Treatment of highly toxic cardboard plant wastewater by a combination of electrocoagulation and electrooxidation processes

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ABSTRACT
The objective of this study was to investigate the removal efficiencies of the electrochemical treatment systems as an alternative for the treatment of cardboard plant wastewater (CPW). In accordance with this purpose, CPW was treated by electrocoagulation (EC) with Al electrodes and the effects of current density (CD), operating time (t), and initial pH (pHi) were investigated. The results showed that EC at optimum treatment conditions (CD: 7.5 mA/cm², pHi: 7.0 and t: 60 min) have limited removal efficiencies for total organic carbon (TOC; 17.1%) and chemical oxygen demand (COD, 14.2%), on the contrary of turbidity (98.7%). Due to the low TOC and COD removal efficiencies, a secondary treatment was needed and the electrocoagulated effluent was subjected to electrooxidation (EO) by using a boron doped diamond (BDD) electrode for investigating the effect of CD, t, and inlet pH. Higher TOC (83.7%) and COD (82.9%) removal efficiencies were obtained by EO under the optimum treatment conditions (CD: 100 mA/cm², pHi: 7.2, C_E: 5.0 g/L Na_2SO_4 and t: 180 min). In addition, a toxicity test was carried out to the raw and treated wastewater under the optimum operating conditions. This study demonstrated that the combination of EC and EO have a satisfactory potential for real industrial wastewater with a high organic content, suspended solids and toxicity.

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1. Introduction
The pulp and paper industry use lignocellulogic materials (wood and/or recycled paper etc.) as a raw material, and produce paper, cardboard and other cellulose-based products. During production of the paper and cardboard, wastewater that has high suspended solids, color, and organic substance in the range from 75 to 275 m³ per ton of product (Jaafarzadeh et al., 2016) is generated. Moreover, this industrial sector wastewater contains the chlorinated lignosulphonic acids, resin acids, phenols and hydrocarbons besides dibenzo-p-dioxin and dibenzofuran, highly toxic and recalcitrant compounds (Kumar et al., 2014). Due to these components, these effluents are extremely hazardous for the ecosystem because they exhibit a strong mutagenic effect, have acute toxicity, cause a decreasing of oxygen, and prevent light penetration. Therefore, various wastewater treatment systems and their combinations have been employed to minimize the negative influence of pulp and paper industry effluents on the environment until now (Birjandi et al., 2014). Inside these treatment systems, coagulation and flocculation processes in which polyaluminium chloride (PAC) and aluminum sulphate used are used very effective for the removal of suspended solids (SS), colloids and toxicity in wastewater. However, there are two problems involving the potential ecotoxicity of metallic coagulants and other toxic components in wastewater: (I) The production of large volumes of toxic sludge, and (II) an increase in metal concentration in treated water are the main disadvantages of these systems. Another alternative treatment system in the paper industry is the biological method (mainly aerated lagoon), which is commonly used due to the low cost and minimal operation requirements. The biological methods are also very effective for the removal of soluble and biodegradable organic pollutants (Pokhrel and Viraraghavan, 2004). However, the existence of bio-refractory components in wastewater, the sensitivity of microorganisms to toxic material, production of high amounts of sludge and lengthy time requirements are the disadvantages of the biological methods (Renault et al., 2009). Due to the mentioned disadvantages, a physico-chemical method is usually needed before a biological method. Furthermore, adsorption, ozonation and membrane filtration of chlorinated phenolic compounds and adsorbable organic halides and chemical oxidation of colorful components were carried out effectively in paper industry wastewater (Pokhrel and Viraraghavan, 2004). However, these processes involve a great deal of disadvantages such as high cost, selective removal and difficulties in practice. On the other hand, due to the increasing fresh water cost and the limited discharge standards of wastewater, the focus of researchers has shifted to relatively new alternatives (Mansour and Kesentini, 2008) such as electrochemical treatment systems. Electrocoagulation (EC), electrooxidation (EO), and electro-fenton (EF) are the most promising...
electrochemical treatment systems.

Due to a great deal of competitive advantages such as no selectivity towards pollutants, low operating cost, easy operable equipment, short operation time, low requirement of chemicals, and low production amount of sludge, the EC process is frequently suggested in literature for the removal of chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), suspended solids (SS), turbidity, and toxicity (David et al., 2015; Makwana and Ahammed, 2016). Generally, a power supply (alternating current; AC or direct current; DC) and electrodes (aluminum or iron) are used during the EC process and anode electrodes are consumed under a potential. Thus, three successful stages during this process are realized: (i) formation of coagulants by electrolytic oxidation of the sacrificial anode electrode, (ii) destabilization of the pollutants, particulate suspension, and breaking of emulsions, (iii) aggregation of the destabilized phases to form flocs. The main reaction at the Al anode is shown as follows (Dastyr et al., 2015; Elabbas et al., 2015; Ezechi et al., 2014; Hamdan and El-Naas, 2014; Makwana and Ahammed, 2016; Mella et al., 2015; Vasudevan, 2012; Zaidi et al., 2016):

$$\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad (1)$$

In addition to aluminum dissolution, oxygen evolution is realized via a reaction (Eqn. 2) at the anode:

$$2\text{H}_2\text{O} \rightarrow \text{O}_2(g) + 4\text{H}^+ + 4e^- \quad (2)$$

At cathode, hydrogen evolution is realized by the following reaction (Eq. (3)) and the formed hydrogen causes the flotation of pollutants. Moreover, the produced hydroxyls ions at cathode generally cause an increase of pH.

$$3\text{H}_2\text{O} + 3e^- \rightarrow 2\text{H}_2\text{O} + 3\text{OH}^- \quad (3)$$

The hydrolysis constants for aluminum cover a very narrow range, and all of the aluminum deprotonations are ‘squeezed’ into an interval of three pH units. Therefore, except for a narrow pH region (approximately 5–8), the dominant soluble species are $\text{Al}^{3+}$ at low pH and $\text{Al(OH)}_3^{4-}$ at high pH (Gencec et al., 2012; Kobya et al., 2014; Kobya and Gencec, 2012). The produced positively charged metal ions ($\text{Al}^{3+}$) in the acidic conditions neutralize the negatively charged pollutants. At about neutral pH (5–8) metal ions hydrolyze to monomeric-polymeric aluminum hydroxides and amorphous species, $\text{Al(OH)}_3$ (sweep coagulation). Monomeric-polymeric species such as $\text{Al(OH)}^{3+}$, $\text{Al(OH)}_2^{4+}$, $\text{Al}_2\text{(OH)}_5^{3+}$, $\text{Al}_3\text{(OH)}_4^{2+}$, $\text{Al}_4\text{(OH)}_6^{2+}$, $\text{Al}_5\text{(OH)}_7^{3+}$, and $\text{Al}_6\text{(OH)}_8^{4+}$ transform initially into $\text{Al(OH)}_3$ and finally polymerize to $\text{Al(OH)}_3$ (Eqs. (4) and (5)) according to the pH of the wastewater and concentration of Al:

$$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3^{4-} + 3\text{H}^+ \quad (4)$$

$$\text{nAl(OH)}_3 \rightarrow \text{Al}_n\text{(OH)}_3\text{n} \quad (5)$$

These hydroxides are excellent coagulants and cause adsorption of pollutants. On the other hand, the formed negatively charged hydroxides such as $\text{Al(OH)}_2^-$ (Eq. (6)) usually reduce the removal efficiencies at high pH values (> 9):

$$2\text{Al} + 6\text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Al(OH)}_4^- + 3\text{H}_3\text{O}^+ \quad (6)$$

Until now, EC technology has been reported as an effective treatment system for industrial wastewater such as electroplating (Kobya et al., 2016), distillery (David et al., 2015), tannery (Elabbas et al., 2015), baker’s yeast production (Gencec et al., 2012) and textile dyeing (Kobya et al., 2014). Therefore, removal of turbidity and toxicity in cardboard plant wastewater (CPW) can be carried out successfully by EC. However, the mineralization of organic components in CPW up to the legal discharge standards of wastewater does not seem possible via EC.

EO is an effective method for the mineralization of organic substances in wastewater, though not for turbidity. Thus, the combination of EC with EO can be a good alternative for treatment of the CPW (Jaaflarzadeh et al., 2016; Zaidi et al., 2016). In addition, EO presents a large number of advantages: (I) the oxidation of pollutants up to the final product or to less toxic by-products in contrast with coagulation, membrane, filtration, and adsorption processes, (II) short oxidation time requirements, no sludge problem, non-selective to toxic and non-biodegradable material in contrast with biological oxidation processes, and (III) addition of chemical reagents not required (except for electrolytes or catalyst addition at low amounts) in contrast with chemical oxidation. EO can be categorized as direct and indirect oxidation. In the indirect oxidation process, oxidizing reagents such as chlorine, hypochlorous acid, hypochlorite, hydrogen peroxide and ozone are formed at the electrodes surfaces and then, destroy pollutants in wastewater. The direct oxidation process involves (I) electron transfer to the pollutants and (II) the forming of hydroxyl radicals on anode’s surface (Särkkä et al., 2015; Wu et al., 2014). When direct and indirect oxidations are compared, direct oxidation has some advantages such as requiring a lower amount of chemical substance and producing no secondary contaminants (Särkkä et al., 2015). The electrocatalytic activity and electrochemical stability of the electrode is a key point for direct oxidation. Although several anode materials have been used in the direct oxidation, the complete mineralization of the pollutants has been possible by use of high oxygen overvoltage anodes such as $\text{SnO}_2$, $\text{PbO}_2$ and boron doped diamond (BDD) (Panizza and Cerisola, 2001). The BDD electrode has been identified as an excellent non-active anode for the removal of pollutants in wastewater (Özcan et al., 2008) and the formation of hydroxyl radical (‘OH) on the BDD anode surface has been reported as the main removal mechanism. Due to having an inert surface and low adsorption capacity, the BDD surface interacts weakly with the ‘OH. During EO with BDD, the complete mineralization of pollutants in wastewater is possible due to the physisorbed ‘OH by the following reactions (Eqs. (7) and (8), R: organic pollutants in wastewater) (Gao et al., 2004; Marco Antonio Quiroz et al., 2006; Martínez-Huitle and Ferro, 2006; Scialdone, 2009; Sires et al., 2014):

$$\text{M} + \text{H}_2\text{O} \rightarrow \text{M(HO)}^+ + \text{H}^+ + \text{e}^- \quad (7)$$

$$\text{M(HO)}^+ + \text{R} \rightarrow \text{M} + \text{mCO}_2 + n\text{H}_2\text{O} + \text{H}^+ + \text{e}^- \quad (8)$$

Although scientists recent attention has focused on EO, there is a lack of information in literature regarding EO: (I) removal efficiencies of EO in different real wastewater (only 20% EO paper in the last 3 years have dealt with treatment of the real wastewater), (II) comparison of the electrodes performance, (III) contribution level on removal efficiencies of EO at a combination of different treatment systems, (IV) removal mechanism, (V) electrical consumption (Sires et al., 2014) and (VI) possible formation of toxic by-products. To the best of the author’s knowledge, the combination of the electrocoagulation (Al electrode) and electrooxidation processes (BDD electrode) has yet to be studied for the treatment of CPW. Moreover, the influence of the EC and EO combination on toxicity of real wastewater has not been investigated sufficiently.

Therefore, the purposes of this study were: (I) present the combination of EC and EO as a competitive alternative for the treatment of industrial wastewater with high suspended solids, organic content and toxicity, (II) investigate the effect of process conditions on removal efficiencies, and (III) calculate the electrical and electrode consumption during these processes.

2. Material and methods

2.1. Wastewater

The wastewater was taken from the starting point of a cardboard plant treatment system. The coated cardboard is made out of recycled paper and the annual cardboard production capacity of the plant has reached 240,000 t (Table 1).
Electrode consumption (ELC, kg/m³, Eq.(10)) were calculated via Faraday’s Law:  

\[ \text{ELC} = \frac{U \times i \times t}{F \times v} \]  

(9)  

During the EC process, three major interaction mechanisms, charge neutralization, adsorption and sweep flocculation are dominant at different pH values (Hamdan and El-Naas, 2014; Jaafarzadeh et al., 2016; Kobya et al., 2016). The optimum values of these parameters are changeable according to the characterization of the wastewater (pH, pollutants species, affinity of pollutants etc.) and species of electrodes (Al, Fe etc.). Therefore, Al electrode was used as a sacrificial electrode in this study and optimum process conditions were evaluated by a series of experiments in order to remove the COD, TOC and turbidity.

3. Results and discussion

As seen in Table 1, CPW has a high organic content, suspended solids and toxicity. In this study, the effect of initial pH (pHi), current density (CD, mA/cm²), and operating time (t, min) were investigated during EC with Al electrode. Following this, the electrocoagulation wastewater was treated by EO processes under different experimental conditions: pHi, CD, t, and electrolyte concentration (C_e) with BDD electrode.

3.1. Effect of processes parameters on EC

It is well known that pHi, CD (A/m²) and t (min) are the major parameters which affect the removal efficiencies in the EC process (Hamdan and El-Naas, 2014; Jaafarzadeh et al., 2016; Kobya et al., 2016; Makwana and Ahammed, 2016). The optimum values of these parameters are changeable according to the characterization of the wastewater (pH, pollutants species, affinity of pollutants etc.) and species of electrodes (Al, Fe etc.). Therefore, Al electrode was used as a sacrificial electrode in this study and optimum process conditions were evaluated by a series of experiments in order to remove the COD, TOC and turbidity.

The effect of pH on treatment efficiencies was examined at 3.0, 4.0, 6.0, 7.0, 9.0, and 10.0 pHs over a period of 60 min. It is clear that when the pH value was altered towards two extremes, the TOC and COD removal efficiencies decreased (Fig. 1a and b). The maximum removal efficiencies were obtained for TOC (16.8%) and COD (10.1%) at pH 7, and for turbidity (97%) at pH 10. The original pHi value (pHi7) of CPW seemed as the optimum one due to the unnecessary pH arrangement and the obtained high removal efficiencies for TOC (16.8%), COD (10.1%) and turbidity (95%, residual turbidity: 38 NTU).

During the EC process, three major interaction mechanisms, charge neutralization, adsorption and sweep flocculation are dominant at different pH ranges and metal concentrations since pH and metal concentration affect the solubility of metal species in wastewater (Fig. 2c, only mononuclear Al species were considered). In low pH values, charge neutralization is dominant and realized by mono metal species such as Al³⁺ which are produced at the anodes. These positively charged metal ions neutralize the anionic charges of pollutants in wastewater and reduce their solubility. Between the pH range 5.0–8.0, amorphous metal hydroxides which have a large specific surface area

### Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (m³/day)⁴</td>
<td>6000–8000</td>
<td>COD (mg/L) 2358</td>
</tr>
<tr>
<td>pH</td>
<td>6.9–7.1</td>
<td>TOC (mg/L) 1006</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>2.27±25</td>
<td>NH₃-N (mg/L) &lt; 0.5</td>
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<tr>
<td>Turbidity (NTU)</td>
<td>783</td>
<td>SO₄²⁻ (mg/L) 241</td>
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<tr>
<td>Total Solids (mg/L)</td>
<td>3000–5850</td>
<td>PO₄³⁻ (mg/L) 2.3</td>
</tr>
<tr>
<td>Settelle Solids (mg/L)</td>
<td>750–850</td>
<td>EC₅₀ 20.11</td>
</tr>
<tr>
<td>Total Suspended Solids (mg/L)</td>
<td>3000–5000</td>
<td>EC₂₀ 6.52</td>
</tr>
</tbody>
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⁴ ELC₅₀ and ELC₂₀: The concentration of wastewater that causes 50% and 20% of bacteria reduction relative to control sample, respectively.

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2.2. The experimental set-up and analytical methods

The EC experiments were realized by a batch process using a 1 L capacity of a reactor made from Plexiglas with dimensions of 12 × 11 × 11 cm. Aluminum (Al) plates (purity > 99.5%) with dimensions of 5.0 × 8.0 × 0.3 cm were used as the sacrificial electrodes. In each run, four Al plate electrodes (two anodes and two cathodes) spaced by 0.5 cm were placed vertically in the reactor and connected at the monopolar parallel mode. All the EC runs were performed with 0.85 L of wastewater at a constant 25°C and 300 rpm (Heidelberg MR 3000D). Before each run, the impurities on the electrode surfaces were removed by a hydrochloric acid-hexamethylenetetramine aqueous solution. The electrodes were dipped into the wastewater to a depth of 80 mm yielding a total effective electrode surface area of 120 cm² (Gengec et al., 2012). Then, the current was arranged at the desired value and the experiment was started. The samples taken from the EC reactor at different operating times were analyzed. At the end of the EC runs, electrical energy consumption (ENC, kWh/m³, Eq. 9) and electrode consumption (ELC, kg/m³, Eq. (10)) were calculated via Faraday’s Law:

\[ \text{ENC} = \frac{U \times i \times t}{F \times v} \]  

(9)  

\[ \text{ELC} = \frac{i \times t \times M_e}{z_A \times F \times v} \]  

(10)  

where U is cell voltage (V), i is current (A), t is operating time (s) and v is volume (m³) of wastewater, M_e is molecular mass of aluminum (26.98 g/mol), z_A is number of electron transferred (z_A = 3) and F is Faraday’s constant (96,487 C/mol).

EO experiments were conducted in batch mode by using an open, undivided, glass cell (12 × 9 × 7 cm). The 0.75 L capacity glass cell was 39 cm². The BDD anode was supplied by DiaCon GmbH, the electrode was used in EO experiments and the effect of processes parameters on EC (t, min) were investigated during EC with Al electrode. Following this, the electrocoagulation wastewater was treated by EO processes under different experimental conditions: pHi, CD, t, and electrolyte concentration (C_e) with BDD electrode.
formed and sweep flocculation of pollutants is possible. Moreover, polynuclear and polymeric species at higher and lower pH values cause adsorption (Elabbas et al., 2015; Gengec et al., 2012; Metcalf and Eddy, 2004). In this study, at 6.0 mA/cm² and 7 pH, the produced Al concentration was calculated by Faraday’s laws (Eqn. 10) as $\times 1.76 \times 10^{-3}$, $3.51 \times 10^{-3}$, $7.02 \times 10^{-3}$, $1.05 \times 10^{-2}$, $1.4 \times 10^{-2}$, $1.76 \times 10^{-2}$, and $2.11 \times 10^{-2}$ molar for 5, 10, 20, 30, 40, 50, and 60 min, respectively. According to these results and Fig. 1c, sweep flocculation seemed as the dominant removal mechanism in this study.

As mentioned before, the pH and the Al concentration affect the species of Al which not only influences the treatment efficiency but also the operating cost of the EC process. According to Faraday Law’s (Eq. (10)), the dissolved amount of coagulant at the anode depends on current density (calculated by dividing the applied current by the active electrode area), and operating time. Moreover, current density and operation time determine the bubble production rate at the electrode, which causes electrofo flotation. For the reasons mentioned above, the effects of current density and operating time were investigated (Fig. 2) in the range of 3.0–12.0 mA/cm² and 0–60 min, respectively. The maximum removal efficiencies at 3.0, 6.0, 7.5, 12.0 mA/cm² during 60 min were obtained as 14.2%, 16.8%, 17.1%, and 18.2% for TOC, 10.2, 11.0, 12.8, 13.8, and 14.1 for COD, and 92.3%, 95.9%, 98.7%, and 98.7% for turbidity, respectively. As seen in results, the increased current density and operating time improved removal efficiencies slightly and caused an increasing of electrical (Fig. 2c) and electrode consumptions. The electrical (Eq. (9)) and electrode consumptions (Eq. (10)) were calculated respectively as 1.85, 5.50, 9.18, 13.90, and 21.30 kWh/m³ and 0.142, 0.284, 0.355, 0.466 and 0.569 kg Al/m³ for 3.0, 6.0, 7.5 and 12.0 mA/cm² during 60 min. Thus, 7.5 mA/cm², 7 of pH, and 60 min were selected as the optimum operating conditions. The EC process was an effective method for the removal of turbidity during the treatment of CPW. In addition, the quality of the EC effluent under the optimum conditions (residual TOC: 834 mg/L; residual COD:2025 mg/L and residual turbidity: 10 NTU) meets the reuse standards for turbidity in the paper industry, which is 14–56 NTU (Terrazas et al., 2010) during the paper bleaching stage. However, the obtained TOC and COD removal efficiencies with the EC were very low when compared with other studies which dealt with the treatment of the paper industries wastewater by EC (Jaafarzadeh et al., 2016). The various used raw materials (recycled paper, wood etc.) and the production conditions of cardboard may cause this phenomenon. As a result, it was determined that the EC could be used efficiently for the removal of high molecular weight dissolved organic matters (Kamali and Khodaparast, 2015), turbidity and suspended solids and it is a competitive alternative to be conducted prior to an oxidation treatment system.

3.2. Effect of processes parameters on EO

During the EO process, the current density is one of the most important driving forces because it not only affects the degradation rate of the EO but also the reactions rate (bubble production rate, O₂ reduction/evaluation rates etc.) (Gengec et al., 2012; Kourdali et al., 2014). Thus, the electrocoagulated CPW at the presence of 2 g/L Na₂SO₄ as the electrolyte was treated at different current densities (from 25 mA/cm² to 100 mA/cm²). When 25, 50, 75 and 100 mA/cm² of the current densities were applied, the removal efficiencies were increased to 47.5%, 66.8%, 77.9%, and 88.2% for TOC and 49.2%, 68.0%, 80.0%, 0.569 kg Al/m³ for 3.0, 6.0, 7.5 and 12.0 mA/cm² during 60 min. Thus, 7.5 mA/cm², 7 of pH, and 60 min were selected as the optimum operating conditions. The EC process was an effective method for the removal of turbidity during the treatment of CPW. In addition, the quality of the EC effluent under the optimum conditions (residual TOC: 834 mg/L; residual COD:2025 mg/L and residual turbidity: 10 NTU) meets the reuse standards for turbidity in the paper industry, which is 14–56 NTU (Terrazas et al., 2010) during the paper bleaching stage. However, the obtained TOC and COD removal efficiencies with the EC were very low when compared with other studies which dealt with the treatment of the paper industries wastewater by EC (Jaafarzadeh et al., 2016). The various used raw materials (recycled paper, wood etc.) and the production conditions of cardboard may cause this phenomenon. As a result, it was determined that the EC could be used efficiently for the removal of high molecular weight dissolved organic matters (Kamali and Khodaparast, 2015), turbidity and suspended solids and it is a competitive alternative to be conducted prior to an oxidation treatment system.

Fig. 1. Effect of pH (CD: 6.0 mA/cm², initial TOC: 1006 mg/L, initial COD: 2358 mg/L, and initial turbidity: 783 NTU) on (a) TOC, (b) COD, (c) turbidity, and (d) Activity–pH diagram for Al(III) species in equilibrium with Al(OH)₃ (amorphous) (Ghernaout et al., 2009; Metcalf and Eddy, 2004; Yılmaz et al., 2007).
and 89.2% for COD during 180 min (Fig. 3a and b), respectively. It is well known that the rise of the current density causes the increase of \( \cdot \text{OH} \) generation on the BDD anode. Therefore, higher removal efficiencies were possible using an increased current density and these results are well in agreement with literature. For instance, Jalife-Jacobo et al. (2015) studied the diazo dye Congo Red (3 L of 100 mg/L) degradation using a BDD anode. They reported that when the current density rose from 7.5 to 50 mA/cm\(^2\) at the presence of Na\(_2\)SO\(_4\), removal efficiencies were increased from 15% to 50%, respectively. Moreover, Jong Young Choi et al. (2010) investigated the effect of the various CD (5, 15, and 25 mA/cm\(^2\)) on the degradation of 1,4-dioxane, a refractory water pollutant with COD = 32 mol O\(_2\)/m\(^3\), by BDD electrode at 5.5 of pH, and the presence of 5 g/L of Na\(_2\)SO\(_4\). They showed that a higher current density had a much faster degradation rate. The complete degradation of 1,4-dioxane occurred at about 18 min at 5 mA/cm\(^2\) and 7 min at 25 mA/cm\(^2\) (the results were seen at graph). As can be seen by these studies, current density in EO systems affect the removal efficiencies depending on other conditions such as pollutant type, the presence of electrolyte, electrolyte species, operating time and pH.

It must be noted that the rise current density from 25 mA/cm\(^2\) to 100 mA/cm\(^2\) (Fig. 3c) not only increased the removal efficiencies but also the electrical consumption (Eqn. 9) from 76.03 kWh/m\(^3\) to 678.28 kWh/m\(^3\) (average volt from 12.93 to 28.99). These higher electrical consumptions should be decreased for economic reasons.

The best way of lowering electrical consumption was to decrease wastewater resistance via the addition of electrolyte into the wastewater. It is well known that adding electrolyte such as NaCl, KCl, Na\(_2\)SO\(_4\), HClO\(_4\), and H\(_2\)SO\(_4\) decreased electrical consumption in all electrochemical treatment processes. In addition to the decreasing electrical consumptions, the inclusion of electrolyte usually causes an increase of removal efficiencies (Jalife-Jacobo et al., 2015). Most studies have shown that the highest removal efficiencies were obtained by usage of NaCl in comparison with other electrolytes. However, it was reported that the usage of NaCl caused the production of many organochlorinated species as intermediates and final products that can be even more harmful than the raw pollutants (Comninellis and Pulgarin, 1991; Gotsi et al., 2005; Sires et al., 2014). Therefore, Na\(_2\)SO\(_4\) was used between 2.0 g/L and 6.0 g/L of concentrations at 7.2 of pH and 100 mA/cm\(^2\) of CD in order to observe the effects of supporting electrolyte on electrical consumption and removal efficiencies. The addition of 2.0, 3.0, 4.0, 5.0, and 6.0 g/L Na\(_2\)SO\(_4\) (Fig. 4a) decreased the potentials of the process (28.99, 25.75, 22.46, 20.07, and 19.06 V) and electrical consumption (678.29, 602.51, 525.64, 469.52 and 446.07 kWh/m\(^3\)), respectively. According to these results, the addition of 5.0 g/L Na\(_2\)SO\(_4\) seemed as an optimum electrolyte concentration due to providing balance between electrical and chemical consumption. These results indicated that electrical consumption could be decreased up to 34% by adding electrolyte. On the other hand, the effect of adding electrolyte into wastewater was commonly reported as not only causing the decrease of electrical consumption but also the increase of removal efficiencies. Generally, significant progresses in removal efficiencies by the forming of radicals and stable oxidants were reported by the usage of Na\(_2\)SO\(_4\) (Eqs. (11) and (12)) (Jalife-Jacobo et al., 2015; Sires et al., 2014):

\[
\text{(11)} \quad \text{SO}_4^{2-} \rightarrow (\text{SO}_2)^\cdot + e^- \\
\text{(12)} \quad (\text{SO}_4)^\cdot + (\text{SO}_4)^\cdot \rightarrow S_2\text{O}_5^{2-}
\]

However, in this study the increasing of electrolyte (2.0, 3.0, 4.0, 5.0, and 6.0 g/L Na\(_2\)SO\(_4\)) caused a slightly decreasing in removal

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Fig. 2. Effect of current density (pH: 7.0, initial TOC: 1006 mg/L, initial COD: 2358 mg/L, and initial turbidity: 783 NTU) on (a) TOC (b) COD and (c) Turbidity.
efficiencies (88.24%, 87.28%, 84.92%, 83.66%, and 83.65% for TOC and 89.2%, 85.8%, 82.6%, 82.86%, and 81.1% for COD) (Fig. 4a and b). The stated decline in removal efficiencies (only 5% for TOC and 8% for COD) showed that the radicals were not formed or the formed radicals $\left( SO_4^{-} \right)$ had an antagonistic effect on the other components in wastewater under tested conditions. Similar to our results, a slight decline or no effect on removal efficiencies during an increased amount of electrolyte was reported in some other studies (Bottesi, 2016; Choi et al., 2010).

The pH of wastewater affects chemical properties of pollutants and the interaction of pollutants with the electrode in EO. Therefore, the effect of the initial pH was investigated in Na$_2$SO$_4$ medium (TOC$_i$: 836 mg/L, COD$_i$: 2025 mg/L, Ce: 5.0 g/L Na$_2$SO$_4$ and CD: 100 mA/cm$^2$). As seen in Fig. 5, after 180 min of electrolysis, the removal efficiencies at pH 2.0, 4.0, 6.0, 7.2, 8.0, and 10.0 were recorded as 78.7%, 79.0%, 82.2%, 83.7%, 84.3% and 85.7% for TOC and 75.0%, 77.1%, 79.4%, 82.9%, 83.0% and 84.0% for COD, respectively. The degradation efficiencies during the EO were slightly higher at > 6 pH than acidic medium. Therefore, EO results showed that the electrocoagulated wastewater could be used in EO without any pH arrangement due to the final pH of electrocoagulated wastewater measured as 7.2 under the optimum process condition of EC, as stated in Section 3.1. Similar to our results, Lissens et al. (2003), Canizares et al. (2004a, 2004b) and Kparal et al. (2007) reported that the oxidation process by BDD electrode is more favourable in neutral and/or alkaline medium. On the other hand, Choi et al. (2010) indicated that pH had no influence on removal efficiencies and Scialdone et al. (2008) reported higher removal efficiencies at an acidic medium. According to this literature, it can be concluded that the effect of pH strongly depends on the nature of the wastewater.

3.3. Evaluation of acute toxicity of wastewater during EC and EO

Generally, the toxicity levels of wastewater are identified by the EC$_{50}$ and EC$_{20}$ values. The EC$_{50}$ and EC$_{20}$ values are the concentration of wastewater that causes 50% and 20% of bacteria reduction relative to a control sample, respectively. In this study, these values were determined according to the ISO Standard Method (21338, 2010) by Vibrio fischeri, a species of bioluminescent bacterium.

The EC$_{50}$ and EC$_{20}$ values of raw wastewater were calculated as 20.11 and 6.52, respectively. It meant that the wastewater had high acute toxicity and when wastewater was evenly diluted at the ratio of 20.11 and 6.52, it caused a 50% and 20% of bacteria reduction in 30 min, respectively. As seen in Table 2, the inhibition ratio for treated wastewater by EC and EO were below 50% for the whole dilution series. These results indicated that the treated wastewater was not toxic (Kováts et al., 2012). Moreover, the measured negative inhibition values demonstrated that better life conditions for bacteria were formed after treatment by EC and EO. The possible way for negative inhibition values is explained by the presence of organic substances (non-toxic or low concentration of toxic compound) which were used as nutrients by bacteria and thus, the amount of bacteria increased. The obtained toxicity test results were quite promising when compared with the literature. In contrast with our findings, some studies which dealt with toxic wastewater reported that toxicity during the EO process rose due to the increase of toxic materials such as organochlorinated species (Chatzisymeon et al., 2006; Gotsi et al., 2005).
4. Conclusions

The EC and EO processes were used to treat cardboard plant wastewater. The optimum process conditions were determined as 7.5 mA/cm², pH of 7.0, and 60 min for EC and 100 mA/cm², pH of 7.2, 5.0 g/L Na₂SO₄ and 180 min for EO. Satisfactory removal efficiencies for turbidity (98.7%), TOC (86.4%) and COD (85.3%) were provided via a combination of EC and EO under the optimum process conditions. Treated wastewater by EC and EO had 347 mg/L of COD, 86.4 mg/L of TOC, 10 NTU of turbidity and 9.2 of pH. It must be noted that EC only provided an effective removal in turbidity. On the other hand, a large fraction of organic component was removed during EO systems. Current density and operating time had an important effect on the removal efficiency for both electrochemical treatment systems. Moreover, both processes showed optimum removal efficiencies at a neutral pH value. Thus, under the optimum processes conditions, a chemical addition for pH arrangement was not necessary in either system. However, the addition of electrolyte during EO was necessary due to causing a decrease of electrical consumption.

According to toxicity test results, EC with Al electrode has an important potential for decreasing acute toxicity in wastewater. In addition, the forming of toxic species, one of the disadvantages of the EO

![Fig. 4. Effect of electrolyte concentration and time on (a) electric potential, (b) TOC and (c) COD removal (CD:100 mA/cm², pH: 7.2, initial TOC: 1006 mg/L, initial COD: 2358 mg/L, and initial turbidity: 783 NTU).](image)

![Fig. 5. Effect of pH and time on (a) TOC and (b) COD removal (CD: 100 mA/cm², Ce: 5.0 g Na₂SO₄/L, initial TOC: 1006 mg/L, initial COD: 2358 mg/L, and initial turbidity: 783 NTU).](image)
E. Gengec

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Table 2

<table>
<thead>
<tr>
<th>Wastewater Dilution Ratios (%)</th>
<th>Inhibition Ratios (Inh %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw EC effluent</td>
</tr>
<tr>
<td>50.00</td>
<td>66.06</td>
</tr>
<tr>
<td>33.33</td>
<td>63.51</td>
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<tr>
<td>25.00</td>
<td>62.46</td>
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<tr>
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<tr>
<td>6.25</td>
<td>12.35</td>
</tr>
</tbody>
</table>

process, was not observed or the concentration of the toxic compound was low and the bacteria were using it as nutrient. It meant that the usage of Na2SO4 was a good choice in terms of toxicity test results. This study demonstrated that the combination of EC and EO processes, which have a great deal of advantages such as easy operable equipment, short operation time, low requirement of chemicals, is a vigorous alternative for the treatment of wastewater with a high turbidity, organic content and toxicity.

Conflict of interest

The author declares that there are no conflicts of interest and affirm that this paper consists of original and unpublished work.

References


