PROCESSING OF ELECTROPLATING EFFLUENT FOR THE RECOVERY OF ZINC AND CHROMIUM USING ION EXCHANGE TECHNIQUE

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Abstract

In order to reduce the pollution and conserve the resources, a process has been proposed to recover zinc and chromium from the electroplating effluent following ion exchange technique. The studies for the extraction of zinc in different contact time, pH of the solution, resin dose, mechanism of adsorption etc. were made for the recovery of zinc from the solution using cationic resin, Lewatit VP OC 1026. The resin, Lewatit VP OC 1026 has been found to be selective for the extraction of zinc from the effluent leaving total chromium in the raffinate. The zinc was effectively eluted from loaded resin with dilute sulphuric acid. The mechanism of extraction of zinc was found to follow the Langmuir isotherm. The chromium was extracted from the raffinate using anionic resin, Amberlite IRA 400 Cl and loaded chromium eluted effectively with 20% NaOH.

Introduction

Different metals are employed for various applications in metallurgical, textile, electroplating, metal finishing chemical industries etc. In these industries, large quantities of effluents containing zinc and chromium along with other metallic constituents viz. copper, nickel, cadmium, iron are generated [1]. These metallic ions are toxic in nature, their discharge not only causes environmental pollution but also adversely affects aquatic and human life as the concentration of these ions is above pollution norm. Different processes viz. solvent extraction, electrodialysis, precipitation, evaporation, ion exchange, etc are used for extraction of metallic values directly from the effluents, wastewater, rinse solutions of different industries [2]. Solvent extraction process is employed for the extraction of metals using organic extractant from the solution more than 800-ppm metallic constituents [3]. In this process, loss of organic extractant takes place due to solubility and entrainment making the process unviable from dilute wastewater. The conventional precipitation process for the removal of metal consumes large quantity of chemicals and generates sludge, which needs costly disposal procedure as landfill. Due to increasing stringent environmental regulation, dumping cost of such materials is also increasing. Recovery of metals will not only conserve the natural resources but also avoid the environmental pollution.

Ion exchange is a proven technique for the purification and separation of metals from aqueous solutions using solid ion exchange resins. It finds major application in the purification of water, extraction of acid from pickle solution, extraction and separation of uranium, copper, nickel, cobalt, gold from different solutions [4]. The process is effective particularly for removal of metallic ions from the dilute solutions (<0.5 g/l) [3] where

precipitation is not efficient. Different organic ion exchange resins are used for the extraction of zinc and chromium from different solutions. This is evident from a number of publications/ patents in different proceedings and journals [5-7]. The studies have been made to improve the loading capacity, selectivity, kinetics of extraction and elution from different solutions containing anions (cyanide, sulphate, nitrate, chloride) and cations. The cation exchange resins viz. dithizone, hydroxamic acid, amidoxime, α-nitroso β-naphthol, aminophosphonate etc have been used for the extraction of zinc and other transition metals (Cu, Ni, Co etc) from the aqueous solutions [8]. Lewatit OC-1026 resin has been reported to have good zinc selectivity, whilst the chelating resins such as Purolite S-930, Metalfix Chelamine and Metalfix Chelosolve showed greater selectivity for the major contaminant ions, Cu, Cd and Pd. These resins however, showed some loss of their functional groups after a small number of repeat cycles. The performance of iminodiacetate resin (Amberlite IRC-718) was comparable with the commercially available Chelex-100 during the sorption and desorption of zinc, cadmium and lead from relatively complex water and sediment samples[9]. Aminophosphonate chelating resin (Duolite C467 produced by Rohm & Haas) [10] has been employed for the removal of zinc from the cyanide containing solution.

The strong and weak base resins exchange the anions from the aqueous solutions. Different authors investigated the adsorption of zinc anions from the cyanide solutions [11]. A strong-base resin having trimethyl ammonium as active group extracted zinc and other metals viz. copper, iron, nickel and gold from the cyanide solution and metals were effectively eluted with a solution containing sulphuric acid and thiourea. Zinc was also removed from the nickel electrolyte using the anion exchange resin (D201) which has good saturation loading at $60^{o}C$ [12]. Different anion exchangers have also been studied for the removal of hexavalent chromium from aqueous solutions [13, 14]. Sengupta et al. [15] reported the selective extraction of $HCrO_4^-$ below pH 6.0 using polystyrene divinylbenzene skelton and functional tertiary amine or ammonium group. Korngold et al. [16] studied the comparative performance of three resins viz. Amberlite 416, Purolite A420 and Relite A-490. Relite A-490 exhibited higher selectivity for chromate and dichromate and found effective to reduce trace concentration of Cr(VI) below permitted level as compared to other two resins in presence of chloride and sulphate ions. A strong basic anion exchanger, Amberlite IRA-400 Cl was used for extraction of Cr(VI) from the chloride solution [17]. Drella [18] reported the removal of Zn(II) and Cr(VI) using Wofatit KPS, strong cation exchanger and Wofatit SBK9, type2, anionic exchanger from the chloride solution respectively. A four-step ion exchange process for chromic acid recovery from waste acid solutions was proposed by Lin and Kiang [13].

In view of the above, ion-exchange process has been used for the extraction of zinc and chromium from electroplating effluent using cationic and anionic resins. Detailed studies viz. contact time, pH, resin dose etc have been made to understand the adsorption phenomena for extraction of zinc using cationic resin, Lewatit VP OC 1026. The raffinate obtained after zinc extraction was used to extract chromium from the solution using anionic resin, Amberlite IRA 400 Cl. The results of the studies are described in the present paper.

Materials and methods

<u>Materials</u>

In the electroplating industries, the effluents containing zinc and chromium are generated during washing of the electroplated materials. The first washing contains high metallic constituent, which is recycled in the electroplating bath. The second wash contains low concentration of metals and discarded as effluent. A composite discarded effluent obtained from M/s Sinha Electrochemical plant, Jamshedpur, India having composition 520 ppm Zn and 17 ppm Cr, 54 g/l Cl was used for experimental purpose. Initially, the synthetic solution containing zinc in required proportion was prepared from their respective chloride salts using distilled water. The chemical reagents such as hydrochloric acid, sodium hydroxide etc were laboratory reagent (L.R.) grade. The cationic resin, Lewatit VP OC1026 (Polystyrene crosslinked matrix with di-2-ethylhexyl-phosphate D2EHPA) and anionic resin, Amberlite IR-400 (Cl) supplied by M/s Rohm & Haas Co., were employed without further purification. The pH of the solution was adjusted by adding dil. hydrochloric acid or sodium hydroxide.

<u>Batch studies in shaking flask</u>

Ion-exchange experiments for the adsorption of metals were carried out in a conical flask using wrist action shaking machine at atmospheric condition. After extraction, resin and raffinate were separated by filtration. Raffinate was analysed to know the concentration of metal in the solution. The metal was eluted from the resin using dilute sulphuric acid/ alkali. The eluted solution containing metal is analysed to check material balance. The regenerated resin was washed with distilled water and used for further experiment.

<u>Studies in column</u>

To carry out adsorption studies in vertical column, the weighed amount of resin was taken in the column. The resin was thoroughly washed with distilled water and then studies were conducted under different concentration of zinc maintaining a constant flow rate at room temperature. The aqueous raffinate was collected in different time intervals. The pH of the feed has been adjusted as per requirement. After adsorption studies, the resin bed was washed with distilled water and loaded metal ions were eluted by passing dilute sulphuric acid/ alkali. The aqueous raffinate and eluted solution were analysed for metal content using cconventional EDTA-titration and Atomic Absorption Spectrophotometer methods.

Results and discussion

Bench scale studies have been carried out under different experimental conditions for the extraction of zinc and chromium from the solution similar to waste effluents. The results of the studies are described below.

<u>Effect of pH</u>

Initially, the effect of pH has been studied for the extraction of zinc from the effluent of electroplating industry containing 0.52 mg/ml Zn and 0.017 mg/ml Cr using Lewatit VP OC 1026 at A/R ratio 100 (ml/ g resin) and 1 hour time. The results presented in Figure 1 show that the zinc was selectively extracted and no chromium(VI) was extracted in the resin.

The extraction of zinc was found to be 25.5% at lower equilibrium pH 1.50. The extraction increased to 46.9% with increase in equilibrium pH of the solution to 4.76 from the effluent of electroplating industry. Further studies have been carried out under different conditions with the model solution similar to electroplating effluent to optimise the process parameters for the extraction of zinc with Lewatit VP OC 1026.
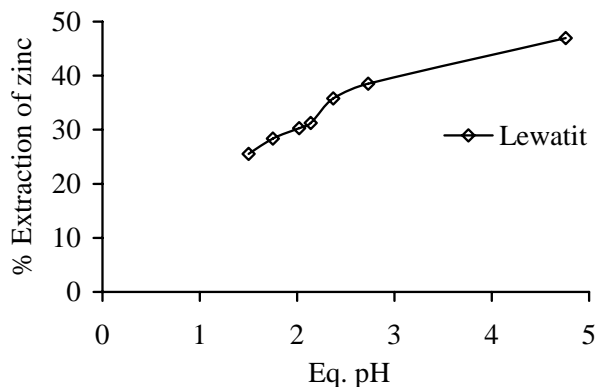

Figure 1. Extraction of zinc from electroplating effluent at different pH
(Exp. Cond.: Wt. of the resin= 1g, Initial pH= 6.22, A/R= 100, t= 1 hr)

Effect of contact time

The effect of time on sorption of zinc was studied from the solution prepared in chloride medium similar to plating effluent containing 0.5 mg /ml Zn having pH 6.00 and 7.26 using Lewatit VP OC 1026. The sorption of zinc increased to 45.2% and 52.9% in five minutes from the lower and higher pH solutions respectively. The equilibrium extraction of 60% was attained in 40 minutes with both aqueous feed solutions. The equilibrium pH of both the solutions after extraction of metal was about 2.0 pH. Subsequent studies have been carried out maintaining a contact time of 60 minutes to attain the equilibrium extraction.

Effect of resin dose

The effect of resin dose on sorption of zinc from the solutions containing 0.20 and 0.50 mg/ml Zn at pH 5.67 has been studied keeping contact time 60 minutes. Resin dose was varied from 0.1 gram to 0.6 gram in 50-ml solution. The results presented in Figure 2, indicate increase in extraction of zinc from 21% to 82% from the solution containing 0.20 mg/ml Zn with increase in resin dose 2 gram/l to 12 gram/l as available sites or surface area increases with higher quantity of resin. On increasing the concentration of zinc in the solution to 0.50 mg/ml Zn, the lower zinc extraction of 20% to 50% was found in the same resin dose due to higher concentration of zinc in the solution. The extraction of zinc ion was found to increase rapidly in the beginning and slowly at the end. An increase in surface area of resin automatically enhances the rate of sorption reaction.
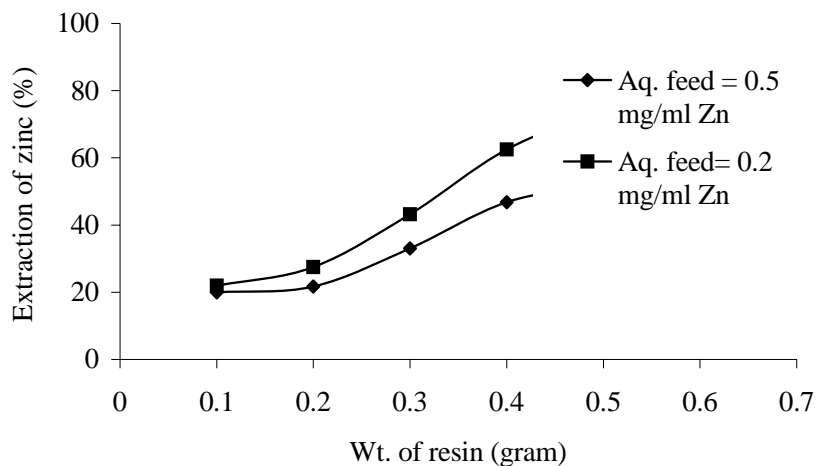
Adsorption of zinc in multi-stages

Figure 2. Effect of resin dose on the extraction of zinc using Lewatit VP OC 1026
(Exp. Cond.: Aq. feed = 50 ml, Initial pH = 5.67, t= 1 hr)

In order to determine the loading capacity of the resin, the Lewatit resin was contacted in different stages with aqueous feed containing 0.1 and 0.2 mg/ml Zn at A/R ratio 400 for 60 minutes. The equilibrium extraction of metal in the resin achieved in five contacts. The results presented in Table-I show the adsorption of 40.6 mg Zn/ g resin from the aqueous feed of 0.10 mg/ml Zn at pH 5.6. The increase in feed concentration from 0.1 to 0.2 mg/ml Zn increased the adsorption capacity of resin from 40.6 to 58.0 mg Zn/g resin due to increase in the equilibrium concentration of metallic ions in the aqueous and resin phases.

Table I. Loading capacity of Lewatit VP OC 1026 for Zinc.
Aq. Feed = 100 ml, Initial pH = 5.57, Resin: Lewatit VP OC 1026,
A/R = 400, Shaking time = 1 hr

Contact No	Aqueous feed: 0.1 mg/ml Zn		Aqueous feed: 0.2 mg/ml Zn	
	Zn in raffinate C_e (mg/ml)	Cumulative loading (q) mg/ g resin	Zn in raffinate C_e (mg/ml)	Cumulative loading (q) mg/ g resin
1	0.0427	22.92	0.1570	17.20
2	0.0860	28.52	0.1679	30.04
3	0.0855	34.32	0.1763	39.52
4	0.0894	38.56	0.1748	49.60
5	0.0948	40.64	0.1790	58.00

The experimental equilibrium data for adsorption of zinc from the aqueous solution of 0.2 mg/ml Zn ion Lewatit VP OC 1026 were analyzed using the Langmuir and Freundlich

equations. The Langmuir sorption model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer sorption without any interaction with the sorbed ionic species.

$$q=(q_m k_1 C_e)/(1+k_1 C_e) \tag{1}$$

Where, C_e = equilibrium concentration of metal in solution (mg/ml), q = amount of material adsorbed on the resin at equilibrium (mg/g resin), k_1 = equilibrium constant related to the affinity of the binding sites for metals or the Langmuir constant

q_m = the resin capacity (mg/ g resin)

$$1/q=[(1/k_1 q_m)(1/C_e)]+[1/q_m] \tag{2}$$

Freundlich model assumes that the uptake or adsorption of metal ions occurs a heterogeneous surface by monolayer adsorpton.The model is described by the following equation:

$$q=k_f[(C_e)]^{1/n} \tag{3}$$

$$\log (q)=(1/n) \log (C_e) + \log k_f \tag{4}$$

The common terms in above equation are described in Langmuir expression and k_f and n are Freundlich constants that can be related to the adsorption capacity and adsorption intensity respectively.
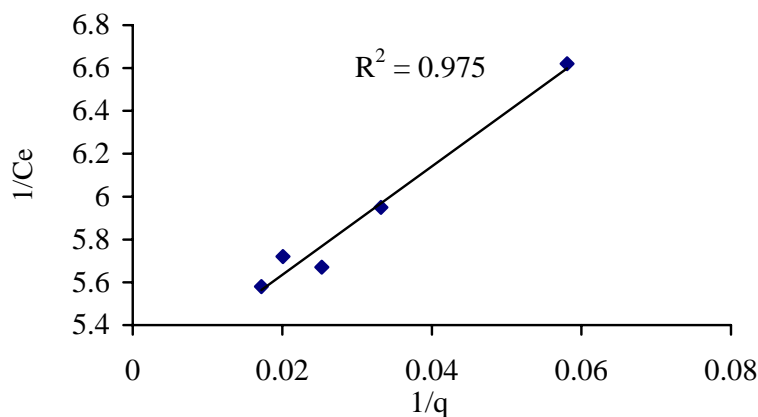

Figure 3. Plot for fitting Langmuir Isotherm with experimental data of Lewatit VP OC 1026 (Exp. Cond.: Aq. Feed= 0.2 mg/ml of Zn, Aq. feed vol.=100 ml, Initial pH= 5.57,Wt. of the resin: 0.25 g, A/R= 400, Shaking time = 1hr)

The correlation co-efficient (R^2) values are 0.924 and 0.975 in case of Freundlich and Langmiur isotherms (Figure 3) respectively. Thus Langmuir isotherm fits the data more satisfactorily for the aqueous of 0.2 mg/ml Zn.

Extraction of zinc in column

In order to carry out extraction of zinc in continuous mode, the studies have been made in a fixed bed column containing 1 g ion-exchange resin, Lewatit VP OC 1026. The aqueous feed solutions containing two different concentrations viz. 0.2 and 0.5 mg Zn/ml were passed through the column at a flow rate of 1 ml/min. The samples were collected at every 50 ml volume for analysis. The extraction of zinc in the resin increased on passing the solution which is evident from Table II and reaches to the saturation loading of 37.8 mg Zn/ g resin on passing 250 ml of aqueous feed of 0.5 mg Zn/ml at pH 5.07. The extraction studies were also carried out with aqueous feed concentration of 0.2 mg Zn/ml at pH 4.82 maintaining the same flow rate of 1 ml/min. The results showed higher equilibrium extraction of 49 g Zn/ g resin on passing 400 ml solution due to equilibrium of metal ion in aqueous and resin phase.

Table II. Dynamic loading of zinc under column with Lewatit VP OC 1026
Resin: - 1 gm, Flow rate = 1ml/min

Cumulative volume(ml)	Cumulative Zn in resin (mg Zn/g resin)	
	Aq. feed=0.5mg/ml Zn, Initial pH= 5.07	Aq. feed=0.2mg/ml Zn, Initial pH= 4.82
50	19.53	16.7
100	29.89	25.47
150	33.64	29.11
200	37.81	32.75
250	37.81	36.33
300	-	38.69
350	-	44.81
400	-	48.14

Extraction of zinc and chromium from effluents

In order to validate the bench scale results, the studies have been carried out in a column containing 2.0 g Lewatit VP OC 1026 using actual electroplating effluent having metal content 520 ppm Zn (0.52 mg/ ml Zn) and 17 ppm Cr (0.017 mg/ ml Cr) at 6.23 pH (Figure 4). Total zinc was found to be extracted from the effluent in the column at flow rate of 1 ml/min. The raffinate free from zinc was then used in the other column containing Amberlite 400Cl. Almost total chromium was extracted in the resin. The loaded zinc and chromium were eluted from the Lewatit and Amberlite resins with 5% sulphuric acid and 20% sodium hydroxide solutions respectively. The eluted solutions containing zinc and chromium could be used to produce their salts by crystallisation.
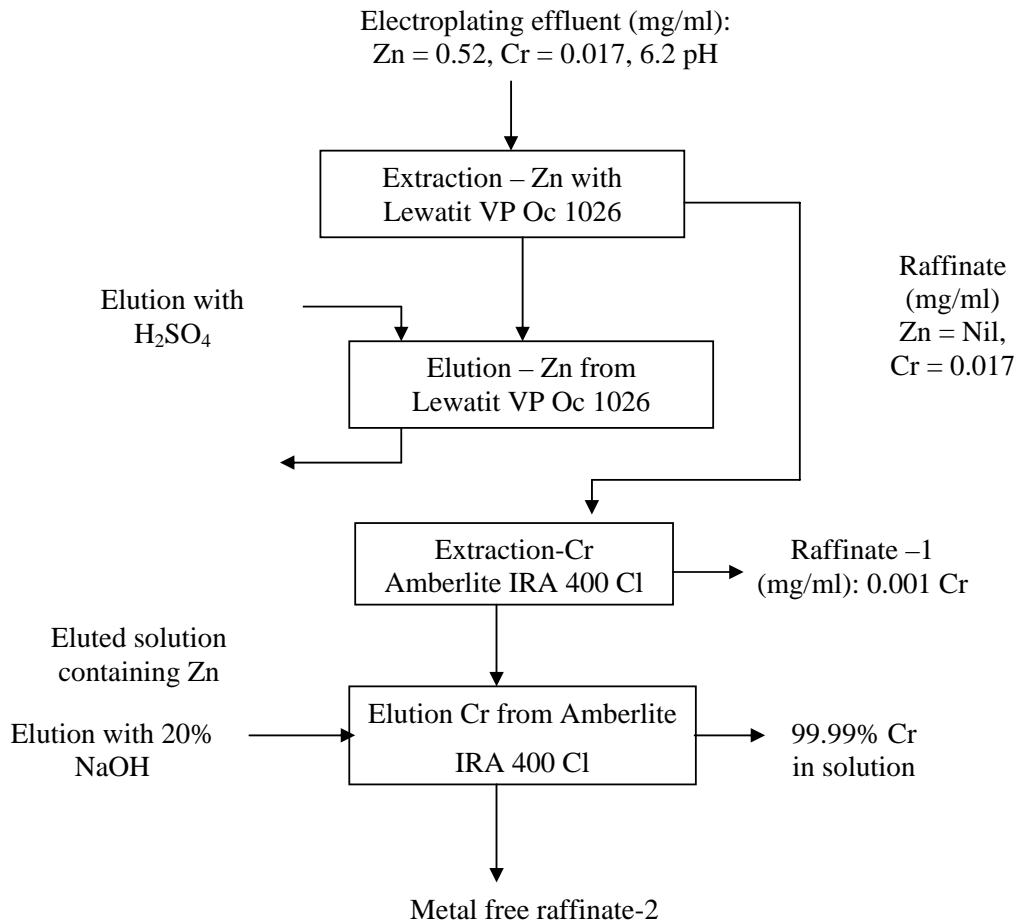
Electroplating effluent (mg/ml):
Zn = 0.52, Cr = 0.017, 6.2 pH

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┌──────────────────────┐
│   Extraction – Zn with│
│   Lewatit VP Oc 1026  │
└──────────────────────┘
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Elution with
H₂SO₄

Raffinate
(mg/ml)
Zn = Nil,
Cr = 0.017

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┌──────────────────────┐
│   Elution – Zn from   │
│   Lewatit VP Oc 1026  │
└──────────────────────┘
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┌──────────────────────┐
│    Extraction-Cr      │
│   Amberlite IRA 400 Cl│
└──────────────────────┘
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Raffinate –1
(mg/ml): 0.001 Cr

Eluted solution
containing Zn

Elution with 20%
NaOH

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┌──────────────────────┐
│  Elution Cr from Amberlite│
│    IRA 400 Cl         │
└──────────────────────┘
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99.99% Cr
in solution

Metal free raffinate-2

Figure 4. Extraction of zinc and chromium from the zinc plating effluent

Conclusions

1. Bench scale studies carried out in shake flask with effluent containing 0.52 mg Zn/ml and
0.017 mg Cr/ml under different pH showed selective extraction of zinc leaving chromium in
the aqueous raffinate. The extraction of zinc was found to increase from lower equilibrium pH
to the higher values from aqueous feed solutions. The extraction of zinc increased with
increase in time and reaches equilibrium in 40 minutes. The extraction also increased from
21% to 82% with increase in resin dose from 2 to 12 g/l.

2. Adsorption of zinc studied in different contacts showed increase in zinc extraction in each
stage. Total zinc loaded in the resin was found to be 40.6 and 58.0 mg/g resin from the
aqueous feeds of 0.1 and 0.2 mg/ml Zn respectively in multi-stage extraction.

3. The sorption reaction for the extraction of zinc from aqueous feed follows Langmiur isotherm as the data fitted more satisfactory than Freundlich isotherm.

4. The batch scale results for metal extraction was validated in continuous mode in fixed bed column. The studies showed the possibility of recovery of zinc and chromium from the industrial effluents by using ion exchange resins viz. Lewatit VP OC 1026 and Amberlite IRA 400 Cl respectively. The process needs scale-up studies and cost calculation before transferring to an industry.

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