Chemical Engineering Journal 281 (2015) 434–443

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Selective iron sorption for on-line reclaim of chromate electroplating solution at highly acidic condition

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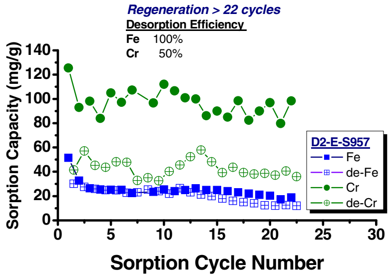
## HIGHLIGHTS

- Maximum Fe contaminant level in chromate electroplating limited below 50 mg/L.
- DEHPA impregnated S957 for selective Fe sorption and on-line reclaim of contaminated chromate bath.
- Complementary sorption selectivity of Fe(III) by DEHPA and S957.
- Improving electroplating performance with enhancing current efficiency and reducing waste water.

## GRAPHICAL ABSTRACT

Stable, Regenerable SIR for Selective Fe Removal from Cr Bath



## ARTICLE INFO

*Article history:*
Received 21 March 2015
Received in revised form 17 June 2015
Accepted 18 June 2015
Available online 3 July 2015

*Keywords:*
Fe selective sorption
DEHPA SIR resin
Sorption isotherm
Cr electroplating
Fe(II)–Fe(III) analysis

## ABSTRACT

On-line reclaim process by selective ion sorption for the purification of highly acidic Fe contaminated chromate electroplating bath has been developed. Among many industrial functional resins, Lewatit VPOC1026 implanted with di-(2-ethylhexyl) phosphoric acid (DEHPA) extractant in the polymeric backbone exhibited the highest selectivity of Fe versus Cr but low sorption capacity of Fe. Impregnation of DEHPA on functionalized S957 resin (a sulfonated mono-phosphonic acid resin) exhibited a much enhanced Fe sorption capacity with high Fe selectivity. The enhancement in the adsorption performance of S957 is due to the selective adsorption of DEHPA for Fe(III) complex formation. For the best electroplating performance, the maximum Fe contaminant level in the chromate electroplating bath was determined as 50 mg/L. The developed process could not only maximize electroplating performance but also minimize the usage of original water and the production of waste water.

## 1. Introduction

Metal corrosion always leads to massive economic loss in gross natural product. It was accounted for around 4–5%. Traditionally electroplating of secondary metal as a protection layer on the surface of metal substrate could improve its corrosion resistance, mechanical hardness and surface smoothness. Chromium (Cr) coating, traditionally the most effective coating, is mostly fabricated by electroplating process or chromate conversion coating (CCC) process using very strong acidic chromate solution (pH < 2). During the electro-deposition of carbon steel or alloy, many metal components of the substrate such as iron (Fe), copper, etc. are apt to leach out into the highly acidic CCC and electroplating bath solutions and accumulate to form contaminants after long service time. Minor contaminants in bath solution particularly Fe could reduce the current efficiency during electro-deposition and downgrade electroplating product quality. To keep the contaminant level as

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http://dx.doi.org/10.1016/j.cej.2015.06.080
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low as possible, electroplating industry usually shortens the service life of CCC bath solution with excessive changeover rate. The typical practice not only requires additional fresh water for preparing CCC bath solution but also generates large amount of Cr waste water solution which are harmful to the Earth.

In principle, it is technology feasible to selectively remove Fe ion impurity from spent electroplating solutions such as Cr pickling solution, electroplating baths, and passivation baths, etc. Some novel adsorbents for selective adsorption of heavy metals have been reported, such as titanate nanoflower for selective sorption of Cd(II) relative to Zn(II) and Ni(II) [1], magnetic MCM41 for selective adsorption of Cr(VI) in magnetic field [2]. In strong acidic electroplating solution, on one hand, sorption equilibrium could be more favorable for desorption to adsorption; on the other hand, hard metal ion has greater sorption affinity than soft metal ion. As such, selective sorption of Fe(II) and Fe(III) ions (intermediate metal ions) from Cr(VI) and Cr(III) (hard metal ions) electroplating solution is a great technology challenge. Many ion-exchange resins are available nowadays for metal sorption. While many chelating resins have been successfully used for removing heavy metals from wastewaters and spent baths, e.g., Lewatit TP-207 [3,4], Dowex M4195, Amberlite IRC748 [5], and Purolite S-950 [6], only few resins, such as Purolite S957 (sulfonated mono-phosphonic resin), have been reported for selective removal of iron ions from Cr(III) passivation bath [7,8].

Metal extraction using organic extractant has been proposed for metal recovery. For example, for the recovery of zinc from Fe(II)–Fe(III) containing spent pickling solution, organophosphorus extractant tributylphosphate (TBP) [9], octylphenyl acid phosphate (OPAP) and di-(2-ethylhexyl)phosphoric acid (DEHPA) were used [10]. The sorption process could be complementary to extraction process in terms of small equipment size, low energy consumption, sustainable operation in acidic solution, etc.

In a recent review paper, Kabay et al. discussed comprehensively the preparation and application of various extractant-containing resins [11]. Two different approaches have been developed for the preparation of extractant-containing solid sorbents. The Levextrel resins were patented using polymerization process, by mixing the extractant with a mixture of monomers (styrene and divinylbenzene), for implanting extractant into polymer backbones. The Levextrel resins available today include extractant TBP, DEHPA and di(2,4,4-trimethylpentyl)phosphinic acid (DTMPPA). The Lewatit VPOC1026 implanted with DEHPA functional group is useful for the extractive sorption of divalent metal ions such as Zn(II), Cu(II) and Cd(II).

Other preparation method so-called solvent-impregnated resin (SIR) by impregnation of extractant on various solid sorbents is versatile and flexible in tailoring the types and contents of extractant, solid sorbent and preparation procedures, etc., providing a wide range of metal separation characteristics. Because of high mobility of ligands, the SIR resin in most of time could perform superior separation property to some widely used ion-exchange resins and chelating resins [12]. Numerous extractants have been used for the preparation of SIR resins, including organophosphorous extractant such as DTMPPA [13], DEHPA [14]; amine group such as tri-n-dodecyl-ammonium chloride [15]; quinolinol/quinone group such as 7-(4-ethyl-methyloctyl)-8-quinolinol (Kelex 100) [16]; and macrocyclic functional group [17]. Some macroporous resins, dodecyl acrylate – divinylbenzene crosslinked polymeric organogels [18] and silica-based composites [19] have been used for solid sorbent. Various SIR solid sorbents have been reported such as DEHPA modified Amberlite 200 for enhanced sorption of Ni, V and Mo [20], DEHPA modified XAD-2 for extraction of Cu ion [12], DEHPA modified HZ-803 for extraction of In(III), Ga(III) and Zn(II) [21], etc.

The present study develops an on-line reclaim process for highly acidic electroplating solution by selective removal of Fe impurity using DEHPA impregnated resins. The SIR modified S957 by DEHPA impregnation exhibited a much enhanced Fe sorption capacity and selectivity, exceeding the DEHPA implanted VPOC1026 resin. The reclaim process could significantly extend the service life of bath solution, reduction of usage of raw materials, fresh water and production of Cr waste water; and also improve the current efficiency during electroplating and electro-deposition product quality.

## 2. Experimental

### 2.1. Materials

Some sorbents (Table 1) including industrial resins and SIR resins were tested in this study. Sodium hydroxide, nitric and hydrochloric acid, and hexane (Merck) were used for the preparation of the different solutions. DEHPA was provided by Tokyo Chemical Industry.

Three industrial electroplating bath solutions provided by local galvanic industry (deployed as B1, B2 and B3 solution) were analyzed by Perkin Elmer model Optical 2100DV Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) for the determination of the concentrations of metals (Cr, Fe, and Cu) and ion chromatography for anions (chloride and sulfate).

The Cr(III)–Cr(VI) and Fe(II)–Fe(III) partitions in the electroplating solution were determined with UV spectroscopy The methodology for the determination of Fe(II)–Fe(III) will be discussed in Section 3.2. For determining Cr partition, the concentrations of

**Table 1**
Description of commercial and modified resins.

| ID | Commercial name | Functional group |
|---|---|---|
| *Group A–SAC resin* | | |
| A200C | Amberlite 200C | Sulfonic acid |
| PK228 | Diaion PK228 | Sulfonic acid |
| *Group B–CKL resin* | | |
| C100 | Amberlite Chelex 100 | Iminodiacetic acid |
| TP207 | Lewatit Mono Plus TP207 | Iminodiacetate groups |
| VPOC1026 | Lewatit VPOC1026 | DEHPA (0.84 mmol/g) |
| S957 | Purolite S957 | Sulfonated monophosphonic acid |
| *Group C–AKL resin* | | |
| P4V | 2% Poly(4-vinylpyridine hydrochloride) | 4-Vinylpyridine hydrochloride |
| DM4195 | Dowex M4195 | Bis-picolylamine |
| *Solvent impregnated resin* | | |
| D2-E-S957 | S957 impregnated with ethanol solution of DEHPA (0.82 mmol/g) | |
| D2-H-S957 | S957 impregnated with hexane solution of DEHPA (0.62 mmol/g) | |
| D2-E-XAD | XAD-2 impregnated with ethanol solution of DEHPA (0.58 mmol/g) | |