

A study on expulsion of cadmium (II) and chromium (III) from electroplating effluent

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Abstract: Chromium and cadmium are toxic heavy metals present in wastewater from electroplating industries. The removal of Cd (II) and Cr (III) by Amberjet, IR 1200, a synthetic ion exchange resin has been studied. The resin was prepared into two cationic forms H^+ and Na^+ . The optimum conditions were concentration, pH, stirring time and resin amount. The exchange capacities, moisture content and optimum conditions of this resin were determined in a batch system. The stirring speed was 50 ppm during all the batch experiments. The initial and final chromium and cadmium amounts were determined using the atomic adsorption spectroscopy. The most preferable value of concentration is 10 mg/L; pH is 5.5, stirring time 30 min, amount of resin 200mg. The maximum removal and recovery for Cd (II) and Cr (III) was seen in Na^+ form of resin.

Keywords: Cadmium, Chromium, heavy metal, water contamination, resin, ion-exchange, extraction, effluent.

Introduction

At present, heavy metal wastes from the electroplating industries are the threat to the environment. Cd (II) and Cr (III) are the common and important pollutants among them. If unnoticed, we would be surfeited with Cd (II) and Cr (III) in the surroundings which will result in serious and permanent damage to the habitat (Hutton *et al.*, 1986; Nriagu, 1988). The maximum permissible limits for these heavy metals are regulated by legislation in each country. In India, the permissible amount for Cadmium and chromium in treated effluent to be let in to surface water sources are 2.0 and 0.1mg/L respectively (EPA notification, S.O. 393(E), 1987). On the basis of these adverse health effects, Cd (II) has been included in the red list of priority pollutants by the Department of Environment, UK (UK red list substances, 1991) and in the black list of EEC Dangerous Substance Directive (EEC black list substances, 1976). US Environment Protection Agency has also classified Cd (II) as group B1 carcinogen (US Environmental Protection Agency, 1999). Cadmium has been designated as category carcinogen by International Agency for Research on Cancer (IARC). As these heavy metals do not decompose naturally; recovery of these is very essential.

Among the various treatment techniques available for the removal of heavy metal ion, the most commonly used ones are ion exchange, adsorption, reduction and precipitation. However, these techniques other than ion

exchange have considerable disadvantages, including incomplete metal removal, expensive equipment and monitoring system, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal (Dragan *et al.*, 2003). The main advantages of using ion exchange resins are their high chemical and mechanical stability, high ion exchange capacity, and ion exchange rate. Synthetic ion exchangers have been widely used in industry for the separation of inorganic ions. Styrene copolymers are one of the most popular precursors for obtaining ion exchangers with different functionalities and morphologies. Functional cross linked polymers, bearing primary amine groups are of great interest because of their high removal capacity (Barnowski *et al.*, 1997; Csoban *et al.*, 1998; Muraviev *et al.*, 2000; Staby *et al.*, 2001; Bai *et al.*, 2003; Neagu *et al.*, 2003).

Another advantage in the ion exchange resin is the possibility of selecting the fixed ligand groups and the degree of cross-linking (Pehlivan *et al.*, 2008). Several studies considering Cr (III) removal using ion exchange resins have been reported in literature. Zhao *et al.* (1998) reported that a new anion exchanger called polymeric ligand exchanger which shows very high chromate selectivity at neutral to alkaline pH would be very effective. Batch shaking adsorption experiments were carried out by Rengaraj *et al.* (2001) to evaluate the performance of IRN77 and SKN1 cation exchange resins in the removal of chromium from aqueous solutions. In another study he reported that the removal of chromium from aqueous solution by ion exchange resins such as 1200H, 1500H and IRN97H (Rengaraj *et al.*, 2003). In the review reported by Dabrowski *et al.* (2004), removal of Cr (III) and Cr (VI) with various commercial resins was explained. The uptake of chromium by ion exchange resins is affected by certain variables such as pH, temperature, initial metal concentration and contact time (Kocaoba *et al.*, 2005; Gode, 2006).

Selective removal and recovery of Cd (II) by microcapsule containing chelating resin was carried out by Dhruv K. Singh *et al.* (2005). Removal of Cd (II) from aqueous solution using pure smectite and Lewatite S 100 and the effect of time and metal concentration was investigated by Bedoui *et al.* (2008). Saito *et al.* (2002) have studied the recovery of Cd (II) ion using microcapsule incorporated bathocuproinedisulphonate-chelate resin.

The aim of the present study is to investigate the removal of Cd (II) and Cr (III) using Amberjet IR 1200.

The reason for the selection of this resin is primarily for its commercial availability and cost. The reusability of this resin is another major advantage. The influence of various parameters like pH, concentration of the metal ions, stirring time and the amount of resin on removal is also examined. From the optimum parameters the removal capacity of the resin was tested with actual electroplating effluent.

Materials and methods

Reagents, resins and equipment

The resin used in this study was Amberjet IR 1200, a strong acid cation exchange resin based on styrene divinylbenzene copolymer matrix obtained from ROHM and HAAS, Philadelphia, U.S.A.

Chromium and cadmium were determined by Atomic Absorption Spectroscopy (AAS), AA-6300, and SHIMADZU, JAPAN. The experiment was done with the following settings: slit, 0.7 nm; flame type, air/acetylene with ratio 3.5/1.5; for chromium with the wavelength 228.8 nm and for cadmium 357.9 nm. All the chemicals used were of AR grade supplied by Ranbaxy Chemicals, India.

Conditioning of resin. The resin was washed with HCl and NaOH solution to remove the chemical residues trapped in the matrixes of resin during their preparation. Then the resin matrix was finally converted into sodium and hydrogen forms using 1M NaCl and HCl. The physicochemical properties and the suggested operating conditions are given in the Table 1.

Determination of ion-exchange capacity. The ion exchange capacity was determined for both Na⁺ and H⁺ forms using column techniques. Accordingly, after loading the sample (3g) into a glass column, the resin was eluted with 20 mg L⁻¹ of chromium or cadmium solutions at a 2BV/h flow rate. The calculated results are given in Table 1.

Table 1. Physicochemical properties, suggested operating conditions and calculated exchange capacities of the resin of Amberjet IR 1200 resin^a

Functional group	Sulphonate
Matrix	Styrene divinyl copolymer
Moisture holding capacity	
Na ⁺ form	43 to 47%
H ⁺ form	49 to 55%
Total exchange capacity (eq/L)	
Na ⁺ form	≥2.00
H ⁺ form	≥1.80
Operating temperature °C	135
Service flow rate (BV/h)	5 to 50
Regenerants (g/L)	
NaCl (10% concn)	50 to 240
HCl (4 to 10% concn)	40 to 150
H ₂ SO ₄ (1 to 8% concn)	40 to 200
Maximum contact time (min)	20
Slow rinse (BV at Regeneration flow rate)	2
Fast rinse (BV at service flow rate)	1 to 3
Total exchange Capacity (eq/L)	
Na ⁺ form	2.00
H ⁺ form	1.80

¹ BV (Bed Volume) = 1 m³ solution per m³ resin.
^a Manufacturer supplied.

Table 2. Analysis of electroplating wastewater

Nature of impurity	Quantity (mg/L)
TDS	74.1
Cu	8
Ni	14
Zn	3.2
Cr	56
Cd	43
Na	182
K	10
Ca	78
pH	2.2

30 min (pH5). Stirring speed was 200 rpm during the batch experiments. All the operations were conducted at room temperature. The contents were filtered and after filtration of the solid phase, the content of chromium and cadmium in the liquid phase was determined by AAS.

Removal and recovery of Cd (II) and Cr (III) from electroplating effluent. The optimum conditions were applied for the removal of Cd (II) and Cr (III) from real electroplating effluent using batch studies. A sample (50ml) of the effluent was taken in a conical flask and treated with 0.2 g of resin for 30 minutes at pH 5.5. The solution was then filtered and the filtrate analyzed for Cd (II) and Cr (III). Next the resin was transferred to another conical flask and treated with 50 ml of 0.05 M HCl solution. After 24 hrs the solution was filtered and the concentration of recovered Cd (II) and Cr (III) was determined in the filtrate.

Table 3. Removal and recovery studies of metal ions using 50 ml electroplating effluent

Metal	Initial Concn (mg)	Amount removed (mg)	Removal (%)	Amount Recovered (mg)	Recovery (%)
Na ⁺ form					
Cd (II)	2.8	2.49	88.9	2.24	89.95
Cr (III)	2.15	1.85	86.04	1.65	89.18
H ⁺ form					
Cd (II)	2.8	2.46	87.85	2.14	86.99
Cr (III)	2.15	1.82	84.65	1.50	82.41

Results and discussion

Operating conditions for the Amberjet IR 1200 resin

Concentration. Cd (II) and Cr (III) concentrations were selected in the range 2 to 50 mg/L for two different ionic forms of the resin.

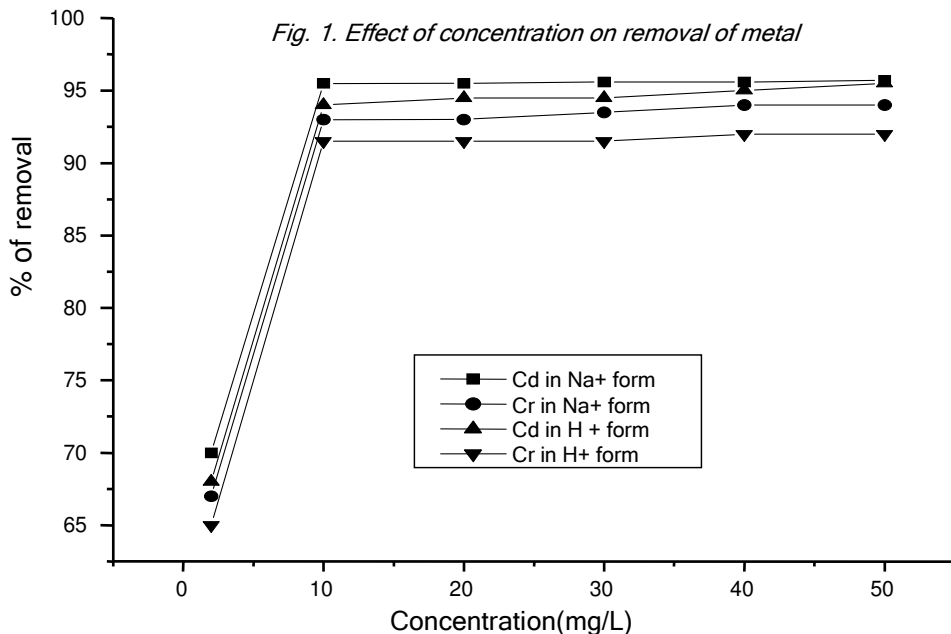
The effect of concentration on metal removal was investigated and the results are shown in Fig.1. It was found that the removal of Cd (II) was higher than Cr (III) for both forms of resin. In both case of ions the removal efficiency increased steadily up to 10 mg/L of the metal ion concentration for both forms of resin. After that there was no notable difference in the removal efficiency. The maximum removal was obtained as 94.5% of Cd (II) and 91.5% of Cr (III) in H⁺ form of resin, 95.5% for Cd (II) and 93% for Cr (III) in Na⁺ form of resin. The optimum

to the formation of hydroxyl complexes of chromium (Cr (OH)₃) (Pehlivan *et al.*, 2008). The optimum pH for the effective removal of Cr (III) was found to be 5.5. It was observed that maximum removal of Cr (III) was 77% for H⁺ form and 79% for Na⁺ form.

In the case of Cd (II) the amount of removal increased from 40 to 90 % as the pH increased from 1 to 6. The decrease in removal with increase in H⁺ ion concentration at low PH, indicates that the removal is via ion exchange (Mohammad Ajmal *et al.*, 2001). After pH

5.5, the rise in pH had no effect on removal of Cd (II) .The maximum removal of Cd (II) was 79.5% and 77.5% in Na⁺ and H⁺ form respectively. 5.5 was the optimum pH for the removal of Cd (II).

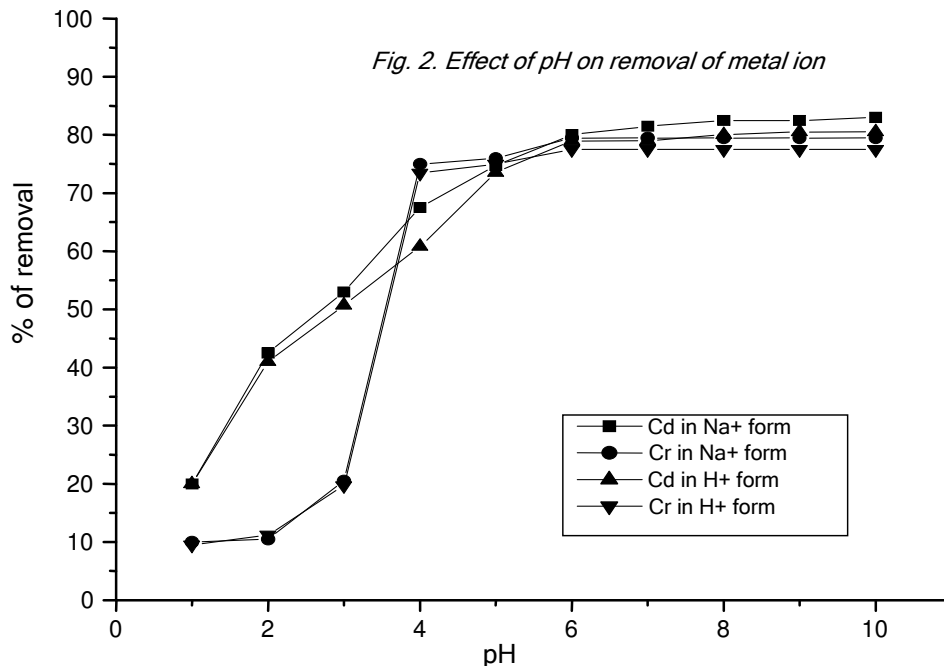
Stirring time: The stirring time range was 5-60 minutes. The effect of stirring time on metal removal was investigated, and the results are given in Fig. 3. Maximum removal of Cr (III) was 82.5% and 81%, for Cd (II) 85% and 83.7% in case of Na⁺ and H⁺ forms respectively. The graph shows the effect of reaction time on the removal metal ions. The removal was increased with an increase in time and attained equilibrium around 30 min. The percentage of metal removal was rapid during the first 20 min after that it rose slowly before attaining saturation value at



concentration fixed for further studies was 10mg/L. **pH:** The removal of Cd (II) and Cr (III) as a function of hydrogen ion concentration was examined in the range of 1-10. The effect of pH on metal removal was determined in batch experiments and the results are given in Fig. 2.

Cadmium removal was much higher than chromium. In case of Cr (III) in the pH range 2 to 2.8 there was little or no removal. This removal trend can be ascribed to the effect of competitive binding between Cr (III) and hydrogen ions for the bonding sites of the resin. At low pH, an excess of hydrogen ions can compete effectively with Cr (III) for bonding sites resulting in a decrease of Cr (III) removal. The percentage removal remarkably increased in the pH range of 3 to 4. The graph shows maximum removal at pH 5.5. The percentage of ion exchange decreased rapidly when the pH increased above 6 which may be due

30 min. A further increase in contact time had negligible



effect on the percentage removal. Very high removal rates were observed at the beginning because of the great number of bonding sites available for exchange operation. The optimum stirring time, 30 min was chosen

for the ion exchange process of two heavy metals Cd (II) and Cr (III) from electroplating waste water. The synthetic resin was converted in to H^+ and Na^+ prior to ion exchange. During the course of the ion exchange process the effect of pH, concentration of metal ion solution, amount of synthetic resin and stirring time were studied. Better ion exchange was obtained for a pH of 5.5, stirring time 30 min, metal ion concentration 10 mg/L and resin amount of 200mg. The sodium form of synthetic resin showed better ion exchange capacity than the H^+ form moreover the two synthetic resins were regenerated after the ion exchange process. Hence, the selected synthetic resin Amberjet IR 1200 performed well for removal and recovery of Cd (II) and Cr (III) from electroplating effluent.

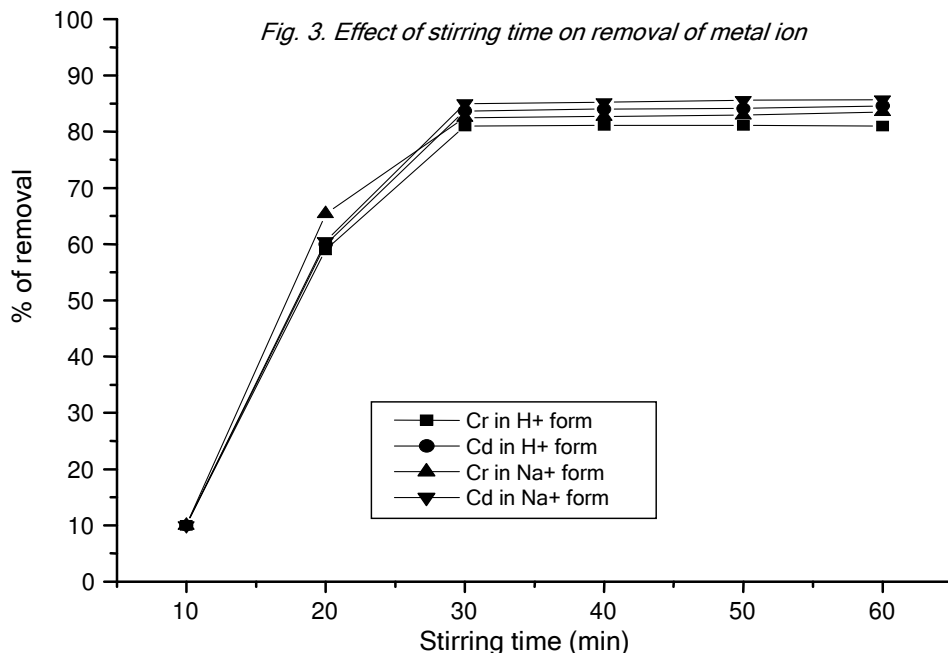


Fig. 3. Effect of stirring time on removal of metal ion

for both resins.

Resin amount. The effect of resin mass on the removal of both metals was investigated. For this purpose, 50 - 1000 mg resin amounts were taken. The results are given in Fig. 4. The figure shows that the amount of metal removed by unit mass increases by increasing the resin amount. An increase in the resin amount resulted in a decrease in the contact time required to reach the equilibrium. Since at 200 mg of resin the removal efficiency reached the maximum, 200 mg was chosen as the optimum resin amount.

Removal and recovery studies of metal ions using electroplating effluent: The results of batch studies of Cd (II) and Cr (III) from electro plating effluent on Amberjet IR 1200 resin both Na^+ and H^+ forms are given in Table 1 and Fig. 5. The graph shows 88.9% removal of Cd (II) in the Na^+ form and 87.85 % in H^+ form. In the case of Cr (III) 86.04 % and 84.65% for Na^+ , H^+ forms respectively. The recovery was about 89.18% and 82.41% for Cr (III), 89.95% and 86.99% for Cd (II) for Na^+ , H^+ forms respectively.

Conclusion

A synthetic ion exchange resin, Amberjet IR 1200, has been selected

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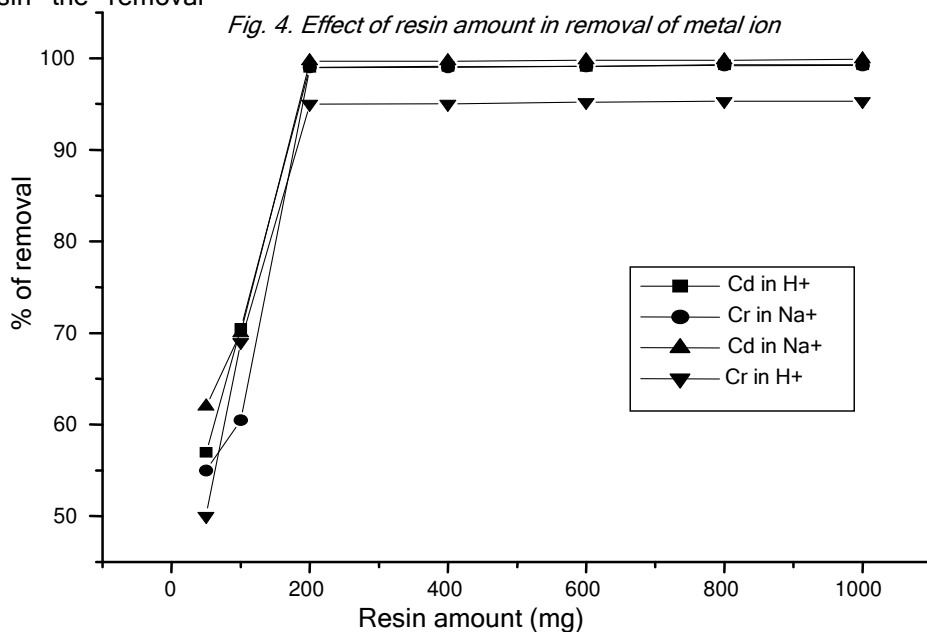
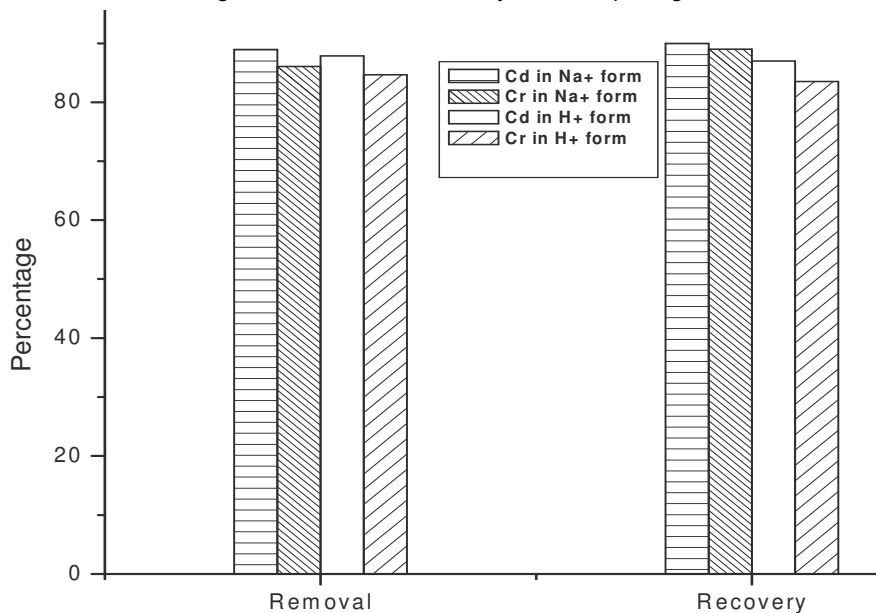


Fig. 4. Effect of resin amount in removal of metal ion



Fig. 5. Removal and recovery in electroplating effluent



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