



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/m², pH 5.0 and operating time of 25.0 min with Al electrode and current density of 60.0 A/m², 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/m³ for Al electrode and from 0.20 to 0.62 kg electrode/m³ for Fe electrode with increasing current density from 10.0 to 100.0 A/m². The energy consumptions were 0.18–11.29 kWh/m³ for Al electrode and 0.24–8.47 kWh/m³ 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.

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1. Introduction

Zinc phosphate (Zn₃(PO₄)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 $4\ ^\circ C$ 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 $27\ ^\circ C$

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 $100\ mm \times 100\ mm \times 100\ mm$ was equipped with four parallel monopolar electrodes; two anodes and two cathodes with the dimensions of $46\ mm \times 53\ mm \times 3\ mm$ for batch and $220\ mm \times 50\ mm \times 4\ mm$ 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 $25\ ^\circ C$ and 200 rpm. The effluent solution from the reactor was collected and then filtered by micropore membrane filter with the pore diameter of $0.45\ \mu m$ 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 $680\ ^\circ C$ 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 $105\ ^\circ C$ 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-

Table 1
Characteristics of zinc phosphate rinse water before and after the EC treatment.

Parameters	Raw rinse water	Batch EC process		Continuous EC process	
		Fe electrode	Al electrode	Fe electrode	Al electrode
pH	3.8	5.6	8.7	7.8	9.6
Zn ²⁺ (mg/L)	40	0.88	1.33	0.45	0.30
PO ₄ -P (mg/L)	120	2.76	1.20	1.20	0.85
SO ₄ ²⁻ (mg/L)	60	48	52	50	55
NO ₃ ⁻ (mg/L)	85	84	83	80	82
Cl ⁻ (mg/L)	100	89	91	75	80
Na ⁺ (mg/L)	105	96	87	95	85
Conductivity (mS/cm)	8.3	5.3	5.1	4.8	4.9
Oil and grease (mg/L)	10	Nil	Nil	Nil	Nil
Turbidity (NTU)	80	5	2	3	2
TSS (mg/L)	240	10	8	5	5
COD (mg/L)	150	45	35	45	35
TOC (mg/L)	20	5	7	10	12

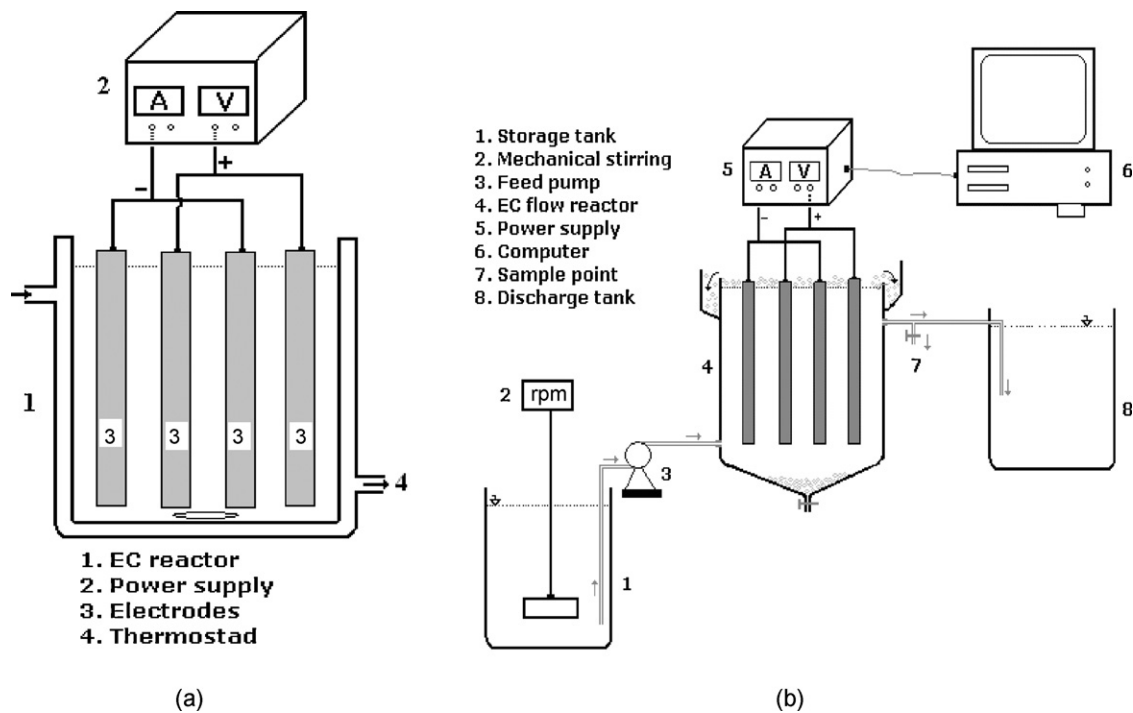


Fig. 1. Experimental setup for (a) batch and (b) continuous EC processes.

lized and separated from the rinse water which the aluminum or iron generated by the electrolysis formed complexes with zinc and phosphate in the sludge. The sludge surface with a number of dents shown in Fig. 2 might tend to entrap microflocs and sludge particles [31,32]. The sludge might consist of formation of insoluble species such as Al(OH)₃, Fe(OH)₂, Fe(OH)₃, FePO₄·2H₂O and AlPO₄·2H₂O or mixed Al(OH)₃-AlPO₄ and Fe(OH)₃-FePO₄ form and Zn(OH)₂, respectively.

3. The EC mechanism [5,33–38]

In the EC process, the coagulant is generated in situ by electrolytic oxidation of Fe or Al electrode as an anode material which produces ions continuously in the system. The released ions neutralize the charges of the particles and thereby initiate coagulation. These ions may remove the undesirable contaminants (metal hydroxide and metal phosphate flocs generated within the effluent) either by chemical reaction and precipitation or by causing the colloidal materials to coalesce and then removed by electrolytic flotation.

Phosphate and zinc from the rinse water might be removed through three main mechanisms during EC [39]:

- chemical precipitation: the formation of the insoluble compounds such as Al(OH)₃, Fe(OH)₂, Fe(OH)₃, Zn(OH)₂, AlPO₄, FePO₄ or Zn₃(PO₄)₂,
- co-precipitation such as FeZn(PO₄), AlZn(PO₄),
- adsorption: the electrostatic binding of soluble phosphate and zinc ions to the external surfaces of the insoluble metal hydroxide.

All three of these mechanisms might contribute towards removal of phosphate and zinc ions.

The main reactions for zinc and phosphate removals at the cathode evolution of hydrogen gas bubbles and hydroxyl ion formation (Eq. (1)) and at the anode are aluminum or iron dissolution (Eqs. (2) and (3)). These observations underline the following removal mechanisms for Zn²⁺ and PO₄³⁻. Moreover, the direct reduction of the metal cations at the cathode surface, OH⁻ ions produces at the cathode precipitate metal ions as hydroxides. This reaction buffers the pH as long as zinc and phosphate ions are precipitated.

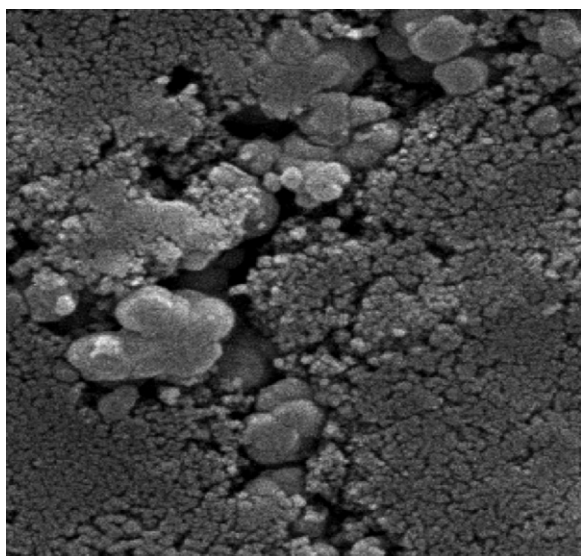
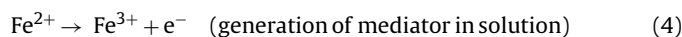
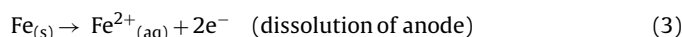
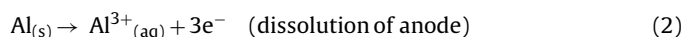
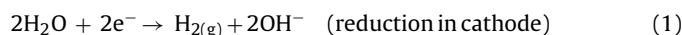


Fig. 2. SEM image of the sludge produced in the EC process.

At acidic pH values, free Al^{3+} ion and $\text{Al}(\text{OH})^{2+}$ hydroxocomplex species are predominate. When pH is between 4 and 9, the Al^{3+} and OH^- ions generated by the electrodes react to form insoluble amorphous $\text{Al}(\text{OH})_3(\text{s})$. Precipitation of phosphate involves the dissolved cations Al^{3+} and Fe^{3+} when iron or aluminum is present in the rinse water, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ or mixed $\text{Al}(\text{OH})_3\text{--AlPO}_4$ and $\text{Fe}(\text{OH})_3\text{--FePO}_4$ form. When the solution pH reaches to optimum pH of zinc (9.0) as a result of cathodic reaction, in the absence of carbonate zinc is completely precipitated as zinc hydroxide. The formation of deposit flocs is dependent on the pH value as well as on the solubility of metal phosphate which increases with increasing pH.

The main electrochemical reactions at the electrodes are:



The rinse water solution becomes green with Fe electrode used and bubbles of gas seen at cathode during the EC process. The effluent gets clear and, a green and yellow sludge are formed. The green and yellow colors are attributed to Fe^{2+} and Fe^{3+} hydroxides.

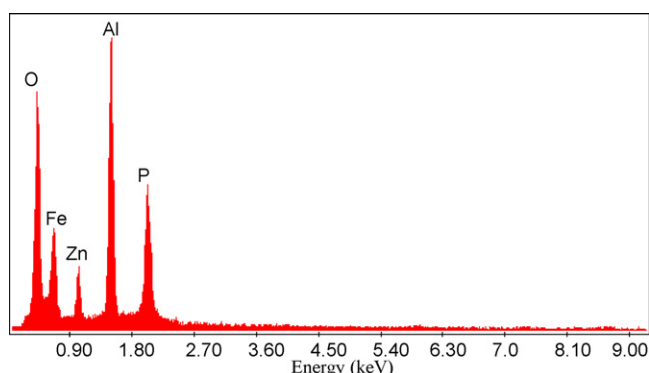
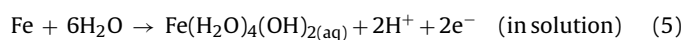
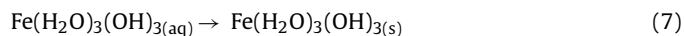
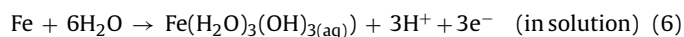
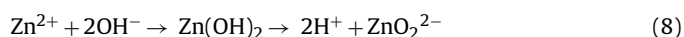


Fig. 3. Energy dispersion spectra of the sludge produced in the EC process.



The principle of phosphorus removal from rinse water is to transfer dissolved phosphates into particulate form by producing chemical precipitates of low solubility. These precipitates are further removed by a solids separation process. The removal mechanism of phosphate by iron/aluminum is mainly precipitation and adsorption depending on solution pH and iron/aluminum concentration. In the case of aluminum electrode, the removal mechanism is due to adsorption of $\text{Al}_x(\text{OH})_y(\text{PO}_4)_z$ (surface complex) into freshly produced $\text{Al}(\text{OH})_3$ ($\text{pH} > 5$). Removal mechanism of phosphate with iron electrode is complicated with respect to solution pH, iron concentration and presence of ferrous and ferric iron, respectively. In the case of ferric iron, at the $\text{Fe}^{3+}/\text{PO}_4$: 1/1 on the molar basis FePO_4 and at higher molar ratio $\text{Fe}_{2.5}\text{PO}_4(\text{OH})_{4.5}$ is precipitated [40]. In the case of ferrous iron $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is precipitated.

Zinc occurs predominantly as Zn^{2+} species at $\text{pH} < 7.5$ and is expected to form hydroxides at $\text{pH} 8\text{--}10$. At $\text{pH} 8.5\text{--}11.5$ and $\text{pH} > 11.5$, the dominant species of Zn^{2+} , $\text{Zn}(\text{OH})_2(\text{aq})$, and $\text{Zn}(\text{OH})_3^-$, respectively [41,42]. Zinc hydroxide, a typical amphoteric hydroxide functions as both an acid and a base:



The hydroxy-complexes $\text{Zn}(\text{OH})_2(\text{aq})$, $\text{Zn}(\text{OH})_3^-$, $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{OH})_5^{3-}$ can be present in a strong alkaline solution.

4. Results and discussion

4.1. Effect of current density

Applied current density is one of the main operating parameters directly affecting process performance and operating cost. Fig. 4 depicted phosphate and zinc removal efficiencies at initial pH 3.0 for Fe electrode and initial pH 5.0 for Al electrode as a function of current density. The phosphate removal at current density in the range 10.0–100.0 A/m^2 were increased from 3.5% to 99.4% for Fe electrode and from 47.8% to 99.3% for aluminum electrode, indicating a higher current density caused a faster phosphate removal (Fig. 4a). The similar behavior was observed with zinc removal (Fig. 4b). It was further noted that there were minor differences in phosphate and zinc removals at the higher current densities. Moreover, higher current density caused high electrical energy consumption and operating cost. Therefore current density at 60.0 A/m^2 was chosen as an optimum current density for the rest of experiments. This was ascribed to the fact that at high current densities, the extent of anodic dissolution of aluminum and iron increased, resulting in a greater amount of precipitate for the removal of pollutants [43]. Removal efficiencies of phosphate and zinc at the optimum current density were 99.0% and 96.7% for Al electrode and 97.7% and 97.8% for Fe electrode, respectively. Moreover, initial pH values with respect to current density during the EC process were increased from 5.1 to 10.6 for Fe electrode and from 4.5 to 10.3 for Al electrode, respectively (Table 2). The amount of metal species formed by dissolution of the anode was calculated from Faraday's law (Eq. (9))

$$C = \frac{MIt}{nFV} \quad (9)$$

where M , I , t , n , F and V are the molecular weight of aluminum (g/mol), the current (A), the electrocoagulation time (s), metal valence (3 for Al, 2 for Fe), Faraday constant (96,500 C/mol) and the working volume of effluent, respectively. Generally an increase

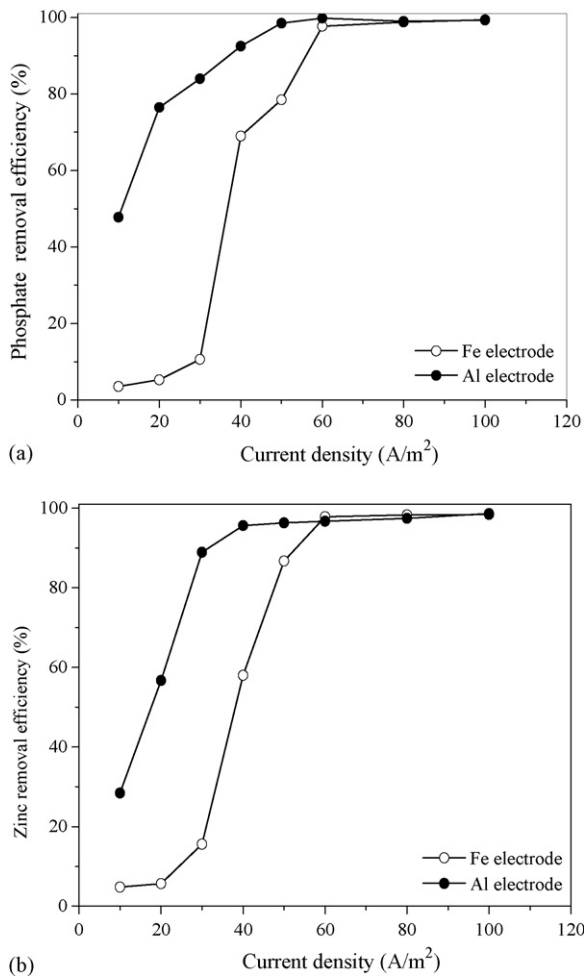


Fig. 4. Effect of current density on phosphate and zinc removal efficiencies for (a) Al and (b) Fe electrodes in the EC process ($t_{EC} = 15$ min and pH 3 for Fe electrode, $t_{EC} = 25$ min and pH 5 for Al electrode).

in current density causes the anodic oxidation to take place more readily, which in turn favors the formation of amorphous aluminum hydroxides species adequately in the vicinity of the electrode as well as in the bulk.

The operating cost (OC) involves costs of chemicals, electrodes and energy consumptions as well as labor, maintenance, sludge dewatering and disposal, and fixed costs [44]. In this preliminary economic investigation, energy and electrode material costs were

taken into account as major cost items in the calculation of the operating cost (US\$/m³). The energy consumed was estimated at a cost of 0.12 US\$/kWh (a). The iron electrode consumption was estimated at a cost of 0.60 US\$/kg (b), whereas a cost of 2.4 US\$/kg was considered for the Al electrode material.

$$OC = aC_{\text{energy}} + bC_{\text{electrode}} + cC_{\text{chemicals}} \quad (10)$$

where C_{energy} (kWh/m³) and $C_{\text{electrode}}$ (kg Al or Fe electrode/m³) are consumption quantities for treatment of the ZPO rinse water. Cost with respect to electrical energy (kWh/m³) was calculated as:

$$C_{\text{energy}} = \frac{UIt_{EC}}{V} \quad (11)$$

where U is cell voltage (V), I is current (A), t_{EC} is the time of EC and V is the volume (m³) of the ZPO rinse water. The electrode consumptions increased from 0.01 to 0.35 kg electrode/m³ for Al electrode and from 0.20 to 0.62 kg electrode/m³ for Fe electrode with increasing current density from 10 to 100 A/m² (Fig. 5a). The energy consumptions were 0.18–11.29 kWh/m³ for Al electrode and 0.24–8.47 kWh/m³ for Fe electrode in the same current density range, respectively (Fig. 5b).

4.2. Effect of charge loading

The mechanisms of EC treatment for the rinse water are very complex since two other possible mechanisms might be involved in which are hydroxide precipitation for zinc and adsorption or precipitation for phosphate removals. All the mechanisms are also related to charge loading (Q_e) [45] which is defined as the charge applied per liter of solution

$$Q_e = \frac{n_h I t}{v} \quad (12)$$

where n_h is number of cells ($n = 4$). The effect of Q_e on phosphate and zinc removals by EC using Al and Fe electrodes was shown in Fig. 6. It was seen from the figure that removal efficiencies of phosphate and zinc for both electrodes rapidly increased over 95.6% by increasing charge loading from 4.0 to 12.0 F/m³ and after that, hardly any changes obtained from removal efficiencies with increasing of charge loading. The optimum charge loading should be at the end of the sharp increase stage. In this case, it was 8.18 F/m³ for Al and 12.29 F/m³ for Fe electrode. The effluent became gradually clear beyond the optimum charge loading values for both electrodes. Over the optimum values there was slight improvement in removals for phosphate and zinc with increment of the charge loading which results from the electrochemical oxidation [45].

Table 2
The variation of initial and final pH of solution.

Initial pH	2	3	4	5	6	7	8	9
Final pH (Fe electrode)	3.3	5.6	6.4	6.8	7.8	8.2	9.3	9.8
PO ₄ -P (%)	6.0	97.7	87.3	25.6	7.5	2.1	1.6	1.2
Zn ²⁺ (%)	6.1	97.8	85.0	13.0	6.4	2.0	1.8	1.50
Final pH (Al electrode)	3.8	6.40	7.6	8.2	9.3	10.1	10.4	10.8
PO ₄ -P (%)	15	91.5	94.5	99.0	94.2	84.5	73.5	48.0
Zn ²⁺ (%)	16.0	87.0	97.2	96.7	94.1	90.0	84.0	52.0
Current density (A/m ²)	10	20	30	40	50	60	80	100
Charge loading (F/m ³)	2.0	4.1	6.1	8.2	9.0	12.3	16.4	20.5
Final pH (Fe electrode)	5.1	5.2	5.3	5.4	5.5	5.6	7.4	9.2
PO ₄ -P (%)	3.5	5.3	10.6	69	78.5	97.7	98.8	99.4
Zn ²⁺ (%)	4.8	5.7	15.6	58	86.7	97.8	98.3	98.4
Final pH (Al electrode)	4.5	5.8	6.9	7.4	7.9	8.2	9.7	10.3
PO ₄ -P (%)	47.8	76.5	84.0	92.5	98.5	99.0	99.0	99.3
Zn ²⁺ (%)	28.4	56.7	88.9	95.6	96.3	96.7	97.4	98.6

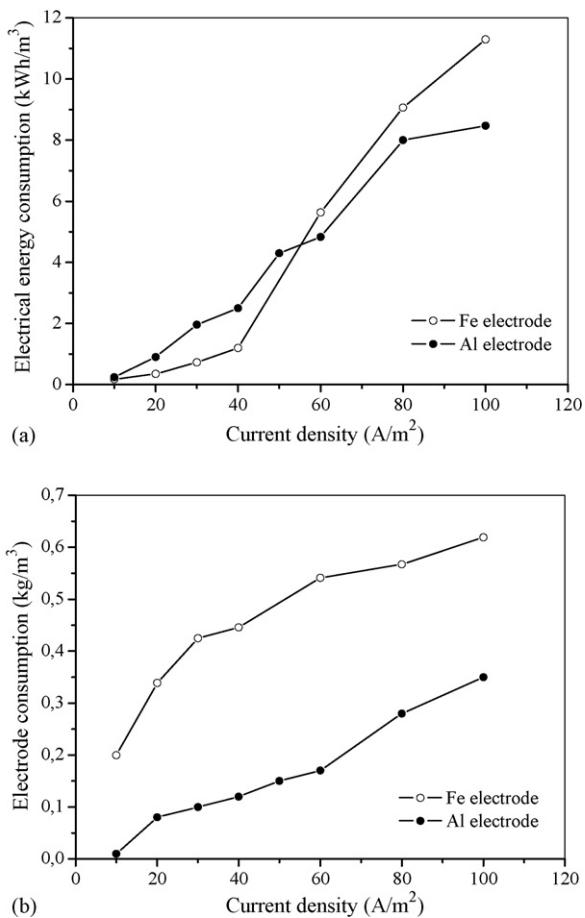


Fig. 5. Effect of current density on energy and electrode consumptions for (a) Al and (b) Fe electrodes in the EC process ($t_{EC} = 15$ min and pH 3 for Fe electrode, $t_{EC} = 25$ min and pH 5 for Al electrode).

4.3. Effect of pH

pH is an important operating factor influencing the performance of electrocoagulation process [10,45,46]. A series of experiments was carried out to evaluate its effect, using solutions containing a sample with an initial pH varying in the range 2.0–9.0 at 60.0 A/m², operating time of 15.0 and 25.0 min for Fe and Al electrodes, respectively. Removal efficiencies of phosphate and zinc

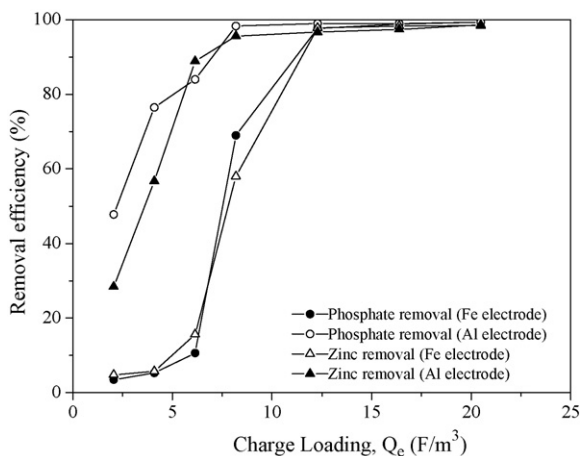


Fig. 6. Effect of charge loading on phosphate and zinc removals in the EC process ($t_{EC} = 15$ min and pH 3 for Fe electrode, $t_{EC} = 25$ min and pH 5 for Al electrode).

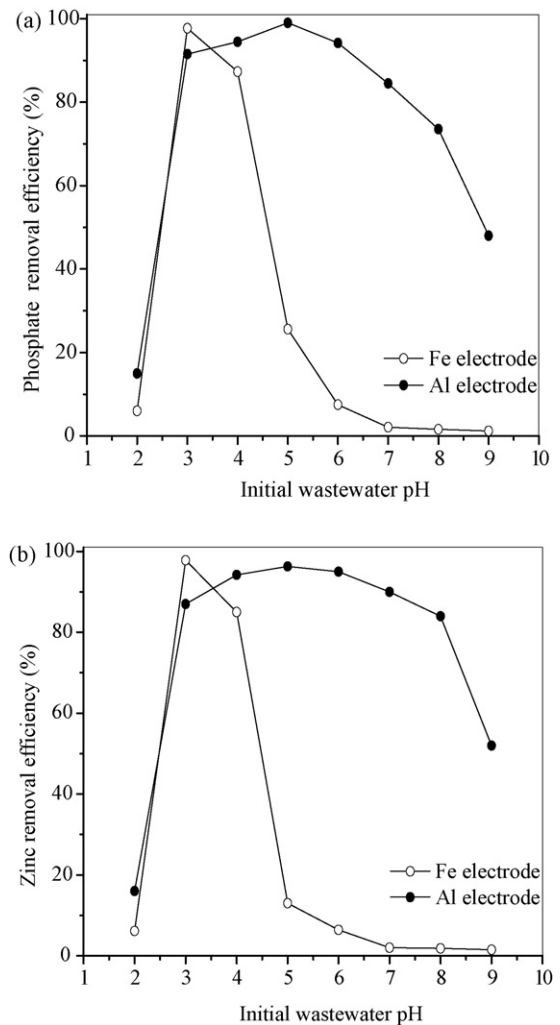


Fig. 7. Effect of initial pH on removal efficiencies for a) phosphate and b) zinc in the EC process ($t_{EC} = 15$ min for Fe electrode and $t_{EC} = 25$ min for Al electrode, CD = 60 A/m²).

for Al and Fe electrodes were shown in Fig. 7; the phosphate and zinc removal efficiencies are obtained from 15.0% to 99.0% and from 16.0% to 96.3% at pH 2.0–5.0 for Al electrode and from 6.0% to 97.7% and from 6.1% to 97.8% at pH 2.0–3.0 for Fe electrode, respectively. This finding is consistent with the previous research [6,18,19,20,47]. The effect of pH on the process performance was explained as follows: the dominant aluminum species were different according to the solution pH; Al³⁺ and Al(OH)²⁺ were dominant at pH 2.0–3.0, and with pH between 4.0 and 9.0, various polymeric species such as Al₁₃O₄(OH)₂₄⁷⁺ were formed and precipitated as Al(OH)₃(s). At acidic pHs, the oxide surfaces exhibited a net positive charge, and adsorption of anionic phosphate and zinc was enhanced by columbic attraction. At higher pHs, the oxide surface had a net negative charge and would tend to repulse the anionic phosphate and zinc in solution. Therefore, the maximum amount of zinc and phosphate removals occurred at pH 3.0 and 5.0. In the case of iron electrode, the complexes (i.e., hydrolysis products) had a tendency to polymerize at pH 3.5–7.0. Insoluble metal hydroxides formed as increase the solution pH which was precipitated as Fe(OH)₂, Fe(OH)₃, Al(OH)₃, FePO₄, Fe₃(PO₄)₂·8H₂O and Zn(OH)₂, respectively. Table 2 showed the effluent pH change of the rinse water with influent pH along with EC process. A pH increase occurred when the influent pH was low. The increase in the pH

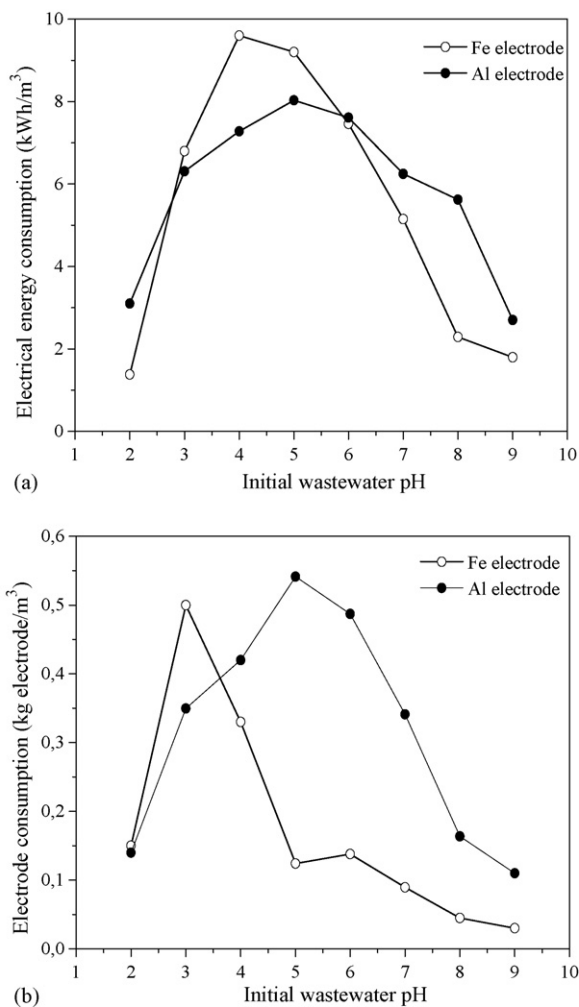


Fig. 8. Effect of initial pH on energy and electrode consumptions for (a) Al and (b) Fe electrodes in the EC process ($t_{EC} = 15$ min for Fe electrode and $t_{EC} = 25$ min for Al electrode, $CD = 60$ A/m²).

during the experiment could be interpreted in terms of the electrochemical and the chemical reactions that took place in the EC reactor. Cathodic water reduction and the chemical dissolution of aluminum and iron electrode increased the pH value.

The electrode consumption values were 0.15–0.50 kg electrode/m³ in the initial pH range 2.0–3.0 for Fe electrode, and 0.14–0.54 kg electrode/m³ in pH 2.0–5.0 for Al electrode, respectively. Values of the energy consumptions at pH 2–5 for Al electrode and pH 2–3 for Fe electrode were 3.10–8.04 kWh/m³ and 1.38–6.80 kWh/m³ (Fig. 8). Above pH 3.0 and 5.0, a decrease in electrical energy and electrode consumptions was detected. This conclusion indicated that pH was very important parameter as it affected the economic applicability of EC process.

4.4. Effect of time

The influence of operating time was explored when the current density was kept constant at 60.0 A/m² and the pH of the wastewater was adjusted to 3.0 and 5.0 for Fe and Al electrodes in phosphate and zinc removals. As seen in Fig. 9a and b, the phosphate and zinc removals increased up to 97.6% and 99.6% for Al in 25 min and 84.2% and 96.6% for Fe electrodes in 15.0 min and further electrogeneration of coagulant flocs had no positive effect on phosphate and zinc removals under the optimum operating time. The optimum operating time for this study was chosen as 25.0 min for Al and

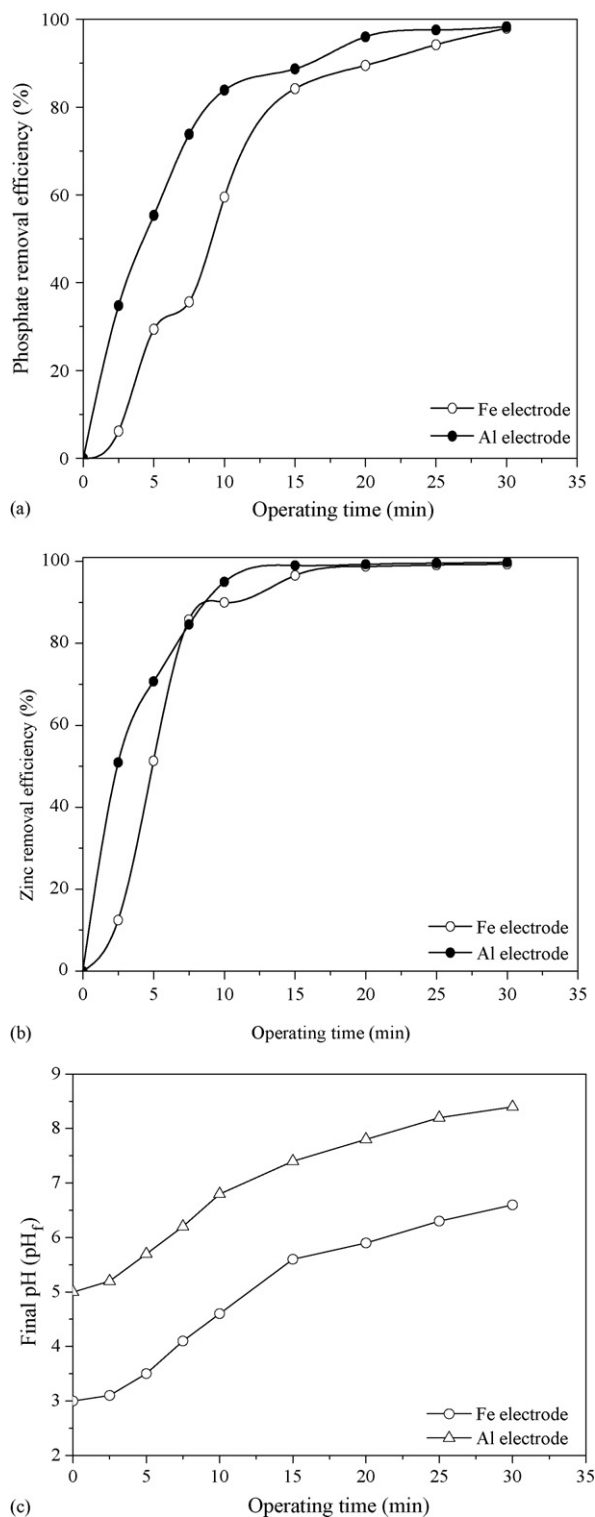


Fig. 9. Effect of operating time on phosphate and zinc removal efficiencies for (a) Al, (b) Fe electrodes and (c) changing of pH with operating time during the EC process (pH 3 for Fe electrode and pH 5 for Al electrode, $CD = 60$ A/m²).

15.0 min for Fe electrodes since the highest removal efficiencies of phosphate and zinc were observed at this time. The operating times for Fe and Al electrodes in the EC process were different since the continual agglomeration of the flocs existed (changing of pH) in a shorter time for Fe electrode than that of Al electrode which eventually settled out from the wastewater. Therefore flocs appeared to stabilize after 15.0 min of operation in the case of Fe electrode.

Table 3

The removal efficiencies and cost parameters of phosphate and zinc as a function of flow rate.

Electrode	Q (mL/min)	Removal efficiency		Effluent pH	C _{energy} (kWh/m ³)	C _{electrode} (kg/m ³)	Amount of sludge (kg/m ³)	OC (\$/m ³)
		Phosphate (%)	Zinc (%)					
Al	50	99.90	99.80	8.4	13.75	0.37	1.51	14.5
	100	99.50	99.60	8.5	8.93	0.27	1.12	9.5
	200	97.83	99.40	8.6	7.78	0.07	0.78	8.0
	400	96.83	99.20	8.8	4.00	0.06	0.71	4.2
Fe	50	99.60	99.30	5.5	12.60	0.59	1.22	12.9
	100	98.50	97.70	5.6	11.30	0.48	0.74	11.5
	200	95.30	95.70	5.8	9.74	0.32	0.53	9.9
	400	85.50	86.10	6.2	5.45	0.18	0.20	5.6

The effect of the operating time on the pH value was also explored (Fig. 9c). The pH value increased as the operating time of EC process was increased due to the OH⁻ ion accumulated in aqueous solution during the process. The increase of pH at acidic condition was attributed to hydrogen evolution at cathodes.

4.5. Comparison of removal parameters with literature

Adhoum et al. [12] investigated the treatability of synthetic samples for the electroplating wastewater containing copper, zinc and hexavalent chromium by EC with aluminum electrodes. Their study revealed that 99.9% removal efficiency for Zn ion was obtained when current density of 16 mA/cm², pH 4 at operating time of 20 min. Irdemez et al. [18] obtained 86% of phosphate removal from wastewater and 0.847 kWh/m³ of energy consumption using iron plate electrodes by EC when the operating parameters were set as current density of 1 mA/cm², 100 mg/L PO₄-P concentration, pH 3 and 50 min. In a separate study, Irdemez et al. [19] conducted optimization study for phosphate removal from wastewater by EC with aluminum plate electrodes. They obtained the optimum conditions for the parameters initial phosphate concentration, initial pH of the wastewater and current density which were 50 mg/L, 4 and 1 mA/cm² at 20 min. They achieved a removal efficiency of 100% under these conditions. Vasudevan et al. [20] studied an EC process for the removal of phosphate from drinking water using mild steel as the anode and stainless steel as the cathode. The results showed that the maximum removal efficiency of 98% was achieved at a current density of 5 mA/cm² and a pH of 6.5. Heidmann and Calmano [22] studied EC of Zn²⁺, Cu²⁺, Ni²⁺, Ag⁺ and Cr⁶⁺ present in aqueous solutions by using aluminum electrodes. Their results showed that zinc could be removed with rate of 2.1 μmol/A s at a current density of 33 mA/cm² and 10 min. Removal of zinc metal plating effluent by EC using stainless steel electrodes was obtained with 66% at current density of 9 mA/cm², pH 6 and 120 min [23]. Bektas et al. [48] achieved the optimum conditions for phosphate removal in aqueous solution by EC using aluminum electrodes as pH 6.2, current density of 10 mA/cm² and initial concentration of 100 mg/L at 20 min. In the present study, phosphate and zinc removal efficiencies at optimum conditions (60.0 A/m², pH 5.0 and 25.0 min for Al electrode and 60.0, pH 3.0 and 15.0 min for Fe electrode) were 97.7% and 97.8% for Fe electrode, and 99.8% and 96.7% for Al electrode. The electrode and energy consumptions varied in the range 0.01–0.35 kg electrode/m³ and 0.18–11.29 kWh/m³ for Al electrode and 0.20–0.62 kg electrode/m³ and 0.24–8.47 kWh/m³ for Fe electrode with increasing current density from 10.0 to 100.0 A/m².

4.6. Effect of flow rate on the removal efficiency

The removal efficiencies and cost parameters of phosphate and zinc as a function of flow rate at the optimum conditions were shown in Table 3. As seen in Table 3, the flow rate increased from 50 to 400 mL/min, phosphate and zinc removal ratios were

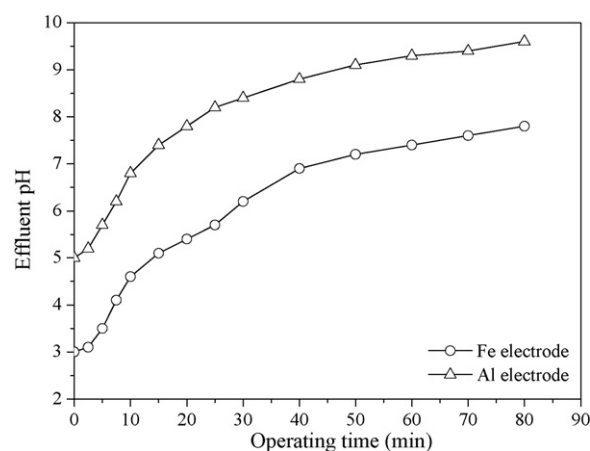


Fig. 10. Changing of effluent pH with operating time for continuous EC process (pH 3 for Fe electrode and pH 5 for Al electrode, CD = 60 A/m², 400 mL/min).

decreased from 99.90% to 96.83% and from 99.80% to 99.20% for Al electrode and from 99.60% to 85.50% and from 99.30% to 86.10% for Fe electrode, respectively. The decrease in removal efficiency with increasing flow rate was quite expected, since slower the flow rate higher the operating time. Higher operating time means the untreated wastewater solution remains in the EC reactor for more time, which in turn provided more time for the reaction. The slower flow rate allowed the coagulant generated by electrochemical oxidation of the anode material and the pollutants in the wastewater to mix properly and thereby improve the rate of coagulation.

The result indicated in Table 3 that energy and electrode consumptions, amount of sludge produced and operating costs were decreased with increasing of the flow rate. The effect of effluent pH with operating time for continuous EC process was shown in Fig. 10. The pH value increased as the operating time of EC process for both electrodes was increased which was responsible for flocs production.

5. Conclusion

The present study was dealt with the effect of operating parameters such as pH, current density and operating time, on phosphate and zinc removals from rinse water of ZPO coating in a batch mode by EC. The results showed that the phosphate and zinc removals were more efficiently achieved by Al electrode at pH 5.0 and Fe electrode at pH 3.0. The highest rate for phosphate and zinc removals was obtained in 25.0 and 15.0 min of operating time, respectively. The energy and electrode consumptions in EC process were increased as current density was increased. Effect of inlet flow rate on removal efficiencies of phosphate and zinc was also studied with continuous mode of operation. Removal rates for phosphate

and zinc were observed to decrease with increasing of inlet flow rate. The dewatered sludge sample was analyzed with SEM and EDX which were conducted to obtain surface morphology and the elements present in the sludge sample.

References

- [1] S. Jegannathan, T.S. Narayanan, K. Ravichandran, S. Rajeswari, Formation of zinc phosphate coating by anodic electrochemical treatment, *Surf. Coat. Technol.* 200 (2006) 6014–6021.
- [2] A.S. Akhtar, K.C. Wong, P.C. Wong, K.A.R. Mitchell, Effect of Mn^{2+} additive on the zinc phosphating of 2024–Al alloy, *Thin Solid Film* 515 (2007) 7899–7905.
- [3] S.L. Zhang, H.H. Chen, X.L. Zhang, M.M. Zhang, The growth of zinc phosphate coatings on 6061–Al alloy, *Surf. Coat. Technol.* 202 (2008) 1674–1680.
- [4] D. Weng, R. Wang, G. Zhang, Environmental impact of zinc phosphating in surface treatment of metals, *Met. Finish.* (1998) 54–57.
- [5] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) science and applications, *J. Hazard. Mater.* 84 (2001) 29–41.
- [6] A.K. Golder, A.N. Samanta, S. Ray, Removal of phosphate from aqueous solutions using calcined metal hydroxides sludge waste generated from electrocoagulation, *Sep. Purif. Technol.* 52 (2006) 102–109.
- [7] E. Oguz, Sorption of phosphate from solid/liquid interface by fly ash, *Colloids Surf. A* 262 (2005) 113–117.
- [8] E. Oguz, A. Gurses, M. Yalcin, Removal of phosphate from wastewaters by adsorption, *Water Air Soil Pollut.* 148 (2003) 279–287.
- [9] H.D. Stensel, Principles of biological phosphorus removal: Phosphorus and nitrogen removal from municipal wastewaters principles and practice, 2nd ed., H. K. Lewis, London, 1991.
- [10] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.* 38 (2004) 11–41.
- [11] K. Kuzawa, Y.J. Jung, Y. Kiso, T. Yamada, M. Nagai, T.G. Lee, Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent, *Chemosphere* 62 (2006) 45–52.
- [12] N. Adhoum, L. Monser, N. Bellakhal, J.E. Belgaied, Treatment of electroplating wastewater containing Cu^{2+} , Zn^{2+} and $Cr(VI)$ by electrocoagulation, *J. Hazard. Mater.* 112 (2004) 207–213.
- [13] N. Meunier, P. Drogui, C. Gourvenec, G. Mercier, R. Hausler, J.F. Blais, Removal of metals in leachate from sewage sludge using electrochemical technology, *Environ. Technol.* 25 (2004) 235–245.
- [14] B. Alyüz, S. Veli, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, *J. Hazard. Mater.* 167 (2009) 482–488.
- [15] A.K. Golder, A.N. Samanta, S. Ray, Removal of Cr^{3+} by electrocoagulation with multiple electrodes: Bipolar and monopolar configurations, *J. Hazard. Mater.* 141 (2007) 653–661.
- [16] C.L. Lai, S.H. Lin, Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication, *Chem. Eng. J.* 95 (2003) 205–211.
- [17] C.L. Lai, S.H. Lin, Treatment of chemical mechanical polishing wastewater by electrocoagulation: system performances and sludge settling characteristics, *Chemosphere* 54 (2004) 235–242.
- [18] S. Irdemez, N. Demircioglu, Y.S. Yildiz, The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes, *J. Hazard. Mater.* 137 (2006) 1231–1235.
- [19] S. Irdemez, N. Demircioglu, Y.S. Yildiz, Z. Bingul, The effects of current density and phosphate concentration on phosphate removal from wastewater by electrocoagulation using aluminum and iron plate electrodes, *Sep. Purif. Technol.* 52 (2006) 218–223.
- [20] S. Vasudevan, G. Sozhan, S. Ravichandran, J. Jayaraj, J. Lakshmi, S. Margrat Sheela, Studies on the removal of phosphate from drinking water by electrocoagulation process, *Ind. Eng. Chem. Res.* 47 (2008) 2018–2023.
- [21] S. Vasudevan, J. Lakshmi, J. Jayaraj, G. Sozhan, Remediation of phosphate-contaminated water by electrocoagulation with aluminium, aluminium alloy and mild steel anodes, *J. Hazard. Mater.* 164 (2009) 1480–1486.
- [22] I. Heidmann, W. Calmano, Removal of $Zn(II)$, $Cu(II)$, $Ni(II)$, $Ag(I)$ and $Cr(VI)$ present in aqueous solutions by aluminium electrocoagulation, *J. Hazard. Mater.* 152 (2008) 934–941.
- [23] I. Kabdasi, T. Arslan, T. Ölmez-Hanci, I. Arslan-Alaton, O. Tünay, Complexing agent and heavy metal removals from metal plating effluent by electrocoagulation with stainless steel electrodes, *J. Hazard. Mater.* 165 (2009) 838–845.
- [24] G. Borbely, E. Nagy, Removal of zinc and nickel ions by complexation membrane filtration process from industrial wastewater, *Desalination* 240 (2009) 218–226.
- [25] H. Kurama, T. Catalarık, Removal of zinc cyanide from a leach solution by an anionic ion-exchange resin, *Desalination* 129 (2000) 1–5.
- [26] F. Arias, T.K. Sen, Removal of zinc metal ion (Zn^{2+}) from its aqueous solution by kaolin clay mineral: a kinetic and equilibrium study, *Colloids Surf. A* 348 (2009) 100–108.
- [27] V.C. Srivastava, I.D. Mall, I.M. Mishra, Removal of cadmium(II) and zinc(II) metal ions from binary aqueous solution by rice husk ash, *Colloids Surf. A* 312 (2008) 172–184.
- [28] S. Veli, B. Alyuz, Adsorption of copper and zinc from aqueous solutions by using natural clay, *J. Hazard. Mater.* 149 (2007) 226–233.
- [29] APHA, Standard Methods for Examination of Water and Wastewater, American Public Health Association, Washington, DC, 1998.
- [30] J.S. Do, M.L. Chen, Decolorization of dye-containing solutions by electrocoagulation, *J. Appl. Electrochem.* 24 (1994) 785–790.
- [31] C.L. Lai, K.S. Lin, Sludge conditioning characteristics of copper chemical mechanical polishing wastewaters treated by electrocoagulation, *J. Hazard. Mater.* 136 (2006) 183–187.
- [32] S. Mahesh, B. Prasad, I.D. Mall, I.M. Mishra, Electrochemical degradation of pulp and paper mill wastewater. Part 2. Characterization and analysis of sludge, *Ind. Eng. Chem. Res.* 45 (2006) 5766–5774.
- [33] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *J. Hazard. Mater.* 100 (2003) 163–178.
- [34] M.J. Yu, J.S. Koo, G.N. Myung, U.K. Cho, Y.M. Cho, Evaluation of bipolar electrocoagulation applied to biofiltration for phosphorus removal, *Water Sci. Technol.* 51 (2005) 231–239.
- [35] W.J. Eilbeck, G. Mattack, Chemical Processes in Wastewater Treatment, John-Wiley and Sons, West Sussex, 1987.
- [36] Z. Zaroual, M. Azzi, N. Saib, E. Chainet, Contribution to the study of electrocoagulation mechanism in basic textile effluent, *J. Hazard. Mater.* 131 (2006) 73–78.
- [37] J.K. Edzwald, J.Y. Bottero, K.J. Ives, R. Klute, Particle alteration and particle production processes, in: J.B. Mc Ewan (Ed.), Treatment Process Selection for Particle Removal, AWWA, IWSA, New York, 1997, pp. 73–123.
- [38] S.D. Faust, O.M. Aly, Chemistry of Water Treatment, Butterworth Publishers, USA, 1983.
- [39] M.I. Aguilar, J. Saez, M. Lorens, A. Soler, J.F. Ortuno, Nutrient removal and sludge production in the coagulation-flocculation process, *Water Res.* 36 (2002) 2910–2919.
- [40] M.J. Yu, J.S. Koo, G.N. Myung, Y.K. Cho, Y.M. Cho, Evaluation of bipolar EC applied to biofiltration for phosphorus removal, *Water Sci. Technol.* 51 (2005) 231–239.
- [41] W. Stumm, J. Morgan, Aquatic Chemistry, 3rd ed., John Wiley & Sons Inc., New Jersey, 1995.
- [42] Y.J. Xue, H.B. Hou, S.J. Zhu, Competitive adsorption of copper (II), cadmium (II), lead (II) and zinc (II) onto basic oxygen furnace slag, *J. Hazard. Mater.* 162 (2009) 391–401.
- [43] C.T. Wang, W.L. Chou, L.S. Chen, S.Y. Chang, Silica particles settling characteristics and removal performances of oxide chemical mechanical polishing wastewater treated by electrocoagulation technology, *J. Hazard. Mater.* 161 (2009) 344–350.
- [44] M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, Operating cost analysis of electrocoagulation of textile dye wastewater, *Sep. Purif. Technol.* 37 (2004) 117–125.
- [45] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, *Sep. Purif. Technol.* 19 (2000) 65–76.
- [46] U.B. Ogutveren, A.S. Koparal, Colour removal from textile effluents by electrochemical destruction, *J. Environ. Sci. Health A29* (1994) 1–16.
- [47] A.L. Bojic, D. Bojic, T. Andjelkovic, Removal of Cu^{2+} and Zn^{2+} from model wastewaters by spontaneous reduction-coagulation process in flow conditions, *J. Hazard. Mater.* 168 (2009) 813–819.
- [48] N. Bektas, H. Akbulut, H. Inan, A. Dimoglo, Removal of phosphate from aqueous solutions by electrocoagulation, *J. Hazard. Mater.* 106 (2004) 101–105.