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Treatment of rinse water from zinc phosphate coating by batch and continuous electrocoagulation processes

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ABSTRACT

Treatment of spent final rinse water of zinc phosphating from an automotive assembly plant was investigated in an electrochemical cell equipped with aluminum or iron plate electrodes in a batch mode by electrocoagulation (EC). Effects of the process variables such as pH, current density, electrode material and operating time were explored with respect to phosphate and zinc removal efficiencies, electrical energy and electrode consumptions. The optimum operating conditions for removal of phosphate and zinc were current density of 60.0 A/m^2, pH 5.0 and operating time of 25.0 min with Al electrode and current density of 60.0 A/m^2, pH 3.0 and operating time of 15.0 min with Fe electrode, respectively. The highest phosphate and zinc removal efficiencies at optimum conditions were 97.7% and 97.8% for Fe electrode, and 99.8% and 96.7% for Al electrode. The electrode consumptions increased from 0.01 to 0.35 kg electrode/m^3 for Al electrode and from 0.20 to 0.62 kg electrode/m^3 for Fe electrode with increasing current density from 10.0 to 100.0 A/m^2. The energy consumptions were 0.18–11.29 kWh/m^3 for Al electrode and 0.24–8.47 kWh/m^3 for Fe electrode in the same current density range. Removal efficiencies of phosphate and zinc were found to decrease when flow rate was increased from 50 to 400 mL/min in continuous mode of operation. The morphology and elements present in the sludge was also characterized by using SEM and EDX.

1. Introduction

Zinc phosphate ($Zn_3(PO_4)_2$) is a crystalline conversion coating that is formed on a metal substrate utilizing the chemical reaction between metal ions that have been dissolved in mineral acids and then diluted with water to form the process solution. It is mainly used for the surface treatment of metal surfaces due to its economy, excellent corrosion resistance, wear resistance and adhesion [1]. Therefore, the zinc phosphate coating process plays a significant role in the automotive and outdoor applications.

The zinc phosphate coating wastewater is accumulated from different processing stages such as degreasing, phosphating, rinsing and cleaning. The presence of various pollutants in the process rinse water such as phosphates, Zn, Mn, etc. leads to serious damage when discharged directly into the environment [2–4]. Almost all automotive industries use this type of conversion coating but zinc phosphate has all been criticized in recent years for introducing phosphorus compounds into surface water systems, encouraging the rapid growth of algae (eutrophication). This will affect the water quality through consumption of dissolved oxygen and destroys aquatic life [5,6]. Hence, the removal is necessary to meet the discharge limit in order to control eutrophication.

A number of treatment methods such as chemical precipitation, adsorption, biosorption, electrocoagulation (EC), ion-exchange and membrane separation have been employed to remove zinc and/or phosphate ions from municipal and industrial effluents [6–14]. EC has the potential to extensively eliminate the disadvantages of the classical treatment techniques to achieve a sustainable and economic treatment of polluted wastewater [15–17]. Therefore, EC has received considerable attention for treatment of wastewater since EC treatment is characterized by simple and easy operated equipment, short operation time, no addition of chemicals and low sludge production, respectively. Iron or aluminum is generally employed as a sacrificial electrode material in EC process. The dissolved metal ions, at an appropriate pH, can form wide ranges of hydrocomplex species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants. Several examples for removals of phosphate and zinc from water and wastewater such as phosphate removal from wastewater using aluminum and iron plate electrodes [18,19], removal of phosphate from drinking water using mild steel as the anode and stainless steel as the cathode [20], remediation of phosphate-contaminated water using aluminum, aluminum alloy and mild steel anodes as the anodes and stainless steel as the cathode [21],

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Nomenclature

CD	current density (A/m^2)
COD	chemical oxygen demand (mg O_2/L)
C_{energy}	energy consumption (kWh/m^3)
$C_{electrode}$	electrode consumption (kg/m^3)
$C_{chemicals}$	chemicals consumption (kg/m^3)
EC	electrocoagulation
F	Faraday's constant (96486 C/mol)
I	operating current (A)
M	molecular weight (g/mol)
n	metal valance used EC
OC	operating cost (US $/m^3)
pH_i	initial pH
pH_f	final pH
Q	flow rate (mL/min)
Q_e	charge loading (F/m^3)
TOC	total organic carbon (mg/L)
TSS	total suspended solids (mg/L)
t_{EC}	operating time (min)
U	electric potential in each cell (V)
V	rinse water volume (L)
ZPO	zinc phosphate

removal of phosphate from aqueous solutions using calcined metal hydroxides sludge waste generated from EC [6], removal of Zn^{2+} present in aqueous solutions using aluminum electrode [22], treatment of electroplating wastewater containing Zn^{2+} [12], heavy metal removals from metal plating effluent with stainless steel electrodes [23], removal of zinc ions from industrial wastewater by membrane filtration process [24], removal of zinc cyanide from a leach solution by an anionic ion-exchange resin [25], removal of zinc metal ion from its aqueous solution by adsorption [26–28], etc. are reported in the literature.

There are a number of studies about removal of zinc and phosphate ions separately from synthetic and industrial wastewater by EC process in the literature but there is no direct study reported on treatment of zinc phosphate rinse water (ZPO). Therefore, this study focuses on the removal and operating costs of ZPO using iron and aluminum as sacrificial electrodes from ZPO by the EC process. Various operating conditions such as pH (3.0–8.0), current density (20–100 A/m^2), electrode material and operating time (5–30 min) in a batch mode are investigated to determine optimum operating conditions. A continuous mode of operation was investigated with flow rates ranged in 50–400 mL/min. The surface morphology and elements present in the dewatered sludge was also explored with scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyzer.

2. Experimental study

2.1. Wastewater samples

Sample of rinse water from ZPO coating was collected from an automotive assembly plant in Turkey. The sample was cooled to 4 °C and then transported to the laboratory for analysis and electrochemical treatment. The wastewater initial pH (3.8) was adjusted by adding the required amount of 0.1 M H_2SO_4 or 0.1 M NaOH. The essential constituents of a ZPO bath were a zinc salt, which was the source of zinc, orthophosphoric acid and an accelerator to speed up the rate of deposition (sodium nitrite was used to avoid polarization of the cathode). The chemical compositions of the bath and its operating conditions were given in constituents per liter: 11.30 mL of H_3PO_4 (85%), 5 g ZnO, 2 g $NaNO_2$, pH 2.7, temperature of 27 °C and operating time of 30 min. The characteristics parameters of the raw and treated wastewater such as the chemical oxygen demand (COD) and total organic carbon (TOC), total suspended solids (TSS), pH, oil and grease, conductivity, turbidity, chloride, zinc, sodium, phosphate, sulphate and nitrate ions, were analyzed as indicated in the Standard Methods for Examination of Water and Wastewater [29] and characterization of ZPO rinse water before and after the EC treatment was shown in Table 1.

2.2. Experimental procedure

The electrocoagulation experiments were carried out in batch and continuous modes with a single-compartment electrochemical reactor (Fig. 1). Aluminum and iron as sacrificial electrodes were used as both anode and cathode, respectively. The reactor thermostated and made from plexiglas with the dimensions of 100 mm × 100 mm × 100 mm was equipped with four parallel monopolar electrodes; two anodes and two cathodes with the dimensions of 46 mm × 53 mm × 3 mm for batch and 220 mm × 50 mm × 4 mm for continuous systems, made of aluminum (99.53% purity) or iron (99.50% purity) plates. The total effective electrode area for batch and continuous modes was 146.3 and 660 cm^2 and an electrode gap of 11 and 20 mm, respectively. The electrical current was applied using a DC digital power supply (Topward 6306D; 30V, 6A) with potentiostatic or galvanostatic operational options. Volumes of the spent final rinse water used for batch and continuous reactors were 850 mL and 3500 mL, respectively. The spent final rinse water was circulated through the EC reactor in the continuous mode by means of a peristaltic pump.

Before each run, electrodes were washed with acetone to remove surface grease, and the impurities on the aluminum or iron electrode surfaces were removed by dipping for 5 min in a solution freshly prepared by mixing 100 mL of HCl solution (35%) and 200 mL of hexamethylenetetramine aqueous solution (2.8%) [30], and dried and re-weighted. All runs were performed at 25 °C and 200 rpm. The effluent solution from the reactor was collected and then filtered by micropore membrane filter with the pore diameter of 0.45 μm at the end of the run.

2.3. Analyses

All chemicals used were analytical grade and used without any further treatment. Distilled water was used in all experiments. Zinc concentration was measured using a PerkinElmer AAS 1100 spectrophotometer at 214 nm. The analysis of phosphate was carried out using the Yellow Vanadomolybdophosphoric Acid Method by UV–vis spectrophotometer (PerkinElmer Lambda 35) according to Standard Methods [29]. The TOC levels were determined through combustion of the samples at 680 °C using a non-dispersive IR source (Tekmar Dohrmann Apollo 9000). The COD concentration was measured by UV–vis spectrophotometer. The pH was measured using AZ 8601 model pH meter.

2.4. SEM and X-ray analyses in the sludge

The flocs were collected over a desired period of time from the reactor and collected samples were filtered by a Whatman no. 41 filter paper before the sludge analysis. The dry weight of the sludge was determined after drying in the oven at 105 °C for 24 h. The morphological feature and chemical analysis of the sludge were evaluated by SEM and EDX. Samples were first gold coated to provide conductivity to the samples, and then the SEM image spectra of the sludge were taken. The results were shown in Fig. 2 for SEM and Fig. 3 for EDX. The existence of oxygen, zinc, phosphate, iron and aluminum present in the sludge was confirmed through EDX examination of the sample. The colloidal matter was destabi-