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The effect of electrodialytic treatment and Na_2H_2EDTA addition on methanogenic activity of copper-amended anaerobic granular sludge: Treatment costs and energy consumption

Jurate Virkutyte [a,*], Ekaterina Rokhina [a], Piet Lens [b], Veeriah Jegatheesan [c]

[a] Department of Environmental Sciences, University of Eastern Finland, Yliopistonranta 1E, 70211 Kuopio, Finland
[b] UNESCO-IHE, Department of Environmental Resources, PO Box 3015, 2601 DA Delft, The Netherlands
[c] School of Engineering and Physical Sciences, James Cook University, Townsville, QLD 4811, Australia

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ABSTRACT

The effect of electrodialytic treatment in terms of a current density, pH and Na_2H_2EDTA addition on the methanogenic activity of copper-amended anaerobic granular sludge taken from the UASB reactor from paper mill was evaluated. Moreover, the specific energy consumption and simplified operational and treatment costs were calculated. Addition of Na_2H_2EDTA (at pH 7.7) to copper-amended sludge resulted in the highest microbial activity (62 mg CH_4-COD g VSS^{-1} day^{-1}) suggesting that Na_2H_2EDTA decreased the toxic effects of copper on the methanogenic activity of the anaerobic granular sludge. The highest methane production (159 %) was also observed upon Na_2H_2EDTA addition and simultaneous electricity application (pH 7.7). The energy consumption during the treatment was 560, 840, 1400 and 1680 kW h m^{-3} at current densities of 0.23, 0.34, 0.57 and 0.69 mA cm^{-2}, respectively. This corresponded to a treatment costs in terms of electricity expenditure from 39.2 to 117.6 € per cubic meter of sludge.

1. Introduction

Sludge management is a serious problem that requires the use of appropriate remediation technologies, especially if the sludge contains significant amount of xenobiotic components, noxious substances and heavy metals (Virkutyte et al., 2005). Sludge has a reuse potential in different fields such as fertilizers, organic matter and biogas production (Ferri et al., 2009). Methanogenic anaerobic digestion is one of the most economically viable techniques for biogas production (Zinatizadeh et al., 2009). Therefore the maintenance of a sufficient methanogenic population in anaerobic digesters is vital for its performance. Methanogenic species types and their relative population levels in sludge depend on the wastewater and sludge characteristics as well as the operational/environmental conditions maintained. Any imposed stress such as change in pH, accumulation of heavy metals, etc. may lead to a change in species types and their relative population levels, which is ultimately reflected in the reactor performance.

Electrokinetic/electrodialytic processes are widely used for soil (Virkutyte et al., 2004), sediments (Virkutyte and Sillanpaa, 2007), water and wastewater (Ferri et al., 2009; Virkutyte et al., 2010) remediation. This method uses direct low-level electric current as the "cleaning agent", combining the electrokinetic movement of ions towards appropriately charged electrodes in the matrix where they form enriched solutions or are reduced to form a deposit on the electrode (Xiu and Zhang, 2009). Also, electric current in combination with microorganisms may be utilized for hydrogen production at the biocathode (Rozendal et al., 2008). Thus, electrodialytic methods have a potential to be used to generate electricity while simultaneously treating contaminated sludge.

Sludge applied to soils as fertilizer often contains a range of various metals and plant nutrients. Some metals, such as Cu, Ni and Zn are essential micro-nutrients for plants and microorganisms, however, these micro-nutrients may be toxic at higher concentrations (Virkutyte et al., 2005). To extract metals from sludge, Na_2H_2EDTA is often used as the chelating agent, since it forms strong complexes with most heavy metals and is relatively inexpensive (about 1.3 € kg^{-1}) compared to other chelating agents (Pociecha and Lestan, 2009).

Herein we evaluate the effect of electrodialytic treatment of anaerobic sludge with a potential to produce biogas. This was done by evaluating current density, pH, addition of Cu^{2+} and Na_2H_2EDTA on the specific methanogenic activity of anaerobic granular sludge. The specific energy consumption during the electrodialytic process and simplified treatment costs were also addressed in the technology assessment.

* Corresponding author. Present address: US Environmental Protection Agency, National Risk Management Research Laboratory, Sustainable Technology Division, 26 West Martin Luther King Drive, MS 419, Cincinnati, OH 45268, USA. Tel.: +1 513 569 7964; fax: +1 513 569 7677.
E-mail address: Virkutyte.Jurate@epa.gov (J. Virkutyte).

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2. Methods

2.1. Source of biomass

Laboratory scale experiments were conducted with granular sludge, which was obtained from a full-scale UASB reactor treating wastewater from paper mills (Eerbeek, Industriewater Eerbeek, The Netherlands). The sludge parameters are presented in Table 1.

2.2. Electrodialytic experiments

The electrodialytic reactor consisted of a cylindrical Pyrex container (diameters 20 cm, length 26 cm) with a distance between the electrodes of 17 cm. The main compartment where sludge specimen (1000 g) was positioned, was separated by, respectively, anion exchange (IAI-204SXZL386) and cation exchange (ICI-61CZL386) semi-permeable membranes from Ionics, Inc. (Virkutyte et al., 2005). Titanium bars (174.3 cm^2) were used as the anode and the cathode (Elektronika-WUR, The Netherlands). The electrodes were connected with a direct current power supply (Hewlett–Packard 613 Altai, Germany) to provide a constant 0.23, 0.34, 0.57 and 0.69 mA cm^{-2} direct current. The voltage fluctuations were monitored with a Fluke 112 multimeter (Fluke, Eindhoven, The Netherlands). Peristaltic pumps (Marlow 502S, Austin, TX, USA) were employed to re-circulate electrolyte solutions. The average flow rate in the electrolytes was maintained at 5 mL min^{-1}. Electrodialytic experiments lasted for 14 days as discussed by Virkutyte et al. (2005).

To test the effect of Cu^{2+} and Na_2H_2EDTA addition on the methanogenic activity, anaerobic sludge was amended with 1000 mg kg^{-1} (wet sludge) of copper and 3.78 g of Na_2H_2EDTA. The sludge was contaminated according to the procedure described by Reddy et al. (1997). Experimental conditions are presented in Table 2.

2.3. Specific methanogenic activity tests

Specific methanogenic activity tests were carried out in 250 mL flasks with 1.2 g of oven dried granular sludge in 30 °C and determined by on-line measurements of the increase in the head-space pressure as a result of methane production as reported in details by Zandvoort et al. (2002). To determine the methane production activity (A_m), the following modified formula was used (Lin and Chen, 1999):

Table 1
Main characteristics of anaerobic granular sludge.

Parameters	Value
Reactor type	UASB
Influent	Paper mill
General characteristics	
Dry weight (%)	17
VSS (% of dry weight)	73
TSS (% of dry weight)	22
Mean density (kg m^{-3})	1040
pH	7.1
Major element content	
Sulfur (mg g^{-1} TS)	41.8
Phosphorus	6.6
Iron	28.7
Copper	0.16
Sludge EPS composition	
Carbohydrates (mg g^{-1} VSS)	7.5
Proteins (mg g^{-1} VSS)	15
Organic carbon content	36.7

Table 2
Experimental conditions.

Parameter	Value
Area of electrodes (cm^2)	174.3
Distance between the electrodes (cm)	17
Voltage (V)	40; 60; 100; 120
Current densities (mA cm^{-2})	0.23; 0.34; 0.57; 0.69
Amount of sludge specimen (kg)	1
Flow rate of electrolytes (mL min^{-1})	5
Duration of experiments (h)	336
Copper concentration (mg kg^{-1} wet sludge)	1000
Na_2H_2EDTA (g)	3.78
Molar Cu^{2+}: Na_2H_2EDTA ratio	1.2:1
pH at the anode after electrodialytic treatment	4.2
pH at the cathode after electrodialytic treatment	7.7

$$A_m = \frac{M_{max} - M_o}{M_{c(max)} - M_{c(o)}} \times 100 \qquad \text{(i)}$$

where A_m was the methane production activity (%), M_{max} and M_o were methane production (mg) at the maximum head-space pressure increase (h) and t_o, respectively, in the control sample without the electricity applied. Specific methanogenic activity of sludge granules was determined by taking the slope of the graph drawn by the methane production against time and expressed as CH_4-COD g VSS^{-1} day^{-1}.

2.4. Analyses

The sludge parameters such as dry weight (expressed in % of wet weight of settled granule), mean density, organic carbon content, pH, sulfur, phosphorus, iron and copper content were determined according to Virkutyte et al. (2005) and Pevere et al. (2009), while volatile suspended solids (VSS), total suspended solids (TSS) as well as extracellular polymeric substances (EPS) of the granular sludge were determined according to Hullebusch et al. (2005).

3. Results and discussion

3.1. Effect of current density, pH, Cu^{2+} and Na_2H_2EDTA addition on the methanogenic activity

The methanogenic activity of sludge with H_2/CO_2 and acetate as the substrate and in the absence of the electric current increased from 11 mg CH_4-COD g VSS^{-1} day^{-1} at 71 h to 48 mg CH_4-COD g VSS^{-1} day^{-1} at 106 h of the methanogenic activity test (Fig. 1a). The effect of the pH change, induced by the electrodialytic treatment on the methanogenic activity was well defined. When electrodialytically treated (pH 7.7) copper-amended sludge was tested for methanogenic activity, the increase in the activity was not significant and augmented to 32 mg CH_4-COD g VSS^{-1} day^{-1} at 50 h (Fig. 1b). The decrease in pH from 7.7 to 4.2 in sludge after a prolonged (14 days) electrical treatment resulted in a sharp decrease in the methanogenic activity to 20 mg CH_4-COD g VSS^{-1} day^{-1} at 104 h (Fig. 1c). Moreover, there was no methanogenic activity observed at 51 h, in comparison to the activity of the sludge at pH 7.7.

The methanogenic activity tests showed that pH and the chelating agent addition were the limiting factors for the methanogenic activity of the sludge, which is similar to the results of Omil et al. (1997), who investigated the methanogenic activity of granular sludge under various experimental strategies. Therefore, the absence of methanogenic activity at pH 4.2 in the sludge (Fig. 1c and d) may be associated with the fact that methanogenic bacteria are sensitive to pH changes and usually require near neutral condi-