Chelating Resin for Indian Electroplating Industrial Waste Water

RITESH .H. PATEL
Asst. Teacher,
Shri A.R.Patel U.M.Shala, Suraj
Gujarat (India)

DR.PRANAV S. SHRIVASTAV
Professor,
School of Science, Gujarat University, Ahmedabad
Gujarat (India)

Abstract:

A macro particular divinylpolystyrene based chelating ion exchanger contains catechol as the functional group has been synthesized. The resin is high capacity against acidic as well as basic media. Physicochemical properties of the resin are examined. Sorption capacities of the heavy metal ions on resin are found to be quantitative in the p^H-range of 1.0-7.0. Sorption kinetics of metal ions on the resin is studied. Under competitive conditions the system shows higher selectivity of Cr(lll) ,Cr(Vl) .The sorption characteristics for Cr(lll) ,Cr(Vl) are studied with a view to utilizing the resin for the removal of Cr(lll) ,Cr(Vl) as well as pre concentration of Cr(lll) ,Cr(Vl) ions from waste water sample by column operation.

Keywords: *Chelating resin, Cr(lll), Cr(Vl), Heavy metals, Pre concentration*

1. Introduction

The trivalent and hexavalent Chromium is often present in electroplating waste water removal of electroplating industrial waste water especially metal tubes and pipes industries in India. Much of the initial focus has been on controlling liquid emission of Cr(lll) ,Cr(Vl) contaminants from electroplating industries which were identified as the single largest sources of Cr(lll) ,Cr(Vl) emissions and specifically targeted by the India Environmental Protection Rule. Cr(lll) is required for normal development of human and animal organisms but Cr(Vl) activates tertogenic processes disturb DNA synthesis and can give rise to mutagenous changes leading to malignant tumors (WHO, Report). Cr(lll) cation predominates in most tissues except the liver. Chromium is associated with nucleic acids and is the subject to the concentration in liver cells. It plays an important role in the metabolism of glucose, certain proteins and fats, is part of enzymes and stimulates the activity of others.

To remove toxic Chromium compounds from sewages there are used such methods as precipitation, membrane process, adsorption and ion-exchange. The maximum limit in drinking water is $0.05 mg/dm^3$ Removal of Cr(lll) ,Cr(Vl) heavy metal ions has been the focus of extensive research. In many cases reduction of heavy metals to low levels is possible. Sorption of heavy metals on inorganic sorbents and carboxyl cation exchangers is not effective at pH values less than 5. metal acidic industrial waste water. The growing problem of heavy metal contamination of natural waters has stimulated a search for new selective ion-exchange and complexing properties of acidic conditions. Chelating resins have received increasing attention as adsorbent for selective pre concentration of dissolved heavy metal from contaminated waste water in preference to non toxic completing Cr ions. Anodizing and electroplating shops produce variable amounts of harmful metals. The toxicity of these metals varies within wide scale. The INDIAN regulatory has recommended for limit for releases from surface finishing plants.

Table: 1 Metal bearing waste water

Metals	Conceg/l
Chromium	0.7
Chromium(IV)	0.2
Copper	0.5
Nickel	1.0
Zinc	2.0
Cadmium	0.2

Effluents can be highly acidic or alkaline. Theoretically, it is possible to reach this limit using conventional cleaning technology e.g. precipitation but optimising the present efficiencies often demands intensification both in the effort and training of waste management teams. Both these activities introduce new costs into the system without increasing production. Usually, there is only one kind transition metals in each separate waste stream, but very often different kinds of wastes are mixed together before metal precipitation.

2. Metal Determination method from sample

- Determination of Cr(VI) from electroplating waste water by using of a spectophometric flow injection system.

A new rapid and sensitive FI method is reported for spectrophotometric determination of trace chromium(VI) in electroplating waste water. The method is based on the reaction of Cr(VI) with sodium diphenylamine sulfonate (DPH) in acidic medium to form a purple complex (λ_{max} = 550 nm). Under the optimized conditions, the calibration curve is linear in the range 0.04–3.8 µg m l^{-1} at a sampling rate of 30 h^{-1}. The detection limit of the method is 0.0217 µg m l^{-1}, and the relative standard deviation is 1.1% for eight determinations of 2 µg ml^{-1} Cr(VI). The proposed method was applied to the determination of chromium in electroplating waste water with satisfactory results.

- Extractive sepration and determination of Cr in electroplating waste water using tribenzylamine.

A simple extractive separation method has been developed for the determination of chromium based on the extraction of Cr (VI) as its ion-pair with tribenzylamine (TBA). The ion-pair is extracted at acidic pH using toluene as the diluent. The concentration of chromium in the organic phase was measured spectrophotometrically at 309 nm. The influence of experimental variables such as pH, sample volume, equilibration time, diverse ions etc. has been studied in detail. The extracted chromium (VI) could be stripped to the aqueous phase using NaOH as the stripping agent. The extracts were characterized using FT-IR spectroscopy. A detection limit of 0.08 µg mL^{-1} could be achieved and the validity of the method was checked in real tannery effluent, electroplating waste water and spiked water samples.

3. Preparation of Chelating Resin

Most of the above special resins are of the chelating type. They are able to form complexes with metals. The picture on the right shows a metal complexed by the iminodiacetic functional group of a chelating resin. The chelating resins make complexes only with multivalent metals. These complexes are very stable. Therefore, these resins have a high selectivity and are capable of removing metals from solution preferentially. See examples in the resin types page, with the corresponding applications.

The activation is more complex, as it requires two successive steps. Also, the chemicals used are more expensive, which explains that anion exchange resins are considerably more expensive than SAC resins. The first step is called **chloromethylation**, and is a reaction between the polymer beads and chloromethyl methylether (which is a very hazardous chemical): Chloromethylation Chloromethylated styrene–divinylbenzene copolymer (6.5 per cent) was prepare. Catechol was sublimed to its purest form before use. For the preparation of chelating resin following procedure was employed: To 10 g of resin I (chloromethylated styrene-divinylbenzene copolymer, 6.5 per cent divinylbenzene), 40 cm^3 of dioxan were added and the mixture was stirred for 1h at room temperature to allow swelling. To this suspension, 8 g of catechol and 5 g of powdered anhydrous zinc chloride (freshly fused) were added.

$CH_3- O - CH_2Cl$

Chloromethyl ether

CH_2Cl CH_2Cl CH_2Cl CH_2Cl
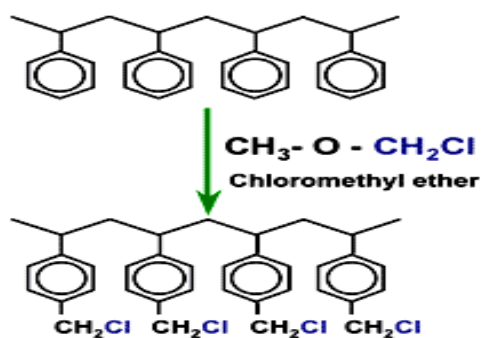
The mixture was then heated to 105-110°C and kept for 12 h with stirring. The product was filtered off and washed with methanol, 10 per cent hydrochloric acid, water and methanol successively. On drying in a vacuum desiccator, 11.4 g of light brown resin (resin II) was obtained.

To 100 cm^3 of 1 M sodium hydroxide containing 4.4 g sodium nitrite, 10 g of resin II was added and the suspension was stirred for 1 h. After cooling to 0°C, 6.6 cm^3 of 38 per cent sulphuric acid was added dropwise to the mixture at 0-5°C with constant stirring. The stirring was continued at 5°C for additional 2 h. The reaction product was filtered and washed with water and methanol. After vacuum drying, 10.6 g of brown resin (III) was obtained.

4. Characterization of Resin

4.1 Stability and Water Regain
To determine the stability, dry resin III (0.5 g) was shaken on a mechanical shaker with 25 cm^3 acid/alkaline solutions of various concentrations for 3 d and then filtered and washed several times with water. After drying the nitrogen content and sorption capacity for the metal ions were determined.

For estimation of water regain values, a sample of 0.5 g dry resin III was immersed in water for 48 h. The resin was then filtered by suction and pressed between filter papers to remove the surface moisture. Weighed amount of the swollen resin was dried at 110°C for 48 h to determine water regain values. The water regain values were calculated based on following expression:

$$EWC = \frac{\text{Wt of the wet resin} - \text{Wt of dry resin}}{\text{Wt of dry}} \quad \text{.......... (1)}$$

4.2 Elemental Analysis
Chlorine content in chloromethylated polystyrene (resin I and II) and the nitrogen content in the final product (resin III) were estimated by the recommended procedures.

4.3 IR Spectra
IR spectra (KBr disks) of chloromethylated polystyrene, polystyrene loaded with catechol and its nitrosocatechol derivative, were recorded on a Perkin Elmer FTIR 160°series spectrophotometer.

4.4 Sorption Studies
The stock metal ion solutions of 5 mg/cm^3 concentration of Cd(II), Pb(II) and Hg(II) were prepared by dissolving their nitrates in distilled water. Standardization of the solutions was carried out gravimetrically or volumetrically by following the available methods[15]. The solutions were diluted, whenever required, using doubly distilled water. The initial pH of the solutions was adjusted with 0.05 mol/L HCl and 0.05 mol/L NaOH, respectively. Batch mode sorption studies were carried out to determine the sorption of metal ions on the resin in the pH range of 1.0–7.0. The weighed quantities of air-dried resins (0.1 g each) were equilibrated with 50 cm^3 of aqueous solution of metal ions at varying concentrations and pH values in stoppered conical flasks by shaking for 24 h. The solution was then filtered and the concentration of metal ion in the filtrate was determined spectrophotometrically by known methods[16]. All experiments were repeated and the average values are presented. The maximum deviation was less than 4 per cent.

The total sorption capacity was calculated from the following expression:

$$\text{Total sorption capacity (mmol/ g)} = \frac{(C_o - C_A)}{W} \quad \text{......(2)}$$

where C_o and C_A are the concentrations of metal ions (mmol) in the aqueous phase before and after equilibration, respectively; V is the volume of aqueous phase (mL) and W is the weight of dry resin. Distribution coefficient values (K_d) for the investigated metal ions at various initial solution concentrations were calculated using batch experiment data as follows:

$$K_{d(i)} = \frac{q_{e(i)}}{C_{e(i)}} \quad \text{..........(3)}$$

where $q_{e(i)}$ is the amount of metal ion sorbed at equilibrium (mol/g) and $C_{e(i)}$ is the equilibrium concentration of metal ion in the solution (mol/mL).

The competitive effect of the metal ions was interpreted through the use of the selectivity coefficient. This coefficient is the measure of the relative selectivity between two competing solutes and is equal to the ratio of their distribution coefficients between the exchanger phase and the aqueous phase:

$$D_{A/B} = \frac{K_{d(A)}}{K_{d(B)}} \quad \text{........... (4)}$$

The rate of metal ion sorption in 0.2 M acetate buffer of respective pH was determined by equilibrating 0.1 g of the resin with 50 cm^3 solution of 100 μg/cm^3 Cd(II), Pb(II) and Hg(II) solutions for various time intervals. The time required for 50 per cent metal uptake was calculated from the per centage retention vs time plots. The mode of diffusion of metal ion through solution towards the resin was determined by the interruption test[17] and was confirmed by the method reported by Nativ.

4.5 Desorption Studies
Desorption of the heavy metal ions from the nitrosocatechol loaded sorbent was carried out by using various acids of different strengths. The sorbent was loaded with heavy metal ions, placed in desorption medium and was shaken mechanically for 15-30 min at room temperature. The final metal ion concentration was determined spectrophotmetrically[16]. The desorption ratio was calculated from the amount of metal ions adsorbed on the sorbent and the final metal ion concentration in the desorption medium as follows:

$$\text{Desorption ratio} = \frac{(\text{Amount of metal ions desorbed to the elution medium})}{(\text{Amount of metal ions adsorbed onto the modified resin})} \times 100 \quad \text{.........(5)}$$

4.6 Column Operation
Compact glass column of ~ 15.0 cm length and 1.0 cm i d was loaded with 3.0 g of the resin. The column was equilibrated at required pH using 0.2 M acetate buffer solution. The breakthrough capacities and interstitial volume were determined, according to the known methods[17,19]. Effect of flow rate was studied and was optimized with a view to utilize the method for the preconcentration of Cd(II) from trace level samples.

5. Results and Discussion
The resin beads of 30-80 mesh size were used throughout the work. The reactions involved in the anchoring of nitroso derivative of catechol on chloromethylated polystyrene are given in Scheme 1. The resin was analysed by various techniques. Estimation of chlorine content in chloromethylated polystyrene (resin I and II) and of the nitrogen content in the final product (resin III) was done by the recommended procedures. The yield calculated for the final product was found to be 60 per cent. The difference in extent of chlorine content in chloromethylated polystyrene and the catechol anchored support is due to the chemical binding of catechol to the support replacing chloride. This was further confirmed by FTIR analysis of chloromethylated polystyrene (I), polystyrene loaded with catechol (II), and its nitrosocatechol derivative (III). The appearance of the characteristic IR absorption bands of nitroso group linked to the benzene ring of catechol at 1350 and 1410 cm^{-1} in the IR spectrum of

resin III is taken as a proof for the presence of the nitroso derivative of catechol in the polystyrene support. The resin shows good thermal stability up to 100°C and chemical stability in 4 M acids and alkalies.

Table: 2 Calibration curve Concentation vs Absorbance λmax : 390nm Mode : Absorbance

Constration of Cr (mg/L)	Absorbance
0	0.000
5	0.218
10	0.439
15	0.655
20	0.872
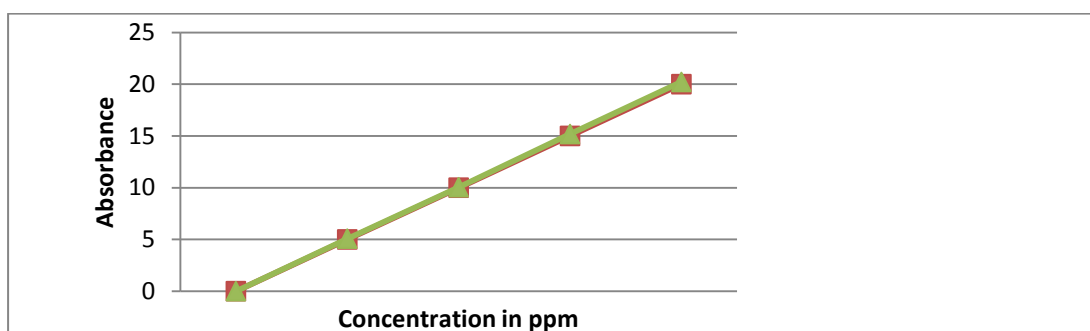
Fig. 1 Concentration Vs Absorbance

Table : 3 Performance of Resin for the removal of Cr at different concentration by batch adsorption method

Conc. of Cr (mg/L)	Initial (Absorbance)	Volume of Solution(ml)	Final Reading (Absorbance)	Cr removed(mg)
5	0.218	50	0.078	0.235
10	0.439	50	0.045	0.501
15	0.655	50	0.185	0.735
20	0.872	50	0.215	1.143

Table : 4 Optimum results for the removal of Cr from effluent of electroplating industries

Metal ions	Amount of metal ions in effluent(mg)	Amount loaded on resin (mg)	Removal (Percentage)	Relative standard deviation(RSD)
Cr^{+3}	1.12	1.071	95.65	1.62
Cr^{+6}	0.186	0.163	87.74	2.16

Table : 5 The adsorption percentage for Cr metal ions on resin (adsorption & desorption)

Metal	Adsorption % number of cylcles.		
	1 cycles	2 cycles	4 cycles
Cr^{+3}	95.65	93.54	93.46
Cr^{+6}	87.74	85.58	85.44

7. Conclusion

A resin was synthesized and their sorptions were studied. The resin showed a very good perfect a very good high kinetic of sorption removing higher than 15 min with both particle sizes of resin studied

considering the small particle size of the resin.

The main advantage of this resin is the contents increase the efficenty of the removal and eventual disadvantage of the loss of efficiency after several processes which is necessary to solve in the near. According to the FT – IR analysis the sorption mean electrostatic interaction followed by complex.

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