Electrooxidation as post treatment of ultrafiltration effluent in a landfill leachate MBR treatment plant: Effects of BDD, Pt and DSA anode types

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ABSTRACT

In this study, ultrafiltration (UF) effluent from a landfill leachate treatment plant (equipped with anoxic-aerobic oxidation and UF) was treated by Electrooxidation (EO) process in a batch reactor using different dimensionally stable electrodes (DSA anodes: Ti/PtO2-IrO2, Ti/RuO2-TiO2, Ti/RuO2-IrO2, and Ti/IrO2-Ta2O5), boron doped diamond (BDD) and Pt as anode and stainless-steel electrode as cathode. The untreated UF effluent had COD and TOC concentrations of 888 mg/L and 398.6 mg/L, respectively. Overall, BDD anode performed better than the other DSA anodes under the tested conditions with removal efficiencies of 64.9–86.8% and 68.2–92.0% for TOC and COD, respectively. The calculated energy consumptions at maximum removal efficiencies were 111.2 kWh per m³ (136.01 kWh/kg COD and 321.27 kWh/kg TOC) at 360 A/m² and 4 h of treatment time for BDD anode. However, TOC and COD removal efficiencies of 31.3–86.8% and 36.5–92.0%, respectively, were obtained for the other DSA anodes at current densities between 60 and 360 A/m² and 4 h of treatment time. Energy consumptions and anode efficiency for DSA anodes ranged from 7.3–111.2 kWh/m³ (15.67–194.87 kWh/kg COD) and 4.40–34.24 g COD/Ah m² (or 1.77–14.62 g TOC/Ah m²). The general COD and TOC removal mechanism well fitted the pseudo first-order kinetic model with $R^2$ of >0.94 particularly for BDD electrode under all applied current densities. The chloride content in the leachate promoted indirect oxidation leading to increased COD and TOC removal efficiencies. Moreover, high performance size exclusion chromatography (HPSEC) was used to evaluate the variation of fractions in wastewater during EO.

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1. Introduction

Leachate from municipal solid waste landfills is a wastewater with complex composition that could result into adverse environmental impacts due to the high concentration of organics, colour, heavy metals, ammonia, chloride, bio-refractory and toxic compounds [1–3]. A lot of methods such as biological treatment, chemical precipitation, chemical oxidation and coagulation–flocculation have been explored for effective treatment of landfills leachate [4–9]. Biological nitrification/denitrification is probably the most efficient and cheapest process to eliminate nitrogen from leachate. However, biological treatment is hampered by the specific toxic substances and/or by the presence of bio-refractory organics. The efficiency of denitrification is reduced due to the limited level of biodegradable organics, particularly in stabilized landfills [10]. Membrane filtration systems, generally used in combination with ultrafiltration (UF) and nanofiltration after biological treatment systems generate high quality permeate but are disadvantaged by the high cost and toxic concentrate production [11]. UF could be used in leachate treatment to remove larger molecular weight ingredients that tend to foul nanofiltration and reverse osmosis membranes, containing organic biodegradable macromolecules and non-biodegradables. However, bio-refractory pollutants such as xenobiotic organics and humic-fulvic acids in landfill leachate are not degraded and removed by biological and UF treatment system stages. These non-biodegradable molecular compounds cause problems in treatment of domestic sewage when the effluent of landfill leachate is...
integrated with municipal wastewater for further treatment [11]. To eliminate these non-biodegradable compounds, an advanced oxidation process is required. In recent years, several advanced oxidation processes (AOPs) have been applied for landfill leachate treatment. These include; ozone and ozone based (O3, O3/UV, H2O2), photocatalytic (UV/TiO2), Fenton and photo Fenton (Fe2+/H2O2, Fe2+/H2O2/UV), ultrasonic oxidation, etc. [12–14]. The treatment of raw leachate by AOPs may be difficult not only due to high pollutant concentration and colour of wastewater, but also high operating cost of AOPs. However, AOPs can be an alternative for effluent of physicochemical and biological treatment systems. The rest of AOPs treatment techniques except for electrooxidation process have a number of disadvantages such as huge space requirements, long operating time, low removal efficiency, highly sensitive to the solution pH, additive chemical reagents causing serious secondary pollution. Electrochemical processes such as electrocoagulation, electrooxidation and electro-Fenton have been widely studied for treatment of landfill leachates [15,16]. Several anode materials have been investigated for EO of sanitary landfill leachates, with BDD being the most studied, followed by Ti/Pt, Ti/SnO2, Ti/PbO2, Ti/RuO2-IrO2, Ti/Pt/SnO2-Sb2O4, and graphite, among others [5,17–32]. For instance, Panizza and Martinez-Huitle [20] compared the effect of electrode materials (BDD and metallic oxides anodes) on electrooxidation of real old landfill leachate. At 400 A/m2 and 2.5 h of EO time, they reported COD and ammonium removals of 95% and 100%, respectively, by BDD anode. On the other hand, PbO2 anode obtained 68% and 100% removals for COD and ammonium, respectively at 4 h, while Ti/Ru-SnO2 anode obtained 35 and 65% removals, respectively after 8 h.

In a related development, Anglada et al. [23,24] treated landfill-leachate by electrooxidation using BDD anodes. At optimum (EO time of 8 h, 450 A/m2), above 90% of COD and 100% of NH4-N removals were recorded. Similarly, Vlyssides et al. [31] reported that EO of landfill leachate by cylindrical Ti/Pt anode and stainless steel 304 cathode achieved COD and NH3-N reduction of 84 and 100%, respectively within 1 h of electrolysis time. This is consistent with the reports by Cossu et al. [3], for EO of biologically pre-treated landfill leachate using Ti/PbO2 and Ti/SnO2 anodes, where the respective COD removals were 91.7% and 60%, with complete removal of NH4-N for both electrodes at 150 A/m2. Chiang et al. [32] applied four different anode materials (graphite, Ti/PbO2, Ti/RuO2-TiO2 and Ti/SnO2–PdO–RuO2) to treat sanitary landfill leachates. The highest COD and ammonium removals were obtained as 92% and 100%, respectively by Ti/SnO2–PdO–RuO2 at 1500 A/m2 and 4 h. This was ascribed to high current efficiency exhibited by this anode due to its high electrocatalytic activity and high O2 evolution overvoltage. In another study using Ti/IrO2 anode for EO of stabilized landfill leachate (pH: 8, COD: 2960 mg/L, TOC: 1150 mg/L, total phenol: 10 mg/L, NH4-N: 14 mg/L, Cl−:6150 mg/L) in the presence of HCO3− as the supporting electrolyte [22], COD, TOC and total phenol removal efficiencies were obtained as 90, 65 and 100%, respectively, at optimum conditions (J = 320 A/m2, T = 80 °C, pH = 3, EO time = 240 min).

All the above studies agree that the main oxidizing agent in the EO of landfill leachates is hypochlorite ion or hypochlorous acid produced by chloride ions, which originate from salt (NaCl) used for meals [33]. The other agent is the hydroxyl radical, resulting from unselective and complete mineralization of organic pollutants by EO at the anode surface [34–36]. Combination of EO with the UF treatment system is therefore, an appropriate option to oxidize the bio-refractory organics in landfill leachate. The use of dimensionally stable anodes (DSA) for wastewater treatment has led to technological improvements thus decreasing operational and investment costs [17,22]. DSA electrodes exhibit high electro-catalytic activity, stability to anodic corrosion, and superior mechanical stability. From above results it can be seen that detailed studies which deal with the treatment of the biological and UF treated landfill leachate by the EO process to enable discharge of wastewater to the receiving environments are needed. The literature studies mostly used BDD anodes in EO studies of sanitary landfill leachates. Notably, in cases were more than one anode were used, BDD exhibited superior qualities, with 100% COD and ammonium removals reported in some studies. Nevertheless, other anode materials also presented very promising results. Apparently, no study evaluated the application of BDD, pt and DSA anode types for electrooxidation of UF effluent from landfill leachate MBR treatment plant. Therefore, the present study was aimed at examining the treatment performance of BDD, Pt and DSA anodes (Ti/PtO2-IrO2, Ti/RuO2-TiO2, Ti/RuO2-IrO2 and Ti/IrO2-Ta2O5) on the UF effluent of a municipal landfill leachate treatment plant, with the evaluation of the variation in fractions in wastewater during EO through HPSEC analysis. The effects of anode type, current density (60–360 A/m2), and the reaction time (0–4 h) on COD and TOC removals from the UF effluent were investigated. Also, specific energy consumptions (as kWh/m3 and kWh/kg removed COD or TOC) and anode performance (as g removed COD or TOC/A h m2) for DSA anodes have been evaluated. We hope that the results of this study shall be of interest to many researchers involved in electrochemical treatment of wastewater.
A 316 AISI stainless steel cathode, having areas of 84 cm\(^2\) (active area) each were used. Both the anodes and cathodes were placed vertically parallel to each other. The electrodes were fixed at 2 cm above the cell bottom. The inter-electrode gap was kept constant at 2.5 cm. Power was provided by a DC power supply (Agilent 6675A model) with current-voltage monitoring and a maximum output of 20 A—120 V. During each experimental run, 0.95 L of wastewater was placed into the reactor. Current was held constant at desired values (i = 0.5—3 A) for each experimental run. During electrochemical oxidation, part of the applied electric energy converted to heat, system temperature increased between 35 and 45 °C. Thus, an adjustment of temperature to normal levels (25—35 °C) was provided via blowing cold air on outer surface of the EO reactor. The samples taken at the different operating times from the EO batch reactor were filtered through a 0.45 \(\mu\)m membrane filter and subsequently analyzed for COD and TOCs. Variations of chloride and ammonium concentrations during EO process were also measured for BDD electrode.

2.3. Analytical method

The COD and TOC were analyzed by the procedures described in the Standard Methods [37]. The COD of the effluent was determined by dichromate open reflux method as per Standard Method 5220-B. The TOC levels were determined through combustion of the samples at 680 °C using a non-dispersive IR source (Shimadzu, TOC-L model) by non-purgeable organic carbon method. The pH and conductivity of solutions before and after EC were measured by a pH (Mettler Toledo Seven Compact) and a conductivity meter (Mettler Toledo Seven Go). All experiments were repeated twice and average data were reported if the test error was below 2%. All the used chemicals were of analytical grade.

The molecular weight distribution (MWD) of pollutants in the wastewater was determined using High performance size exclusion chromatography (HPSEC) with a Hewlett-Packard HPLC 1100-series system equipped with a refractive index detector (RID) (G1362A, Agilent), a diode array detector (DAD, G1315A) and two ultra-hydrogel (Waters, Product Number: AT011535 and WAT011525) columns. The sample injection volume was 100 \(\mu\)L and Ultra-pure water at a flow rate of 1 mL/min was used as the mobile phase. Polysaccharide (Pullulan) standards of known different molecular weights (186, 100, 48, 23.7, 12.2 and 58 kDa) were chosen to calibrate the columns. The RID measures changes in refractive index, in terms of “Refractive Index Units (nRIU)” whereas DAD is a type of UV—Vis detector that performs measurements in absorbance unit (AU) at any wavelength. Weight-average molecular weight \((M_w)\) and number-average molecular weight \((M_n)\) were calculated from the data using the following equations and the calculations were processed with Chem Station software.

\[
M_w = \frac{\sum n_i M_i^2}{\sum n_i} \quad (1)
\]

\[
M_n = \frac{\sum n_i M_i}{\sum n_i} \quad (2)
\]

where; \(M_i\) and \(n_i\) are the molecular weight and the height of each \(i\)-th fraction eluted at the \(i\)-th volume in the chromatogram, respectively. The polydispersity index (PDI) or heterogeneity index, is a measure of the distribution of molecular mass in each polymer sample. PDI is calculated from \(M_w/M_n\).

3. Results and discussion

3.1. Theoretical background of EO

The mechanism of electrochemical degradation of organic matter at metal oxide anodes has been suggested by Comninellis [35]. Water is electrolyzed by anodic catalysis to produce absorbed hydroxyl radicals.

\[
\text{MO}_x + \text{H}_2\text{O} \rightarrow \text{MO}_x(\cdot\text{OH})_{\text{ads}} + \text{H}^+ + e^- \quad (3)
\]

The adsorbed hydroxyl radicals at metal oxide (MO\(_x\)) electrodes (except for BDD and Pt) may form chemisorbed active oxygen.

\[
\text{MO}_x(\cdot\text{OH})_{\text{ads}} \rightarrow \text{MO}_x + \text{H}^+ + e^- \quad (4)
\]

Meanwhile, the hydroxyl radicals will react with each other to form molecular oxygen to complete the electrolysis of the water molecules.

\[
\text{MO}_x(\cdot\text{OH})_{\text{ads}} \rightarrow \text{M} + \text{O}_2 + \text{H}^+ + e^- \quad (5)
\]

By applying a current corresponding to the anode potential close to the region of oxygen evolution, the organic pollutants (R) present in landfill leachate can be oxidized via mechanisms illustrated in equation (6) by reaction with physiosorbed hydroxyl radicals \(\text{MO}_x(\cdot\text{OH})\) formed according to equation (3):

\[
\text{MO}_x(\cdot\text{OH})_{\text{ads}} + \text{R} \rightarrow \text{MO}_x +\text{CO}_2 +\text{H}_2\text{O} +\text{inorganic ions} \quad (6)
\]

The physiosorbed hydroxyl radicals \(\text{M}(\cdot\text{OH})\) cause unselective...
oxidation of organics, resulting into complete combustion. Furthermore, hypochlorite (another strong oxidant) may be produced in many wastewaters containing chlorides. The chloride present in wastewater water is electrochemically converted to strong oxidants such as chlorine/hypochlorite at anode. The electrochemical oxidation of chloride ions present in the landfill leachates may produce gaseous chlorine, hypochlorous acid, or hypochlorite (indirect oxidation):

**Anodic reactions:**

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^- \quad (7) \]

Consequently, the reaction equation (8) is realized at equilibrium.

\[ \text{Cl}_2(g) + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (8) \]

\[ \text{HOCl} + \text{R} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{H}^+ + \text{Cl}^- \quad (9) \]

Cathodic reactions:

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad (10) \]

\[ \text{OCl}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^- \quad (11) \]

Considering that the studied landfill leachates contained significant amounts of chloride ion (3–8 g/L), it can be accepted that this contributed to the oxidation of organics in the solution [16,36].

**Fig. 2.** COD and TOC removals from UF effluent with BDD, Pt and different DSA anodes.
3.2. Effect of anode materials and treatment time

The anode material is one of the most important parts in an electrochemical oxidation process. Six anode materials (BDD, Pt, Ti/PtO₂-IrO₂, Ti/RuO₂-TiO₂, Ti/RuO₂-IrO₂, and Ti/IrO₂-Ta₂O₅) were used in this study. Fig. 1 shows the COD and TOC removal efficiencies of these anodes according to EO time (0–240 min) at current density of 360 A/m² (applied current, i = 3 A, Electrod = 84 cm²). It can be observed that the TOC and COD removals increased with the increase in EO time. TOC and COD removals at EO time of 4 h and 360 A/m² were measured as 86.8% and 92.0% for BDD, 67.2% and 70.6% for Ti/RuO₂-TiO₂, 62.1% and 67.1% for Ti/RuO₂-IrO₂, 62.2% and 66.6% for Pt, 59.7% and 64.7% for Ti/PtO₂-IrO₂, and 47.2% and 52.6% for Ti/IrO₂-Ta₂O₅, respectively. According to above results, the lowest COD and TOC removals from UF effluents was observed with Ti/IrO₂-Ta₂O₅ anode. Also, Fig. 1 reveals that the performance of BDD was better than that of the other DSA anodes tested in this study. This is due to the weak adsorption of the hydroxyl radicals which are very reactive to the organic compounds, on the inert surface of the BDD anode. BDD is a “non-active” anode which does not provide any catalytic active site for the adsorption of reactants and/or products from the aqueous medium; hence the anode serves only as an inert substrate, which can act as a sink for the removal of electrons in the electrochemical oxidation.

At 140 min of EO process with BDD anode, the TOC and COD removals were 79.7% (81.1 mg/L) and 82.9% (152.4 mg/L), respectively. However, at 240 min (4 h) the TOC and COD removals increased to 86.8% (52.6 mg/L) and 92.0% (70.8 mg/L), respectively. In addition, the TOC removal efficiency for all DSA anodes was slightly lower than that of COD, which suggests that some part of organic compounds was degraded to other organics rather than completely mineralized to CO₂ and H₂O.

Furthermore, the colour removal efficiency for UF effluents by all DSA anodes at EO time of 4 h was almost 100%. The colour removal was faster than the COD and TOC removals, which showed that chromophoric groups of organic pollutants in UF effluents were easily degraded by EO. This indicated the effective decolorization ability of electrochemical oxidation.

3.3. Effect of applied current density

Current density, the current per unit area of electrode, may be the most frequently referred term in an electrochemical process because it controls the reaction rate [16,19,35,36]. Current densities used in the reviewed publications which dealt with EO process for landfill leachate ranged from 50 to 5400 A/m² [12,20–31]. Generally, 50 A/m² is the minimum current density required for effective oxidation of organics. Fig. 2 shows TOC and COD removals from the UF effluent by DSA anodes as a function of EO time at different current densities. When the current density and the EO time was increased, the residual COD and TOC concentrations for all the used DSA anodes decreased. In addition, COD and TOC removal efficiencies of UF effluent for different anode materials at different current densities is presented in Table 2. For EO time of 4 h and current density of 60, 120 and 360 A/m², the COD removal efficiencies were obtained as 68.2, 84.9, and 92.0%, respectively for BDD; 45.9, 58.1 and 66.6%, respectively for Pt; 52.7, 55.9 and 64.7%, respectively for Ti/PtO₂-IrO₂; 46.6, 61.4 and 70.6%, respectively for Ti/RuO₂-TiO₂; 51.1, 61.1 and 67.1%, respectively for Ti/IrO₂-Ta₂O₅; 36.5, 48.1 and 52.6%, respectively for Ti/IrO₂-Ta₂O₅. It is clear from the obtained results that COD and TOC removal performance highly depended on applied current density (Fig. 2 and Table 2), which is in well-agreement with literature. This trend could be due to the increase in generation rate of hydroxyl radical with current density, which eventually enhanced degradation of organic compounds from the UF effluent. Moreover, increased current density during EO enhanced active chlorine species generation, which was probably responsible for subsequent removal of organic pollutants [38]. The residual COD and TOC removal efficiency for BDD anode increased from 68.2% (282.6 mg/L) to 92.0 (70.8 mg/L) and 64.9% (140.1 mg/L) to 86.8% (52.6 mg/L) respectively for increase in current density from 60 to 360 A/m² (Fig. 2).

Li et al. [38], reported noticeable effect of current density on COD and TOC removal efficiencies from leachate under high chloride ion concentration (3000 mg/L) compared to low chloride ion concentration (1650 mg/L). This phenomenon again proves the key role of indirect oxidation during EO of leachate. Additionally, Morea and Bertazzoli [39], reported that colour removal efficiencies from leachate also strongly depended on current density. Removal efficiency of colour at 1160 A/m² was five times more than that at 130 A/m² with 3 h of electrochemical process. Indirect oxidation of wastewater using chlorine/hypochlorite requires a high chloride concentration, typically larger than 3000 mg/L [39]. Hence, addition of chloride ion is frequently necessary in EO of wastewaters.

### Table 2

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<th>R&lt;sub&gt;e&lt;/sub&gt; TOC (%)</th>
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CE: Current efficiency (Faradic yield), SEC: Specific energy consumption, U: average voltage between electrodes, η: Anode efficiency.
including landfill leachate.

The efficiency of the EO process depends on the specific energy consumption (SEC) for the reduction of 1 kg of organic matter (in terms of COD or TOC), which is one of the most important economic factors. The SEC was calculated by the following equations [19,20]:

\[ SEC(kWh/m^3) = \frac{U \times i \times t}{10^3 \times V} \]  
(12)

\[ SEC(kWh/kg COD) = \frac{U \times i \times t}{10^3 \times V \times (COD_0 - COD_t)} \]  
(13)

\[ SEC(kWh/kg TOC) = \frac{U \times i \times t}{10^3 \times V \times (TOC_0 - TOC_t)} \]  
(14)

where COD_0 and COD_t are the chemical oxygen demand at initial EO time and at given EO time t (kg O_2/L), respectively, U is the voltage applied, i the current (A), t is the treatment time (hour) and V is the volume of solution (0.95 L). In this study, SEC for all DSA anodes increased from 15.67 to 194.87 kWh/kg COD (or from 38.00 to 483.76 kWh/kg TOC) for increase in current density from 60 to 360 A/m² (Table 2). The highest SEC was 194.87 kWh/kg COD (or 483.76 kWh/kg TOC) at 360 A/m² by Ti/IrO₂-Ta₂O₅ anode, and the lowest SEC was 15.67 kWh/kg COD (or 38.00 kWh/kg TOC) at 60 A/m² with Ti/PtO₂-IrO₂ anode. The maximum COD and TOC removal efficiency was obtained using BDD anode, increasing current density from 60 to 360 A/m² resulted into an increase of SEC from 26.22 to 136.01 kWh/kg COD (from 61.41 to 321.27 kWh/kg TOC or from 15.9 to 111.2 kWh/m²). This trend could be explained by the increase of applied current (from 0.50 to 3 A) with average voltages (from 7.54 V to 8.80 V for BDD anode) and amount of removed kg COD and TOC for these changes in current density. For the commercialization of EO process, lower values of SEC are important. The results showed that at low current density the performance would be cost-effective but needs long treatment time, while at high current density it was highly efficient but costlier. Therefore, SEC value should be optimized according to COD and TOC discharge criteria.

The anode efficiencies (η) for the EO of the UF effluent is shown in Table 2. It has been calculated from the following equations in grams (g) of COD and TOC removed (COD_r, TOC_r) per hour per ampere per square meter [31,40,41].

\[ \eta(g COD/Ah/m^2) = \frac{(COD_0 - COD_t) \times V}{i \times t \times S_{anode}} \]  
(15)

\[ \eta(g COD/Ah/m^2) = \frac{(TOC_0 - TOC_t) \times V}{i \times t \times S_{anode}} \]  
(16)

For BDD anode, the anode efficiencies were calculated as 34.24 g COD/Ah m² (14.62 g TOC/Ah m²) at 60 A/m², 21.31 g COD/Ah m² (21.31 g TOC/Ah m²) at 120 A/m², and 7.70 g COD/Ah m² (3.26 g TOC/Ah m²) at 360 A/m². On the other hand, the anode efficiencies for the DSA anodes except BDD varied between 4.40 and 26.44 g COD/Ah m² and 1.77–10.90 g TOC/Ah/m². When the EO time and
current density was increased, the anode efficiency decreased rapidly for all current density values. This gradual decrease of anode efficiency indicates the increasing difficulty in oxidation of residual organics and inorganics in the UF effluents by the DSA anodes.

The Instantaneous Current Efficiency (ICE, in %) or Faradic efficiency of the electrolysis, was calculated from the values of the COD using the following equation [35]:

\[
ICE = \frac{[\text{COD}]_t - [\text{COD}]_{t+\Delta t}}{8 \times i \times \Delta t} \times F \times V
\]

where \([\text{COD}]_t\) and \([\text{COD}]_{t+\Delta t}\) are the COD values at \(t\) and \((t + \Delta t)\) (in g O₂/L), respectively. \(i\) is the current intensity (A), \(F\) is the Faraday constant (96487 C/mol), \(V\) is the volume of the electrolyte solution (L), and \(8\) is the equivalent weight of oxygen. ICE values at 4 h of electrochemical treatment time of UF effluent at different current densities with the DSA anodes are presented in Table 2. As seen in Table 2, the ICE decreased with increase of current density for all the anodes, this could be explained by the parasitic reactions, which are well detailed in literature [42–44].

3.4. Electrooxidation kinetics for COD and TOC removal

The COD and TOC removal process was analyzed to determine the classical kinetic mechanism that best describes their removal processes (see Fig. 3). In electrochemical treatment, the COD and TOC removal rates are proportional to the concentration of the organic pollutant and the amount of oxidants formed [3, 45, 46]. The general removal mechanism well fitted the pseudo-first-order kinetic model (equation (16)) with \(R^2\) of 0.96, 0.98 and 0.97 at current densities of 60 A/m², 120 A/m² and 360 A/m², respectively for TOC removal by BDD anode, whereas for COD removal; \(R^2\) of 0.94, 0.98, and 0.98, respectively were obtained for the same variations in current densities (Table 3).

\[
\ln(C_t) = \ln(C_0) - k(t)
\]

where \(C_0\) and \(C_t\) are the concentration of COD or TOC (mg/L) at time \(t\) (min) and 0 (min) respectively, \(k\) is the reaction rate constant.

As it can be seen in Table 3, the first-order model rate constant \((k_1)\) varied from 0.0044 to 0.01 min⁻¹ for increase in current density from 60 to 360 A/m² for COD removal, and for TOC removal mechanism, the rate constant varied from 0.0039 to 0.0082 min⁻¹ under the same condition. The rate constants in both cases showed great dependence on the applied current density. This could be explained by the fact that increasing current density enhances chlorine generation, which undergoes subsequent reactions to form hypochlorite, enhancing indirect oxidation. Furthermore, studies by Cossu et al. [3] on electrochemical treatment of sanitary landfill leachate by catalytic anodes reported \(k_1\) in the final stages of the reaction to be lower than \(k_1\) in the initial stages of the reaction. This was attributed to the presence of more easily oxidizable compounds in the initial stages of the process.

The effluent pH decreased during the first 40 min of electro-oxidation, and then began to rise rapidly until 100 min where it remained fairly constant for the rest of the experiment (Fig. 4a). Previous studies in electrochemical treatment of wastewater by BDD anode also reported a similar trend [47, 48]. The initial decrease in pH in this study could be due to the formation of hypochlorous acid (HClO) and hypochlorite (HOCl), which are produced by the oxidation of chloride ions.

![Fig. 4](https://example.com/figure4.png)

**Fig. 4.** Changes of pH, conductivity, chloride and NH₃-N ion concentrations during electrooxidation of UF effluent using BDD anode (j = 360 A/m²).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(j) (A/m²)</th>
<th>Kinetics for COD (k_1 \times 10^3) (1/min)</th>
<th>(R^2)</th>
<th>Kinetics for TOC (k_1 \times 10^3) (1/min)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD</td>
<td>60</td>
<td>4.40</td>
<td>0.941</td>
<td>3.87</td>
<td>0.962</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>7.30</td>
<td>0.983</td>
<td>6.55</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>10.01</td>
<td>0.977</td>
<td>8.24</td>
<td>0.967</td>
</tr>
<tr>
<td>Ti/RuO₂-TiO₂</td>
<td>60</td>
<td>2.60</td>
<td>0.996</td>
<td>2.29</td>
<td>0.979</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.31</td>
<td>0.952</td>
<td>2.96</td>
<td>0.958</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>4.54</td>
<td>0.903</td>
<td>2.41</td>
<td>0.975</td>
</tr>
<tr>
<td>Pt</td>
<td>60</td>
<td>2.19</td>
<td>0.831</td>
<td>1.43</td>
<td>0.796</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.05</td>
<td>0.946</td>
<td>2.14</td>
<td>0.847</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>4.21</td>
<td>0.952</td>
<td>3.61</td>
<td>0.937</td>
</tr>
</tbody>
</table>

![Fig. 5](https://example.com/figure5.png)

**Fig. 5.** Molecular weight distribution of Raw wastewater before EO process.
Fig. 6. Molecular weight distribution of wastewater obtained by RID during EO process via BDD and Ti based electrode.
acid as illustrated in equation (8). The pH later increases due to oxidation of hypochlorous acid, and the subsequent release of more hydroxyl ions than protons into the solution due to cathodic and anodic reactions. The solution conductivity was also measured during the EO process (Fig. 4a). The ionic conductivity of the solution generally showed an exponential decrease during the EO process. These results were expected since the decrease in concentration of ions such as chloride and ammonium in the electrolyte occurred, hence decreasing the electric conductivity of the sample.

Two distinct zones can be seen in the chloride concentration profile (Fig. 4b). The first zone exhibits a slow decrease in chloride concentration and the second zone shows a rapid decrease in chloride concentration. This trend could be explained by the fact that electrochemical oxidation of wastewaters containing chloride ions results to the formation of “active chlorine” during indirect oxidation. At acidic pH, the depletion of chloride concentration seems to be accelerated by gaseous chlorine evolution at the anode and aqueous chlorine is the predominant species in solution. Moreover, a strong choline odor was detected at acidic pH (~5 for this experiment). However, chloric acid and chlorate ions are the predominant species at alkaline pH, hence chloride concentration decreases due to chlorate formation [49,50]. The NH\textsubscript{4}\(\textsuperscript{+}\) concentration showed a rapid decrease for the first hour of the experiment and then remained fairly constant (Fig. 4b). This could be due to reaction of NH\textsubscript{4}\(\textsuperscript{+}\) and HOCl to generate volatile chloramines. From Fig. 4b, as the Cl\textsubscript{-} concentration decreases towards the end of the process, ammonium removal rate becomes negligible. Studies by Cabeza et al. [27] and Li and Liu [38] indicated the oxidation of ammonia was primarily due to the indirect oxidation by HOCl, which is in turn controlled by the chlorine evolution rate at the anode.

3.5. Effect of anode materials and time on molecular weight distribution

High performance size exclusion chromatography (HPSEC) is widely used to understand the mechanism of wastewater treatment systems because it allows monitoring of molecular weight (MW) changes of pollutants in the wastewater during treatment. In this study, HPSEC with two different detectors, RID and DAD, was used to evaluate the variation of fractions in wastewater during EO. The difference between the refractive index of a sample in the sample cell and the mobile phase in the reference cell is measured by RID and reported as nRIU. Molecular weight distribution calibrated with standards were calculated according to RID results because RID is suitable for detecting all components in wastewater. The \(M_{\text{w}}\), \(M_{\text{n}}\) and PDI values of raw wastewater were calculated by RID as 2.0085 \(\times\) 10\textsuperscript{6}, 7.7227 \(\times\) 10\textsuperscript{4} and 2.6007 \(\times\) 10\textsuperscript{4}, respectively. The results in Fig. 5 showed that pollutants in wastewater have a very wide molecular weight distribution (100~100,000 g/mol). Moreover, three peaks (peak 1 = 100~200 g/mol, peak 2 = 200~1000 g/mol and peak 3 = 40,000~100,000 g/mol) were monitored from the raw wastewater. Of these peaks, the area of peak 2 was 89.3% of the total area. In addition, the HPSEC results obtained with BDD and Ti/RuO\textsubscript{2}–TiO\textsubscript{2} electrodes between 30 min and 5 h during EO are given in Fig. 6a, b, c, d. It can be seen that for BDD electrode, complete removal of pollutants with molecular weight of about 90~10,000 g/mol was not realized within 5 h of EO process. Similarly, for the Ti/RuO\textsubscript{2}–TiO\textsubscript{2} electrode, complete removal of pollutants with molecular weight of about 20~50,000 g/mol was not realized during 5 h of EO treatment. Furthermore, there was a rather broad and shallow increase in the amount of contaminants having a molecular weight of 100 g/mol in the Ti/RuO\textsubscript{2}–TiO\textsubscript{2} electrode. The \(M_{\text{w}}\), \(M_{\text{n}}\) and PDI values of 5-hour treated wastewater by BDD were measured as 8.4355 \(\times\) 10\textsuperscript{2}, 2.1488 \(\times\) 10\textsuperscript{1} and 3.9257 \(\times\) 10\textsuperscript{2}, respectively whereas for Ti/RuO\textsubscript{2}–TiO\textsubscript{2} electrode, these values were 2.3367 \(\times\) 10\textsuperscript{4}, 1.0042 \(\times\) 10\textsuperscript{2} and 2.3270 \(\times\) 10\textsuperscript{2}, respectively. These results have supported the success of BDD electrodes in EO treatment and proved BDD as an effective electrode not only for treatment of high molecular weight (HMW) fractions but also low molecular weight (LMW) compounds. In addition, BDD electrode converted the HMW fractions to LMW fractions faster than other DSA electrodes.

Although RID is sensitive to all components, it has lower sensitivity compared to DAD. Moreover, DAD provides good sensitivity for light-absorbing compounds especially for chromosphere groups. On the other hand, DAD is disadvantaged by its unsuitability for detecting components without UV–Vis absorption such as sugar, alcohol and inorganic ions. For these reasons, chromatogram of wastewater obtained by RID (Figs. 5 and 6) were different from that of DAD (Figs. 7 and 8). DAD results at 254 nm are taken as an indication of the presence aromatic compounds. The destruction of the aromatic rings become evident in Fig. 8. As seen in Fig. 8, the anodes are inadequate for removal of HMW organic fractions.

4. Conclusion

In this paper, electrochemical oxidation of UF treatment stage effluent from a landfill leachate treatment plant has been studied at different current densities in a batch cylindrical reactor using different DSA anodes. For the BDD anode, COD and TOC concentration decreased from 888.1 mg/L to 70.8 mg/L (92% removal) and 398 mg/L to 52.6 mg/L (86.8% removal), respectively after EO time of 4 h at current density of 360 A/m\textsuperscript{2}. The energy consumption for all the DSA anodes at 4 h of EO time greatly varied from 7.6 to 111.2 kWh/m\textsuperscript{2} depending on the applied current density. TOC and COD removal efficiencies of 31.3~86.8% and 36.5~92.0%, respectively, were obtained with the other DSA anodes at current densities between 60 and 360 A/m\textsuperscript{2} and 4 h of EO treatment. Furthermore, anode efficiencies were 7.70, 5.58, 5.42, 5.91, 5.61 and 4.40 g COD/Ah m\textsuperscript{2} for BDD, Pt, Ti/PtO\textsubscript{2}–IrO\textsubscript{2}, Ti/RuO\textsubscript{2}–TiO\textsubscript{2}, Ti/RuO\textsubscript{2}–IrO\textsubscript{2}, and Ti/IrO\textsubscript{2}–Ta\textsubscript{2}O\textsubscript{5}, respectively. Boron doped diamond (BDD) anode performed better than the tested DSA anodes under all examined conditions. Moreover, hypochlorite formed from chloride ions (after about 1 h at high current density of 360 A/m\textsuperscript{2}) during the EO process plays an important role in the oxidation of bio-refractory organic compounds in UF effluent of the landfill.

![Fig. 7. Molecular weight distribution of raw wastewater obtained by DAD.](image-url)
Fig. 8. Molecular weight distribution of wastewater obtained by DAD during ED process using BDD and Ti based electrode.
leachate. According to the HPSEC results, the BDD electrode more effectively treated high molecular weight fractions compared to other DSA anodes. The removal mechanism well fitted pseudo first-order kinetic model with R² of 0.96, 0.98 and 0.97 at current densities of 60 A/m², 120 A/m² and 360 A/m², respectively for TOC removal by BDD anode, whereas for COD removal; R² of 0.94, 0.98, and 0.98, respectively were obtained for the same variations in current densities. The COD and TOC removals kinetics were greatly boosted by the increase in the applied current density. The COD concentration was reduced below the discharge limit to natural current densities. The COD and TOC removals kinetics were greatly enhanced for the same variations in COD and TOC removals by BDD anode, whereas for COD removal; R² of 0.94, 0.98, and 0.98, respectively for COD removal; R² of 0.98 for the same variations in COD and TOC removals by BDD anode.

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