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Comparison of electro-oxidation (BDD anode and Ti/Pt cathode) and electro-coagulation (aluminum electrodes) for the treatment of raw landfill leachate

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ABSTRACT

The current work examines the efficiency of electro-oxidation (EO) and electro-coagulation (EC) on removing chemical oxygen demand (COD) and ammonia nitrogen from landfill leachate using boron-doped diamond and Ti/Pt electrodes in EO and aluminum electrodes in EC. After 250 min of electro-processing time at current density of 40 mA/cm^2, pH 7.53 and initial COD 5,440 mg/L, a COD removal efficiency of 93% was recorded with EO and 80% with EC, respectively. Ammonia nitrogen was efficiently removed by the applied electro-oxidation process and reached 82% after 200 min reaction time. The results of this study showed that removal of organics and ammonia nitrogen was successfully achieved rendering the electrochemical processes of interest for landfill leachate processing.

Keywords: Electrochemical processes; Landfill leachate; Boron-doped diamond; Aluminum; Wastewater treatment

1. Introduction

Landfilling is widely applied for the disposal of solid waste. During the last decade in Greece, 82% of solid waste ended up in landfills, while 15% was recycled, and the remaining was composted (Hellenic Ministry of Environment and Energy, www.ypen.gov.gr). Landfills generate leachates, characterized by high concentration of organic compounds, ammonia, inorganic salts, heavy metals and other contaminants. The chemical composition of leachates varies with the landfill age and the degree of refuse stabilization inside the landfill body. Treatment technologies for landfill leachate purification are based on physical (e.g., ultrafiltration and reverse osmosis), biological (e.g., aerobic) and chemical processes (e.g., coagulation). It is widely accepted however, that landfill leachates purification up to disposal or reuse standards, is difficult unless a combination of treatment processes is implemented [1]. Recent studies showed that the removal of both organic and inorganic compounds from landfill leachate is possible by implementing electrochemical processes, such as electro-oxidation and electro-coagulation [2–4].

Electro-oxidation is based on direct and indirect oxidation of organics and ammonia [5]. The process is mainly accomplished using boron-doped diamond (BDD) electrodes as the anode [6,7]. EO oxidizes organic compounds

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into CO_2 and water and thus minimizes the formation of excess sludge, compared to aerobic biological processes. Panizza and Martinez-Huitle [7] reported that BDD achieved complete chemical oxygen demand (COD), colour and ammonium removal from landfill leachates mainly due to the electro-generation of hydroxyl radicals and active chlorine species. During direct anodic oxidation, the pollutants were initially adsorbed onto the anode's surface and then oxidized by the electrons transferred [8]. During indirect oxidation, the organics are reacted with the generated active chlorine species (ClO^-, HClO, and Cl_2) and hydroxyl radicals ($OH^•$) [9]. BDD also exhibits high current efficiency which is accompanied with lower energy costs compared to other electrodes [7]. The energy consumption during landfill leachate processing was between 50–134 kWh/m^3 for electro-oxidation using BDD anodes [7,10–12]. Cabeza et al. [13] reported complete COD removal from a landfill leachate after 8 h processing time at 60 mA/cm^2. The required time was further decreased to 6 h with increasing current density to 90 mA/cm^2. Similarly, Can et al. [14] reported 100% COD removal after 5 h processing time at 125 mA/cm^2. At lower current density (e.g., 25 mA/cm^2) COD removal decreased to 75% at 8 h processing time. Similar behaviour was reported for ammonia oxidation [7,11,13]. The oxidized ammonia nitrogen was mainly converted to nitrogen gas (75%) and nitrates (30%) [12]. Clearly, increasing the current density and processing time results in a major process improvement.

Electro-coagulation is an advanced electrochemical process that combines electrochemical methods with conventional chemical coagulation to remove organic and inorganic compounds from wastewaters [15]. In contrary to conventional coagulation, the coagulants are generated in-situ by dissolving the sacrificial anode [16]. The rate of coagulant release is affected by the applied electric current. During electro-coagulation, hydrogen bubbles are generated at the cathode which contributes to the flotation of flocculent matter and suspended solids [17]. During electro-coagulation of landfill leachate, the generated coagulant sludge was significantly increased from 16% to 60% v/v with increasing current density from 12 to 40 mA/cm^2 [18]. The coagulant sludge is usually separated from the treated effluent either by sedimentation [19,20] or centrifugation [21]. Based on previous studies, maximum COD removal during landfill leachate electro-coagulation ranged between 60%–70% while the process was operated at short reaction time (commonly between 30 and 60 min) [18,22,23]. Ammonia removal efficiency was lower compared to COD and this was mainly attributed to the short reaction time.

Aim of this work was to evaluate the performance of mature landfill leachate electro-oxidation using BDD as the anode and Ti/Pt as the cathode, since relevant data were not found in the literature. Besides, cathodes used for mature leachate processing were stainless steel [7], tantalum [12], silver [24] and BDD [10]. Therefore, different experiments were conducted to evaluate the effect of processing time and current density on COD and ammonia removal efficiency. For comparison, the landfill leachate was also treated by electro-coagulation using aluminium electrodes as anode and cathode.

2. Materials and methods

2.1. Leachate and reagents

The leachate samples used for this study were obtained from a sanitary landfill located in North Greece. The site was in operation since 2005 and received both municipal, industrial, and agro-industrial wastes and sludges. The reagents used for pH adjustment (HCl, NaOH) and the supporting electrolyte (NaCl) were all of analytical grade (Merck).

2.2. Experimental design and apparatus

All the electrochemical experiments were carried out in batch mode, at room temperature using a cylindrical glass electrochemical reactor, with 300 mL working volume and a magnetic stirrer (Thermodyne, Nuova II STIR PLATE) (Fig. 1). Electro-coagulation treatment was performed using two commercially aluminum plates (2024 aluminum alloy) with size 8 cm × 5 cm × 0.3 cm and an effective area of 25 cm^2 each. The electro-oxidation process was performed using BDD as the anode and Ti/Pt electrode as the cathode. The inter-electrode distance was 1 cm, and the electrodes were placed vertically parallel to each other. The electrodes were connected to a DC power supply (STELLTRAFO, PHYWE SystemeGmbh & Co, Germany) to provide constant current and a multimeter (VOLTCRAFT 91) to measure electric potential and current.

The electrochemical treatment efficiency was studied for different electro-processing times (50, 100, 150, 200, and 250 min) and current densities (10, 20, and 40 mA/cm^2). Every 50 min of electro-processing time, liquid samples were extracted from the reactor medium, filtered with Whatman paper, and analyzed for pH, electrical conductivity, chemical oxygen demand (COD), and ammonia nitrogen (NH_4–N). COD measurements were performed using a COD thermoreactor (TR 420, MERCK) and a spectrophotometer (Spectroquant Pharo100, MERCK), according to the Standard Methods for Examination of Water and Wastewater [25].

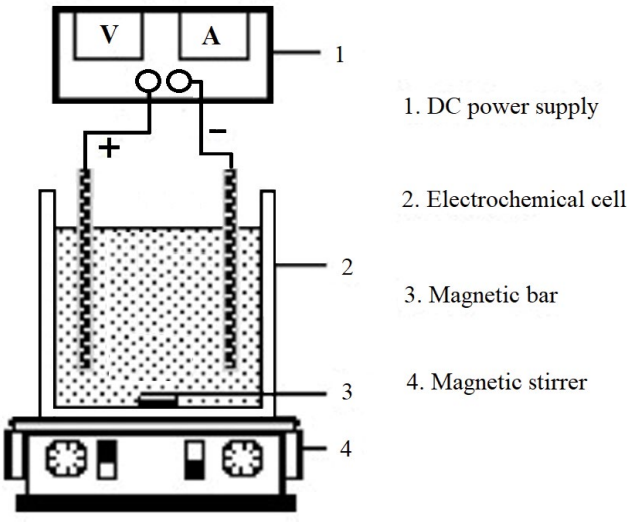

Fig. 1. Schematic representation of the experimental setup used for the study.

3. Results and discussion

3.1. Landfill-leachate characteristics

Table 1 show the physicochemical properties of the landfill-leachate used for the study. The biochemical oxygen demand (BOD)/COD ratio was equal to 0.15, indicating that the landfill was old. The leachate's electrical conductivity was relatively high (24.3 mS/cm) and this was attributed to the implementation of reverse osmosis (RO) for landfill-leachate processing (with RO concentrate recirculation back onto the landfill body). Similar composition of landfill leachate samples was reported in Brazil [22], Turkey [14], Spain [13], Poland [12] and Portugal [11]. In those cases, landfill leachate was characterized by neutral to alkaline pH (between 7.8 and 8.4), high electrical conductivity (between 8 and 27 mS/cm) and chloride concentrations (between 1.5 and 3.0 g/L). The increased salinity of landfill leachate is generally considered beneficial for the implementation of electrochemical treatment processes since the addition of a supporting electrolyte can be minimized or avoided.

3.2. Effect of electro-processing time and current density on COD removal efficiency

Tables 2 and 3 demonstrate the effect of electro-processing time on COD removal for electro-oxidation and electro-coagulation of landfill leachate, respectively. The effect of operating time was initially studied at 40 mA/ cm^2 current density. It is well known that with increasing reaction time, there is a respective increase of the electrochemically produced oxidants which improve the efficiency of the process. According to the experimental results it was possible to achieve around 90% COD removal efficiency within 250 min reaction time. Similar COD removal efficiency at 4 h was reported by Panizza and Martinez-Huitle [7], Can et al. [14] and Cabeza et al. [13] using BDD anodes and stainless steel cathodes. In their studies, however, the required current density for complete COD removal was significantly higher (up to 125 mA/cm^2). According to the data provided in Table 3, electro-coagulation with aluminum electrodes resulted in an overall COD removal of around 33% after 50 min reaction time which increased to 80% after 250 min (at 40 mA/cm^2 current density). Previous studies for landfill leachate electro-coagulation using aluminum electrodes were performed at short reaction times (30 min at 50 mA/cm^2 [18], 60 min at 38 mA/cm^2 [26] and 120 min at 50 mA/cm^2 [23]). In these cases COD removal ranged between 40 and 70% comparable to the results of this work.

Table 1
Physicochemical properties of mature landfill-leachate used for this study

Parameter	Value
pH (–)	7.53
EC (mS/cm)	24.3
COD (g/L)	5.44
BOD (g/L)	0.82
TS (g/L)	15.2
VS (g/L)	3.86
NH_4–N (mg/L)	774

Table 2
COD removal as a function of reaction time for landfill leachate electro-oxidation using BDD anode and Ti/Pt cathode, at a current density 40 mA/cm^2

Time (min)	pH	Temperature (°C)	COD (mg/L)	Removal (%)
0	7.53	28	5,440	0
50	7.35	39	4,243	22
100	7.82	39	3,264	40
150	8.11	39.2	1,686	69
200	8.35	40.5	979	82
250	8.40	41	381	93

Table 3
COD removal as a function of processing time for landfill leachate electro-coagulation using aluminum electrodes (anode and cathode) at a current density 40 mA/cm^2

Time (min)	pH	Temperature (°C)	COD (mg/L)	Removal (%)
0	7.53	28	5,440	0
50	8.91	34	3,645	33
100	9.15	37	2,122	61
150	9.22	38	1,523	72
200	9.23	39	1,306	76
250	9.30	39.5	1,088	80

The applied current density perhaps is the most significant parameter in the electro-oxidation process since it often controls the overall reaction rate [6]. The data presented in Fig. 2 reveal that COD removal efficiency is increasing with the applied processing time and current density. In the case of electro-oxidation using BDD anode and Ti/Pt cathode, after 250 min of electrolysis time the COD removal efficiency reached 69%, 83%, and 93% with increasing current density from 10 to 20 and 40 mA/cm^2, respectively. A comparison between EO and EC show that at short reaction time (<150 min), electro-coagulation is more effective in removing organic compounds from landfill leachate. This is attributed to the coagulation/ adsorption of organics onto the electrogenerated aluminium compounds. As such, COD removal reached a plateau after 150 min reaction time, since further increasing the coagulant dosage had no positive effect on treatment performance.

3.3. Ammonia removal efficiency

One of the most critical problems in landfill leachate processing is nitrogenous compounds. In mature landfill leachates, ammonia nitrogen concentrations may vary from 200 mg/L [26] up to 2,700 mg/L [12]. Fig. 3 shows the ammonia nitrogen removal efficiency as a function of electro-processing time and current density. Ammonia removal was generally attributed to oxidation by the generated free chlorine species [27]. The data presented in Fig. 3 reveal that with increasing current density, ammonia removal was significantly improved. Indeed, after 200 min electro-processing time with BDD and Ti/Pt electrodes at the higher current density (40 mA/cm^2), NH_4–N removal efficiency reached 82% (from 774 to 141 mg/L). Similar results were reported by Panizza and Martinez-Huitle [7] (95% ammonia removal at 40 mA/cm^2) and Cabeza et al. [13] (65% removal at 90 mA/cm^2).

3.4. Comparison with previous studies

Table 4 summarize the results from previous electro-oxidation and electro-coagulation studies for the treatment of mature landfill leachate. The data were selected according to the landfill leachate composition and the type of electrodes used for electrochemical treatment. According to Table 4 mature landfill leachate was characterized by an average COD = 3,800 (±1,130) mg/L, NH_4–N = 1,430 (±950) mg/L, pH = 7.9 (±0.5), and electrical conductivity 19.0 (±7.5) mS/cm. Electro-oxidation studies revealed that after 4 h reaction time COD removal ranged between 50% and 100%, while NH_4–N decreased at slightly lower rate (40% and 86%). Experiments conducted using stainless steel cathodes showed complete COD removal at high current density (90 and 125 mA/cm^2). The use of Ti/Pt cathode (this work) resulted in high COD removal at a current density of 40 mA/cm^2. Finally, a tantalum (Ta) cathode achieved only 50% COD removal while operated at low current density (25 mA/cm^2). Electro-coagulation using aluminum electrodes resulted in significantly lower COD and NH_4–N removal, compared to electro-oxidation (Table 4).

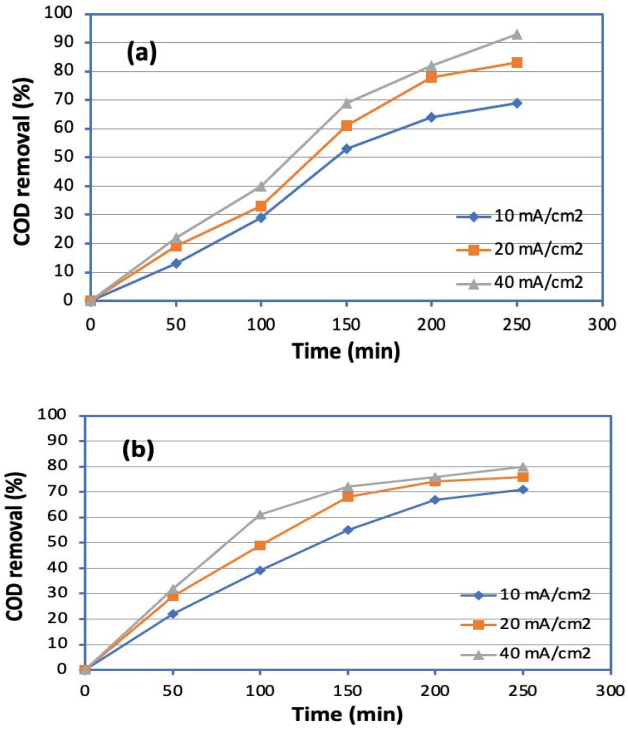

Fig. 2. COD removal efficiency (%) vs. time at various current densities for landfill leachate processing: (a) electro-oxidation using BDD anode and Ti/Pt cathode and (b) electro-coagulation using aluminium anode and cathode.

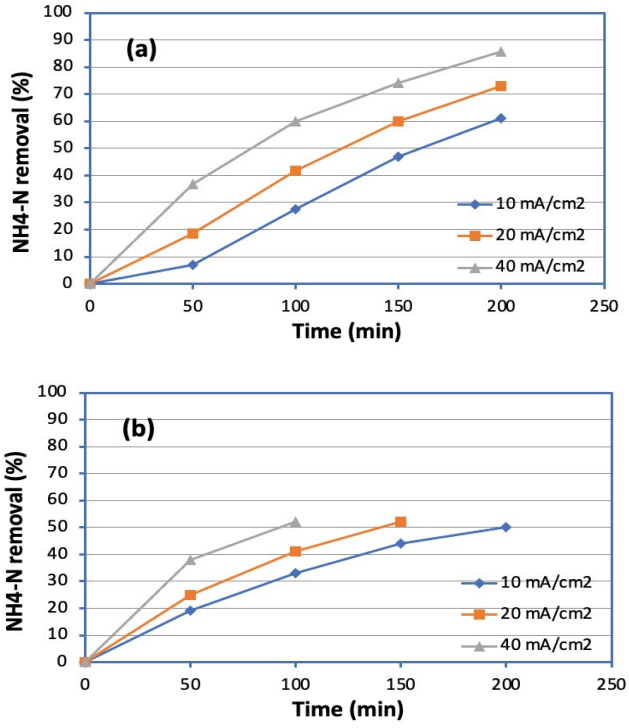

Fig. 3. NH_4–N removal efficiency (%) vs. time at various current densities for landfill leachate processing: (a) electro-oxidation using BDD anode and Ti/Pt cathode and (b) electro-coagulation using aluminium anode and cathode.

Table 4
Performance of electrochemical treatment of raw landfill leachate using electro-oxidation and electro-coagulation

pH (–)	EC (mS/cm)	COD (mg/L)	NH_4–N (mg/L)	Anode material	Cathode material	Time (min)	Current (mA/cm^2)	CODr (%)	NH_4–Nr (%)	References
Electro-oxidation										
8.00	22.0	3,500	2,500	BDD	SS	240	70	45	56	[11]
7.80	27.6	4,225	2,770	BDD	Ta	240	25	50	40	[12]
8.00	24.5	4,660	NR	BDD	SS	240	125	98	NR	[14]
8.40	12.8	4,430	1,930	BDD	SS	240	90	90	65	[13]
7.50	24.3	5,440	774	BDD	Ti/Pt	250	40	93	86	This study
Electro-coagulation										
6.90	NR	2,566	386	Aluminium	Aluminium	50	3	33	25	[28]
7.90	7.9	4,212	1,648	Aluminium	Aluminium	90	13	40	NR	[22]
8.24	9.9	1,747	216	Aluminium	Aluminium	60	36	NR	30	[26]
7.50	24.3	5,440	774	Aluminium	Aluminium	50	40	31	38	This study
						150	40	68	52	This study

NR – not reported, SS – stainless steel

Besides, the applied reaction time remained between 50 and 90 min (compared to 250 min for electro-oxidation). When the reaction time increased to 150 min (this study) process efficiency was significantly improved both concerning the removal of COD and NH_4–N.

In order to evaluate the electrochemical treatment of landfill leachate, the specific energy consumption and the respective costs involved needs to be considered. Electrochemical processing of mature landfill leachate resulted in a specific energy consumption of 55 and 140 kWh/m^3 leachate (equivalent to 14 and 28 kWh/kg COD removed) for electro-oxidation and electro-coagulation respectively. This accounts for 5.5 and 14 €/m^3 leachate respectively (considering an electricity price 0.10 €/kWh), and it is within the same range reported in previous studies [7]. Indeed, the specific energy consumption for landfill leachate electrooxidation using BDD anodes was between 20 and 90 kWh/m^3 [10,14,24] and 26 to 110 kWh/kg COD removed [4,12]. In the case of electro-coagulation the specific energy consumption was significantly lower, compared to electro-oxidation, as demonstrated by the results of both this work (14 kWh/kg COD removed) and previous studies (between 1 and 11 kWh/kg COD removed) [21,23].

4. Conclusions

Electro-oxidation and electro-coagulation processes were implemented at lab-scale to treat raw landfill leachate. Process efficiency was affected by the applied reaction time and current density. Electro-oxidation using BDD anode and Ti/Pt cathode was more efficient in decreasing ammonium nitrogen concentrations compared to electro-coagulation. After 250 min of treatment time, the electro-oxidation process achieved over 90% COD and 80% ammonium nitrogen removal compared to 80% and 50% for the electro-coagulation. The specific energy consumption was calculated equal to 14 and 28 kWh/kg COD removed for electro-coagulation and electro-oxidation respectively.

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