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Separation and recovery of valuable metals from real mix electroplating wastewater by solvent extraction

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ABSTRACT

Recycling of electroplating wastewater is very important because of the large amounts of wastewater generated, the enormous economic value and large environmental concerns when conventional neutralization–precipitation processes are used to dispose of the wastewater. This work describes the recovery of valuable metals from industrial wastewater collected at a galvanizing industrial site using a solvent extraction process. Several extractants such as DEHPA, TBP, LIX 984N-C, Cyanex 272 and Aliquat 336 were tried for the separation and recovery of valuable metals from the wastewater. Optimum extraction parameters for zinc, copper, iron, nickel and chromium were determined as 10% Aliquat 336, 5% LIX 984N-C, 10% DEHPA, 15% LIX 984N-C and 10% Cyanex 272 in kerosene at equilibrium pH 1.45, 1.20, 1.00, 5.25 and 6.00 with 99.6%, 100%, 100%, 99.9% and 100% extraction efficiencies at almost 100% selectivity, respectively. These extraction efficiencies were attained at two extraction stages for zinc, copper and chromium and at one extraction stage for iron and nickel. Copper-loaded LIX 984N-C, iron-loaded DEHPA, nickel-loaded LIX 984N-C and chromium-loaded Cyanex 272 were stripped with 450 g/L, 2 M, 150 g/L and 1 M H_2SO_4 respective strip solutions with relative 100% stripping efficiencies. A two-stage process stripped the zinc-loaded Aliquat 336 with a 2 M NaOH solution with 100% efficiency. Based on the data, a flow sheet for the separation of the five metal ions is provided.

1. Introduction

During many plating operations, a substantial amount of bath solution adheres to a plated work piece as it leaves the plating tank. In this manner, valuable materials are lost as "drag-out" into the subsequent cascade rinse tanks. These contaminated rinse solutions, which are called electroplating wastewater, contain different concentrations of iron, copper, zinc, chromium and nickel with high concentrations of acids, sulfate, Cl^- ions, etc. that are considered persistent, bioaccumulative and harmful substances. Because of the serious threat to human health and ecological systems, these contaminants must be removed from wastewater before discharge to the environment (Liu et al., 2013; Sarangi et al., 2007). Precipitation of metal ions in the wastewater as hydroxides, under appropriate pH conditions, is one of the most conventional methods used and is considered the most economical. This treatment, however, generates huge amounts of heavy metal sludge or slime as a secondary environmental pollutant. Considering the limited landfill space around the world and the prices of highly valuable metals, sludge generating processes should be reduced by newly developed recycling techniques to address these issues (De Souza et al., 2006; Eyupoglu and Kumbasar, 2014).

Recently, different physicochemical processes such as ion exchange (Juang et al., 2006), biological processes (Kumar et al., 2012), liquid membranes (Ren et al., 2007), solvent extraction techniques (Bachmann et al., 2010; El-Nadi and El-Hefny, 2010; Huang and Tanaka, 2009; Kul and Çetinkaya, 2009; Torras et al., 2012), electrowinning (Dutra et al., 2008), electrocoagulation (Akbal and Camc, 2011), adsorption (Calero et al., 2014; Danish et al., 2011a, 2011b; Liu et al., 2013; Tong and Xu, 2013), emulsion liquid membranes (Eyupoglu and Kumbasar, 2014), ion exchange (Cavaco et al., 2007; Juang et al., 2006), sorption (Danish et al., 2011a,2011b; Kumar et al., 2012), hollow fiber renewal liquid membranes (Ren et al., 2007), electrodialysis (Benvenuti et al., 2014; Li et al., 1999), and emulsion pertraction technology (Diban et al., 2011) have been applied for the extraction of heavy metals from diluted or concentrated synthetic or real electroplating wastewater. Comparing the solvent extraction technology (SX) with other available options, it has the advantage that a large volume of wastewater can be treated, and metals in the wastewater can be selectively recovered as metal salts by crystallization or metal plates by electrowinning.

Generally, the large volume of electroplating wastewater from plating plants in organized galvanizing industrial sites is collected in a wastewater treatment plant at the site to treat the water by conventional neutralization–precipitation processes. Approximately 250 tons/day of wastewater is treated at these treatment sites. SX is the most suitable process to selectively remove and recover valuable metals (Cu, Zn, Ni, Cr and Fe) from a large volume of electroplating wastewater. However, there have been no studies regarding the selective recovery and removal of Cu, Zn, Ni, Cr and Fe from complex electroplating

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wastewater obtained from wastewater treatment plants at organized galvanizing industrial sites. Therefore, selective parameters were studied in this work for Cu, Zn, Ni, Cr and Fe recovery from these sites by SX using LIX 984N-C, Aliquat 336, DEHPA, TBP, LIX 7820 and Cyanex 272.

2. Experimental

2.1. Solutions, reagents and materials

The chemical properties of electroplating rinse bath solutions, which are the source of wastewater, depend on various factors such as the surface area of the work piece, the raw materials used, the material concentrations in the plating bath and the cleaning period of the rinse bath. Therefore, 10 L of aliquot was taken from the first tank of the wastewater treatment plant of an organized galvanizing industrial site, which has 200 electroplating plants, every day for 10 days. Therefore, 100 L of composite real mix electroplating wastewater was used to complete all of the extraction experiments. The chemical properties of the samples are presented in Table 1. A chemical analysis was performed using a BGC Sigma model atomic absorption spectrophotometer (AAS). A Hanna HI 221 model pH meter was used to measure the pH of the solutions.

Solvent extraction reagents (LIX 984N-C, Aliquat 336, DEHPA, TBP, LIX 7820 and Cyanex 272) were dissolved in commercially available kerosene without further purification to prepare the organic phase. LIX 984N-C reagent, a 1:1 volume blend of LIX 860N-IC and LIX 84-IC, is a mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime in a high flash point hydrocarbon diluent; this reagent easily forms water insoluble complexes with various metallic cations. It is a more concentrated form of LIX 984N. Aliquat 336 is a quaternary ammonium salt that contains a mixture of C_8 (octyl) and C_{10} (decyl) chains with C_8 predominating. Di-(2-ethylhexyl)phosphoric acid (DEHPA) is an organophosphorus compound with the formula $(C_8H_{17}O)_2PO_2H$. The yellow liquid is a diester of phosphoric acid and 2 ethylhexanol. Tris (2,4,4-trimethylpentyl) phosphine oxide (Cyanex-272) is a phosphinic acid.

2.2. Procedure of solvent extraction

Each experiment, unless otherwise stated, was completed at room temperature by mixing 25 mL of an organic mixture with 25 mL of an aqueous phase in a 100 mL separatory funnel at a constant shaking speed of 300 rpm for 15 min with a mechanical shaker (IKA yellow line RS 10 control). The organic phase to aqueous phase (O/A) ratio was taken as unity, unless otherwise stated. At the end of each experiment, the separated and filtrated aqueous phase was analyzed by AAS to determine the metal concentration in the aqueous phase, and the metal concentration in the organic phase was calculated by subtracting its value from the total. The percent extraction and stripping efficiency of metals were calculated from these results. The variation in multiple readings from the same sample was generally within 4%, while that of the duplicated experiments ranged from 2% to 5%.

3. Results and discussion

The aim of this study was not to determine all of the optimum solvent extraction parameters of each metal in the wastewater, such as the ratio of organic phase to aqueous phase, the counter current extraction and stripping stage. The main aim of this work was to determine

Table 1
Chemical properties of wastewater inlet to treatment plant.

pH	Cu (mg/L)	Zn (mg/L)	Ni (mg/L)	Cr (mg/L)	Fe (mg/L)	CN^- (mg/L)	$SO_4^{=}$ (g/L)	Cl^- (g/L)
1.60	1527	689	462	264	147	70	3.5	3.5

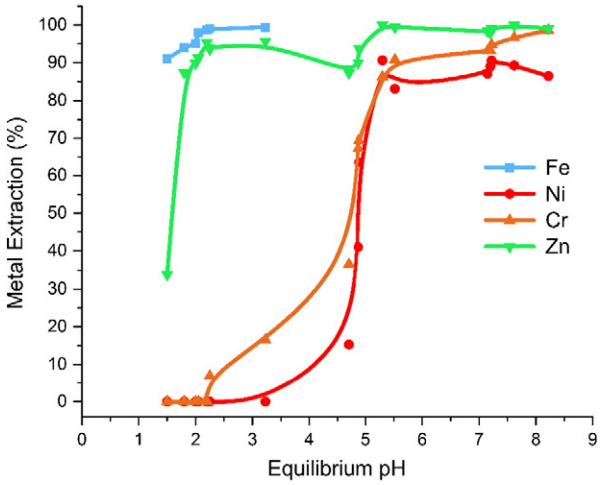

Fig. 1. Influence of the equilibrium pH in the extraction of Zn, Fe, Ni and Cr in the wastewater with 0.1 mol/L DEHPA.

the type of extractant and equilibrium pH values for the selective extraction of zinc, copper, iron, nickel and chromium in the industrial wastewater described in Section 2.1.

In pretests, NaOH and Na_2CO_3 solutions were used to increase the pH of the wastewater. According to these pretests, the Na_2CO_3 solution resulted in a clearer aqueous phase with no precipitate formation at high pH. Therefore, the Na_2CO_3 reagent was chosen as the pH-adjusting agent.

3.1. Separation and recovery of zinc

The wastewater pH was 1.60, and DEHPA and CYANEX 272 were two of the most convenient extractants for the selective zinc extraction from wastewater at a 1.60 pH value. Because their selective zinc extraction capability was high at low pH values (~2.0 and 2.5-3.0, respectively), the selective zinc extraction from the wastewater was carried out with 0.1 M DEHPA and the 10 vol.% Cyanex 272 organic phases. The percentage extraction of metal ions at different equilibrium pH values is shown in Figs. 1 and 2. As expected, although DEHPA and CYANEX 272 extracted zinc at pH 2.05 and 2.67 with 95% efficiency, respectively, the coextraction of Fe with zinc occurred as shown in these figures. The extraction behavior of Zn and iron in 0.1 M DEHPA and the 10 vol.% Cyanex 272 organic phases was very similar. Therefore, selective extraction studies of zinc from the wastewater using DEHPA

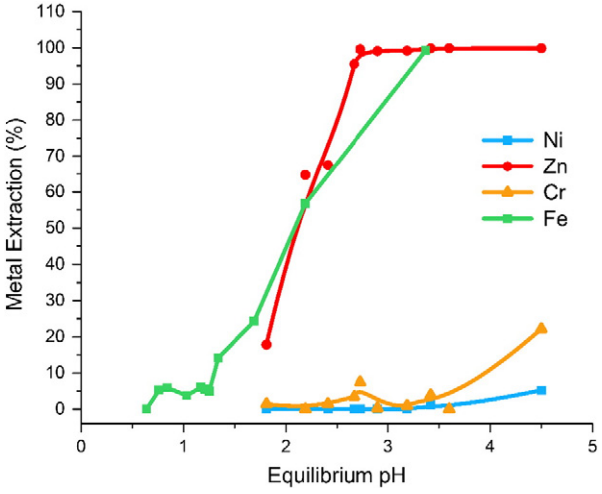

Fig. 2. Influence of the equilibrium pH in the extraction of Zn, Fe, Ni and Cr in the wastewater with 10 vol.% Cyanex 272.