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Removal of Salicylic Acid from Aqueous Solutions Using Various Electrodes and Different Connection Modes by Electrocoagulation

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Removal of salicylic acid (SA) from aqueous solutions using hybrid aluminum and iron electrodes (eight different combinations) and three different connection modes (monopolar parallel (MP-P), Monopolar series (MP-S) and bipolar series (BP-S)) by electrocoagulation was investigated in this study. The effects of electrocoagulation parameters such as hybrid electrode combination, initial pH, current density, initial salicylic acid concentration, air injection flow, solution conductivity and connection mode on SA and COD removal efficiencies were evaluated. Optimum operational conditions at 10 min operating time were found to be as: Al-Al-Al-Al (anode-cathode-anode-cathode) electrode combination, the initial pH of 6, current density of 50 A/m^2, salicylic acid concentration of 100 mg/L, air injection mode of 2 L/min and connection mode of monopolar series (MP-S). Under these conditions, removal efficiencies for salicylic acid and COD were respectively observed as 95.1% and 85.97%. Moreover, the UV absorbance was determined before and after the treatments by electrocoagulation (EC) process. The operating costs including electrodes, energy and chemicals were calculated as 0.0156 €/m^3. Sludge generation of EC process was also analyzed by scanning electron microscope (SEM) imaging, Fourier Transform Infrared Spectroscopy (FT-IR), XRD (X-raydiffraction) and amorphous Al hydroxides were encountered in the sludge. As to conclude, electrocoagulation through different electrode combinations and connections modes was found to be quite efficient for removal of salicylic acid from aqueous solutions.

Keywords: Electrocoagulation, Removal of Salicylic acid, Hybrid Fe-Al electrode, Electrode connection mode, Operating cost.

1. INTRODUCTION

Anti-inflammatory drugs are among the common potentially toxic contaminants in aquatic environments. These drugs have various negatives impacts on aquatic life and humans [1]. Aspirin

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(Acetylsalicylic acid, $C_9H_8O_4$) produced by German Bayer Company is the most common anti-inflammatory worldwide [2]. A large part of aspirin is transformed into a metabolite, commonly into salicylic aside. Salicylic acid (SA) is a prominent pharmaceutical intermediate to produce acetylsalicylic acid (aspirin), sodium salicylate, salicylamide, acethxybenzamide, and phenyl salicylate [3]. Recently, several other anti-inflammatory drugs were developed and produced by the other companies. The amount of aspirin manufactured worldwide is more than 5000 tons every year [2]. Besides, increasing SA production results in increasing amount of SA-contained industrial wastewater [3]. Salicylic aside is discharged as waste via toilet into sewage system. Salicylic acid is a hazardous substance encountered in wastewaters mainly through byproducts, human and veterinary drugs, paper milling and cosmetic industries. Salicylic acid removal from wastewaters requires advanced treatment technologies. Therefore, alternative technologies should be investigated to remove salicylic acid and metabolites from wastewaters.

In recent years, several studies were carried out to investigate salicylic acid removal from wastewaters. Most of them focused on degradation of salicylic aside through advanced treatment and adsorption processes such as combined membrane and carbon nanotube [3-4], modified Na-montmorillonite sorption [5-7], electrochemical processes [8-9], UV/H_2O_2/oxygen systems [10]. Electrocoagulation (EC) is one of the most effective techniques for removal of pollutants from wastewaters. EC process has some advantages over the other methods such as high removal efficiency, no chemical addition, reduced sludge generation, versatility, energy efficiency, safety, selectivity, amenability and lower operating costs. The EC process treats pollutants from wastewaters with sacrificial anodes dissolved to release iron and aluminum coagulant into solutions. The process realized in three main steps; (1) electrolytic reaction, (2) formation of coagulants in aqueous phase, (3) adsorption of soluble or colloidal particles on coagulants and removal by sedimentation or flotation [11-13]. Commonly, low-cost and easily accessed iron or aluminum electrodes are used in EC process [14-16].

The anode and cathode reactions during EC process can be presented as follows;

Anode side: $Al \longrightarrow Al^{3+}{}_{(aq)} + 3e^{-}$ (1)

$Fe \longrightarrow Fe^{3+}{}_{(aq)} + 2e^{-}$

Cathode side: $3H_2O + 3e^{-} \longrightarrow \frac{3}{2}H_2 + 3OH^{-}$ (2)

In solution

$Al_{(aq)}{}^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H_{(aq)}{}^{+}$ (3)

$Fe_{(aq)}{}^{3+} + 2H_2O \rightarrow Fe(OH)_{2(s)} + 2H_{(aq)}{}^{+}$

These metal flocs will react to form various hydroxide and/or polyhydroxide species depending on medium pH (such as $Al(OH)^{2+}$, $Al(OH)_2{}^{+}$, $Al_2(OH)_2{}^{4+}$, Fe $(OH)_2$ hydroxides species; $Al_6(OH)_{15}{}^{3+}$, $Al_7(OH)_{17}{}^{4+}$, $Al_8(OH)_{20}{}^{4+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$, $Al_{13}(OH)_{34}{}^{5+}$), $Fe(H_2O)_6{}^{2+}$, $Fe(H_2O)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2{}^{4+}$ and $Fe_2(H_2O)_6(OH)_4{}^{4+}$ [17-19]. Metal hydroxide flocs have large surface areas which are highly beneficial for rapid adsorption of soluble organic compounds onto floc surface and these flocs can easily be removed from aqueous medium by sedimentation and flotation [19-21].

The EC process have been employed for various purposes such as to remove pollutants from drinking waters, to remove arsenic and heavy metals from industrial wastewaters, for treatment of textile wastewater, oily wastewater, slaughterhouse wastewater and restaurant wastewaters. However, only one study was come across in literature dealing with simple electrocoagulation process. Chou et al [9] investigated removal of SA from aqueous solutions with Al electrode and a removal efficiency of 88.7% was achieved under operational conditions of 1.2 mA/cm^2, 0.005 N support solutions, 298 K temperature and 60 min process duration. But the parameters effective in EC process such as initial pH, electrode type, current density, electrode connection mode, air injection flow, initial SA concentration, support solution concentration, operation time, operating cost and sludge generation were not investigated, Electrocoagulation time was quite long and EC operating costs were very high in that study. Thus, removal of SA by electrocoagulation process should also be investigated in terms of both technical and economical aspects.

In present study, effects of electrode types (eight different hybrid electrode combinations), initial pH (4-10), current density (25-150 A/m^2), initial SA concentration (50-500 mg/L), solution conductivity (500-1500 µs/cm), air injection flow (0-6 L/min) and electrode connection modes (monopolar parallel-series and bipolar series) were investigated in a batch mode. Optimum operating conditions for the highest SA removal were also investigated. Moreover, sludge characterization was also performed and operating costs were calculated.

2. MATERIAL AND METHOD

The SA solutions were prepared by dissolving appropriate amount of SA ($C_7H_6O_3$) (with a molecular weight of 138.121 g/moL and purity of 99%) supplied from Sigma-Aldrich. Experiments were all carried out in a batch mode using a 1000 mL Plexiglas reactor with vertical Fe-Al electrodes spaced 20 mm apart and dipped into the reactor (Figure 1) [22].

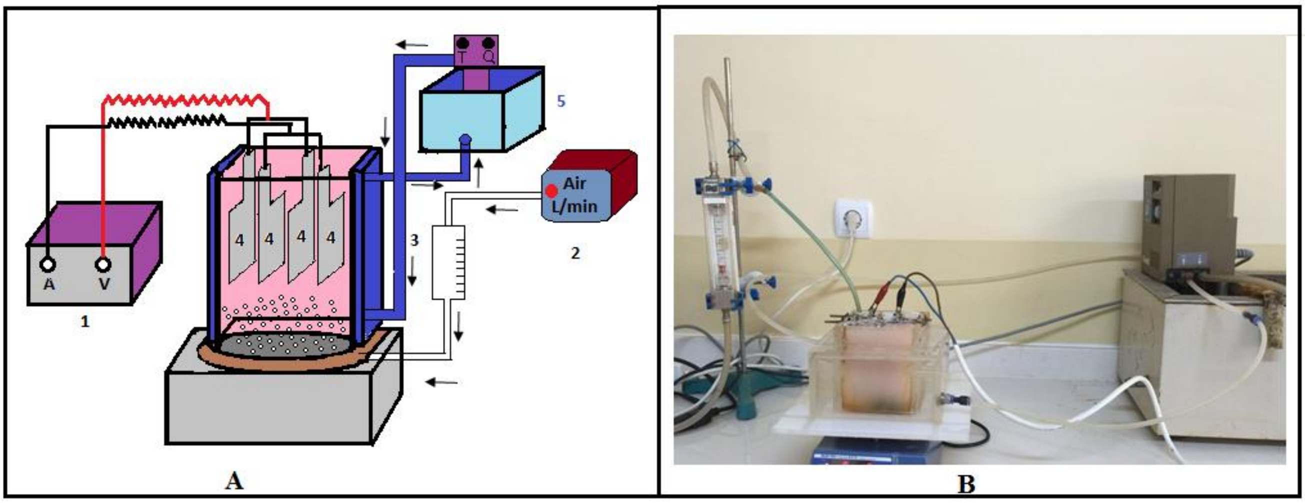


Figure 1. Schematic diagram (A) and photograph (B) of electrocoagulation process (1. Power supply, 2. Air flowmeter, 3. EC reactor, 4. Al, Fe or Al-Fe hybrid electrodes, 5. Water circulator).

To run the experiments, electrodes made of aluminum and iron plates with dimensions of 50x70x2 mm (99.5% purity) were ordered in pairs (Anode-Cathode-Anode-Cathode). The EC experiments were conducted with both only aluminum and iron and also hybrid electrodes as two anodes and two cathodes in eight different combinations as of Fe-Al-Fe-Al, Fe-Al-Al-Fe, Al-Fe-Fe-Al, Al-Fe-Al-Fe, Fe-Al-Al-Al, Al-Fe-Fe-Fe hybrid electrodes and Al-Al-Al-Al or Fe-Fe-Fe-Fe electrodes. A digital DC power supply (Alpha 10A-50V) equipped with galvano-static operational options was used [23-25]. The effects of different electrode connection modes on pollutant removal were experimented at three electrode connection modes. The hybrid electrodes were connected in MP-P, MP-S and BP-S connection modes (Figure 2) [11, 22, 26, 27].

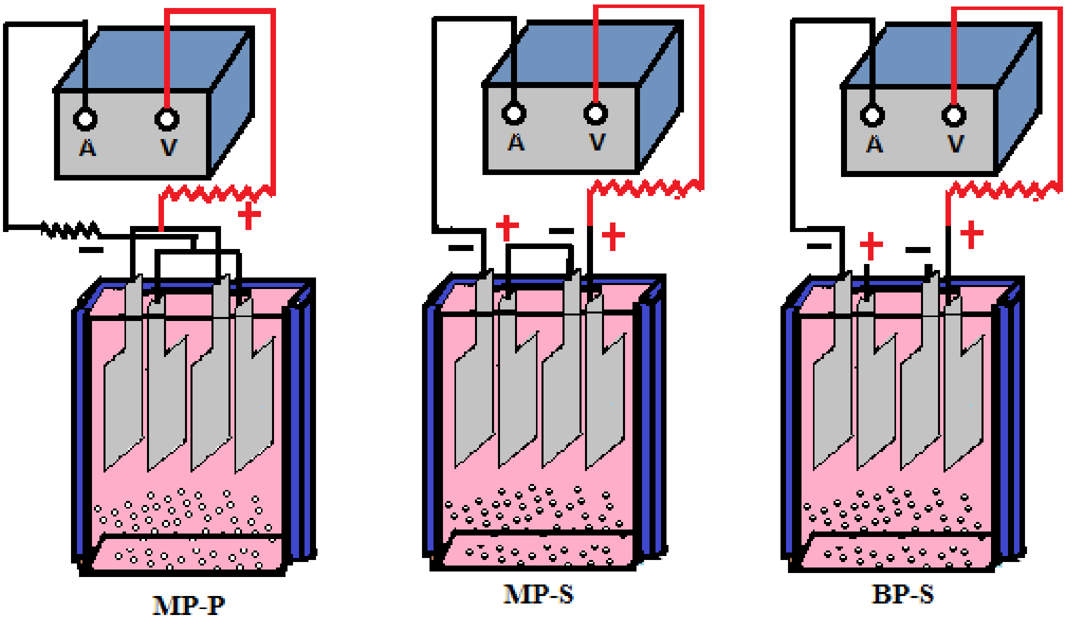


Figure 2. Schematic diagram of three different electrode connection modes.

Entire experiments were carried out at a constant temperature (25°C) via a water circulator and with 1000 mL of wastewater solution. Before each run, organic impurities and oxide zone at the electrodes were cleaned by dipping for 2 min into a solution freshly prepared by mixing HCl solution (35%) and hexamethylenetetramine aqueous solution (2.80%) [28]. Electrodes were then washed with deionize water and dried in an oven.

Chemical oxygen demand (COD) analyses were carried out in accordance with standard analysis methods [29]. The UV-Vis spectrum was measured by using a UV-Vis spectrophotometer (Merck spectroquant Pharo 300, German). The pH and conductivities of samples were measured with a pH meter (C931, Consort, Belgium) and a conductivity meter (340i, WTW, German). The salicylic aside concentration of the solution was calculated with a calibration curve, prepared by plotting the absorbances at 297 nm versus different salicylic acid concentrations.

The SA and COD removal efficiencies (%) were calculated by using the following equation, Eq. (4).

$$\text{The removal efficiency } (\%) = \left(\frac{(C_0 - C)}{C_0}\right) x100 \qquad (4)$$

Sludge generated by EC process was dried in the oven at 105^0C then was analyzed by a Bruker powder X-ray diffractometer (XRD) equipped with a sealed tube copper target (Cu-K=1.54059 Å) and used by Bruker GADDS software. Fourier Transform Infrared Spectroscopy (FTIR) for sludge samples was used a Bio Rad FTS 175 C spectrophotometer and recorded in the range 4000-600cm^{-1}. In addition to, the sludge samples were analyzed using scanning electron microscope imaging (SEM) (Philips XL30S-FEG).

Operating costs are the most significant limiting factors for the application of any wastewater treatment methods. EC process has quite low operating costs. As reported in earlier studies, operating costs generally include material (mainly electrodes) costs, electrical energy cost, labor, maintenance and other costs [28-30]. In present study, the operating costs were composed of electrodes, electrical energy, chemical costs and air pump cost. So, energy, electrode and chemical consumption costs are taken into account as major cost items [28]. Calculation of operating cost was formulated as follows;

Operating Cost **=** *aEnergy consumption* + *bElectrode consumption* + *cChemical consumption* + *dAir Injection consumption*

where, energy consumption and electrode consumption are consumption quantities per m^3 of the treated water. Unit prices, *a, b, c and d* provided for Turkish Market in February 2016 are as follows; electrical energy price is 0.092 €/kWh, electrode material price is 0.85 €/kg for iron, 1.65 €/kg for aluminium and chemical cost is 0.73 €/kg for NaOH and 0.29 €/kg for H_2SO_4.

The electrode and energy consumptions in EC process were calculated by using the following equations;

$$\text{Energy}_{\text{consumption}} = \frac{(\text{V.I.t})}{\text{v}} \qquad (5)$$

where ,Energy$_{\text{consumption}}$ is energy consumption (kWh/m^3), V is voltage (Volt), I is current (Ampere), t is EC time (s) and v is volume of the treated wastewater (m^3). According to Faraday’s law, electrode material consumption and charge loading are calculated with the following equations;

$$\frac{\text{Faraday}}{\text{m}^3} = \frac{(\text{I.t})}{(\text{F.v})} \qquad (6)$$

$$\text{Electrode}_{\text{consumption}} = \frac{(I.t.M_w)}{(z.F.v)} \qquad (7)$$

where, F is Faraday’s constant (96485 C/mol), M_w is the molar mass of iron (56 g/mol), aluminium (27 g/mol) and z is the number of electron transfer (zFe:2, zAl:3).

3. RESULT AND DISCUSSION

SA removal through electrocoagulation process with Al and Fe electrodes was investigated and optimum operating conditions were tired to be determined in this study. Experiments were carried out with different types of electrodes (eight different configurations), initial pH of 4-10, current density of 25-75 A/m^2, initial SA concentration of 50-500 mg/L, support solution conductivity of 500-1500 µs/cm, air injection flow rate of 0-6 L/min, electrode connection mode of (MP-P, MP-S, BP-S) and operation duration of 0-45min.

3.1 Effect of electrode type

Type of electrode is the most significant parameter specifying system performance in electrochemical processes. Such significance was also pointed out in previous studies [31-34]. The amount and type of metal hydroxide flocs play significant roles in removal efficiency of EC process. Higher efficiencies were reported in recent studies for processes using different types of hybrid electrodes [31, 32]. In present study, to investigate the effects of electrode type on SA removal efficiency of EC process, aluminium and iron electrodes were experimented in eight different combinations as Anode-Cathode-Anode-Cathode (Fe-Al-Fe-Al, Fe-Al-Al-Fe, Al-Fe-Fe-Al, Al-Fe-Al-Fe, Fe-Al-Al-Al, Al-Fe-Fe-Fe hybrid electrodes and Al-Al-Al-Al or Fe-Fe-Fe-Fe) at initial pH of 6, current density of 50 A/m^2, initial SA concentration of 100 mg/L, support solution conductivity of 1000 µs/cm, air injection flow rate of 2 L/min and electrode connection mode of MP-P.

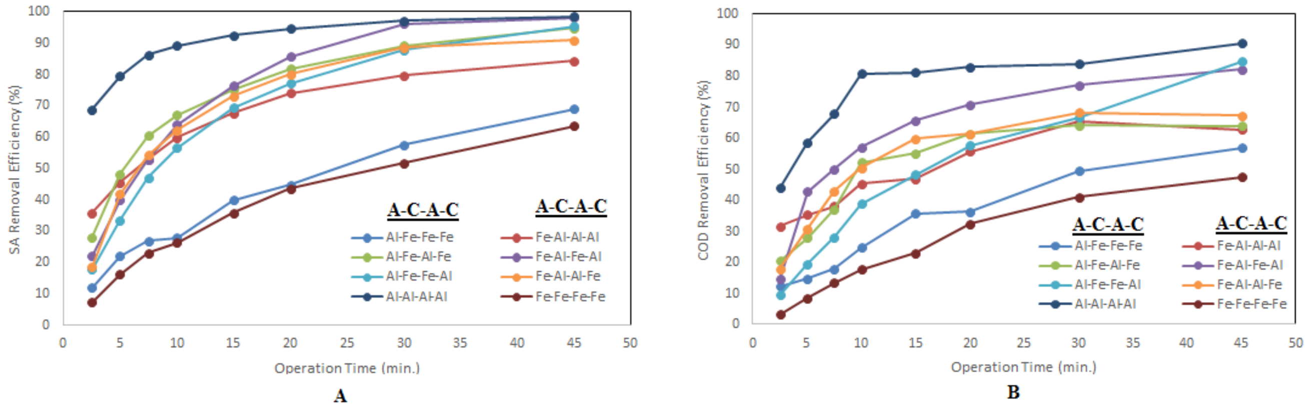


Figure 3. Effect of hybrid electrode types on removal efficiency for SA (A) and COD (B) (A: Anode, C: Cathode) (Operating conditions: pH = 6, current density = 50 A/m^2, SA concentration = 100 mg/L, air injection flow = 2 L/min, solution conductivity = 1000µs/cm, and electrode connection mode = MP-P).

Effect of electrode type on SA removal is presented in Figure 3. The greatest SA removal efficiency was observed in the shortest time with the EC process using Al-Al-Al-Al electrodes. SA removal was obtained as 89.27% in 10 min, 86.29% in 7.5 min and 79.5% in 5 min process durations. High removal efficiencies were observed during the initial 10 min. of the EC process. Remarkable changes were not observed in removal efficiencies later on. A similar trend was also observed for COD parameter. The greatest COD removal efficiency (80.79%) was observed in 10 min. EC process. The least SA and COD removals were observed in EC process using Fe-Fe-Fe-Fe electrodes (respectively as 17.65% and 26.4%). Current findings revealed that removal efficiencies in EC process with hybrid electrodes were lower than the process using only Al electrodes and higher than the process using only Fe electrodes. Al electrodes yielded better performance than Fe electrodes for SA removal in EC process. Such a case can be expressed by the efficiency of Al hydroxide monomeric and polymeric forms created during the EC process. The flocs might have adsorbed the SA. In general, adsorption, coprecipitation and flotation play an effective role in pollutant removal in EC process. Chou et al [9] in a study for SA removal used Al-Al electrodes at current density of 1.2 mA/m^2, support solution of 0.005N, initial SA concentration of 100 mg/L and EC duration of 60 min and achieved a SA removal of 88.7%. Similarly, high removal efficiency was observed in this study with Al electrodes. The higher removal efficiencies in shorter durations were because different parameters were used and reflected on EC process of the present study. Besides, cost of 10 min EC process was calculated as 0.008 €/m^3. Considering the operating costs and performance criteria, Al-Al-Al-Al electrodes and 10 min EC duration was found to be suitable for better SA removal efficiencies.

3.2 Effect of initial pH

In all electrochemical processes, pH specifies the type of metal hydroxide flocs to be formed in the reactor [15, 24, 34-35]. To investigate the effect of pH on SA removal, initial pH of SA-polluted water samples were adjusted to desired values. In EC processes with Al electrodes, initial pH levels were changed between 4-8 and then the effects of pH on SA removal were investigated. The effects of different initial pH levels on SA and COD removal are presented in Figure 4.

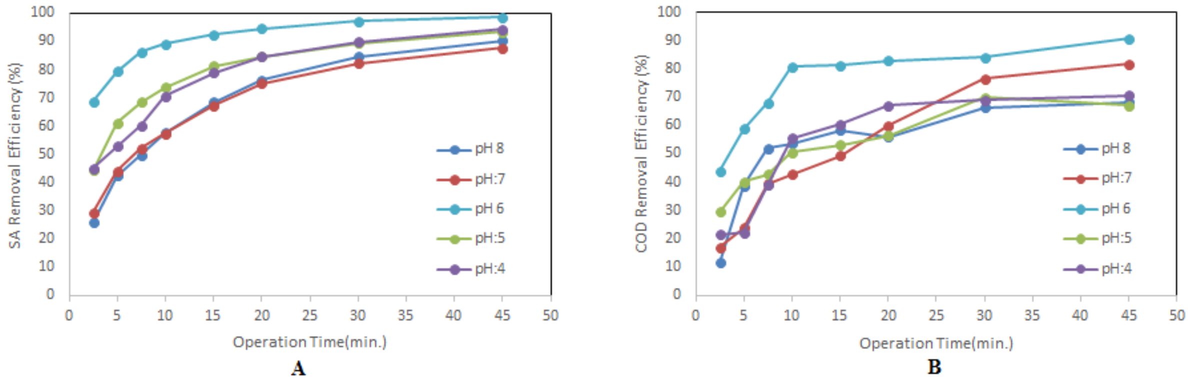
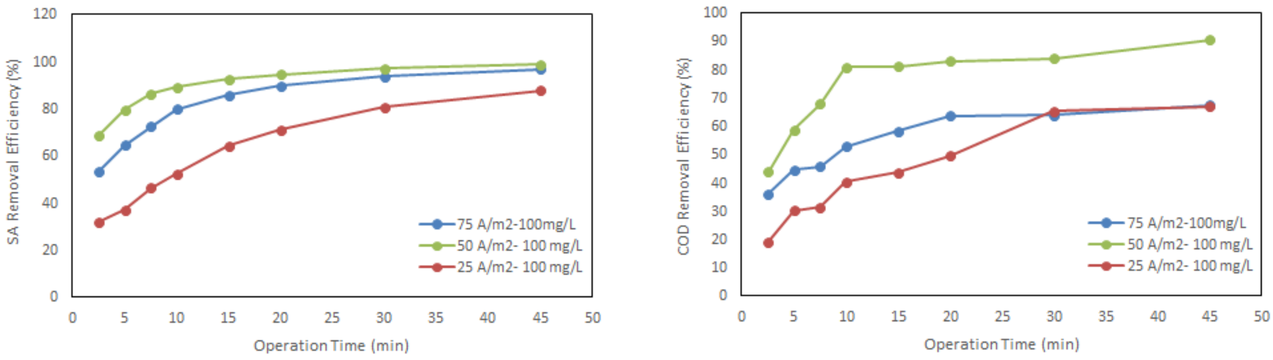


Figure 4. Effect of initial pH levels on removal efficiencies for SA (A), and COD (B) (Operating conditions: Al-Al-Al-Al electrode, current density = 50 A/m^2, initial SA concentration: 100 mg/L, air injection flow = 2 L/min, solution conductivity = 1000µs/c, and electrode connection mode = MP-P).

The greatest SA removal (89.27%) was achieved at an initial pH of 6. Lower SA removal efficiencies were observed at pH levels above and below this value. Aluminium ions formed through anodic dissolution are precipitated in hydroxide form. The pH values before and after the EC process varied between 4.5–8.8. Slight increase in pH levels in EC process are related to OH ions produced at cathode electrode and H_2 gas released from the cathode (Eq 2). Therefore, slight increases may be observed in pH levels with the OH ions produced in electrolytic reactor and the solution may turn into an alkaline form. These ions also constitute aluminium hydroxide forms. It was reported in previous studies that optimum pH levels in EC process varied between 5-8, in other words $Al(OH)_3$ flocs formed at slightly neutral or fully neutral pH levels were quite effective in pollutant removal. On the other hand, $Al(OH)_4$ flocs formed at alkaline conditions (pH>9) had lower pollutant removal efficiencies than $Al(OH)_3$ flocs [24, 25, 34, 35]. Similarly, high removal efficiencies were observed in this study for SA and COD at slightly alkaline initial pH levels (pH of 6).

3.3 Effect of current density

Current density is a significant parameter specifying and controlling reaction rate in electrochemical processes. Current density is especially significant in electrocoagulation process in finding coagulant generation and bubble production rates and floc sizes[37-40]. In present study, current density was arranged between 25-75 A/m^2 to identify the effects of current density on SA removal in EC process and the effects of current density on SA removal are presented in Figure 5.



A **B**

Figure 5. Effect of current density on removal efficiency for SA (A), and COD (B) (Operating conditions: Al-Al-Al-Al electrode, initial pH = 6, initial SA concentration: 100 mg/L, solution conductivity = 1000µs/cm, air injection flow = 2 L/min and electrode connection mode = MP-P).

SA and COD removal efficiencies increased with increasing current densities (Fig 5A, B), but decreasing efficiencies were observed after 50 A/m^2. The greatest removal efficiencies were observed at 50 A/m^2 (89.27% for SA and 80.79% for COD). According to Faraday's law, ion efficiency in anode and cathode increases with increasing current density. Then, metal hydroxide formation will also increase with that increase in current density. These metal hydroxide flocs ultimately result in higher pollutant removal efficiencies. Moreover, amount of removal of SA depends on the generated metal hydroxide flock form. The removal of SA from aqueous solutions can be explained that SA reacts with aluminum ions to form insoluble compounds and adsorbed with aluminum hydroxide flocks. When the current density increased, the amount of generated aluminum ions and aluminum hydroxide flock also increased. So the removal of SA rate increased. In addition to, for removal of pollutants is important $Al(OH)_3$ (eq.3) which have huge surface area and adsorption is very positive. The sludge generated during EC process was identified $Al(OH)_3$ flock form by XRD (section 3.7). Bubble formation rates and bubble sizes are also quite effective in pollutant removal. The decrease in pollutant removal efficiencies after a certain current intensity is mainly resulted from disintegration of flocs by high bubble formation rates and large bubble sizes. Therefore, selection of optimum current density is the critical issue to achieve high pollutant removal efficiencies in EC process. In present study, optimum current density for SA and COD removal was selected as 50 A/m^2. Operating cost for 10 min operation was calculated as 0.008 €/m^3 for 50 A/m^2, 0.005 €/m^3 for 25 A/m^2 and 0.015 €/m^3 for 75 A/m^2.

Electrode passivation is another significant issue in electrocoagulation process. Desired metal hydroxide complexes cannot be formed when there is a passivation layer over the electrodes of the process. Such a layer also increases applied potential and residual energy. Then with this layer, both removal efficiency of the process decreases and energy cost increases. Electrode passivation in electrochemical processes can be detected through monitoring current efficiency [23-25]. In EC process, current efficiency can be calculated as follows (Eq. 8):

$$C_{\text{current efficiency}} = \frac{C_{\text{experimental electrodeconsumption}}}{C_{\text{theoricialelectrodeconsuption}}} \times 100 \qquad (8)$$

Where, $C_{\text{current efficiency}}$ is current efficiency, $C_{\text{experimental electrodeconsumption}}$ is consumption of electrode during EC process. $C_{\text{theoricialelectrodeconsuption}}$ is theoretically calculated consumption of electrode. Throughout EC process, $C_{\text{current efficiency}}$ should be higher than 100%. A $C_{\text{current efficiency}}$ of less than 100% indicates a passivation. Current efficiency values never went blow 100% in this study and the values varied between 100–120%. Possible passivation can be prevented through replacing anode and cathode electrodes in certain periods.

3.4 Effect of initial SA concentration

Initial SA concentrations were arranged between 50-500 mg/L to investigate the effects of initial concentrations on SA and COD removal efficiencies and the results are presented in Figure 6. Low initial concentrations yielded higher removal efficiencies and decreasing efficiencies were observed with increasing initial SA concentrations. Removal efficiencies decreased after 100 mg/L initial concentration. Under constant current density, a certain level of metal hydroxide concentration and pollutant removal capacity can be achieved. Then the removal of a certain pollutant concentration will be achieved in short periods, but slow rates and less removal efficiencies will be experienced at higher concentrations. Current findings revealed under 50 A/m^2 constant current density and 10 min EC duration that SA and COD removal efficiencies were respectively observed as 89.50 and 75.80% for 50 mg/L, as 89.50 and 80.79% for 100 mg/L, as 31.2 and 55.6% for 150 mg/L and finally as 22.57 and 48.53% for 500 mg/L. Based on these findings at 50A/m^2 current density, optimum initial SA concentration was identified as 100 mg/L.

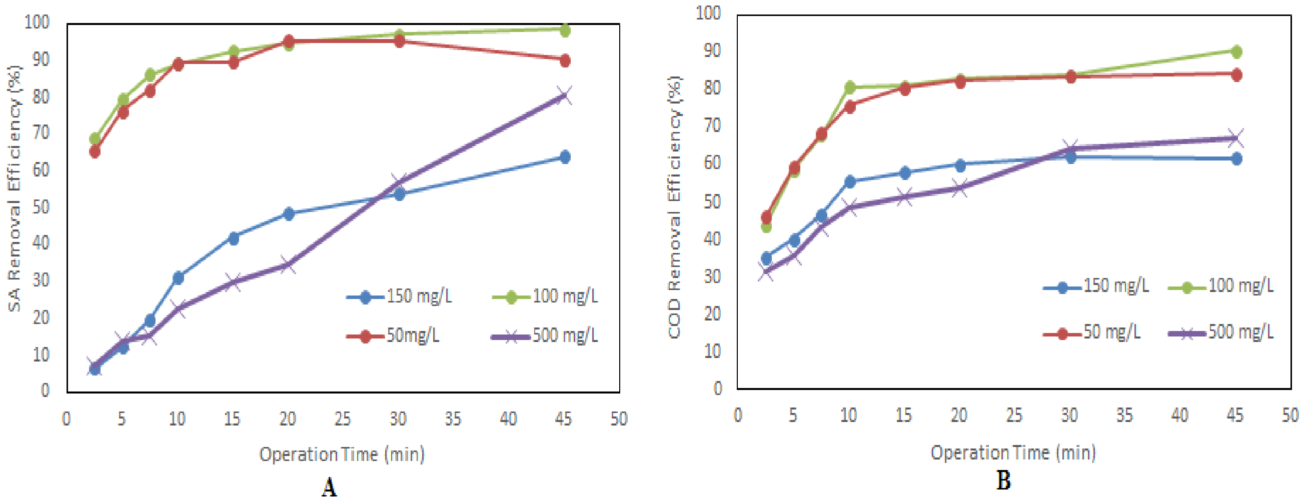


Figure 6. Effect of initial SA concentration on removal efficiency for SA (A) and COD (B) (Operating conditions: Al-Al-Al-Al electrode, initial pH = 6, current density = 50 A/m^2, air injection flow = 2 L/min, solution conductivity = 1000µs/cm, and electrode connection mode = MP-P).

3.5 Effect of air injection flow

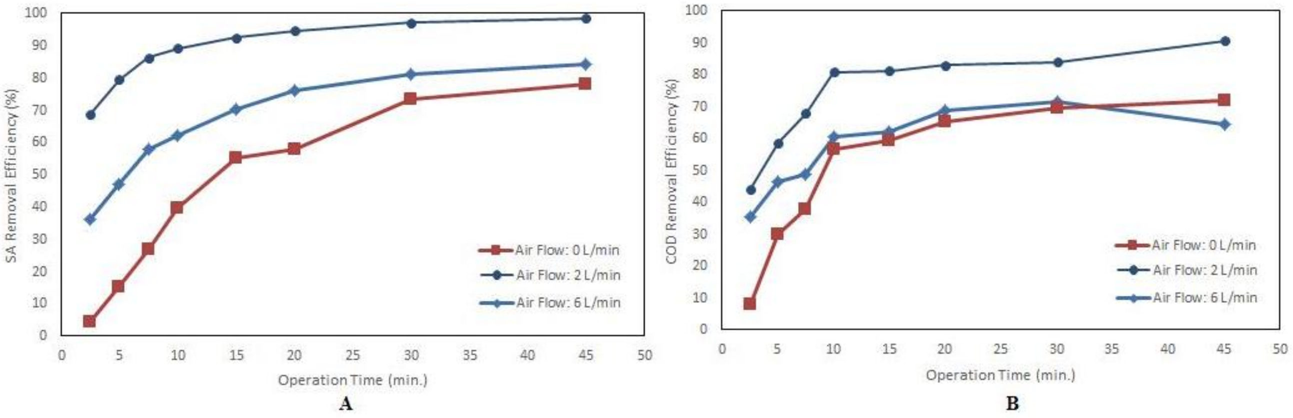


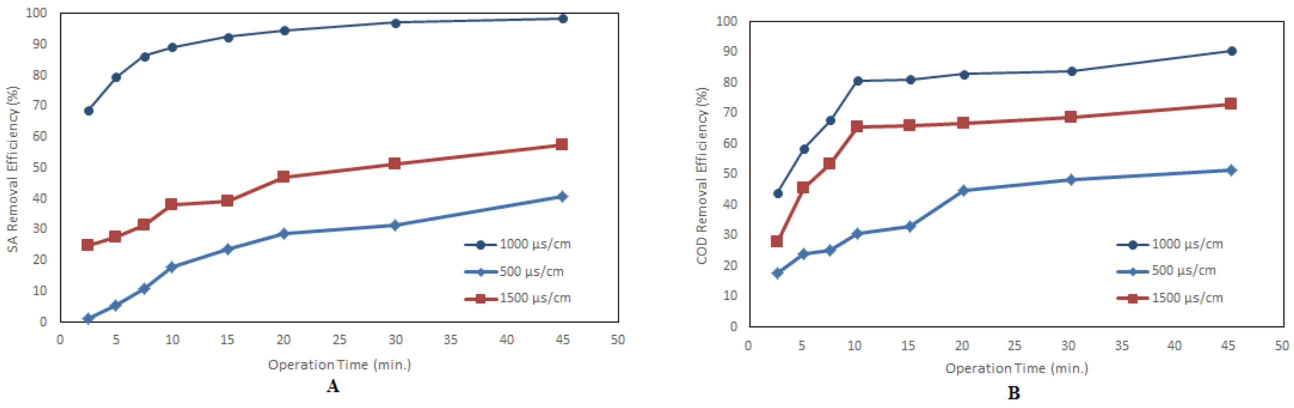
Figure 7. Effect of air injection flow on removal efficiency for SA (A) and COD (B) (Operating conditions: Al-Al-Al-Al electrode, initial pH = 6, current density = 50 A/m^2, solution conductivity = 1000µs/cm, and electrode connection mode = MP-P).

In this study, the effects of air injection flow on SA and COD removal efficiencies were investigated since air injection flow was indicated as an effective parameter in EC process. Experiments were conducted at air injection flow rates of between 0-6 L/min. Air injection both increases metal oxidation rate and capacity and supports coagulation/flocculation process through providing sufficient mixture and turbulence [35]. With air injection, dissolved oxygen oxidizes metals and supports metal hydroxide formation. All these processes improve pollutant removal from wastewaters. Previous studies reported improved pollutant removal efficiencies with air injection [22, 41, 42].

Effects of air injection on SA and COD removal efficiencies are presented in Figure 7. Air injection had positive impacts on pollutant removal efficiency. SA and COD removal efficiencies of 10 min. EC process for unaired, 2 L/min and 6 L/min air injection rates were respectively observed as 40.2-89.27-60.2% and 30.6-40.2-80.79%. Pollutant removal efficiencies increased with increasing air injection rates, but decreases were observed after 2 L/min. Lower efficiencies at higher air injection rates were because of disintegration of metal flocs with more and larger bubbles formed at higher air injection rates. In any case, it can be stated herein that air injection improved pollutant removal efficiency of EC process.

3.6 Effect of Solution Conductivity

In EC process, electrical conductivity of aqueous solutions is directly related to the voltage applied to the process [8, 43, 44]. Energy is the greatest cost item in EC processes. Thus, low voltage levels are desired to reduce operating costs. Therefore, electrical conductivity of the solution should be kept at a certain level. Support solutions (KCl, $NaSO_4$, NaCl) can be supplemented if the conductivity is too low. The effects of NaCl support solution on SA and COD removal efficiencies are presented in Figure 8.



A B

Figure 8. Effect of solution conductivity on removal efficiency for SA (A) and COD (B) (Operating conditions: Al-Al-Al-Al electrode, initial pH = 6, current density = 50 A/m^2, air injection flow= 2L/min, and electrode connection mode = MP-P).

Table 1. EC experiment results for different solution conductivities

Conductivity (µS/cm)	Voltage (V)	$Energy_{consumption}$ (kWh/m^3)	Removal percentage (%)		Current Efficiency (%)
			SA	**COD**	
500	13.4	22.4	17.99	30.71	110
1000	10.0	18.3	37.91	65.70	105
1500	8.1	12.1	89.27	80.79	92

Increased removal efficiencies were observed with increasing electrical conductivity of the solution. Applied voltage and consequently energy costs also decreased with increasing conductivities (Table1). Besides, with the use of NaCl, electrochemical Cl was produced and thus disinfection was provided. On the other hand, high NaCl conductivities (1500 µs/cm) may facilitate rusting corrosion. Such an impact may then result in local corrosions over electrode surfaces and may passivate some sections of electrode surfaces [21, 36, 45]. Low current density (Table 1) and removal efficiencies for SA and COD (Figure 8) were considered to be resulted from such impacts.

3.7 Effect of electrode connection mode

The efficiency of electrocoagulation process is greatly depend on dissolution of electrodes of the system [22, 24, 26, 27]. Dissolution forms metal hydroxide flocs. Amount of dissolved metal ions increases with increasing active anode surface area. According to literature, there are three types of connection modes in EC process (monopolar parallel-series and bipolar series) [11, 26, 27]. SA and COD removal efficiencies were investigated with Al-Al-Al-Al electrode types at three different electrode connection modes, 0-45 min process intervals, initial pH of 6, current density of 50 A/m^2, air injection flow of 2 L/min and solution conductivity of 1000 µs/cm (Figure 9). While similar removal efficiencies were achieved with monopolar connection modes, lower efficiencies were observed in bipolar connection mode. The greatest removal efficiency was obtained from MP-S mode as 95.1% for SA and 85.97% for COD. Removal efficiencies in MP-P and BP-S connection modes were respectively observed as 80.79 and 49.25% for SA and 89.27 and 46.59% for COD. Operating costs and pollutant removal efficiencies calculated for different connection modes are provided in Table 2.

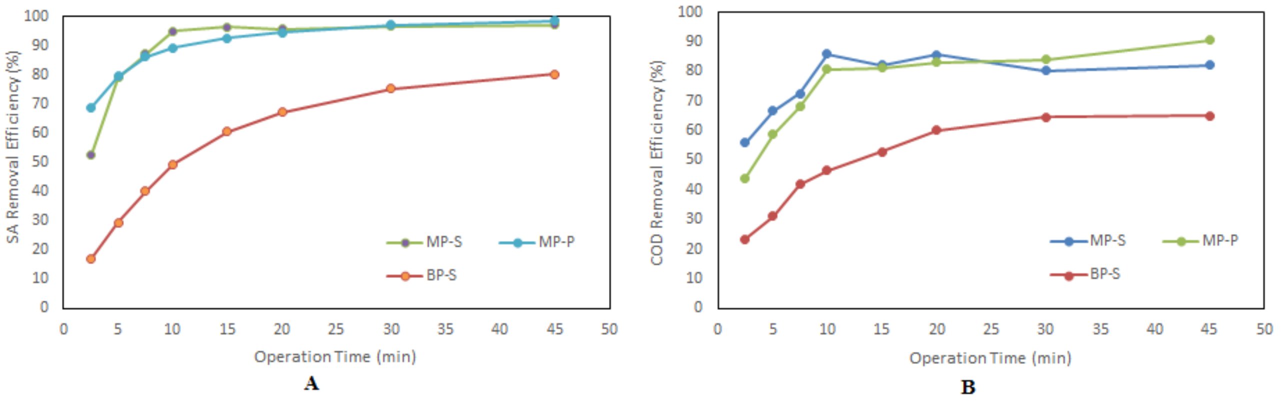


Figure 9. Effect of electrode connection mode on removal efficiency for SA (A), and COD (B) (Operating conditions: Al-Al-Al-Al electrode, initial pH = 6, curent desity = 50 A/m^2, air injection flow= 2L/min. and solution conductivity= 1000µs/cm).

Operating cost for 10 min process duration was calculated as 0.008 €/m^3 for MP-P mode, 0.0156 €/m^3 for MP-S and 0.0156 €/m^3 for BP-S connection mode. Higher operating cost of MP-S connection mode was also reported in similar studies [24, 26, 27]. High operating costs of series connection modes are commonly resulted from high potential difference between the electrodes and consequent high voltages. Such an increase in voltage also increases electricity costs.

Table 2. Removal efficiencies and operating costs at different connection modes and operation times.

	Operation Time (min.)							
	2.5	5	7.5	10	15	20	30	45
MP-P								
SA (% removal)	68.81	79.50	86.29	89.27	92.55	94.66	97.20	98.62
COD (% removal)	44.01	58.70	67.98	80.79	81.20	82.95	84.04	90.60
Operating Cost (€m^3)	0.039	0.004	0.006	0.008	0.012	0.016	0.025	0.037
Sludge production (kg/m^3)	0.05	0.08	0.012	0.016	0.15	0.25	0.35	0.63
MP-S								
SA (% removal)	52.74	79.01	87.20	95.1	93.66	95.82	96.77	97.08
COD (% removal)	55.80	66.70	72.60	85.97	82.10	85.50	80.30	82.00
Operating Cost (€/m^3)	0.039	0.078	0.117	0.156	0.234	0.312	0.467	0.701
Sludge production (kg/m^3)	0.04	0.07	0.011	0.14	0.18	0.23	0.34	0.57
BP-S								
SA (% removal)	23.39	30.99	41.95	46.59	52.79	60.10	64.52	65.11
COD (% removal)	16.95	29.27	40.09	49.25	60.43	67.20	75.34	80.25
Operating Cost (€/m^3)	0.039	0.078	0.117	0.156	0.234	0.312	0.468	0.702
Sludge production (kg/m^3)	0.03	0.06	0.08	0.10	0.16	0.21	0.31	0.49

The UV-Vis spectra of the raw and the treated wastewater with different reaction times at optimum operational conditions (Al-Al-Al-Al electrode type, initial pH of 6, current density of 50 A/m^2, SA concentration of 100 mg/L, solution conductivity of 1000µs/cm, air injection flow of 2 L/min and connection mode of MP-S) are presented in Figure 10.

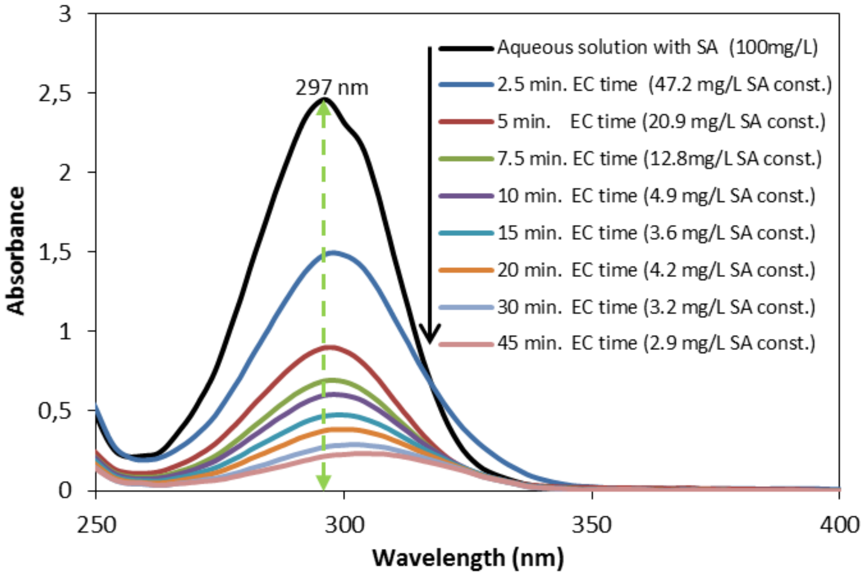


Figure 10. UV-Vis spectra of the raw and treated water at 2.5-45 min reaction times.

Several strong peaks were observed over the range of 200-400 nm corresponding to maximum absorption wavelength band of pollutants for single-ring aromatic compounds such as polycyclic aromatic hydrocarbons and heterocyclic nitrogen compounds. Furthermore, it is interesting to note that the overall absorbance of the curve decreased significantly with the increase of EC operation time, which may be due to the removal of pollutants with metal hydroxide flocs of organic compounds. The lowest peaks of the effluent by ECP were observed at 5-45 min. However, there are no changes in peaks of the spectra corresponding to components of the treated wastewater with operation time of 20 min. Figure 9 suggests that organic compounds of SA aqueous solution were oxidized and decomposed, and not completely mineralized through EC process. Some organic compounds were not destroyed during the EC process. As seen in Figure 10, the EC process was fairly effective for the removal of SA from aqueous solutions.

3.7 Characteristic of EC sludge

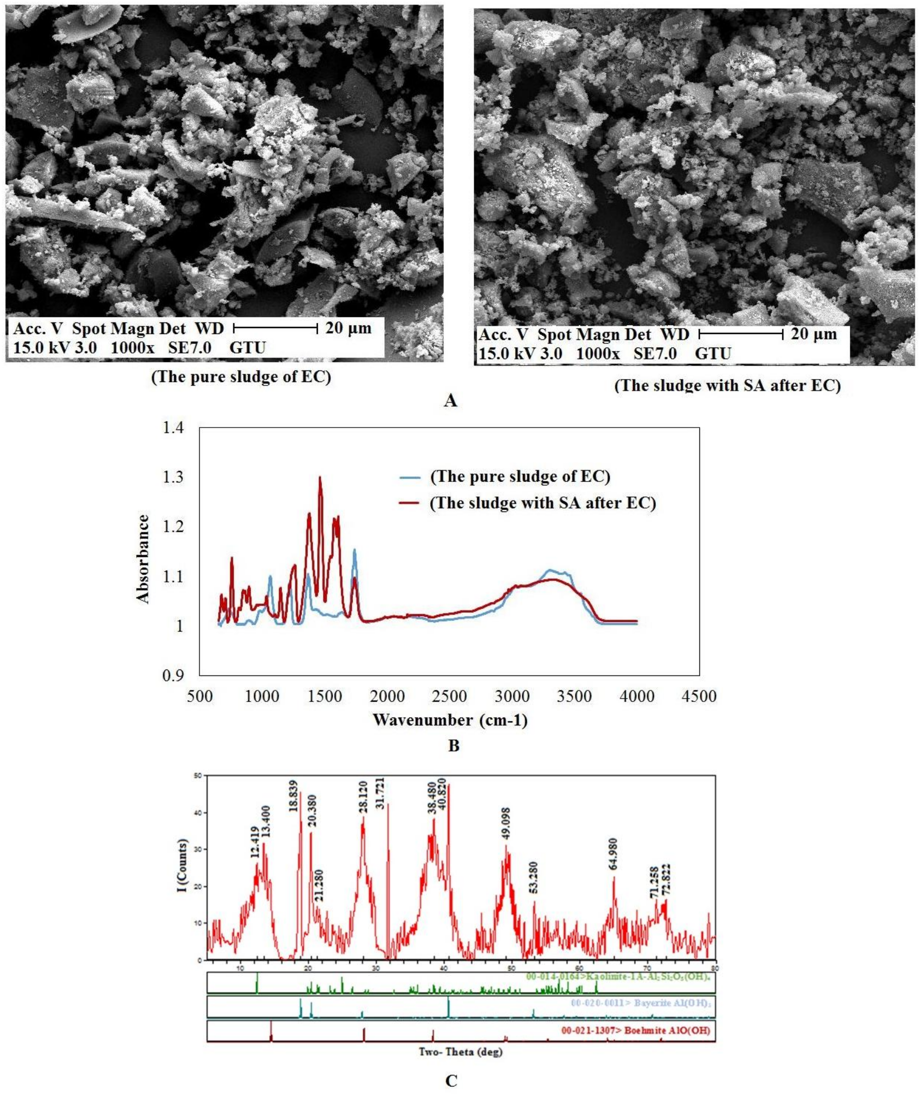


Figure 11. (A) SEM micrograph, (B) FT-IR spectrum and XRD analysis of EC sludge after removal of SA from aqueous water solution using Al-Al-Al-Al electrode pairs.

Sludge generation is another important parameter of EC process. Pollutants are removed from the wastewaters mostly in the form of sludge. Sludge generation of EC process varied with electrode connection modes. Increased SA and COD removal efficiencies also increased sludge generation since pollutants were effectively removed from the wastewater by adsorption and coprecipitation on metallic sludge. The amount of sludge produced at 10 min operation time was obtained as 0.10 kg/m^3 for BP-S, 0.016 kg/m^3 for MP-P and 0.014 kg/m^3 for MP-S.

The SEM imaging (SEM, Philips XL30S-FEG) of the resultant sludge is presented in Figure 11 (A-B). Process sludge had a size range of 20-60µm and were mostly amorphous. As it was indicated in earlier researches, other elements of the resultant sludge came from support electrolyte and chemicals used in the experiments [24-26]. The XRD of the EC sludge in Figure 11 (C) showed that existences of kaolinite ($Al_2Si_2O_5(OH)_4$), bayerite ($Al(OH)_3$ and boehmite ($AlO(OH)$) were present in the sludge sample. In the FT-IR spectrum of sludge, generated the removal of SA in EC process, the peaks observed at range of 1100- 1750 cm^{-1} can be assigned to carbohydrate (C-O C-C C-O-C) and carbonyl (C-O). The peaks at range of 3200-3300 cm^{-1} present bonded and non-bonded hydroxyl groups. These groups play role to adsorbed water. The obtained SEM, XRD and FT-IR analyses results indicated that SA in aqueous solution were linked with aluminum hydroxide and the generated sludge after EC process contained SA components.

4. CONCLUSIONS

SA removal from the aqueous solutions through EC process was investigated in this study. Among the parameters effective in EC process, effects of electrode type, initial pH, current density, SA concentration, air injection flow, solution conductivity and electrode connection mode were also investigated. Based on current findings, electrode type of Al-Al-Al-Al, initial pH of 6, current density of 50 A/m^2, SA concentration of 100 mg/L, solution conductivity of 1000µs/cm, connection mode of MP-S and process duration of 10 min were identified as optimum operational conditions. Under these conditions, 95.1% SA removal efficiency and 85.79% COD removal efficiency was attained. Operating cost under such conditions at 2.5-45 min operating times was calculated as 0.0039-0.701 €/m^3. Values of the sludge for operating times of 2.5-45 min in EC process were 0.04-0.57 kg/m^3. As to conclude, EC process with Al electrodes and different connection modes yielded quite high removal efficiencies for SA and COD.

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