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Electro-Oxidation of Anaerobic Digester Effluent Results in Solids Separation by Electro-Flotation Combined with COD and Ammonia Oxidation

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Abstract

Electrochemical oxidation can provide a post-treatment alternativeto remove recalcitrant organics, ammonia and disinfect effluents from anaerobic digestion facilities. In this work we examined the electrochemical oxidation of a raw anaerobic digester effluent by using Boron Dopped Diamond (BDD) anode and Ti/Pt cathode at different current densities (25, 50 and 70 mA/cm^2). The digester effluent was characterized by a chemical oxygen demand (COD) concentration of 23 g/L, total suspended solids 15 g/L, ammonia nitrogen 1800 mg/L and electrical conductivity 14 mS/cm. Mass balance calculations revealed that the percentage of COD transferred to the foam increased from 41 to 58 and 72% with increasing current density from 25 to 50 and 70 mA/cm^2. The remaining liquid after 4.5 h electro-processing time was characterized by low COD (between 1.8 and 4.2 g/L) and ammonia nitrogen concentration (between 48 to 540 mg/L). This is in accordance with the Hellenic digestate reuse standards in agriculture (as an organic fertilizer) where COD concentrations should be less than 4.5 g/L. The results from this study demonstrate that electro-separation of digestate solids is favoured at high current densities followed by oxidation of organics and ammonia.

Keywords: Electrooxidation; Anaerobic digestion; Wastewater treatment.

1. Introduction

Anaerobic digestion technology enables organic waste treatment combined to biogas production; the latter can be utilized for heat, electricity, and transportation purposes [1]. The European Union goal to increase the consumption of biogases from 18 to 54 bil m^3 $CH_4$by 2050 [2] requires a factor 2 to 3 more anaerobic digestion facilities from around 19,000 plants currently in operation [3].

Organic wastes treated in anaerobic digestion facilities are often characterized by high suspended solids concentrations and low or medium biodegradability (e.g. lignocellulosic biomasses and manures) [4-6]. The generated anaerobic effluents (i.e. digestates) thus retain high concentrations of solids, recalcitrant organics, ammonia, soluble salts, odours and pathogenic microorganisms, therefore additional processing is often necessary [7-10]. Under field conditions, digestate processing includes separation of solids (e.g. by means of a screw press) followed by a stabilization (storage) lagoon for the liquid fraction. Indeed, the efficiency of lagoon treatment is questionable especially for effluents characterized by high organic matter content, ammonia and salinity, such as those arising from manure and agricultural digesters.

Electrochemical processes are considered of interest for industrial wastewater treatment [11-14]. These technologies have been successfully applied to enhance the biodegradability of recalcitrant organics, to oxidize ammonia and sulphides and to disinfect anaerobic effluents from pathogenic microorganisms [15-19]. Electrooxidation (EO) using boron-doped diamond (BDD) electrodes can directly oxidize organic compounds and ammonia [20,21]. Indirect oxidation is also possible via the formation of active chlorine species (ClO^-, HClO, and Cl_2) or hydroxyl radicals ($OH^\cdot$) [22,23]. EO oxidizes organic compounds into CO_2 and water thus avoiding problems related to excess sludge production.

Katsoni A. [24] studied the combined anaerobic digestion and electrooxidation (using BDD anode) for cheese industry wastewater treatment. The anaerobic treatment process achieved a COD removal efficiency between 90-95% with an effluent COD = 0.3-0.4 g/L, while the electrooxidation resulted in complete COD removal within 3-4 h processing time. Baker's yeast wastewater, having an initial COD of 15 g/L was treated anaerobically and this was decreased to 3.5 g/L [17]. The authors studied the effect of current density (6.6, 13.3, 26.6 and 40 mA/cm^2) on the electrooxidation process efficiency. For current densities higher than 26.6 mA/cm^2 the removal of COD was almost complete within 3 h processing time [17]. Finally, electrochemical treatment of livestock digester effluent was efficient for its disinfection from pathogenic microorganisms [12].

Aim of this study was to evaluate the performance of an anaerobic digestion facility treating dairy manure and digestate quality during long-term operation. Digestate was further treated by electrochemical oxidation using a BDD anode and a Ti/Pt cathode.Since digestate was characterized by a large fraction of organics, solids and ammonia the study aimed to evaluate the fate of COD, ammonia and solids at different applied current densities.

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2. Material and Methods

2.1. Anaerobic digester design and operation

The anaerobic digester consisted of a plug-flow reactor with 50 m^3 working volume. The anaerobic digester was operated over a 300 days periodunder mesophilic conditions (38-39 ^oC) while treating mainly screened dairy manure. The applied hydraulic retention time was between 5 and 10 d. The effluent from the PFR after solids separation by sedimentation was used in electrochemical studies.

2.2. Electrochemical treatment design and apparatus

All electrochemical experiments were carried out in batch mode, at room temperature, using a cylindrical glass electrochemical reactor, with 250 mL working volume equipped with a magnetic stirrer (Thermodyne, Nuova II STIR PLATE). Electrooxidation was performed using a boron-doped diamond (BDD, DiaCCon GmbH, Germany) anode and a Ti/Pt cathode electrodewith size 8 x 5 x 0.3 cm and an effective area of 25 cm^2 each. The inter-electrode distance was maintained at 1cm, 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) measuring electron potential and current.

During processing, the electrochemical treatment efficiency was studied for different processing times (90, 180 and 270 min) and current densities (12, 24, and 36 mA/cm^2). Every 90 minutes of electro processing time, liquid samples of 3 mL 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, MERK) and a spectrophotometer (Spectroquant Pharo100, MERCK), according to the Standard Methods for Examination of Water and Wastewater [25].

3.Results and discussion

3.1. Anaerobic digester performance

In Table 1 we summarize the average physicochemical properties of digester influent and effluent during the study period. The data reveal a considerable decrease in wastewater suspended solids from 26 to 11 g/L (i.e. 58% reduction) and soluble COD concentration from 18 to 6 g/L (i.e. 67% reduction).

Figure 1 show the evolution of ammonia, suspended solids and the electrical conductivity of the digestate. Digestate composition was relatively constant especially considering the concentration of suspended solids and the electrical conductivity. In order to comply with theHellenicstandardsfor digestate reuse in agriculture (as an organic fertilizer) suspended solids and COD concentrations should be less than 5 and 4.5 g/L respectively, thus additional treatment is necessary.

3.2. Oxidation of organics and ammonia during electrooxidation

Figure 2 show the concentration of COD and ammonia nitrogen during electro-oxidation treatment of anaerobic digester effluent at different current densities. Digestate COD concentration showed a gradual decrease with increasing current density and processing time. The addition of sodium chloride was essential to increase current density higher than 25mA/cm^2. Under these conditions, the increase in COD removal efficiency was attributed to indirect oxidation induced by the chloride radicals. Besides, NaCl has been reported to improve indirect oxidation of organics and to enhance process efficiency due to the formation of chlorine and hypochlorite intermediates [20,22,26] . Katsoni A. [27] reported COD removal of 70% without salt addition, and this value increased to 100% when 1.7 and 3.3 g/L NaCl were supplemented. Fernandes A. [28] showed a significant increase of COD removal efficiency (after 6 h electrolysis at 50 mA/cm^2) from of 43 to 60% with the addition of 3 g/L NaCl into the reactor.

Table 1. Physicochemical properties of the anaerobic digester influent and effluent during the study period. The data represent average values and standard deviation.

Parameter	Influent	Effluent
pH	7.17 ± 0.09	7.88 ± 0.14
EC (mS/cm)	12.0 ± 1.3	14.5 ± 1.1
TSS (g/L)	32.5 ± 13.3	15.2 ± 1.6
VSS (g/L)	26.6 ± 7.6	11.1 ± 1.1
PO_4-P (mg/L)	107 ± 7	48 ± 5
NH_4-N (mg/L)	Nd	1020 ± 280
TCOD (g/L)	32.8 ± 7.0	23.0 ± 2.0
SCOD (g/L)	18.2 ± 3.5	6.0 ± 0.6

The final COD concentration (of this study) after 4.5 h processing time was below digestate reuse standards (< 4.5 g/L) for all applied current densities.Moreover, the effluent was characterized by negligible total suspended solids, color and turbidity (see Figure 2). Similarly, electrochemical treatment was efficient in decolorizing an anaerobic digester effluent [29,17,19]. Previous studies showed that BDD electrodes were especially suitable for electrooxidation applications since they were characterized by high activity, high oxygen evolution potential, electrochemical stability, high corrosion stability, good conductivity, and they were inert in tough conditions [11,21]. Compared to other electrodes, they were the most suited for producing free radicals and performing oxidation with very high current efficiencies [30,31].

Ammonia present in anaerobic digester effluent showed a considerable decrease with the applied electrooxidation treatment. Ammonia removal was almost complete after 4.5 h processing time at high current densities. However, ammonia removal displayed a lower rate compared to COD. Ammonia removal by EO is generally attributed to oxidation by the electro-chemically generated free chlorine species (equations 1 to 3 and 4) [20,23,26] :

$$2Cl^- \rightarrow Cl_2 + 2\ e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \quad (2)$$

$$HOCl \rightarrow ClO^- + H^+ \quad (3)$$

$$2NH_4^+ + 3\ HOCl \rightarrow N_2 + 3\ H_2O + 5H^+ + 3\ Cl^- \quad (4)$$

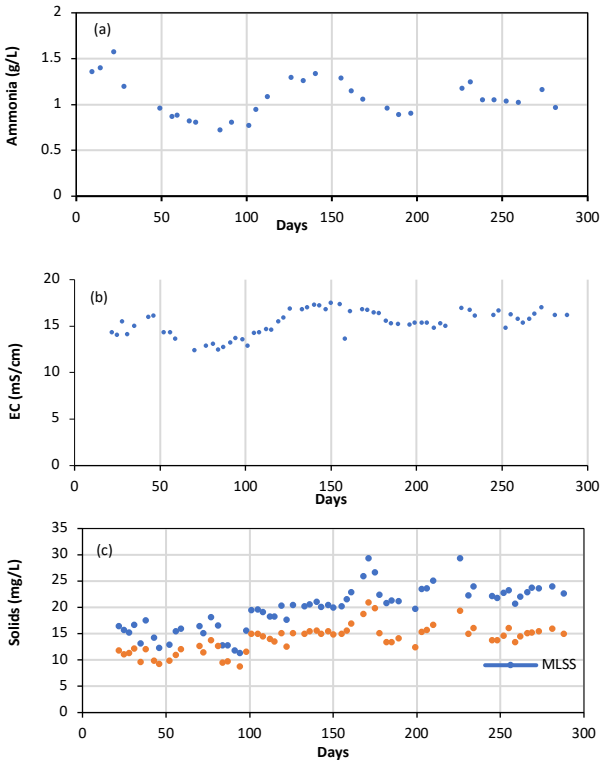

Fig.1. Evolution of (a) ammonia nitrogen, (b) electrical conductivity and (c) suspended solids concentrations of the anaerobic digester effluent during the study period

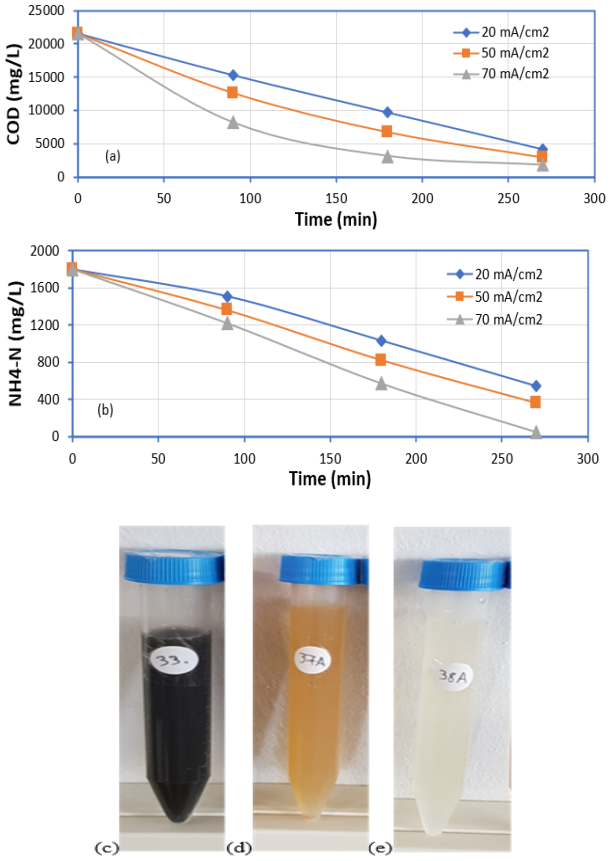

Fig. 2. (a)Evolution of COD and (b) ammonianitrogenconcentrations during electrochemical oxidation (BDD anode and Ti/Pt cathode) of the anaerobic digester effluent. Photographic representation of (c) raw digestate and the liquid effluent after (d) 90 min and (e) 270 min electrooxidation.

3.3. Digestate solids separation by electro-flotation

During the electro-oxidation process, hydrogen gas bubbles generated at the cathode contributed to the flotation of digestate particulate matter. According to the data presented in Table 2, there was a significant decrease (~ 35%) of the initial digestate volume which was transferred into the generated foam. A mass balance revealed that with increasing current density, the amount of organics transferred to the foam increased from initially 41 to 58 and 72% (Figure 3). As such the actual percentage of COD oxidized was 48, 34 and 23% with increasing current density from 25 to 50 and 70 mA/cm^2 respectively. Based on the above, it was evident that electro-separation of digestate solids was favored at high current densities [32] showed that electrooxidation resulted in protein and aliphatic matrix modification which induced changes in the release of water and improved digestate dewaterability.The remaining liquid (as described in section 3.2) was characterized by low COD concentration, and this was further decreased with processing time and increasing current density.

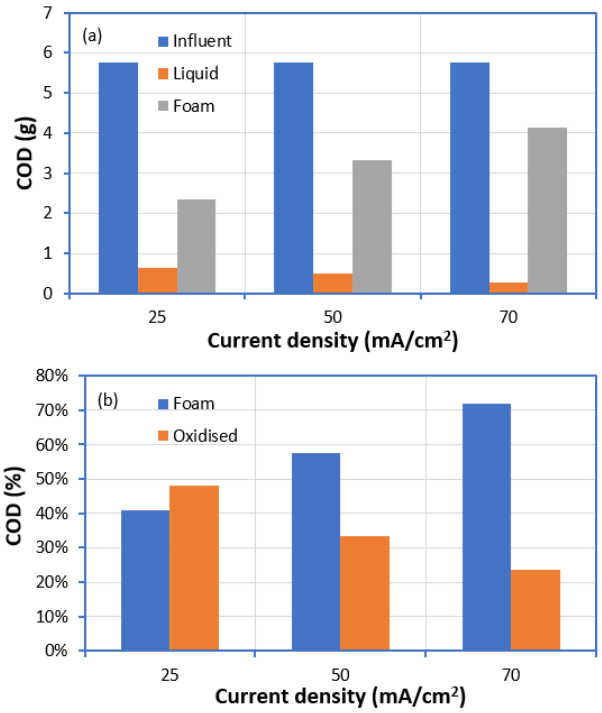

Fig. 3.(a) Mass balance of influent, effluent and foam COD, and (b) percentage of COD transfer to the foam and oxidized,by the applied electrooxidation process at different current densities after 4.5 h processing time.

Table 2. Performance of electro-oxidation of the anaerobic effluent by applying different current densityafter 4.5 h processing time.

Parameter	25mA/cm^2	50mA/cm^2	70mA/cm^2
V initial (mL)	250	250	250
V final (mL)	150	175	150
V foam (mL)	100	75	100
NaCl (g)	0.0	1.0	2.0
pH (-)	7.80	7.38	6.50
EC (mS/cm)	12.0	20.5	23.0
COD total (g/L)	4.2	2.9	1.8
COD soluble (g/L)	2.8	1.3	0.4
COD foam (g/L)	23.6	44.2	41.3

4. Conclusions

Electrochemical oxidation of anaerobic digester effluent was possible by implementing a BDD anode and a Ti/Pt cathode at current densities between 25 and 70 mA/cm^2. Generation of hydrogen gas bubbles at the cathode resulted in digestate particulate matter flotation, while the amount of solids transferred to the foam increased with increasing current density. The remaining liquid after 4.5 h processing was characterized by low COD and ammonia nitrogen concentrations, negligible color and solids concentration. Final COD was far below the standards set by the Hellenic legislation for digestate reuse in agriculture.

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