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Short Communication

Influence of solids on the removal of emerging pollutants in electrooxidation of municipal sludge with boron-doped diamond electrodes

J.A. Barrios *, A. Cano, J.E. Becerril, B. Jiménez

Treatment and Reuse Group, Instituto de Ingeniería UNAM, Circuito Escolar, Ciudad Universitaria, 04510, México, D.F., Mexico

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ABSTRACT

Electrooxidation of waste activated sludge (WAS) was performed using boron-doped diamond (BDD) electrodes to evaluate the removal of emerging pollutants: 4-[2-(4-hydroxyphenyl) propan-2-yl]phenol (bisphenol A); nonylphenols (including isomers); and (5-chloro-2-(2,4-dichlorophenoxy)phenol) (triclosan). The applied current density was 28.5 mA cm^{-2}, and the treatment times evaluated were 60, 120, and 180 min. Partial degradation of selected emerging pollutants was obtained with efficiencies of 51% for bispenol A, 69% for nonylphenols, and 62% for triclosan. Organic matter was partially oxidized, mainly in the soluble phase. Most of the organic matter (78%) and emerging pollutants (>98%) were found to associate with solid particles in WAS, which limited the efficiency of the process.

1. Introduction

Wastewater sludge management is a major concern for treatment facilities due to its potential impacts on public health and the environment, as well as the associated handling and disposal costs. Wastewater sludge contains >90% water with the remainder consisting of organic matter, nutrients, and trace elements. It also concentrates pollutants and significant amounts of pathogens [1]– [3]. Recently, research has focused on the presence of emerging pollutants in sludge [2] as some of these may affect the endocrine system [4,5]. Furthermore, some of these compounds may end up in soils where sludge is land applied [6].

The electrooxidation technique has proven to be a suitable treatment process because it offers advantages such as the environmental compatibility, versatility, energy efficiency, amenability to automation, and in particular it has high efficiency in destroying persistent organic pollutants in water, wastewater, and sludge [7]. The process may oxidize organic compounds through two main routes: (i) a direct process, in which the organic molecules are oxidized after adsorption onto the electrode surface; or (ii) an indirect process, in which the oxidation is carried out in the bulk solution by electrogenerated oxidants [8,9]. Among these various oxidants, the hydroxyl radical (•OH) is one of the most powerful, and is produced by the oxidation of water on certain anodes, such as boron-doped diamond electrodes [7].

Based on the above, this work focused on the electrooxidation of municipal sludge with boron-doped diamond (BDD) anodes to evaluate the removal of organic matter, including three emerging pollutants (triclosan, bisphenol A, and nonylphenols), and provide information on the influence of sludge solids on their degradation.

2. Material and methods

2.1. Collection and characterization of sludge samples

Waste activated sludge (WAS) was obtained from a 2 m^3/s activated sludge wastewater treatment plant in Mexico City. Samples were collected in glass containers and cooled to 4 °C before transportation to a certified laboratory for characterization and treatment. Sludge was characterized for pH, conductivity, total and volatile solids, as well as total and soluble chemical oxygen demand (COD), all of which were determined according to the Standard Methods for the Examination of Water and Wastewater [10]. Soluble COD was determined by centrifuging sludge samples at 1400 g for 20 min and then filtered through a 0.45 μm membrane. Particulate COD was determined as the difference between total and soluble COD. For the evaluation of emerging pollutants, two grams of dried sludge (60 °C) were mixed with diatomaceous earth and then processed through an accelerated solvent extraction

* Corresponding author.
E-mail address: jbarriosp@iingen.unam.mx (J.A. Barrios).

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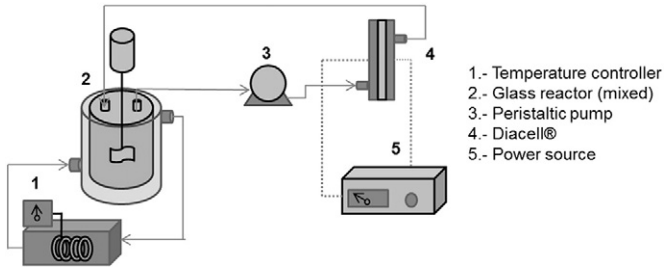

Fig. 1. Experimental set-up.

(ASE) equipment. Extraction conditions were 100 °C and 1500 psig, using a solvent mixture of acetone, hexane, and acetic acid (50:50:2, % v/v). To clean the samples, a solid-phase extraction (SPE) with Strata X phases and an acetone elution were performed. Analytes were derivatized and analyzed via gas chromatography–mass spectrometry with an HP 6890 gas chromatograph coupled to an HP 5973 selective mass detector following the protocols described in [11]. Bisphenol A, nonylphenols and triclosán were selected due to their extensive use, their toxicological effects, including endocrine disruption, and their physicochemical properties [12].

2.2. Experimental procedure

Electrooxidation tests were performed in a Diacell® electrochemical cell (WaterDiam, Switzerland) using boron-doped electrodes (surface area: 70 cm^2; electrode gap: 2 mm). 1 L samples of sludge were continuously mixed in a glass reactor at a low speed (100 rpm; Fig. 1). The system worked in total recirculation mode (2.8 L/min), with a peristaltic pump (JP Selecta Percom N-M328) at constant temperature (25 °C). Power was supplied by a Delta Elektronika ES030-10. Operating conditions are based on previous reports [13] where current densities applied to reduce emerging pollutants in industrial sludge ranged between 20 and 40 mA cm^{-2} and a treatment time of 60 min was applied. Even though current density plays an important role in the generation of hydroxyl radicals and other oxidants which allow direct and indirect oxidation, when working at very high values, efficiency does not increase linearly. This behavior is due to the undesirable secondary reaction of the water electrolysis and the generation of oxygen and OH^-, which may compete with the mineralization of organic matter [14]. For this reason, a current density ($\boldsymbol{j}$) of 28.5 mA cm^{-2} was selected which is consistent with values reported for the mineralization of bisphenol A in water (14.3 to 35.7 mA cm^{-2}) [15] and the capacity of the power source. Treatment times evaluated were 60, 120 and 180 min.

3. Results and discussion

Waste activated sludge used in the electrooxidation tests exhibited slight variations in pH, as well as in total and volatile solids since it was sampled on different dates Table 1. However, in all samples, >99% of the volume was water, while the rest was composed of solid particles

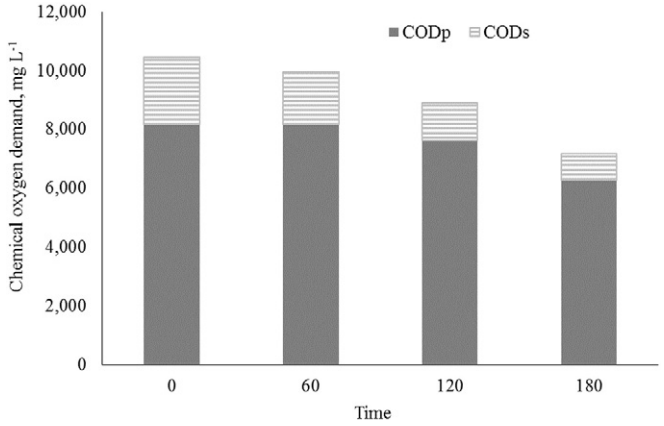

Fig. 2. Change in soluble and particulate COD in electrooxidation tests ($\boldsymbol{j}$: 28 mA cm^{-2}).

(total solids: 0.80%). Volatile solids, an indicator of the amount of organic matter in the sludge, were 80.7% of the total solids since the sludge is mostly biomass. Values of total COD (10,440 mg/L) reflect the large amount of organics present in the sludge. It should be noted that organic matter removal is be affected by the characteristics of the sludge, such as the initial COD concentration and total solids content. The former has an impact on final removal while the latter requires an intimate contact between the solid particles and the proximity of the electrode as discussed below. The decrease in COD is accompanied by a decrease in total solids and volatile solids, due to the oxidation of organic matter, including (at least partially) emerging pollutants.

The effect of treatment time is observed in the reduction of organic matter measured as volatile solids and total COD. The minimum reduction of volatile solids (VS) obtained in this work was 13% after 60 min of electrooxidation. This value is higher than that reported by [16] of <4% reduction of VS after 240 min of electrochemical treatment of WAS (pH: 6.9; TS: 0.82%) with RuO/Ti electrodes. However, their objective was the improvement of biodegradability of the sludge for an aerobic digestion process, rather than the degradation of emerging pollutants.

Fig. 2 shows the change in soluble and particulate COD for raw sludge (time = 0) and treated sludge at different times. It may be observed that the process has a better efficiency for the oxidation of soluble organic matter, rather than the oxidation of the particulate organic matter. This is clear after 60 min of treatment where particulate COD (CODp) is equal to the initial value ($t = 0$) and oxidation is only observed for soluble COD (CODs). At 120 and 180 min of electrooxidation, alone, a slight degradation of CODp was achieved (6.7 and 23.3%, respectively). It should be noted that in non-active electrodes, such as BDD, direct oxidation occurs in a thin layer close to the electrode surface where the highly-reactive and short-lived hydroxyl radical is being generated and the process becomes mass transfer controlled [17]. Based on these concepts, to fully oxidize organic matter in sludge through direct oxidation, all the solid particles would need to reach the proximity of the electrode where electrooxidation takes place. This was not achieved

Table 1
Electrooxidation results at different treatment times ($\boldsymbol{j}$: 28.5 mA cm^{-2}).

		60 min		120 min		180 min	
Parameter	Raw sludge	Value	Removal	Value	Removal	Value	Removal
pH	6.6	6.29	–	6.39	–	6.46	–
Total solids %	0.80	0.76	5%	0.69	14%	0.65	19%
Volatile solids, % of total solids	80.7	74.0	13%	72.0	23%	70.8	29%
COD_{total} (mg L^{-1})	10,440	9940	5%	8910	15%	7180	31%
$COD_{soluble}$ (mg L^{-1})	2260	1770	22%	1275	44%	910	60%
$COD_{particulate}$ (mg L^{-1})	8180	8170	0.1%	7635	6.7%	6270	23.3%
Bisphenol A (ng L^{-1})	194.3	155.7	20%	147.9	24%	95	51%
Nonylphenols (ng L^{-1})	1583	577	64%	533	66%	485	69%
Triclosan (ng L^{-1})	1193	881	26%	477.6	60%	443	63%