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Electrooxidation treatment for removal of emerging pollutants in wastewater sludge

J.A. Barrios [a,*], E. Becerril [a,1], C. De León [b,2], C. Barrera-Díaz [b,2], B. Jiménez [a,1]

[a] Treatment and Reuse Group, Instituto de Ingeniería UNAM, Circuito Escolar, Ciudad Universitaria, 04510 México, D.F., Mexico
[b] Centro Conjunto de Investigación en Química Sustentable, UAEM-UNAM, Carretera Toluca-Atlacomulco, Km 14.5, Unidad El Rosedal, C.P 50200 Toluca, Estado de México, Mexico

HIGHLIGHTS

- Electrooxidation removed emerging pollutants in industrial wastewater sludge.
- Sorption of emerging pollutants to solids limit electrooxidation efficiency.
- 90% of the organic matter is associated to sludge solids.
- Process performance is mass transfer limited and requires good mixing conditions.
- Degradation of selected emerging pollutants reached 73–89%.

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ABSTRACT

Management of wastewater sludge continues to pose a challenge as its generation is rising as a result of an increase in wastewater treatment and because its quality varies widely. Lately, emerging pollutants have gained importance based on their persistence and potential risk once they enter the environment. Different treatment processes have been proposed to reduce their concentration, such as electrooxidation. Electrooxidation using boron doped diamond electrodes has properties that make them suitable for a wide variety of applications, including wastewater and sludge. Electrooxidation was applied to sludge from a wastewater treatment plant receiving industrial discharges located in Toluca, México. Different pH and current densities were tested at the laboratory and, based on soluble chemical oxygen demand (sCOD) reduction, operating conditions were set at a pH of 3 and a current density of 40 mA cm^{-2} during 1 h. Oxidation of organic matter was limited by the concentration of solids during treatment as phased separation (flotation) occurred due to gas generation and additional tests were performed to overcome this situation. 4,4′-(Propane-2,2-diyl)diphenol, Nonylphenol, and 5-chloro-2-(2,4-dichlorophenoxy)phenol were removed by 73%, 89%, and 82% under improved test conditions. Sludge volatile solids were degraded 23% and total COD 27%. Overall, the proposed process represents a promising technology to reduce emerging pollutants in wastewater sludge.

1. Introduction

As a result of improvements in global sanitation, the amount of sludge that must be managed will increase [1]. Growing concerns about sludge management arise not only because of the costs associated to its treatment and disposal (up to 60% of operation and maintenance costs; [2]), but also based on the presence of harmful pathogens and a new kind of contaminants, namely, emerging pollutants [3].

Emerging pollutants, or micropollutants, include tensoactive substances, personal care products, pharmaceuticals, hormones, phthalates, and flame retardants. These pollutants reflect the diversity of products that society is using and the careless way in which people abuse and discharge them into sewage system. Moreover, these pollutants represent an environmental risk as some of them may have harmful effects on aquatic environments as well as on animal fertility [4].

Abbreviations: BDD, boron doped diamond (electrodes); BPA, 4,4′-(propane-2,2-diyl)diphenol; COD, chemical oxygen demand; NP, Nonylphenol; TCS, 5-chloro-2-(2,4-dichlorophenoxy)phenol.

* Corresponding author. Tel.: +52 55 56233600x8681; fax: +52 55 56233600x8694.
E-mail address: jbarriosp@iingen.unam.mx (J.A. Barrios).
[1] Tel.: +52 55 56233600x8681; fax: +52 55 56233600x8694.
[2] Tel.: +52 722 2173890; fax: +52 722 2175109.

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Many of these pollutants, such as pharmaceuticals, are not easily removed during biological or chemical wastewater treatment, and may reach the environment [5]. In addition, pharmaceuticals and hormones are of particular interest as they can cause biological responses at very low concentrations [6].

However, sludge generated during treatment has a composition similar to that of wastewater, since more than 90% of the sludge (liquid phase) is water, and thus many of those pollutants end up within this matrix. Their concentration in sludge varies widely among countries or even wastewater treatment plants [7] but evidence suggest the need to control and monitor their levels to reduce environmental risks, especially when sludge is reused in agricultural applications [8]. Conventional treatment processes, such as anaerobic or aerobic digestion, composting, or lime stabilization, are not capable of removing most of these pollutants as their presence has been documented in wastewater sludge treated by those routes [3,6,9].

Alternative treatment processes have been studied to reduce the concentration of emerging pollutants in wastewater and sludge. One of them is electrooxidation, a process that is aimed to mineralize organic compounds. In this process a direct current is applied in an electrochemical cell, then an electrochemical conversion or combustion is developed and free radicals are generated [10]. Free radicals are responsible for degrading organic pollutants, and, in particular, hydroxyl radicals (·OH) account for attacking organic compounds such as phenol and hormones [11].

The main mechanism of electrooxidation, is reported as one of the simplest technologies for mineralizing pollutants when stable anode materials are used, and boron doped diamond (BDD) electrodes have been reported as the "most active anode for oxidation of various pollutants" [12]. In addition, BDD electrodes have high anodic stability, a wide working potential window, and low stable voltammetric background current in aqueous media [13,14].

Although, there are some studies that report BDD electrooxidation for removal of emerging pollutants in secondary effluents [11], with respect to sludge and to the best of the authors' knowledge, this process has been applied only for stabilization and conditioning [15] but not for the removal of emerging pollutants. Thus, this work presents the results obtained when electrooxidation with BDD electrodes is applied to sludge under laboratory conditions.

2. Material and methods

2.1. Collection of sludge samples

Waste activated sludge was obtained from an industrial plant that treats 400 L s^{-1} of wastewater generated by more than 165 industries located in Toluca, State of Mexico. The plant includes the following processes: degritting, screening, flow equalization, primary sedimentation, activated sludge, clarification, dissolved air flotation, disinfection, as well as sludge thickening, dewatering and incineration. Samples were obtained directly from the sludge wasting/returning pipe. Therefore, the chemical composition of this effluent is rather complex. Samples were collected in plastic containers and cooled down to 4 °C, then transported to the laboratory for analysis and treatment.

2.2. Electrochemical reactor

A batch cylindrical electrochemical reactor was constructed for the electrooxidation. The reactor cell contained 2 parallel monopolar Boron Diamond Doped electrodes (BDD film supported on a niobium substrate). Each electrode was 20.0 cm by 2.5 cm with a surface area of 50 cm^2. A direct-current power source supplied the system with 0.5, 1.0 and 2.0 A, corresponding to current densities of 10, 20, and 40 mA cm^{-2}, based on previous work [16–19]. Sludge samples were mixed using a magnetic stirrer to reduce liquid–solid phase separation. The sludge volume used was 0.6 L at each experiment and the system was operated on batch mode. Fig. 1 shows a diagram of the experimental setup.

2.3. Electrooxidation tests

Sampled sewage sludge contains more than 98% of water and less than 2% of solids. As a result, the initial evaluation of the treatment in the liquid phase of the sludge was determined by analysis of the soluble chemical oxygen demand (sCOD; mg L^{-1}). This parameter was determined by the open reflux method according to the American Public Health Association (APHA). However, once the optimal conditions were found, raw and treated sludge samples were analyzed for pH, total solids, and total COD, using the standard methods for the examination of water and wastewater procedures [20].

2.4. Zeta potential measurements

The zeta potential determination of raw and treated sludge was performed using a Zetasizer Nano-Z series (Malvern Instrument GmbH, UK). Sludge samples were injected into a folded capillary cell and introduced into the equipment. The zeta potentials reported here were calculated from the average of three separate injections per sample.

2.5. UV–vis spectra

UV–vis spectra were obtained from samples of raw and treated sludge (under improved mixing conditions) using a double beam Perkin-Elmer 25 spectrophotometer. The scan rate was 960 nm s^{-1} within a 900–200 nm wavelength range. The samples were scanned in quartz cells with a 1 cm optical path.

2.6. GC–MS analyses

Gas chromatography samples were prepared with an accelerated solvent extraction followed by solid phase extraction with derivatization since this technique reduces extraction time and volume, compared to Soxhlet systems, and it is adapted from a technique reported elsewhere [21]. Samples were analyzed with an HP 6890 gas chromatograph coupled to an HP 5973 selective

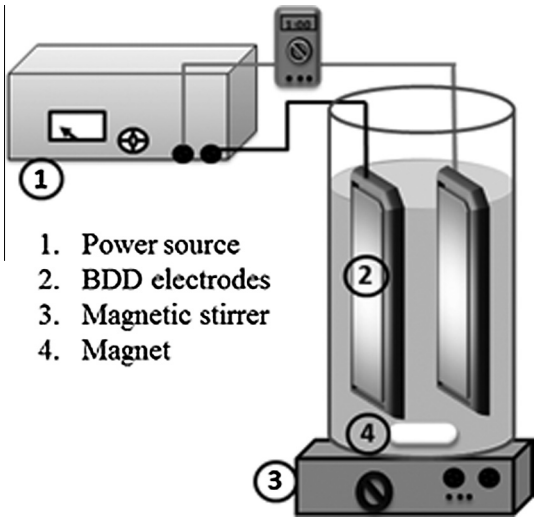

Fig. 1. Schematic diagram of the electrooxidation reactor.