh D, Rawat NS (1997) Adsorption of heavy metals on treated and untreated low grade bituminas coal. Indian J Chem Technol. 4:39-41
Suemitsu R, Venishi R, Akashi I, Nakana M (1986) The use of dye-stuff-treated rice hulls for removal of heavy metals from wastewater. J Appl Poly Sci. 31:75-83
Sureshkumar MK (2000) Heavy metal biosorption by bacterial cells: a case of cadmium removal. Proc Nat Symp On Environment Bangalore Univ, Bangalore, June 5-7 p 142-145.
Turner RC, Marshal C (1972) Accumulation of zinc by sub- cellular fraction of root of *Agrotis tennis* Sibith in relation to zinc tolerance. New Phytol 71: 671-676
Zouboulis AI, Kydros KA (1993) Use of red mud for toxic metals removal, The case of nickel. J Chem Technol Biotechnol 58:95-101