Treatment of vinegar industry wastewater by electrocoagulation with monopolar aluminum and iron electrodes and toxicity evaluation
Seval Yılmaz, Emine Esra Gerek, Yusuf Yavuz and Ali Savaş Koparal

ABSTRACT
We present electrocoagulation (EC) treatment results of vinegar industry wastewater (VIW) using parallel plate aluminum and iron electrodes, and analyze the toxicity of the treatment processes. Due to the chemical complexity of vinegar production wastewater, several parameters are expected to alter the treatment efficiency. Particularly, current density, initial pH, Na₂SO₄ as support electrolyte, polyaluminum chloride (PAC) and kerafloc are investigated for their effects on chemical oxygen demand (COD) removal. Following several treatment experiments with real wastewater samples, aluminum-plate electrodes were able to reach to a removal efficiency of 90.91% at pH 4, 10 mg/L PAC and an electrical current density of 20.00 mA/cm², whereas iron-plate electrodes reached to a removal efficiency of 93.60% at pH 9, 22.50 mA/cm² current density. Although EC processes reduce COD, the usefulness of the system may not be assessed without considering the resultant toxicity. For this purpose, microtox toxicity tests were carried out for the highest COD removal case. It was observed that the process reduces toxicity, as well as the COD. Consequently, it is concluded that EC with aluminum and iron electrodes is COD removal-wise and toxicity reduction-wise a plausible method for treatment of VIW, which has high organic pollutants.

Key words | COD, electrocoagulation, toxicity, vinegar industry wastewater

INTRODUCTION
Water is no longer a free commodity for the society. In fact, the cost of water is, now, almost the same as other raw materials used in the industry. Almost all the water used in the industry is discharged in the form of wastewater. Uncontrolled discharge of industrial wastewater leads to many important environmental problems and this situation is harmful to human beings. For this reason, it is necessary to reduce the use of water, treat the wastewater to reuse or provide discharge standards before discharging wastewater (Ranade & Bhandari 2014). Despite the fact that industrial wastewater characteristics vary among different sub-sectors, chemicals, pharmaceuticals, rich organic content in the form of sugars, proteins and oils and fats are dominant industrial sub-products. One of the basic sub-sectors of industrial wastewater is the food industry, and vinegar has an important share within the food industry. Since vinegar is heavily used as a food preservative or condiment in other food industries its demand has increased substantially in the last decade worldwide, increasing the corresponding wastewater (Qi et al. 2014; Schlepütz & Büchs 2014).

Like other industrial wastewater cases, vinegar has high organic pollutant load. During vinegar production, acetic acid bacteria stoichiometrically oxidize ethanol to acetic acid and water. Resulting hazardous products are typically discharged to the sewerage system and are only partially treated using biological wastewater treatment techniques. Unfortunately, traditional methods mostly fail to efficiently treat such wastewater, due to their inherent acidity and heavy pollution load (Valero et al. 2014). For instance, the vinegar industry wastewater (VIW) was previously studied by us through chemical coagulation with alum (Al₂(SO₄)₁₈H₂O) and iron(III)-chloride (FeCl₃·6H₂O). In those previous chemical coagulation studies with alum, 41.82% chemical oxygen demand (COD) removal was observed at pH 7 and 75 mg/L alum concentration, whereas iron(III)-chloride reached to a removal efficiency of only 30.77% at pH 9,
100 mg/L iron(III)-chloride (Yilmaz 2013). Due to these low removal rates, it is necessary to develop and implement innovative and efficient methods for the treatment of such wastewaters. In this study, an attempt to apply advanced treatment techniques was made for VIW, with an aim of environmental and economical sustainability.

A popular treatment method for the food industry is biological treatment, which includes anaerobic process, oxidation ponding, trickling filters, and activated sludge removal. However, pollutant type, pollution load and the volume of wastewater varies dramatically, depending on the food product. Therefore, usefulness of this technique requires specific experimentation (Di Berardino et al. 2000; Ranade & Bhandari 2014). For the case of vinegar wastewater, the acidity of the medium was observed to render this method almost obsolete. An immediate alternative for such wastewater media is known to be application of electrochemical processes (An et al. 2017; Franco et al. 2017; Baran et al. 2018). Certain advantages of the electrocoagulation (EC) method allow the use of this method in the treatment of many industrial wastewaters. For this reason, a lot of research is being conducted in this area with electrocoagulation method being the process type, particularly using aluminum (Al), iron (Fe), or hybrid Al/Fe electrodes (Feng et al. 2003; Chen 2004; Nariyan Sillanpää & Wolkersdorfer 2017; Devlin et al. 2018).

The main chemical reactions occurring in aluminum electrodes during electrocoagulation process are as follows.

At the anode, aluminum oxidation occurs,

\[
Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3e^{-} \quad (1)
\]

At the cathode, water reduction occurs,

\[
3H_2O(l) + 3e^{-} \rightarrow 3/2H_2(g) + 3OH_{(aq)}^- \quad (2)
\]

At acidic conditions,

\[
Al_{(aq)}^{3+} + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3H_{(aq)}^+ \quad (3)
\]

At alkaline conditions,

\[
Al_{(aq)}^{3+} + 3OH_{(aq)}^- \rightarrow Al(OH)_3(s) \quad (4)
\]

According to reactions (1)–(4), electrodes provide metal dissolution and water oxidation/reduction at different conditions. In the electrocoagulation processes, pH of wastewater (electrolyte) directly affects solubility of metal hydroxide compounds. At low pH, aluminum anode generates cationic monomeric species such as Al\(^{3+}\) and Al(OH)\(_3\).

When iron electrodes are used, Fe(OH)\(_{3(n)}\) (\(n = 2\) or 3) is formed. Typical reactions are provided in Equations (5)–(8) and more details can be reached from the following.

Anode:

\[
4Fe_{(s)} \rightarrow 4Fe_{(aq)}^{2+} + 8e^{-} \quad (5)
\]

\[
4Fe_{(aq)}^{2+} + 10H_2O(l) + O_{2(g)} \rightarrow 4Fe(OH)_3(s) + 8H_{(aq)}^+ \quad (6)
\]

Cathode:

\[
8H_{(aq)}^+ + 8e^{-} \rightarrow 4H_2(g) \quad (7)
\]

Overall:

\[
4Fe_{(s)} + 10H_2O(l) + O_{2(g)} \rightarrow 4Fe(OH)_3(s) + 4H_2(g) \quad (8)
\]

The resulting Fe(OH)\(_{3(n)}\) remains in water in the form of a suspension, which requires further removal by electrostatic methods followed by coagulation (Mollah et al. 2001; Chen & Hung 2010).

Keeping these two reaction types in mind, this study focuses on performance comparisons of aluminum and iron electrodes for the electrocoagulation treatment of VIW. Many studies can be found that use aluminum and iron electrodes for the treatment of other industrial wastewaters (Koparal et al. 2008; Yavuz et al. 2011; Valente et al. 2014; Wahida & Zularisam 2017; Devlin et al. 2018; Nariyan Wolkersdorfer & Sillanpää 2018; Nawarkar & Salkar 2019). However, the literature for the treatment of VIW by electrocoagulation process is slim (Kargi & Arikan 2013; Gerek et al. 2016; Gerek et al. 2017), with no particular emphasis on electrocoagulation with Al or Fe. Besides, simultaneous consideration of the toxicity right after the treatment process was not a commonly encountered research style, except for a select group of studies on different wastewater types (Ma et al. 2017; Paździior et al. 2017; Baran et al. 2018).

To further extend the research content, a scanning electron microscopy (SEM) is used to observe the surface structure of electrodes before and after the treatment. Consequently, the results of the experiments performed at laboratory scale make a solid contribution to the literature regarding the treatment of VIW. The target of the present
study is to examine the treatability of VIW by EC using aluminum and iron electrodes and to explore the effects of varying operating parameters such as the applied contact time, current density, initial pH of wastewater, dosages of Na₂SO₄, polyaluminum chloride (PAC) and keraflc. Aluminum and iron electrodes are cross-examined through these parameters. High removal efficiency values are obtained. Additionally, toxicity evaluations show that the treatment processes have positive effect on the toxicity reduction. The cross experimental results are expected to provide insight for the food industry wastewater treatment community regarding necessity of simultaneous COD and toxicity analysis.

MATERIALS AND METHODS

Sampling and characterization of vinegar industry wastewater

In order to attain realistic and acceptable results, real VIW were used in our experiments. The VIW samples were obtained from a vinegar manufacturing plant located in Izmir/Turkey. We collected 50 L of wastewater samples, each, in two separate days within the same production season of the manufacturing plant. The samples were refrigerated at 4°C to keep biochemical properties throughout experimental studies. The influent pollution parameters measured from these two days indicate that the structure of wastewaters do not vary within the production season. The average influent parameters were given in Table 1.

Experimental setup

Laboratory scale treatment experiments were conducted with batch electrolysis tanks that include aluminum and iron electrodes (see Figure S1 in the Supplementary Material, available with the online version of this paper). In order to come up with optimum working conditions (at room temperature), various process parameters were carefully adjusted. The initial pH value of the wastewater was adjusted using H₂SO₄ (Merck, Germany) and NaOH (Merck, Germany), while pH and conductivity levels were monitored with a pH and conductivity meter (Thermo Scientific Orion STAR A215 model, USA).

The available reactor tank is a 500 mL cylindrical glass reactor with a magnetic stirrer (Falc Instruments F60 model, Italy) installed in our laboratory. A monopolar electrolysis electrode structure consisting of six aluminum or iron plates (three connected as anode and the other three connected as cathode) is constructed (see Figure S1 component 4 in Supplementary Material). These parallel plate electrodes were set up vertically, immersed to a 4 cm depth and the inter electrode distance was adjusted to 0.3 cm. The total immersed area of electrodes was observed to be approximately 100 cm². At the end of each experiment run, the electrode surfaces were cleaned with diluted HCl (Merck, Germany). The electrolysis power supply is a DC power supply (Statron type 3262, 0–5 A/0–80 V, Germany), which is capable of injecting constant level currents that can be adjusted according to the desired current density. In order to achieve symmetric and homogenous erosion at the electrode sides, a pole changer (Yavuz et al. 2011) was used to switch the polarity of the electrodes at certain time intervals and coagulants are generated uniformly by symmetric consumption of electrodes.

Analysis

The analysis methodologies for COD assessments, toxicity evaluations (via Vibrio fischeri) and SEM imaging are explained in detail in Parts S.1., S.2. and S.3. of the Supplementary Material, respectively (available online).

RESULTS AND DISCUSSION

In this section, we present experimental results for electrochemical treatment of VIW with EC methods using aluminum and iron electrodes at several electrochemical parameter settings. The efficiencies were first evaluated according to the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw wastewater</th>
<th>After electrocoagulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.00</td>
<td>7.00 Al</td>
</tr>
<tr>
<td>Electrical conductivity (mS/cm)</td>
<td>2.00</td>
<td>3.10 Al</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>10,000</td>
<td>900 Al</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>4,800</td>
<td>370 Al</td>
</tr>
<tr>
<td>BOD/COD</td>
<td>0.48</td>
<td>0.41 Fe</td>
</tr>
<tr>
<td>Color Pt-Co</td>
<td>2.98</td>
<td>0.16 Fe</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>27.4</td>
<td>1.80 Fe</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>150.19</td>
<td>45.37 Fe</td>
</tr>
</tbody>
</table>

Table 1 | Pollution parameters of vinegar industry wastewater (influent; effluent)
percentage removal of COD during the treatment process. Once the best COD removal conditions were obtained, the corresponding treatment results were further investigated for their toxicity, which is also a critical parameter for sustainable treatment of VIW. During the treatment process, the energy consumption values were also monitored. The experiments show that the proposed process is an efficient approach to VIW treatment in terms of COD removal and toxicity reduction, as explained in the following subsections.

**EC treatment studies**

**Effects of current density**

It is well known that one of the most important parameters affecting the performance of electrochemical systems is the electrical current density. The current applied in the EC system determines the amount of Al\(^{3+}\) and Fe\(^{2+}\) ions and forming coagulants. Thus, as the applied current density increases, more Al\(^{3+}\) and Fe\(^{2+}\) ions dissolve in the solution and the rate of formation of M(OH)\(_n\) increases (Yavuz et al. 2014). As expected, an increase in applied current density caused an increase in removal efficiency, thanks to the increased formation of metal ions, which play an important role in the precipitation (Önder et al. 2011). Due to physical limitations of the power supplies and working environment, current density values of 17.50, 20.00 and 22.50 mA/cm\(^2\) were applied to the electrochemical reactor to examine their effects and current density studies were first accomplished at the original pH values (~4.00) for both electrode types. Critical observations are explained separately for both electrode types below.

Al-plates: The effect of the current density on the COD for aluminum electrodes can be seen in Figure 1(a). Current density studies were accomplished at the original pH values (~4.00) and the final pH values were observed to vary around 6.0 and 7.0. The COD removal efficiency values were 50.00%, 80.90% and 81.10% for current density values of 17.50, 20.00 and 22.50 mA/cm\(^2\), respectively. There was no significant difference in COD removal efficiency values at the current densities of 20.00 and 22.50 mA/cm\(^2\), hence a current-wise saturation was observed. Since the current density applied to the electrochemical reactors is directly proportional to the consumption of electric energy, a useless increase in current density causes an increase in the energy consumed per m\(^3\) of treated wastewater (Yavuz et al. 2011). Particularly, the energy consumption values for current densities of 17.50, 20.00 and 22.50 mA/cm\(^2\) were evaluated as 40.9, 55.7 and 65.0 kWh/m\(^3\) treated wastewater, respectively. Using the present average electrical energy price of €0.11 per kWh in Turkey (Anon n.d.), the costs of energy consumed per m\(^3\) of treated water for 75 min were calculated as €4.50, €6.13, and €7.15 for current densities of 17.50, 20.00 and 22.50 mA/cm\(^2\), respectively. Since COD removal efficiencies did not significantly change by increasing the current density, no significant difference in COD removal efficiency was observed for current density values of 20.00 and 22.50 mA/cm\(^2\).

- **Figure 1** | Current density dependency figures of COD removal efficiency versus time (C\(_o\) = 10,000 mg/L VIW; pH = ~4.00) for (a) Al-plates, (b) Fe-plates; pH dependence figures of COD removal efficiency versus time for (c) Al-plates (C\(_o\) = 10,000 mg/L VIW, I = 20.00 mA/cm\(^2\)) and (d) Fe-plates (C\(_o\) = 10,000 mg/L VIW, I = 22.50 mA/cm\(^2\)).
density from 20.00 to 22.50 mA/cm², the lower energy consumption point of 20.00 mA/cm² was found advisable for further studies. Selection of a lower current density for optimal energy vs. COD removal operation point was also encountered in various different applications in the literature (Wahida & Zularisam 2017). The experiment durations were also set according to energy-versus-COD removal efficiency. Since the COD removal rates were observed not to improve (providing a flat and saturated COD removal rate) after 75 min electrolysis for all current densities, the experimental results are presented within 0–75 min range.

Fe-plates: The dependence of COD on current density for iron electrodes can be seen in Figure 1(b). The graph indicated that 22.50 mA/cm² has a clearly higher COD removal effect. COD removal efficiency values were 50.0%, 62.9%, 71.3% for the current density values of 17.50, 20.00 and 22.50 mA/cm², respectively. This expected behavior is explained by the fact that the treatment efficiency was mainly affected by charge loading which equals \( I \times t \), where \( I \) is the applied current, \( t \) is the application time (Önder et al. 2007; Nariyan et al. 2017; Changmai Pasawan & Purkait 2019; Hansen et al. 2019). Similar to the Al-plate case, the COD removals reached a plateau after 60 min, therefore the results are presented at the 60-min process output. At the end of the 60-min electrolysis, energy consumption values for current densities of 17.50, 20.00 and 22.50 mA/cm² were 50.09, 58.00 and 77.50 kWh/m³ treated wastewater, respectively. Consequently, the costs of energy consumed per m³ of treated water for 60 min were calculated as €5.51, €6.38, and €8.53 for current densities of 17.50, 20.00 and 22.50 mA/cm², respectively. This time, due to its clear COD removal advantage, operation at 22.50 mA/cm² was found advisable for the rest of the studies.

Effects of initial pH

The original pH of the wastewater could have a positive or negative effect on the treatment performance, as it affects the stability of various hydroxide species formed in the system. Likewise, changes in the pH values can change the surface charge of the particles, and this has the effect of removing the colloidal dispersed organics from solution (Yavuz et al. 2011). Laboratory experiments were performed by changing the initial pH value to investigate the effects of initial pH of wastewater on EC process for both electrode types. During the experiments, only the initial pH was set and was no further controlled. Yet, pH progress was monitored throughout the electrolysis.

Al-plates: Taking the optimal current density of 20.00 mA/cm² from the previous experimental stage, three different initial pH values were selected; ~4 (original pH of the wastewater), 7, and 9. The variation of the COD removal efficiency for aluminum electrodes with the initial pH values are given in Figure 1(c). COD removal efficiencies of 80.90%, 65.40% and 40.50% for original pH value, pH 7 and pH 9 were obtained for this case, respectively. This means that the original (which is relatively acidic) pH can be considered suitable for the experiments. This situation was also an economical and efficient option for the system since no added chemicals were required to adjust pH. Many previous studies related to EC using aluminum electrodes have shown that the maximum COD removals were observed at neutral pH 6–7 (Bensadok et al. 2008; Deghles & Kurt 2015). However, in this study original pH (~4.00) was observed to be clearly more effective on the removal of COD. On the other hand, starting with an original pH value of 4, the pH value was observed to increase during the reactive phase, then to stabilize at pH close to 7. This increment in pH can be attributed to the electrolysis process resulting in hydrogen evolution and production of OH⁻ ions which are partially buffered by various Al hydroxides forms (Al Aji et al. 2012). It can be argued that the effect of the initial pH is further significant in an electrocoagulation process. A gel layer forms on the anode surface, especially in high concentrations and in high initial pH, which is expected to affect aluminum hydrolysis (Koparal et al. 2008). Therefore, an efficiency reduction can be caused by formation of gel layer on the surface of the anode at pH values of 7 and 9. Due to this gel formation, Al³⁺ ion transfer seems to be slower. To prevent gel formation and to provide a symmetric erosion, a pole changer was employed during experiments. According to the above observations, the original pH of the wastewater (~4.00) was chosen as the initial pH for the rest of the studies, which is in accordance with the results of Changmai et al. (Changmai et al. 2019).

Fe-plates: This setup works according to the formation of Fe(OH)₃ due to the reaction of Fe³⁺ generated at the anode and OH⁻ ions generated at the cathode for iron electrodes. Insoluble hydrous ferric oxide is known to be produced over a pH range of 3.0–13.0 (Önder et al. 2007). Similar to the Al-plate case, the corresponding optimal current density (22.50 mA/cm²) was taken and the initial pH values were varied. The variation of COD removal efficiencies according to the initial pH values are presented in Figure 1(d). The iron-plate experiments produce removal efficiencies of 71.30%, 78.01% and 93.60%, respectively,
for the original pH = 4, pH = 7 and pH = 9 initial settings. Due to these removal levels, it can be seen that iron electrodes provide better COD removal performances at relatively higher pH values. This result is in accordance with the literature explaining that the majority of iron complexes (coagulants) are formed at higher pH values (Al Aji et al. 2012; El-taweel & Nassef 2015). The different initial pH dependencies of Al and Fe electrodes show that initial pH dependency of EC systems cannot be fixed to a constant rule. The energy consumption efficiencies also vary with the initial pH level. We have observed that initial pH levels which provide better removal efficiencies also provide better (lower) energy consumption levels. For example, if aluminum electrodes are used, the original (acidic) pH level was favorable for COD removal, and the lowest energy consumption of 55.70 kWh/m³ was obtained (whereas the inefficient pH = 9 causes a consumption level of 63.50 kWh/m³). Conversely, if iron electrodes are used, high pH (pH = 9) initial level provides a better COD removal with the lowest energy consumption of 47.06 kWh/m³ (whereas the inefficient acidic pH starting level causes an energy consumption of 77.50 kWh/m³).

Effects of Na₂SO₄

The conductivity of the wastewater can affect the electrochemical treatment because it is directly related to the ease of electron transmission in the medium. Consequently, there is a direct relationship between the electrolyte concentration and the solution conductivity. As the concentration of Na₂SO₄ increases, the conductivity of the solution increases (Khosa et al. 2013). Na₂SO₄ was added to increase the electrical conductivity of the wastewater and to observe the effect of the concentration on the COD removal efficiency.

Al-plates: Further experiments were carried out with the addition of Na₂SO₄ (0, 2.5, 5 and 10 mM) under the previously optimized experimental conditions of pH = 4 and current density of 20.00 mA/cm². Electrical conductivities of VIW for 0 mM, 5 mM and 10 mM Na₂SO₄ were measured as 2.03 mS/cm, 5.26 mS/cm and 7.88 mS/cm, respectively. The experimental results show that there was no significant effect of the addition of Na₂SO₄. This can be due to the fact that the original electrical conductivity of VIW was high enough to perform electrochemical reactions, and additional Na₂SO₄ was not necessary. Consequently, the rest of the studies were carried out without Na₂SO₄ to avoid chemical addition and unnecessary chemical consumption.

Fe-plates: Again, further experiments were carried out with the addition of Na₂SO₄ (0, 2.5, 5 and 10 mM) under the corresponding optimal conditions of pH = 9 and current density of 22.50 mA/cm². COD removal efficiencies of 95.58%, 93.62%, 90.76 and 92.81% were achieved for 0, 2.5, 5 and 10 mM Na₂SO₄. Such irrelevance between removal efficiency and additional Na₂SO₄ amount was also observed in the literature (Gengec 2017). Due to the relatively inconsistent effects of support electrolytes, further energy consumption analysis was performed to better conclude which support electrolyte level could be advisable. After 60 min electrolysis, energy consumption values for 0, 2.5, 5 and 10 mM Na₂SO₄ were measured as 47.06, 39.19, 38.25 and 29.53 kWh/m³ treated wastewater, respectively. Such decrease in energy consumption with additional Na₂SO₄ is a typical observation in the literature (Huda et al. 2017). The costs of energy consumed per m³ of treated water were calculated as €3.18, €4.31, €4.21, and €3.25 for 0, 2.5, 5 and 10 mM Na₂SO₄. According to the marginal differences in the energy costs and due to the above COD removal results, it is concluded that there is no significant improvement increase due to additional Na₂SO₄. This can, again, be attributed to the fact that electrical conductivity of VIW was high enough for the electrolysis.

Effects of keraflocc

In coagulation–floculation based water treatment processes, coagulant aids are used to improve the performance of the primary coagulant and to make the process more economical. When keraflocc (which is an organic polymer with anionic charge) is added as the coagulant aid, floculation, hence floc sedimentation and organic removal performance, is expected to improve (Zhao et al. 2012; Oladoja 2016).

Al-plates: Further experiments were carried out by adding keraflocc under optimal experimental conditions at dosages of 0, 5, 10, 15, and 20 mg/L (see Figure S2(a) in the Supplementary Material, available with the online version of this paper). The resulting COD removal efficiency values were obtained as 80.90%, 89.20%, 89.50%, 82.80%, and 78.60% for the respective keraflocc dosages. Two keraflocc concentrations (5 and 10 mg/L) were observed to exhibit a similar (and relatively high) performance trend, with their final removal efficiency values being virtually the same. After 75 min electrolysis, energy consumption values for keraflocc concentration of 5, 10 mg/L were 52.53 and 49.59 kWh/m³ treated wastewater, respectively. Consequently, to avoid excessive chemical consumption, 5 mg/L keraflocc dose was found advisable.
Fe-plates: Again, further experiments were carried out by adding kercaflo under the corresponding optimal experimental conditions at dosages of 0, 5, 10, and 15 mg/L (see Figure S2(b) in Supplementary Material). The resulting COD removal efficiency values were 93.58%, 82.76%, 86.21%, and 89.66% for the kercaflo concentration detailed above in increasing order. After 60 min electrolysis, where final energy consumption values for kercaflo concentration of 0, 5, 10, and 15 mg/L were 47.06, 35.06, 37.97 and 43.78 kWh/m³ treated wastewater, respectively. Besides the marginal reduction of energy consumption, there is no supportive effect of kercaflo addition on COD removal. For this reason, further studies were performed without kercaflo to avoid chemical addition and redundant chemical consumption.

Effects of PAC

In order to improve organic substance removal efficiency, coagulant-aid addition was performed with an aim of increased particle size and instability. PAC is a pre-polymerized Al(III) chemical which contains a series of hydrolysis and polymeric species carrying a relatively large and high cationic charge. Reinforced surface activity and improved charge neutralization capacity of PAC are expected to make it influential on COD removal efficiency. PAC is known to have the following benefits: fast aggregation velocity, bigger and heavier flocs and lower dosage requirement (Tezcan Un et al. 2009; Sudoh et al. 2015). Consequently, PAC was also used to test the removal efficiency variations in our experiments.

Al-plates: Figure S3(a) (in the Supplementary Material, available online) shows the removal efficiencies of COD versus time at different PAC dosages. From the figure, it can be seen that 10 mg/L PAC addition improved the removal efficiency from 80.90% to 90.91%. After 75 min electrolysis, energy consumption values for 0 mg/L PAC and 10 mg/L PAC concentrations were 55.70 and 42.42 kWh/m³ treated wastewater, respectively. The costs of energy consumed per m³ of treated water were calculated as €6.13 and €4.67 for without PAC and 10 mg/L PAC concentrations. Apart from this clear advantage, it was observed that the flocs formed during this process exhibited a larger surface and increased the settlement capability of the flocs. It is concluded that the addition of 10 mg/L PAC is efficient for removal of COD. However, any further increase in PAC concentration caused no improvement in the removal of effluent COD.

Fe-plates: Different PAC concentrations were used in the experiments: 0, 5, 10 and 20 mg/L PAC (see Figure S3(b) in Supplementary Material). The final COD removal efficiency values were 93.58%, 79.95%, 85.54%, and 89.66% for the PAC concentrations in the same given order. After 60 min electrolysis, energy consumption values for 0, 5, 10 and 20 mg/L PAC concentrations were calculated as 47.06, 41.91, 38.06 and 35.81 kWh/m³ treated wastewater, respectively. The costs of energy consumed per m³ of treated water were, therefore, calculated as €5.18, €4.61, €4.19 and €3.94 for 0, 5, 10 and 20 mg/L PAC concentrations. Apart from a slight decrease in energy consumption, additional PAC was observed to cause no removal efficiency improvement, therefore PAC addition was concluded to be unnecessary.

Overall results

Considering the above experimental results, the optimum performances of Al and Fe plates can be summarized as in Table 1.

The results in Table 1 indicate that all of the pollution parameters are significantly reduced using both electrode types, with a slight advantage for Fe electrodes. The BOD/COD ratio stays in the range of ‘average biodegradable’ (i.e. 0.4 ~ 0.5) before and after the treatment (Nagwekar 2014). The electrode consumption costs are evaluated according to Demirbas and Kobya (Demirbas & Kobya 2016). At the optimal settings, the process consumes 2.10 kg of Al and 5.86 kg of Fe per m³ treatment. At the corresponding costs of €1.76/kg for Al and €0.44/kg for Fe, the material cost for Al and Fe are €3.69/m³ and €2.58/m³, respectively. Combining this cost to their electrical energy consumptions, total EC costs for Al and Fe electrodes become €8.36/m³ and €7.76/m³, respectively, showing that Fe electrode is not only marginally more efficient at treatment, but also more economical. This result is in accordance to the previous literature (Wahida & Zularisam 2017; Xu et al. 2017).

Toxicity evaluation

As indicated in the introduction, a major contribution of this study is the simultaneous monitoring of EC treatment by means of COD removal efficiency and toxicity behaviors. Toxicity assessment had gained interest as a result of treatment attempts for wastewaters that contain toxic and biologically intact particles. A commonly used method is bacteria tests before and after the treatment stages (Kokkali & van Delft 2014; Yang et al. 2016). A motivation to consider toxicity for this particular case of vinegar production is the formation of acetaldehyde in the intermediate steps. This byproduct is usually discharged within the final
wastewater and makes the effluent toxic. The reactions that cause acetaldehyde during vinegar production are listed below.

Ethyl-alcohol oxides with air to form acetaldehyde:

\[ C_2H_5-OH + \frac{1}{2} O_2 \rightarrow CH_3CHO \text{ (acetaldehyde)} + H_2O \]  

(9)

Acetaldehyde gains water to become hydro-acetaldehyde:

\[ CH_3CHO + H_2O \rightarrow H_2C-CH(OH)_2 \]  

(10)

Hydro-acetaldehyde dissolves to acetic acid and water:

\[ H_2C-CH(OH)_2 \rightarrow CH_3-COOH \text{ (acetic acid)} + H_2O \]  

(11)

Due to enzymatic oxidation, an excess energy arises:

\[ +\frac{1}{2} O_2 \text{ acetaldehyde dehydrogenase } DH_0 = -483 \text{ kj} = -118 \text{ kcal} \]

yielding the eventual equation to be (Elgün 2011):

\[ C_2H_5-OH + \frac{1}{2} O_2 \rightarrow CH_3-COOH + H_2O + 118 \text{ kcal} \]  

(12)

At their corresponding optimal settings (optimality according to COD removal as described above), the two reactor plate types were evaluated for their efficiencies in toxicity reduction. Microtox® bioassay tests were applied to analyze the toxicity of the VIW treated for certain times in the electrochemical reactor, including time zero under optimum experimental conditions. The relative toxicity results are given in Figure 2(a) and 2(b) as a function of time, which shows a visible decrease in the toxicity levels in time. Toxicity reduction was, therefore, observed to be an important achievement and an advantage of EC process with aluminum and iron electrodes.

Al-plates: According to Figure 2(a), toxicity decreases within the first 10 min and after 30 min shows a stable pattern of less than 0.4 RTI. This corresponds to 60% toxicity reduction as compared to the initial toxicity value of VIW.

Fe-plates: According to Figure 2(b), toxicity decreases within the first 10 min and after 20 min shows an almost stable pattern of less than 0.05 RTI. This corresponds to a 95% toxicity reduction relative to the initial toxicity value of VIW.

The final toxicity levels show that Fe electrodes have a clear advantage in terms of toxicity reduction. It must be noted that the initial toxicity levels of the wastewater samples are significantly high, and the graphs are showing only the relative decrease. Our results indicate that, for VIW treatment with electrocoagulation, there is a clear relation between COD removal and toxicity removal successes. This is somewhat in contradiction to previous works which found no significant correlation between
COD and 24 h-LC50 toxicity values before and after treatment for different types of wastewaters (Välitalo et al. 2017; Gholami-Borujeni Nejatzadeh-Barandozi & Aghdasi 2018). Our positive correlation claim between COD and toxicity can also be proven by the positive inclinations of the COD-vs-toxicity graphs for both plates given in Figure 2(c) and 2(d).

SEM images

A final erosion analysis was made on the electrodes to see the consumption of plates during the reactions. The surface structure of electrodes was analyzed through surface electron microscopy (SEM) analysis. The SEM images of aluminum electrodes shown in Figure S4(a) and S4(b) correspond to before (unused) and after the treatment plate surfaces, respectively (see Figure S4(a) and S4(b) in the Supplementary Material, available online). Figure S4(a) clearly shows a homogenous and relatively flat structure of aluminum plate electrodes, whereas Figure S4(b) exhibits a visible material loss. Yet, the used plate shows a homogenous consumption of aluminum material from the surface during the electrocoagulation process. This homogenous erosion may be attributed to the use of a pole changer during experiments, because the pole changer prevents/avoids a polymeric film layer formation on the surface of the electrodes. Iron electrodes were also observed to yield a similar usage pattern on the SEM images.

CONCLUSION

This work presents results of a simultaneous analysis of COD removal and toxicity assessment for EC treatment of VIW at various parametric levels of electrode type (aluminum and iron), electrical current density, initial pH, additive Na2SO4, kerafloc and PAC. For all experiments, the real life VIW had approximately 10,000 mg/L COD. First, the optimal parametric conditions for parallel aluminum and iron plate electrodes were achieved for maximum COD removal efficiency, then these settings were tested for their toxicity reduction performances.

- Al-plate results indicate that 75 min electrolysis was sufficient for these systems to reach equilibrium conditions, since insignificant variations in COD removal were observed after this time. The best experimental conditions determined in these electrochemical studies were as follows: current density 20.00 mA/cm²; original pH (~4.00), without any supporting electrolyte or kerafloc addition; PAC concentration 10 mg/L. Under these conditions, 90.91% COD removal from VIW was achieved. At this setting, the treatment consumed 42.42 kWh/m³ energy and COD value after 75 min electrolysis was 901.4 mg/L from VIW, which was found to be successful.

- Fe-plate results indicate that 60 min electrolysis was sufficient for these systems to reach equilibrium conditions, since insignificant variations in COD removal were observed after this time. The best experimental conditions determined in these electrochemical studies were as follows: current density 22.50 mA/cm²; pH 9, without any chemical addition. Under these conditions, 93.58% COD removal from VIW was achieved. The treatment consumed 47.06 kWh/m³ energy and COD value after 60 min electrolysis was 700 mg/L from VIW, which was found to be even more successful in terms of COD removal efficiency.

- The experiments show that EC using monopolar aluminum or iron electrodes is a convenient way for effective removal of COD from VIW and achieves faster removal of pollutants in comparison to chemical coagulation, where several hours and more chemical addition are needed.

- As a critical contribution, toxicity tests for the proposed treatment methods were carried out. Similar to the COD removal advantage, the toxicity analysis show that these plates are plausible for reduction of toxicity, with a visible advantage of the iron electrode. Our experiments also show that COD removal success has a clear correlation with the toxicity removal rate.

- Since the initial COD and toxicity levels of VIW is extremely high, although the reductions with the proposed EC systems are above 90%, it may be advisable to try EC in cascade with other advanced methods to further reduce the discharge COD and toxicity down to urban limits. Such combinations are proposed as future studies to follow this work.

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REFERENCES

Al Aji, B., Yavuz, Y. & Savaş Koparal, A. 2012 Electrocoagulation of heavy metals containing model wastewater using
Gerek, E., Savaş Koparal, A. & Gerek, Ö. N. 2016 Energy Footprint and Efficiency of Electrochemical Vinegar Wastewater Treatment Under Variable Reactor Types. 8th EGE Energy Symposium, Afyonkarahisar, Turkey.
Nariyan, E., Wolkersdorfer, C. & Sillanpää, M. 2018 Sulfate removal from acid mine water from the deepest active


