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APPLICATION OF ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (EAOPS) FOR TREATMENT OF CONCENTRATE FROM PSYCHROPHILIC ANAEROBIC DIGESTER UNITS

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Abstract: This study applied electrochemical advanced oxidation processes (EAOPs) like electro-oxidation and electrocoagulation to treat the concentrate deriving from a psycrophilic anaerobic municipal organic solid waste digester units. The concentrate or effluent from anaerobic digestion units contains high concentrations of organics and suspended materials. As a result, such concentrate poses a formidable challenge for treatment in conventional wastewater treatment facilities. Recently, EAOPs have demonstrated a promising ability to reduce a variety of pollutants from wastewater efficiently. The EAOPs have the advantage of not requiring the addition of chemical reagents in the treatment process, and these can also be easily implemented by integration in an automated treatment system. Hence, a quick and efficient treatment for high strength wastewater is possible with EAOPs. This study used an open cylindrical glass electrolysis cell with Boron-Doped Diamond (BDD) as the anode and stainless steel as the cathode for the electrooxidation process. The electrolysis cell also contained an aluminum plate in bipolar arrangement for the electrocoagulation process. The electrooxidation and electrocoagulation process stabilized the organics, both dissolved and particulate, in the wastewater. Preliminary tests were conducted to assess the effects of different operational parameters (e.g., current density, treatment time) of the electrolytic cell on the overall treatment efficiency. Based on the preliminary results, combined electro-oxidation and electrocoagulation processes demonstrated great potential for treating the concentrate from anaerobic municipal organic solid waste digester units.

1 INTRODUCTION

Anaerobic digestion (AD) is an engineered method designed to decompose organic solid waste through the synergistic action of a consortium of microbes under oxygen-free condition (Kalysuzhnyi, S;Veeken, A; Hamelers 2000, Li et al. 2011). It offers an appealing treatment option for agricultural wastes, food wastes, and wastewater sludge as it can simultaneously be applied to reduce the pollution load from wastes and recover renewable energy (Chen et al. 2008). AD processes are classified by key operating parameters and design featuresT such as continuity (batch vs. continuous), operating temperature (psychrophilic, mesophilic, and thermophilic), reactor design (plug-flow, complete-mix, and covered lagoons), and solid content (wet or dry) (Li et al. 2011, Environment Canada 2013). The dry/high solids AD process usually treats solid waste with less than 80% moisture content and the feedstock have a total solids content higher that 15-20% (Rapport, J.; Zhang , R.; Jenkins, B M; Williams 2008, Environment Canada 2013). The high solids AD processes are advantageous than wet AD in terms of use of smaller sized reactors, low energy requirements for heating, minimal material handling, lower parasitic energy

loss, and shows comparable biogas production to wet AD systems (Luning et al. 2003, Guendouz et al. 2008).

The fresh feedstock in a high-solid AD process is inoculated in the reactor to speed up the reaction processes. It is a much faster process than degradation of solid wastes in a landfill, but slower than in wet AD (Martin et al. 2003). The concentrate or leachate from AD reactor is usually recycled to inoculate the fresh feedstock (Rapport, J.; Zhang , R.; Jenkins, B M; Williams 2008, Environment Canada 2013). Leachate recycling enables the colonization of the bacteria throughout the digester by providing a passive transport mechanism for microbial communities. This provides the operational benefit of reduced handling costs and higher reactor volume utilization (Li et al. 2011). Any surplus of concentrate from AD process is directed to a wastewater treatment plant for further treatment before discharge (Environment Canada 2013). The concentrate produced from anaerobic digestion of organic solid waste contains high concentrations of organics, nutrients, and total solids. Its quality is inferior to usual municipal wastewater quality received in most wastewater treatment plants. Hence, there is a scope for developing effective treatment schemes for concentrates deriving from anaerobic digesters treating municipal organic solid wastes.

The present study considered the use of electrochemical advanced oxidation processes (EAOPs) like electrooxidation (EO) and electrocoagulation (EC) as a quick and efficient means to treat the concentrate from a psychrophilic dry AD system managing municipal organic solid wastes. Application of psychrophilic dry AD systems provides low-cost solid waste management options in cold climates (Massé et al. 2014, Rajagopal et al. 2017). These electrochemical processes avoid any addition of external chemicals to purify the wastewater and hence can be considered a "cleaner" technology than many conventional treatments. Also, these processes require less skilful supervision and can be easily integrated as parts of a more extensive treatment operation. EO process use derivatives of oxygen as an oxidizer. The direct action of electric current is used to oxidize or reduce species exclusively at the electrodes, with the indirect action generating an oxidant, which reacts electrochemically with the species in solution. The possible dominant species of oxidants include superoxide ($O_2^{\circ-}$), hydrogen peroxide (H_2O_2), ozone (O_3), atomic oxygen (O°), hydroxyl radical (OH°), hydroperoxyl radical (HO_2°), molecular oxygen (O_2) and singular oxygen ($^1O_2$) (Ferro 2006, Sultana et al. 2018). On the other hand, EC involves the generation of coagulants in situ by electrically dissolving metal ions (aluminum or iron) at the anodes (Chen 2004). The nascent metal ions are very efficient coagulants and quickly form large particulate flocs, which in turn can chemically adsorb pollutants from wastewater (Shen et al. 2003).

Preliminary results of the combined application of EO and EC for treatment of concentrate from a psychrophilic dry AD reactor have been reported in this paper. Treatment performances of EO and EC regarding chemical oxygen demand (COD) and electrical conductivity removal from concentrate originating from a psychrophilic AD system treating municipal organic solid wastes demonstrated excellent potential for application of these EAOPs.

2 MATERIALS AND METHODS

2.1 Characterization of AD Concentrate Sample

The concentrate from a dry psychrophilic AD system treating mixed food waste with cow manure was used in the present study. The AD system was installed near Sherbrook, Quebec, Canada and was operated at a low temperature (20 – 25 ^oC). This temperature range has been reported to be psychrophilic in the literature for anaerobic digestion systems (Massé et al. 2014, Rajagopal et al. 2017). The characteristics of the concentrate are presented in Table 1. It is evident from the data that the concentrate contained high concentration of organics and nutrients.

Table 1: Physicochemical characteristics of the concentrate from a dry psychrophilic AD system

Parameter (Units)	Mean Value (± Standard Deviation)
pH	7.63 ± 0.17

Parameter (Units)	Mean Value (± Standard Deviation)
Conductivity (mS)	29.30 ± 1.70
Chemical Oxygen Demand (mg/l)	10658 ± 253
Total Nitrogen (mg/l)	994.50 ± 16.24
Total Kjeldahl Nitrogen (mg/l)	964.25 ± 17.89
Ammonia Nitrogen (mg/l)	767.86 ± 26.91

2.2 Experimental Set-up

An open, cylindrical glass cell with one anode and one cathode in a vertical alignment and monopolar parallel connection was used at room temperature (22 ± 2 °C) for electrochemical treatment. BDD (Fraunhofer USA, Inc.) and stainless steel electrodes (with effective surface area of 25 cm2) were used as anode and cathode, respectively. In addition to the monopolar arrangement of anodes and cathodes, an aluminum electrode was placed in a bipolar arrangement between the anode and cathode. The distance between the different electrodes were kept at 5 mm. A sample of 450 ml volume was added to the cell. A DC power supply (E364xA, Agilent Technologies, Rockaway, NJ, USA) was used for all experiments and the experiments were performed in galvanostatic mode. The electrochemical experiments were conducted for 12 hours at an applied current intensity of 0.6 A and 0.8 A. Samples were collected at different intervals (0, 2, 4, 6, 8, 12 hours) to measure the studied parameters. The BDD, aluminum, and stainless steel electrodes were cleaned by immersion in 1 M H2SO4 for 30 minutes after each experiment to remove any adsorbed molecules at the electrode surface, if any, and after that the electrodes were rinsed with deionized (DI) water until the pH of the water on the electrodes was observed to be neutral (Abdessamad et al. 2013). Rinsing the electrodes with sufficient DI water ensured removal of acid on the electrode surfaces and prevented the electrodes from becoming polarized.

2.3 Analytical Measurements

This paper reports preliminary data of COD and conductivity removal from the concentrates. COD was measured by reactor digestion method using Hach kits (London, Ontario, Canada) and the concentration was obtained using a spectrophotometer (DR 2800, HACH) (HACH 2012). The pH and conductivity of the collected samples were measured using a pH meter and a conductivity meter (both from Oakton Instruments, Vernon Hills, IL, USA), respectively.

3 RESULTS AND DISCUSSIONS

3.1 Electrical Conductivity Reduction with Application of Combined EO-EC

Figure 1 shows the electrical conductivity profile of the AD concentrate with application of combined EO-EC treatment at an applied current intensity of 0.6 A. Visual observation of the concentrate during the EO-EC treatment revealed foam generation in the first 8 hours of treatment, which may be due to electrofloatation occurring in the cell. After this initial period visible flocs were observed in the reactor cell, and the samples collected for analysis also had flocs in them, which settled rapidly in the collection container. With increasing treatment time the rate of decrease of electrical conductivity was observed to be higher.

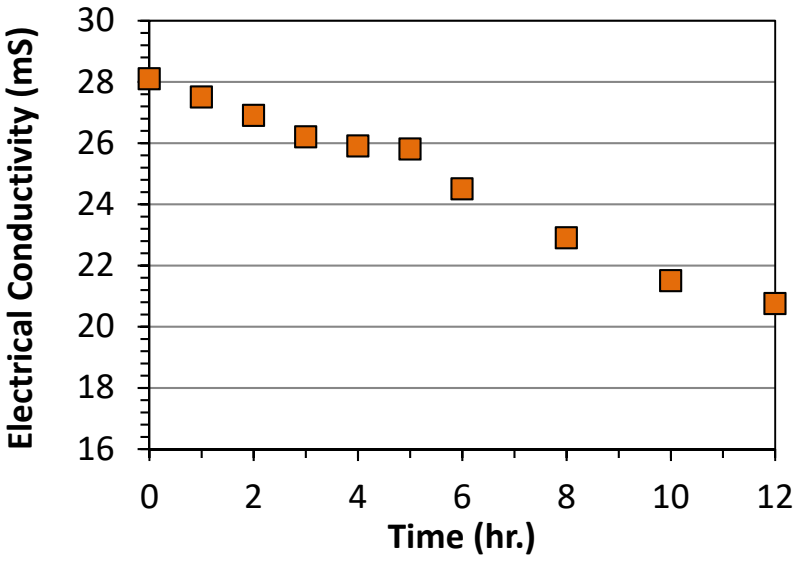


Figure 1: Electrical conductivity profile of Psychrophilic AD concentrate with application of combined EO-EC treatment at an applied current intensity of 0.6 A.

3.2 COD Reduction with Application of Combined EO-EC

COD profiles were obtained for two different applied current intensities: 0.6 A and 0.8 A. Figure 2 indicates the normalized COD reduction profile in the concentrate with time for the two applied current intensities.

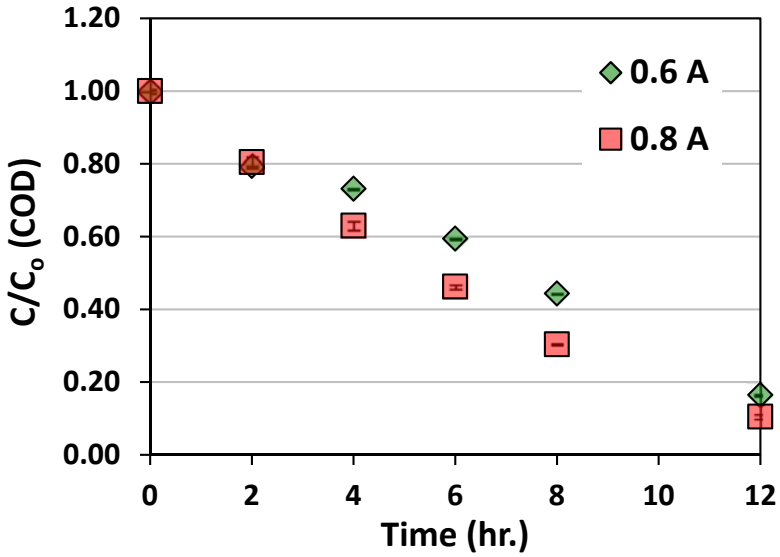


Figure 2: Variation with time of the normalized COD for the combined EO-EC treatment of Psychrophilic AD concentrate at applied current intensities of 0.6 A and 0.8 A.

The COD reduction enhanced with increased applied current intensity. In the initial few hours the effect of increased current intensity on COD reduction was not noticeable. However, the differences were more prominent in the following part, as up to 14% more removal was observed at 8 hours with 0.8 A applied current intensity. Over the extended duration of treatment, the enhanced effect of increased applied current intensity was evident.

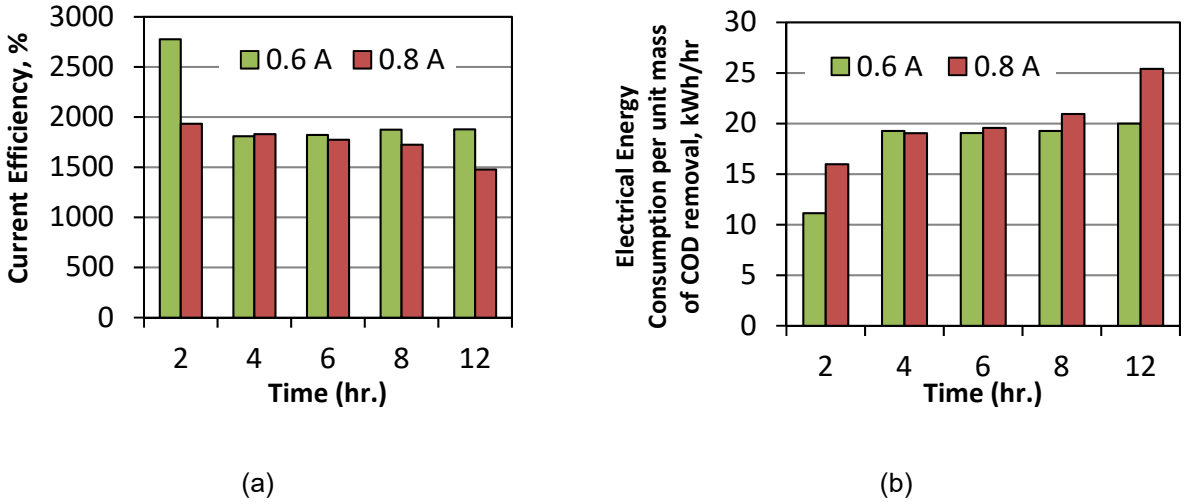
3.3 Instantaneous Current Efficiency and Specific Energy Consumption with respect to COD removal

The instantaneous current efficiency (ICE, %) and the specific energy consumption per unit mass of COD removal (KWh kg^{-1}) for different applied current intensities (shown in Figure 3(a) and Figure 3(b), respectively) were calculated using the following equations (Eq. 3-1 and Eq. 3-2, respectively) (Li et al. 2014):

[3-1] $$ICE = \frac{[(\mathrm{COD})_0 - (\mathrm{COD})_t]}{8It} \mathrm{FV}$$

[3-2] $$E = \frac{UIt}{1000\ \mathrm{V} \times \Delta\mathrm{COD}}$$

Where, COD0 and CODt are the solution COD values at time t=0 and t=t, respectively (mg/l), ∆COD = (COD0 – CODt) (mg/l), V is the solution volume (liter), F is Faraday constant (96,485 C/mole), I is the applied current (A), 8 is the oxygen equivalent mass (g/eq), and U is the applied voltage (V)



(a) (b)

Figure 3: Current efficiency, % (a) and Specific electrical energy consumption per unit mass of CID removal, kWh/kg (b) for the combined EO-EC treatment of Psychrophilic AD concentrate at applied current intensities of 0.6 A and 0.8 A.

It can be observed that both the specific current consumption and current efficiency values for 0.6 A and 0.8 A applied current intensities remained somewhat similar between 4 – 8 hours of treatment. At 12 hours the current efficiency value decreased and the specific electrical energy consumption value increased for higher applied current (i.e. 0.8 A). This may be due to oxidation of readily electro-oxidizable organics at the beginning part of the treatment; as a result the recalcitrant fraction of COD did not decrease later at the same rate even at increased current intensity.

3.4 Observation of Electrode Fouling in EO-EC

Some fouling was observed in the cathode stainless steel electrode during the treatment experiments. No fouling was observed on the BDD anodes. The bipolar aluminum electrode demonstrated decay on the surface facing the stainless steel electrode and some fouling occurred on the surface facing the anode electrode.

4 CONCLUSIONS

The present study showed great potential for the application of combined EO-EC process for treatment of high strength concentrate derived from psychrophilic dry AD systems. COD decreased rapidly in the first 8 hours of treatment. With applied current intensity of 0.8 A the COD reduction rate decreased after 8 hours of electrolysis. This may be due to conversion of all organics to complexes recalcitrant to electrooxidation, which were not oxidized at the same rate. Overall the COD was reduced to 84% and 90% of initial value after 12 hours of electrolysis with 0.6 A and 0.8 A applied current intensity, respectively. Based on the preliminary observed data, further experimental investigations will be carried out to observe removal of nitrogen and organic loads from AD concentrates. Scaling up of the combined EO-EC process for treating large volume of wastewater will be a critical issue. Such scale up would require proper electrode arrangement throughout the reactor and sufficient mixing in the reactor to circulate the wastewater around the electrodes. Failure to ensure proper circulation of wastewater in the electrochemical reactor might result localized treatment of wastewater in the reactor, which will not remove overall organic load from the wastewater.

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