Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

RECOVERY OF COPPER (II) AND CHROMIUM (III,VI) FROM ELECTROPLATING-INDUSTRY WASTEWATER BY ION EXCHANGE

Sibel Yalçin[a]; Reşat Apak[a]; Jülide Hizal[a]; Hüseyin Afşar[b]
[a] Department of Chemistry, Faculty of Engineering, Istanbul University, Avcilar, Istanbul, Turkey [b] Department of Chemistry, Faculty of Science and Letters, Yildiz Technical University, Şişli, Istanbul, Turkey

Online publication date: 31 August 2001

To cite this Article Yalçin, Sibel , Apak, Reşat , Hizal, Jülide and Afşar, Hüseyin(2001) 'RECOVERY OF COPPER (II) AND CHROMIUM (III,VI) FROM ELECTROPLATING-INDUSTRY WASTEWATER BY ION EXCHANGE', Separation Science and Technology, 36: 10, 2181 — 2196
To link to this Article: DOI: 10.1081/SS-100105912
URL: http://dx.doi.org/10.1081/SS-100105912

SEPARATION SCIENCE AND TECHNOLOGY, 36(10), 2181–2196 (2001)

RECOVERY OF COPPER (II) AND CHROMIUM (III,VI) FROM ELECTROPLATING-INDUSTRY WASTEWATER BY ION EXCHANGE

Sibel Yalçin,[1] Reşat Apak,[1,*] Jülide Hizal,[1] and Hüseyin Afşar[2]

[1]Department of Chemistry, Faculty of Engineering, Istanbul University, Avcilar, 34850, Istanbul, Turkey
[2]Department of Chemistry, Faculty of Science and Letters, Yildiz Technical University, Şişli, Istanbul, Turkey

ABSTRACT

Two laboratory-scale separation processes have been developed for the recovery of copper (II) from acidic and cyanide-containing alkaline wastewater of electroplating industries. Acidic bath wastes were treated with Dowex 50X8, a strongly acidic cation-exchange resin, and the retained copper was eluted with H_2SO_4. The cyanide-containing alkaline bath waste was first oxidized with excessive hypochlorite, then neutralized, and recovered by the use of Amberlite IRC-718 chelating resin. Copper was eluted with H_2SO_4.

The two different valencies of chromium have been recovered from electroplating-industry wastewater by different separation processes: The predominant valency, Cr(VI), was retained on a strongly basic Dowex 1X8 resin and eluted with a NaCl and

*Corresponding author. E-mail: rapak@istanbul.edu.tr

NaOH solution. Alternatively, Cr(III), either existing originally in electroplating-industry waste-rinse mixtures or converted from Cr(VI) by reduction with Na_2SO_3, could be recovered by a weakly acidic Amberlite IRC-50 resin and eluted with a solution containing H_2O_2 and NaOH. Where plating industry wastes contain high levels of organic contamination, Cr(VI) would be naturally reduced to Cr(III) upon acidification, and it may be more economical to recover all chromium as Cr(III).

Key Words: Copper (II); Chromium (VI); Chromium (III); Recovery; Removal; Electroplating-Industry Wastewater; Ion Exchange; Wastewater Treatment

INTRODUCTION

Copper and chromium are important constituents of modern alloys, and these elements are quite abundant in untreated wastewaters of iron and steel, leather tanning, metal plating, textile, battery, electrowinning, and metal-finishing industries. Both elements pose a contamination risk to the natural environment (1,2) because at trace level amounts they are essential micronutrients to biota while at more elevated concentrations they may be toxic or carcinogenic (such as Cr(VI))(3). Chromium speciation basically involves the Cr(III) and Cr(VI) oxidation states; the latter is of much more of environmental concern because of its toxicity (4). Thermodynamic and kinetic considerations predict that $[Cr(H_2O)_5(OH)]^{2+}$ and $[Cr(H_2O)_4(OH)_2]^{+}$ species of the trivalent state and $HCrO_4^-$ and CrO_4^{2-} species of the hexavalent state should be the predominant forms of chromium in natural waters at common pH levels (5,6). The maximum tolerable limits of Cr(VI) (0.05 mg/L), of Cr(III) (0.17 mg/L), and of Cu(II) (1.0 mg/L) in drinking water have been specified by the World Health Organization and Environmental Protection Agency standards (7–9).

Ion exchange processes have been frequently used for the treatment of wastewater containing copper and chromium and for the recovery of these elements (10). Cr(III) has been removed from leather tanning effluents by a 4-step adsorption process involving oxidation-reduction reactions between Cr(III) and Cr(VI) and utilizing anion- and cation-exchanger resin columns (11). In another study, tanning effluents were treated with a carboxylic-acid cation exchanger for the removal of Cr(III). Elution followed by regeneration was not carried out by mineral acids (HCl, H_2SO_4, etc.) but by H_2O_2 in an alkaline medium (12–15) for preventing surface passivation of the resin beads and prolonging the useful life of the resin.

Hexavalent chromium held by a strongly basic anion resin was eluted by the use of strong reducing agents. For performing the reductive elution of Cr(VI), var-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

ious reductant solutions, such as 9% ascorbic acid in 1 M HCl (16), hydroxylamine in 1 M H_2SO_4 (17), ammonium ferrous sulfate in 1 M HCl (18), 10% $NH_2OH \cdot HCl$ (19), 5% Na_2SO_3 in 0.1 M HCl (20), and 0.01M Na_2SO_3 in 0.1 M H_2S0_4 (21), were used.

In cases where reducing agents were not preferred, Cr(VI) elution from the strongly basic anion exchanger was realized by salt solutions containing relatively high anion concentrations, such as 2 M KNO_3 (22), 1 M NaCl (18), 1 M KSCN (23), and 0.4 M $NaClO_4$ (24). Other than ordinary salts, the use of a 8–10% Na_2CO_3 solution or the more effective mixture of Na_2CO_3 and $NaHCO_3$ (25,26) has the advantage of combining basicity with a high anion concentration.

The uptake of chromate-containing wastewater by a strongly basic resin in OH-form, regeneration of the resin with NaOH, and production of chromic acid coupled to removal of excessive NaOH by the use of an acidic resin can be represented by a series of chemical reactions (10):

$$2ROH + H_2CrO_4 \rightarrow R_2CrO_4 + 2H_2O$$

$$R_2CrO_4 + 2NaOH \rightarrow 2ROH + Na_2CrO_4$$

$$2RH + Na_2CrO_4 \rightarrow 2\,RNa + H_2CrO_4$$

$$RH + NaOH \rightarrow RNa + H_2O$$

When chrome-plated parts are removed from the bath, the adhering film of chromic acid–plating electrolyte passes to the rinse water. As a result, bath waste combined with rinse water can be evaluated for the recovery of chromic acid.

As for the recovery of Cu(II) from plating effluents, strongly acidic resins normally prefer Cu^{2+} to Na^+ and other alkali metal cations, but it is not feasible to recover trace Cu(II) from solutions containing major amounts of alkali metal ions. In such cases, chelating resins (e.g., having iminodiacetate functional groups) are very effective for copper recovery, especially when other relatively stable complex-forming ligands, such as EDTA (ethylenediaminetetraacetate), citrate, and organic compounds, are present in the solution (10). However, recovery of copper from acidic solution obtained from leaching operations in copper production is not usually feasible with conventional chelating resins. In that case, *N*-(hydroxylalkyl)picolyamine–type resins may be used to concentrate Cu(II) from acidic solutions, but these resins require much higher acidity to be regenerated (27–29).

The main form of copper in cyanide-containing plating-bath wastes is the $Cu(CN)_3^{2-}$ complex species. Although anion exchangers may show a high selectivity for the cyanide complex of copper, special regeneration procedures employing both an acid and caustic may be required, bringing the risk of generating extremely toxic HCN gas (10).

In the Istanbul Metropolitan Ikitelli Organized Industrial Area, the electroplating industries produce high levels of metal-contaminated wastewater that may contain heavy metal ions (200–900 ppm), such as Cu(II), Ni(II), Cr(III,VI), as

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

well as acids, bases, salts, and cyanide. Thus the aim of this work was to design simple ion-exchange processes (of laboratory scale) to solve the wastewater treatment problems of individual plating plants and to develop combined processes for the treatment of mixtures (as these bath-rinse effluents are frequently mixed in the area). Connected to these aims, both simple acidic and cyanide-containing alkaline bath wastes containing copper were treated. Also, both valencies of chromium, individually or in mixtures, were treated.

MATERIALS AND METHODS

The chemicals $CuCl_2 \cdot 2H_2O$, $CrCl_3 \cdot 6H_2O$, $K_2Cr_2O_7$, H_2O_2, Na_2SO_3, HCl (concentrated), H_2SO_4 (concentrated), NaOH, NaCl, CH_3COONa, NaOCl were of E. Merck, analytical reagent grade. The ion exchangers used were as follows: Dowex 50X8 (H-form) strongly acidic cation-exchange resin, Dowex 1X8 (Cl-form) strongly basic anion-exchange resin, Amberlite IRC-50 weakly acidic cation-exchange resin, and Amberlite IRC-718 weakly acidic, chelating, cation-exchange resin. The strongly acidic and basic resins were converted to the Na- and OH-forms when required. The electroplating-industry wastewater samples were supplied from plants located in the Istanbul Ikitelli Organized Industrial Area.

The ion exchangers filled glass thermostatic columns of ϕ 9.5 mm and 25 cm^3. All pH levels were adjusted by the use of a Metrohm E 512 pH meter equipped with a glass electrode. Metal (copper and chromium) analyses were performed with a Varian 220AA-Spectrometer using an air-acetylene flame. When the analysis of a Cr(III) and Cr(VI) mixture was required, Cr(VI) was adsorbed on a melamine-formaldehyde resin and eluted with 0.1 M sodium acetate. Total chromium was analyzed after H_2O_2 oxidation, as described elsewhere (30).

For the recovery of Cu(II) from synthetic, acidic, copper-plating wastewater with strongly acidic, Dowex 50X8 resin, 1 L of 400 ppm Cu(II) solution adjusted to pH 1 was passed through a 4 g resin column at 2.6 mL/min. The capacity of the resin was saturated after the flow of 950 mL Cu(II) solution. (See Fig. 1.) The retained copper was eluted with 75 mL of 1 M H_2SO_4, and the resin breakthrough capacity was found as mg Cu/g resin. An acidic copper-plating wastewater sample containing 400 ppm Cu(II) was run simultaneously (Fig. 1).

For the recovery of Cu(II) from synthetic, alkaline, copper-plating wastewater (containing cyanide) with weakly acidic, chelating, Amberlite IRC-718 resin, the resin capacity was found by passing 700 mL of 450 ppm Cu(II) solution (at pH 2.5) through 4 g resin at 1.3 mL/min.

For oxidation–ion exchange treatment of synthetic, alkaline, plating wastewater, 2.7 g $CuCl_2 \cdot 2H_2O$ and 3.1 g NaCN were dissolved in water to convert copper to the $Cu(CN)_3^{2-}$ complex and leave some free excessive cyanide in

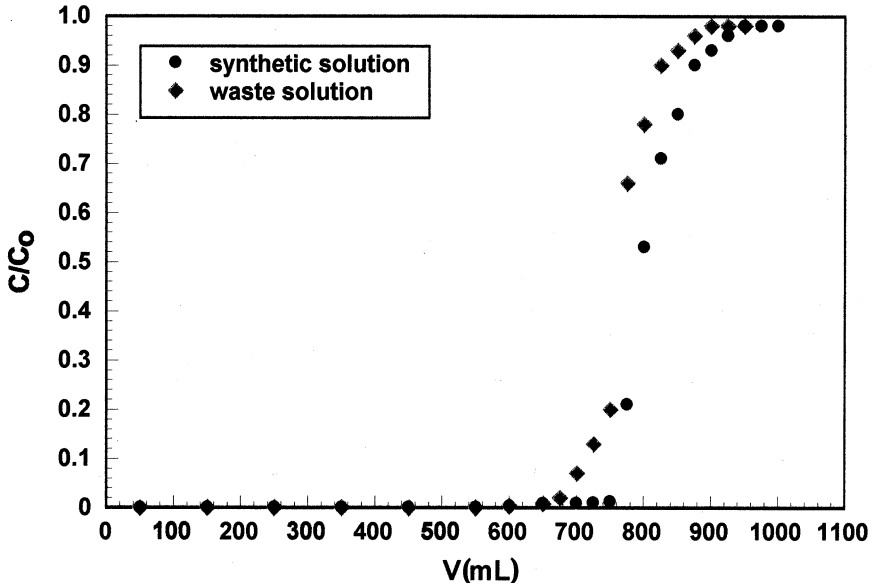

Figure 1. Breakthrough curves of synthetic and real acidic copper-plating wastewater on a Dowex 50X8 strongly acidic cation exchanger. Solution pH : 1.0; Cu(II) concentration: 400 ppm; amount of resin: 4 g; throughput rate: 2.6 mL/min. C/C_o represents concentration of Cu in the effluent to that in the influent solution.

solution. This solution was treated with 85 mL of 2 M hypochlorite solution (containing 37.25 g NaOCl per 250 mL solution) and left overnight. The final alkaline suspension was treated with 1 M H_2SO_4 to dissolve the copper (II) precipitate; the pH was adjusted to 2.5; and 1 L water was added to yield a 1,000 ppm copper solution. A 450-ml aliquot of this solution was diluted to 1 L with water. Seven hundred milliliters of this final solution (containing 450 ppm Cu) was passed through 4 g of resin at 1.3 mL/min to confirm the previously found capacity of the resin. Simultaneously, a real alkaline wastewater sample containing 450 ppm copper (II) was treated with excessive NaOCl, treated with 1 M H_2SO_4 to yield a final pH of 2.5, and passed through the resin column under identical conditions. (See Fig. 2 for breakthrough curves.) The retained copper from each separation was eluted with 50 mL of 1 M H_2SO_4.

For finding the capacity of the Dowex 1X8 strongly basic resin for chromate (VI) and for testing the treatability of plating wastewater containing chromate, a 5,000 ppm Cr(VI) stock solution (containing 7.07 g $K_2Cr_2O_7$ per 500 mL) was pH adjusted and diluted tenfold to yield a 500-ppm Cr(VI) working solution at pH 2; 2,000 mL of this final solution was passed through a 5-g resin column at 2.5 mL/min to yield the breakthrough curves (see Fig. 3). Because an elution trial

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

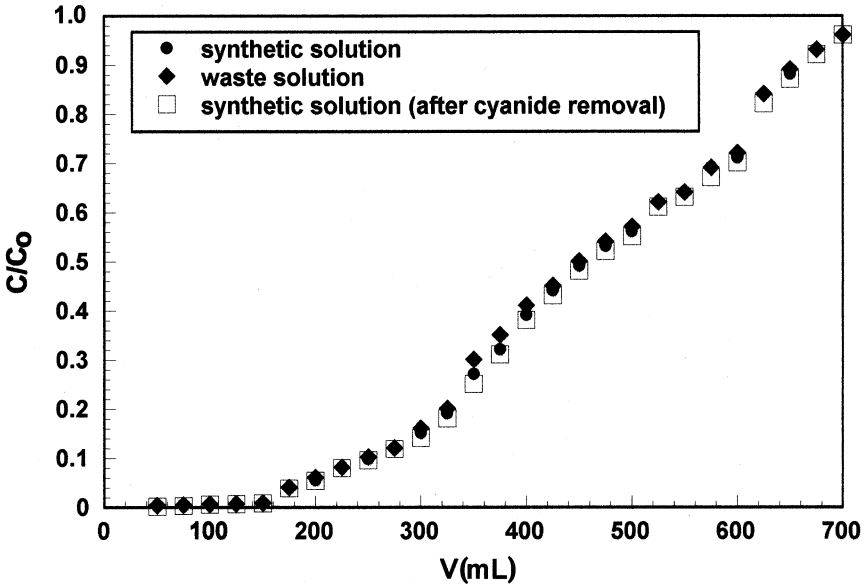

Figure 2. Breakthrough curves of synthetic and real alkaline copper-plating wastewater (after NaOCl oxidation of cyanide and followed by neutralization) on an Amberlite IRC-718 weakly acidic cation exchanger. Solution pH: 2.5; Cu(II) concentration: 450 ppm; amount of resin: 4 g; throughput rate: 1.3 mL/min.

with 1 M NaOH was not efficient, complete elution was realized by using 125 mL of a mixture solution containing 15% NaCl and 1 M NaOH.

For testing the treatability of Cr(III) effluents with a Dowex 50X8 strongly acidic resin, 300 ppm of Cr(III) solution (prepared from $CrCl_3 \cdot 6H_2O$) at pH 3.4 was passed through 4 g of resin at 2.6 mL/min. The resin capacity was determined after eluting the retained chromium with 1.5 M H_2SO_4.

For testing the treatability of effluents containing Cr(VI) by the use of a reduction-cation exchange procedure, 5 mL of 1 M H_2SO_4 and 2.5 mL of 2 M Na_2SO_3 were added to 30 mL of 5,000 ppm Cr(VI) stock solution (originally at pH 2). The mixture was diluted to 500 mL with water to obtain a Cr(III) solution at approximately pH 3. A 625-mL volume of this final solution (containing 300 ppm of converted Cr(III)) was passed through a 5.4-g, Amberlite IRC-50, weakly acidic resin bed at 1.3 mL/min to obtain the breakthrough curve (See Fig. 4) enabling the calculation of the resin capacity. The same reduction was performed on the Cr(VI)-plating wastewater (originally at pH 2), and 600 mL volume of the final 300-ppm Cr(III) solution at approximately pH 3 was enough to saturate the same amount of resin (Fig. 4). The retained Cr(III) was eluted with 300 mL of an oxidizing mixture solution consisting of 0.15 M H_2O_2 and 0.01 M NaOH.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

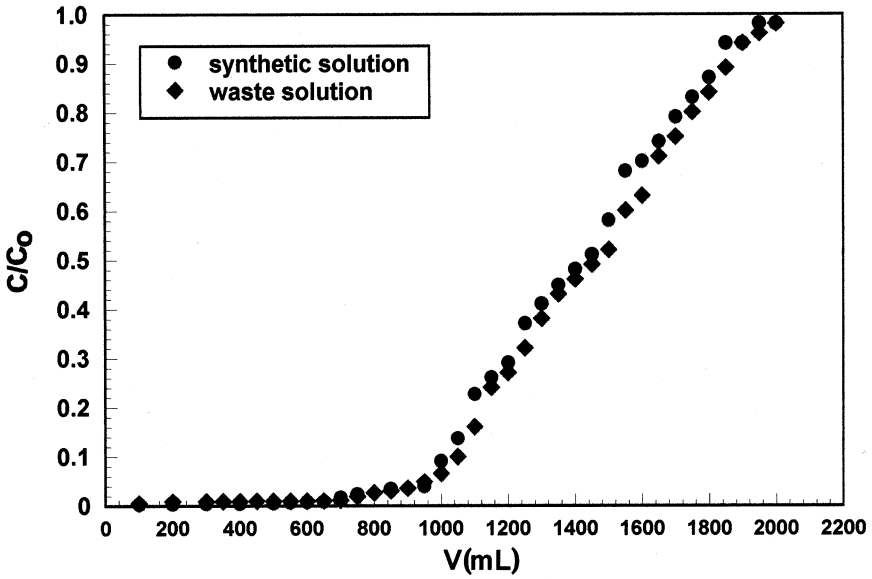

Figure 3. Breakthrough curves of synthetic and real acidic chrome-plating wastewater on a strongly basic Dowex 1X8 anion exchanger. Solution pH: 2.0; Cr(VI) concentration: 500 ppm; amount of resin: 5 g; throughput rate: 2.5 mL/min.

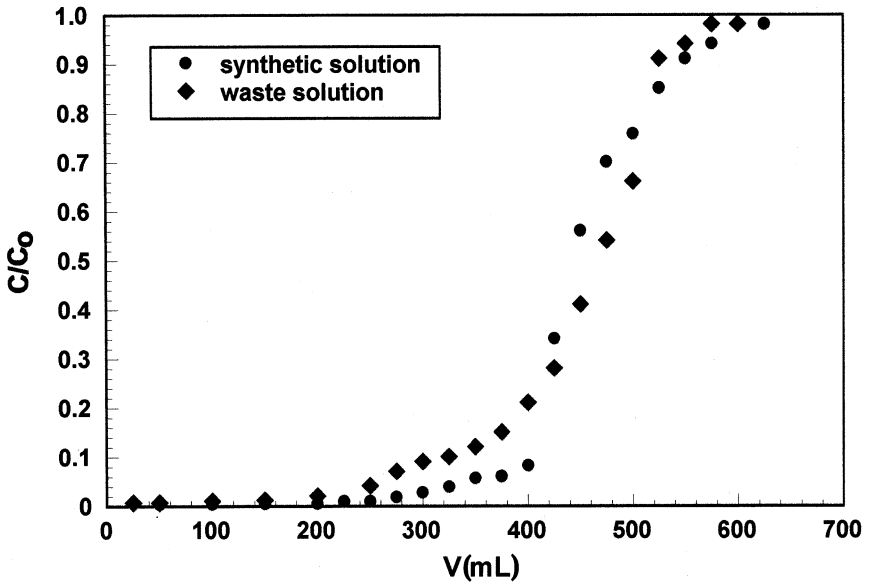

Figure 4. Breakthrough curves of synthetic and real chrome-plating wastewater (after Na_2SO_3 reduction of chromate in acidic medium and followed by neutralization) on an Amberlite IRC-50 weakly acidic cation exchanger. Solution pH: 3.0; Cr(III) concentration: 300 ppm; amount of resin: 5.4 g; throughput rate: 1.3 mL/min.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

All adsorption and desorption data were obtained from 3–5 experiments, and the efficiencies are given within 95% confidence limits as mean ± [standard deviation x $t_{.95}$/ (number of measurements)$^{1/2}$].

RESULTS AND DISCUSSION

Experiments on the treatability of copper-electroplating industry wastewater obtained from the Istanbul Ikitelli Organized Industrial Area showed that acidic wastewater could be treated with a Dowex 50X8 strongly acidic, cation exchanger, and after the oxidation of bound- and free-cyanide with NaOCl, alkaline (cyanide-containing) wastewater could be treated with an Amberlite IRC-718 chelating resin. The postulated reaction scheme for oxidation and ion exchange is as follows:

$$Cu^{2+} + 4CN^- \rightarrow Cu(CN)_3{}^{2-} + 1/2\ (CN)_2$$

$$CN^- + OCl^- \rightarrow CNO^- + Cl^-$$

$$2CNO^- + 3OCl^- + H_2O \rightarrow 2CO_2 + N_2 + 3Cl^- + 2OH^-$$

$$2R\text{-}N\text{-}(CH_2COOH)_2 + Cu^{2+} \leftrightarrow [R\text{-}N\text{-}(CH_2COO)_2]_2Cu + 2H^+$$
(on chelating resin)

$$2R\text{-}SO_3H + Cu^{2+} \leftrightarrow (R\text{-}SO_3)_2Cu + 2H^+ \text{ (on strongly acidic resin)}$$

The breakthrough curves presented in Fig.1 enable the calculation of the strongly acidic resin capacity for Cu(II) at pH 1 as 1.25 mmol/g. The 400 ppm acidic, plating wastewater that contained Cu (pH 1) was treated with the resin, and the overall efficiency of uptake and elution was 93.3 (± 0.43)% (294 mg Cu recovery on 4 g resin). When the retained Cu(II) was eluted with 75 mL of 1 M H_2SO_4, the first 50 mL-portion of the eluant was responsible for 99.7 (± 0.23)% of the total recovery, while the remaining eluant volume (25 mL) desorbed the rest of copper (0.3%). Economical reasons may dictate the acid elution method from acid resins may be preferentially chosen for the recovery of the overwhelming proportion of Cu(II); as long as its capacity for the metal is not seriously affected, the resin may be reused for repetitive adsorption-desorption cycles. Generally, strongly acidic cation exchangers with a high degree of cross-linking have excellent chemical stability and a life expectancy of up to 5 years (31).

After hypochlorite oxidation of the synthetic alkaline Cu(II) solution containing cyanide, a reaction shown to leave no residual cyanide (32), the chelating resin (Amberlite IRC-718) capacity for Cu(II) at pH 2.5 was 0.78 mmol/g. This amount is slightly less than that obtained for pure Cu(II) solution at the same pH (0.81 mmol). The iminodiacetate-based Amberlite resin is particularly useful for Cu(II) recovery from complex solutions (33,34) because, per the Irwing-Williams order, Cu(II) is the strongest complex-forming divalent metal ion among the first-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

row transition elements. For example, the selectivity factor of Cu(II) on IRC-718 resin relative to Ca^{2+} is approximately 2,300 (35). The selection of the working pH was made on the basis of assuring the dissolution of the hydrolytic copper (II) precipitate upon hypochlorite oxidation. Above approximately pH 3, the hydrolytic Cu(II) precipitate could partly suspend in solution forming a colloidal solution, which would negatively affect overall copper recovery. The breakthrough curves of pure, synthetic, and real samples are shown in Fig. 2 and represent overall copper yield efficiency of 99.0 ($\pm$ 0.39)%. Elution of copper from the chelating resin was made with 50 mL of 1 M H_2SO_4, yielding a desorption efficiency of 99.9 ($\pm$ 0.25)%.

Chelating ion exchangers, such as the iminodiacetic acid–functionalized IRC-718 resin, have been tested for stability upon prolonged exposure to EDTA. After 3,000 cycles at room temperature, the resin compressed and lost 36% of its original Cu(II)-retention capacity (36).

Chromium (VI) removal from aqueous media by reduction to Cr(III) followed by $Cr(OH)_3$ precipitation, though seemingly practical and cost-effective, may not be efficient for dilute solutions nor environmentally acceptable because Cr in the disposed sludge may be oxidized and mobilized into groundwater (37). Thus, synthetic electroplating-industry wastewater, which consisted of simulated effluents of an organized industrial area, was used, and removal of individual metal contaminants by selective ion-exchange processes was both efficient and environmentally friendly.

Cr(III,VI) recovery from aqueous solution by ion exchange may be more difficult than expected due to the complexity of Cr speciation (e.g., polymeric species, sulfato- and other anionic complexes of hydrolytic Cr ions) created as a function of pH, concentration, and storage time (38).

On quaternary ammonium–functionalized basic resins, a small fraction of Cr(VI) is reduced to nonadsorbed Cr(III) in H_2SO_4 solutions of 0.01–4 N (39). This reaction would negatively affect the separation of Cr as well as the stability of the resin (40). However, the use the anion exchange resin in the hydroxide form (at higher pH) may increase the alkalinity of the resin bed, which in turn may entail the precipitation of metal hydroxides (such as $Cr(OH)_3$).

Because sulfate and chloride salts would normally accompany chromate in plating effluents, the selectivity of chromate over these anions is important in ion-exchange recovery. The preferred resin should have a polystyrene, rather than polyacrylate, matrix, and high degrees of cross-linking, hydrophobicity, functional group basicity, and longer alkyl groups bound to quaternary amines all increase the selectivity of chromate over sulfate (37).

Generally, as a result of an equilibrium phenomenon characteristic of some unusual interactions between the anion exchanger and chromate species at acidic pH, an early Cr(VI) breakthrough is observed when a strongly basic anion exchanger is used during a fixed-bed column run. Thus, the total available chromate-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

removal capacity cannot be fully utilized in conventional single-unit, fixed-bed runs (41). Chromate-sulfate and chromate-chloride isotherms at slightly acidic pH are unfavorable (concave upward) for two strongly basic anion exchangers and may also lead to early breakthroughs (37).

Cr(III) recovery by cation exchangers are problematic because of its strong adsorption on acidic resins, such as Dowex 50, and the need for strong acid elution (42) or oxidative desorption (43). Chelating resins have also been used with limited success due to the slow kinetics of Cr(III) retention (44,45) and difficulty in pH control.

Because Cr-plating effluents are basically composed of hexavalent chromium, the design of ion exchange treatment was focused on chromate (VI) removal. Typical Cr-plating wastewater (at approximately pH 2) contained 200–900 ppm Cr in the hexavalent form. However, some minor amounts of Cr(III), either originally present in such effluents or converted from Cr(VI) by reduction with organic matter, should also be treated. In this regard, strongly basic resins offer greater Cr(VI) removal capacity at acidic pH as measured by removed Cr atoms per exchange site (37). The capacity of the strongly basic Dowex 1X8 resin for 500 ppm Cr(VI) synthetic solution at pH 2 was found as 2.78 mmol/g. The Cr(VI) uptake efficiency of the anionic resin at pH 2 was 98.0 ($\pm$ 0.35)%, and the retained Cr could be quantitatively recovered (with an efficiency of 99.9 ($\pm$ 0.27)%) by using 125 ml of a 15% NaCl and 1 M NaOH mixture solution. (See Fig. 3 for breakthrough curves.) A lower concentration of NaCl in the eluting mixture solution (such as 10% NaCl in 1M NaOH) required a higher volume for quantitative Cr recovery; for example, 220 mL of this mixture eluted Cr with 99.8 ($\pm$ 0.39)% efficiency. When $NaNO_3$ was replaced with NaCl, even better results were obtained; 150 mL of 5% $NaNO_3$ in 1 M NaOH yielded 99.9 ($\pm$ 0.24)% Cr recovery, and 100 mL of 10% $NaNO_3$ in 1 M NaOH yielded 99.9 ($\pm$ 0.20)% Cr recovery. The use of NaCl (or $NaNO_3$) along with NaOH weakens the adsorption tendency of the trapped Cr(VI) followed by ultimate elution (46). A single eluting solution containing both NaOH and NaCl may deprotonate the ion exchange–held $HCrO_4^-$ and exchange CrO_4^{2-} with Cl^- in the resin phase (37).

A low level of chromate leakage compared to that associated with weakly basic resins is an advantage of using a strongly basic resin for Cr(VI) removal; however the necessity of using greater amounts of NaOH in regeneration is a drawback (29). Quaternary ammonium groups of strongly basic anion exchangers may be partly converted into tertiary amines on prolonged standing in strongly alkaline solutions. The life expectancy of a particular anionic resin may involve such chemical characteristics as the aqueous influent (e.g., other trace metals, anions, oxidizing agents, and dissolved O_2), presence of fouling substances, and regeneration level (31). Then the treatability of Cr(III) contaminants was investigated by passing 750 mL of 300 ppm Cr(III) solution (prepared from $CrCl_3 \cdot 6H_2O$) through 4 g of Dowex 50X8 strongly acidic resin bed at pH 3.4 and using

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

a throughput rate of 2.6 mL/min. A breakthrough capacity of 0.83 mmol/g was found for the strongly acidic resin.

The uptake of Cr(III) by the strongly acidic cation-exchanger resin strongly depended on the aqueous phase speciation of Cr(III) with respect to pH. The Cr(III) uptake efficiency at pH 2.7 was 98.3%. The species distribution calculations for Cr(III) within the studied concentration (300 ppm total Cr(III) (47)) revealed that 92% of Cr(III) is solely in the $[Cr(H_2O)_6]^{3+}$ form while 8% is in the hydroxo-complex $[Cr(H_2O)_5OH]^{2+}$ form. However, Cr(III) recovery efficiency was 99.9 ($\pm$ 0.18)% at pH 3.4 and the speciation diagram indicated that 70% was $[Cr(H_2O)_6]^{3+}$ and 30% was $[Cr(H_2O)_5OH]^{2+}$. The $[Cr(H_2O)_6]^{3+}$-$[Cr(H_2O)_5OH]^{2+}$ conjugate acid–base buffer system may prevent the extreme pH drop that would normally occur as a result of the H^+ release associated with Cr^{3+} uptake (3 H^+ liberated per Cr^{3+} retained), thereby maintaining Cr removal efficiency. In regard to overall Cr(III) removal efficiency, best results were obtained in buffer media containing both $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5OH]^{2+}$ species at appreciable levels. When the basicity was increased to pH 4.8, the Cr(III) uptake efficiency was maintained at 99.9 ($\pm$ 0.14)%, but the relative amount of $[Cr(H_2O)_4(OH)_2]^+$ should have increased at the same time. The anticipated increase in $[Cr(H_2O)_4(OH)_2]^+$ was expected to give rise to some surface-precipitated hydroxo-Cr(III) species, e.g., $Cr(OH)_3$, which would be adsorbed irreversibly on the resin and would not be recovered by acid elution. Though the Cr(III) uptake efficiency was about the same for both 3.4 and 4.8 pH values, Cr desorption proved to be lower for the latter. At pH 3.4, the retained Cr(III) could be eluted with 140 ml of 1.5 M H_2SO_4 at a throughput rate of 1 mL/min. The first 100-mL portion of the sulphuric acid solution released 99.0 ($\pm$ 0.46)% of bound chromium while the rest (40 mL) eluted an additional 0.6%, making the overall recovery 99.6%. For 100% elution, a total acid volume of 170 mL was necessary. This need for additional eluent is not surprising because Cr(III) has a strong adsorption affinity for the strongly acidic resin (42). The Cr(III) retained at pH 4.8 required more concentrated H_2SO_4 for desorption than did the Cr(III) retained at the lower pH; that is, at pH 4.8, 100 mL of 3M H_2SO_4, flowing at 1 mL/min, was needed to release 99.0 ($\pm$ 0.47)% Cr. For successful Cr(III) release, the Cr-saturated resin should be contacted with acid for nonprolonged periods. If the resin is left standing in acid, the hydrolyzed and surface-precipitated hydroxo-Cr(III) species would be irreversibly adsorbed.

In addition to adsorption-desorption studies with synthetic Cr(III) solutions, the treatability of Cr(VI), the predominant form of Cr in plating effluents, by reduction with Na_2SO_3 to Cr(III) and cation-exchange recovery of the latter was tested. After the reduction of Cr(VI) in acidic medium according to the reaction

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

the recovery of the converted Cr(III) by the use of Dowex 50X8 resin was tried. The recovery efficiency was 10% for 300 ppm (converted) Cr(III) solution, which is much less than that for pure Cr(III) solutions. This low efficiency was attributed to complexes formed by $SO_4^{2-}$and Cr(III). Some anions, such as sulfate, phosphate, acetate, and oxalate are known to form relatively stable complexes with Cr and prevent its recovery (3). Thus, Cr(III) removal from real solutions by the use of strongly acidic cation exchanger would not be a suitable process, and treatability of Na_2SO_3-reduced solutions was further tested by using Amberlite IRC-50 weakly acidic cation-exchange resin. Because this resin in H^+ form could not quantitatively recover Cr(III), the weakly acidic resin was converted to the Na^+ form by treating it with 0.1 M NaOH. The necessity for the partial conditioning of weakly acidic cation exchangers in the salt form by means of NaOH treatment has been reported in literature (48). The RCOOH weak acidic groups of the resins could, at pH $\geq$ pK_a, decationize wash solutions of galvanized products that had been submitted to acid metal plating.

Preliminary experiments revealed that the IRC-50 resin was successful for Cr(III) removal in a sulfated medium. For Na_2SO_3-reduced Cr solutions containing 300 ppm Cr(III), the breakthrough capacity of the resin was 0.47 mmol/g at pH 3 and a throughput rate of 1.3 mL/min. Cr(III) converted from real wastewater by Na_2SO_3 reduction was tested under identical conditions as the preliminary experiment to yield the breakthrough curves, shown in Fig. 4, at a Cr-removal efficiency of 98.3 ($\pm$ 0.38)%.

Some irreversible adsorption on the resin was observed, and the use of a 0.15 M H_2O_2 and 0.01 M NaOH mixture as eluant was required (12,13). Oxidative elution (49) effectively overcame the difficulties encountered in Cr(III) desorption (50). The retained Cr(III) could be quantitatively released upon oxidation to Cr(VI) in alkaline medium because the CrO_4^{2-} anion would be rejected by the cation exchanger. At 0.8 mL/min, 300 mL of a 0.15 M H_2O_2 and 0.01 M NaOH mixture solution was capable of eluting chromium in the hexavalent state at an efficiency of 95.1 ($\pm$ 0.36)%. For completely recovering Cr remaining in the solid resin phase, 100 more mL of the eluant was necessary. Practically all the Cr (98.1 ($\pm$ 0.49)%) retained by the resin could be eluted using 130 mL of the 0.15 M H_2O_2 and 0.1 M NaOH mixture solution. However, the higher concentration of alkali, in the presence of the H_2O_2 oxidant, could react with the resin particles over an extended period causing some structural changes in the resin. As a result, use of this mixture is not a recommended approach to achieve higher efficiency. Another method of using more dilute (e.g., 0.001 M NaOH) alkali combined with 0.15 M H_2O_2 yielded unquantitative recovery results. Therefore, 400 mL of the 0.15 M H_2O_2 and 0.01 M NaOH mixture solution was determined as the optimal volume and eluant, respectively.

Amberlite IRC-50 carboxylic-acid resins possess good chemical stability in acid, neutral, and alkaline solutions, and are relatively resistant to oxidizing agents

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

(51). Their oxidative degradation rate is inversely proportional to the degree of cross-linking, e.g., 1.4×10^{-2} meq $\cdot$ g^{-1} $\cdot$ h^{-1} for 8% divinylbenzene containing types (31). It was suggested by Petruzelli et al. (12,13) that the carboxylate functional abilities of the weakly acidic resins, once converted into polyvalent metal form, could not be easily regenerated by using conventional chemicals, such as acids and bases, because partial regeneration by mineral acids caused surface passivation of the resin beads. The passivity was created by sudden conversion of the outer shells in H-form,

$$(RCOO)_3Cr + 3H^+ \rightleftarrows 3RCOOH + Cr^{3+}$$

Recovery of chromic species by the use of NaOH was also inefficient due to the strong affinity of the $RCOO^-$ group for polyvalent metal (Cr(III)) species. Thus, the following reactions can be proposed for the uptake and release of Cr(III):

$$3RCOONa + Cr^{3+} \rightarrow (RCOO)_3Cr + 3Na^+$$

$$2(RCOO)_3Cr + 3H_2O_2 + 10NaOH \rightarrow 2Na_2CrO_4 + 6RCOONa + 8\ H_2O$$

Also, the same researchers (12,13) found the use of weakly acidic resin in the Na form the most beneficial for Cr(III) uptake. As observed in this study, some kind of a Brønsted buffer (RCOOH resin partly in Na form at optimal working pH, i.e., pH 3) would be necessary to prevent the sudden decrease in pH that would retard further metal uptake if only the H-form of the resin were used ($3H^+$ ions would be normally liberated per every Cr^{3+} held by the adsorbent). Weakly acidic resins are very sensitive to solution pH and are not able to take up metal ions in acidic environments, i.e., at pH$<<$pKa of RCOOH (29).

CONCLUSIONS

A combined treatment scheme for the recovery of copper and chromium from electroplating-industry wastewater has been proposed that is applicable to small and medium metal-plating plants. Thus, when the amounts of rinse water are relatively small, recycling of copper and chromic acid may be economical in such plants, and consequently, the municipal sewage system would not be severely contaminated with these toxic pollutants. The proposed treatment system is also environmentally superior to the classical Cr(VI) reduction followed by $Cr(OH)_3$ precipitation with lime in which Cr in the disposed sludge may be oxidized and mobilized into groundwater.

Two laboratory scale processes have been developed for copper: Cu(II) from acidic plating wastewater is recovered by a strongly acidic cation exchanger and eluted with H_2SO_4, while cyanide-containing alkaline plating effluents are first oxidized with NaOCl and neutralized, and Cu(II) is retained on an iminodiacetate-type chelating resin and eluted by H_2SO_4. The selective uptake of Cu(II)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

by the iminodiacetate-based resin from a complex mixture (i.e., alkaline bath waste constituents) has been fully exploited.

Two laboratory scale processes have been designed for the two valencies of Cr. Cr(VI) from acidic plating waste-rinse water is taken up by a strongly basic anion exchanger and eluted with a NaOH and NaCl mixture. Both original and reduced Cr(III) can be recovered by the use of a weakly acidic cation exchanger at optimal pH and eluted by H_2O_2 and NaOH, which also provides for resin-saving oxidative regeneration. The combined process capable of treating both valencies of Cr-contaminants is useful because plating bath-rinse effluents are frequently mixed in the organized industrial area studied in the presented research and in those in other countries (52).

Chromium (VI) was recovered at acidic pH on a strongly basic resin due to increased chromate selectivity at this pH. However, the total chromate removal capacity of such resins cannot be fully utilized in conventional single-unit fixed-bed runs because other competing ions in the influent (SO_4^{2-}, Cl^-, etc.) would always lead to an early, gradual CrO_4^{2-} breakthrough at acidic pH. Therefore, the original CrO_4^{2-} was reduced with Na_2SO_3 to Cr(III) and total Cr (initial and reduced Cr(III)) was recovered with a weakly acidic cation exchanger.

Because both Cr(III), on a weakly acidic cation exchanger and Cr(VI), on a strongly basic anion exchanger resin, would show high adsorption affinities, multi-complex eluting solutions were used to weaken affinities; for example, the H_2O_2 and NaOH solution affected Cr(III) release by oxidation to the cation exchanger–rejected chromate, and NaOH and NaCl mixture affected Cr(VI) release by acid-base neutralization. Quantitative redox and neutralization reactions constitute the driving force of these complex elutions by shifting weak equilibria to completion.

ACKNOWLEDGMENT

The authors would like to thank the Research Fund of Istanbul University for supporting this work under Project 1194/070998.

REFERENCES

1. Patterson, J.W. *Waste Water Treatment Technology*; The University of Tennessee: Tennessee, USA, 1975; 43–85.
2. Nriagu, J.O.; Nieboer, E. *Chromium in the Natural and Human Environments*; Wiley: New York, 1988.
3. Collins, C.H.; Pezzin, C.H.; Rivera, J.F.L.; Bonato, P.S.; Windmöller, C.C.; Archundia, C.; Collins, K.E. J. Chromatog. A **1997,** *789,* 469,
4. Lees, P.S.J. Environ. Health Perspect. **1991,** *92,* 93.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

5. Elderfield, H. Earth Planet. Sci. Lett. **1970,** *9,*10.
6. Tan, H.K.S. Sep.Sci.Tech. **1998,** *33,* 1089.
7. Mc Kee, E.J.; Wolf, W.H. *Water Quality Criteria*, Publication No.3-A; California, USA; 1972.
8. Chapman, D. *Water Quality Assessments*; University Press: Cambridge, U.K., 1996; 80–82.
9. Kemmer, F.N.; McCallion, J., Eds. *The NALCO Water Handbook*, Mc Graw-Hill: New York, 1979; 35-2,3.
10. Freeman, H.M., Ed. *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill: New York, 1989; 6.66-68.
11. O'Dwyer, F.T.; Thomas, F.; Hodnett, K.B. J. Chem. Tech. Biotechnol. **1995,** *62,* 30.
12. Petruzzelli, D.; Santori, M.; Passino, R.; Tiravanti, G. International Conference on Ion-Exchange, Tokyo, Japan, 1991.
13. Petruzzelli, D.; Alberga, L.; Passino, R.; Santori, M.; Tiravanti, G. Reactive Polymers **1992,** *18,* 95.
14. Petruzelli, D.; Tiravanti, G.; Santori, M.; Passino, R. Water Sci. Tech. **1994,** *30,* 225.
15. Petruzelli, D.; Passino, R.; Tiravanti, G. Ind. Eng. Chem. Res. **1995,** *34,* 2612.
16. Brunfelt, O.A.; Steinnes, E. Anal.Chem. **1967,** *39,* 833.
17. Shigetomi, Y.; Hatamoto, T.; Nagoshi, K.; Yamashige, T. Nippon Kagaku, Kaishi **1976,** *4,* 619.
18. Pankow, J.F.; Janauer, J.E. Anal. Chim. Acta **1974,** *69,* 97.
19. Papadopoulou, C.; Kanias G.; Hadzistelios, I. J. Radioanal. Chem. **1976,** *31,* 389.
20. Pakholkov, S.V.; Panikarovskikh, E.V. Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. **1967,** *10,* 168.
21. Yamashige, T.; Izawa, H.; Shigetomi, Y. Bull. Chem. Soc. Jpn. **1975,** *48,* 715.
22. Marino, F.D.; Ingle, D.J. Anal. Chem. **1981,** *53,* 294.
23. Stella, R.; Genova, N.; Di Casa, M.; Gallorini, M.; Orvini, E. J. Radioanal. Chem. **1976,** *34,* 59.
24. Fritz, S.J.; Sickafoose, P.J. Talanta **1972,** *19,* 1573.
25. Mulokozi, M.A. Analyst **1972,** *97,* 820.
26. Mulokozi, M.A. Talanta **1973,** *20,* 1341.
27. Grintsead, R.R. J. Metals **1979,** *31,* 13.
28. Jones, K.C.; Pyjoer, R.A. J. Metals **1979,** *31,* 19.
29. Bolto B.; Pawlowski, L. Environ. Protection Eng. **1985,** *11,* 1.
30. Demirata, B.; Tor, I.; Filik, H.; Afsar, H.; Fresenius J. Anal.Chem. **1996,** *356,* 375.
31. Kunin, R. *Ion Exchange Resins*, Wiley: New York, 1958; 353–361.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

32. Gümüş, G.; Demirata, B.; Apak, R. Talanta **2000**, in press.
33. Maurelia, G.R.; Zamora, C.R.; Gonzales, M.M.; Guevara, B.M.; Diaz, C.G. Afinidad **1998,** *55,* 57.
34. Muraviev, D.; Gonzalo, A.; Valiente, M. Anal. Chem. **1995,** *67,* 3028.
35. Wang, L.K.; Wang, M.H.S., Eds. *Handbook of Industrial Waste Treatment*; Marcel Dekker, Inc.: New York, 1992; Vol. 1, 159.
36. Beatly, S.T.; Fischer, S.T.; Hagers, D.L.; Rosenberg, E. Ind. Eng. Chem. Res. **1999,** *38,* 4402.
37. Sengupta, A.K. *Ion Exchange Technology: Advances in Pollution Control;* Technomic Publ. AG.: Basel, Switzerland, 1995; 115–147.
38. Collins, C.H.; Pezzin, S.H.; Rivera, J.F.L.; Bonato, P.S. J. Chromatog. A **1997,** *789,* 469.
39. Strelow, F.W.E.; Bothma, C.J.C. Anal. Chem. **1967,** *39,* 595.
40. Weiner, C. Schiele, Fresenius' Z. Anal. Chem. **1971,** *169,* 271.
41. Sengupta, A.K.; Clifford, D. Ind. Eng. Chem. Fundam. **1986,** *254,* 249.
42. Collins, C.H.; Collins, K.E.; Ackerhalt, R.E. J. Radioanal. Chem. **1971,** *8,* 263.
43. Sleater, G.A.; Freeman, D.H. Anal. Chem. **1970,** *42,* 1666.
44. Maeda, H.; Matsumoto, Y.; Egawa, H. Nippon Kagaka Kaishi **1982,** *11,* 1, 825.
45. Szczepaniak, V. Chem. Anal. (Warshaw) **1963,** *8,* 843.
46. Ou-Yang, G.L.; Jen, J.F. Anal. Chim. Acta **1993,** *279,* 329.
47. Ramos, L.R.; Rubio, F.L.; Coronado, G.M.R.; Barron, M.J. J. Chem. Tech. Biotechnol. **1995,** *62,* 64.
48. Liberti, L.; Millar, J.R. *Fundamentals and Applications of Ion Exchange;* Martinus Nijhoff Publ.: Dordrecht, Netherlands, 1985; 34–35.
49. Davis, M.H.; Grossman, V.B. Anal. Biochem. **1971,** *44,* 339.
50. Mulokozi, A.M.; Mosha, D.M.S. Talanta **1975,** *22,* 239.
51. Kunin, R.; Barry, R.E. Ind. Eng. Chem. **1949,** *41,* 1269.
52. Sapari, N.; Idris, A.; Ab. Hamid, N.H. Desalination **1996,** *106,* 419.

Received March 2000
Revised July 2000

Request Permission or Order Reprints Instantly!