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Effect of electrochemical treatments on the biodegradability of sanitary landfill leachates

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ABSTRACT

The application of combined electrocoagulation/anodic oxidation processes to improve the biodegradability of a leachate from an intermunicipal sanitary landfill was evaluated. Electrocoagulation (EC) experiments were performed with iron consumable electrodes, and the influence of the initial pH and of the electrocoagulation time were studied. In the anodic oxidation (AO) assays, a boron-doped diamond anode was used, and three applied current intensities were tested. The influence of the electrocoagulation pretreatment experimental conditions on the anodic oxidation performance was also evaluated. For the experimental conditions tested, there was an increase in the ratio between biochemical oxygen demand and chemical oxygen demand, BOD_5/COD, from 0.30 up to 0.88. The concentrations of iron, chromium and zinc were monitored during the combined treatment. During EC, chromium was almost completely removed, and zinc was partially removed; the remainder of the zinc was removed during AO. The concentration of iron increases during EC and decreases during AO; the removal of iron increases with the AO applied current density.

1. Introduction

Several types of pollutants can be found in the composition of sanitary landfill leachates, such as heavy metals, organic and inorganic compounds; some of these pollutants are refractory and toxic [1,2]. The composition and concentration of the pollutants are primarily influenced by the nature of the solid wastes deposited, the climatic conditions and the age of the sanitary landfill [3,4]. One of the major problems in sanitary landfill leachate treatment is the low biodegradability of the leachate, especially the mature leachates, because of the presence of recalcitrant and non-biodegradable organic substances [5,6]. Biological processes, used commonly to treat sanitary landfill leachates, have limited effectiveness when the ratio between the biological oxygen demand and the chemical oxygen demand, i.e., BOD_5/COD ratio, also known as the biodegradability index, is lower than 0.5 [3]. A possible solution for the treatment of sanitary landfill leachates with such properties is the use of an oxidation process as a pre-treatment to convert initially recalcitrant and non-biodegradable organic substances into more readily biodegradable intermediates [5,7,8].

Over the past 20 years, there have been several studies reporting the application of technologies based on oxidation processes to eliminate the color, reduce the organic load and, simultaneously, improve the biodegradability of the landfill leachates [4,5,9–19].

Yilmaz et al. studied the improvement in the BOD_5/COD ratio and the removal of COD and color from young municipal landfill leachate using the Fenton process [15]. The experimental results have shown a BOD_5/COD ratio increase from 0.58 to 0.64 and COD and color removals of 55.9% and 89.4%, respectively. An evaluation of the Fenton and the ozone-based advanced oxidation processes as a pre-treatment for mature landfill leachates showed that ozone in combination with hydrogen peroxide was the best oxidation approach tested, with COD removal reaching 72% and the BOD_5/COD ratio increasing from 0.01 to 0.24 [11]. A comparative study of the UV–Fenton, the UV–H_2O_2 and the Fenton reaction processes on landfill leachate was also reported, showing that the UV-Fenton process is the most effective approach to enhance the biodegradability index (from 0.17 to 0.60) and to eliminate the color of the leachate [16]. A solar photo-Fenton process combined with a biological nitrification and denitrification system was also proposed for the decontamination of a landfill leachate and was found to be efficient in the treatment of leachates, enhancing the biodegradability index and making possible a subsequent treatment by a biological oxidation process [17]. The application of a Fenton-like zero valent iron process on landfill leachates treatment was also tested, using iron shavings as the catalyst, which was shown to be a suitable and economical solution, leading to COD removals up to 60% [18].

Another promising electrochemical method used in wastewater treatment is the anodic oxidation (AO) process [20–25]. Deng and Englehardt present an overview of the electrochemical oxidation processes used to treat landfill leachates [20]. Although different

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materials are being used as anodes in the oxidation of persistent pollutants, the best results are obtained with boron-doped diamond (BDD) anodes, due to their unique chemical, electrochemical and structural stabilities that allow their use at high potentials where most organic pollutants can be oxidized [26]. Zhao et al. proposed a synergistic combination of the biochemical treatment and the electrochemical oxidation of landfill leachate with sectional treatment on a BDD electrode that was highly efficient and energy saving, with biodegradability index improvements from 0.016 to 0.51, toxicity reductions from 82.5% to 30.2% and Total Organic Carbon (TOC) removals of 83.1% [27].

Another possible method of improving the biodegradability of sanitary landfill leachates is the removal of part of the recalcitrant and non-biodegradable organic substances. Although there are no reports in the literature that describe the use of electrocoagulation (EC) to improve the biodegradability of sanitary landfill leachates, several studies show that electrocoagulation is a promising method to remove heavy metals, arsenic, dyes and other persistent pollutants that were not sufficiently removed by conventional treatments [28]. In addition, EC techniques, using aluminium and iron electrodes, presented better performance than the chemical coagulation process in the treatment of landfill leachate, showing that it can be successfully used as part of a combined treatment [29].

In EC processes, the coagulating ions are produced ‘in situ’ and they are involved in three successive stages [30]: (i) formation of the coagulants by electrolytic oxidation of the ‘sacrificial electrode’, (ii) destabilization of the contaminants, particulate suspension and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs. The generation of metallic ions involved in the first stage of EC is dependent on the applied potential/current intensity and on the pH and the conductivity characteristics of the wastewater. The main processes that occur in the electrolytic system when iron anodes are used can be described by the reactions (1)–(4). At the anode, the Fe^{2+} is formed due to the oxidation of Fe, according to reaction (1). At the cathode, H_2 gas is formed from the reduction of the protons in the acidic medium (reaction (2)) or from water reduction in the alkaline medium (reaction (3)). In both cases, the pH increases during electrolysis, and the Fe^{2+} ions can react to form iron hydroxides (reaction (4)).

$$\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{2+}(aq)} + 2\mathrm{e^-} \tag{1}$$

$$2\mathrm{H^+(aq)} + 2\mathrm{e^-} \rightarrow \mathrm{H_2(g)} \tag{2}$$

$$2\mathrm{H_2O(l)} + 2\mathrm{e^-} \rightarrow 2\mathrm{OH^-(aq)} + \mathrm{H_2(g)} \tag{3}$$

$$\mathrm{Fe^{2+}(aq)} + 2\mathrm{OH^-(aq)} \rightarrow \mathrm{Fe(OH)_2(s)} \tag{4}$$

In solution, iron ions hydrolyze and, depending on the medium pH, different polymeric hydroxides may be formed. The consumable iron anodes are used to continuously produce polymeric hydroxides close to the anode, which are excellent coagulation agents and have a strong affinity for colloids, dispersed particles and ionic species and cause flocculation. The formed flocs can be removed by sedimentation or flotation [28,31]. In the case of complex mixtures containing organic and inorganic matter, such as sanitary landfill leachates, simultaneously to the process described above, the cathodic reduction of the metal ions present in the suspension may also occur in the EC cell, with the consequent deposition of metals over the cathode.

The generally low biodegradability of the leachates from sanitary landfills shows that their biological treatment typically requires an extra aid, with chemical or physical pre-treatment or post-treatment procedures. The aim of this study was to evaluate the application of electrocoagulation and anodic oxidation in a combined process for the improvement of the biodegradability of a leachate from an intermunicipal sanitary landfill. During EC treatment, large quantities of iron are introduced into the suspension; therefore, the iron concentration was also monitored during the combined treatment, as well as the concentrations of chromium and zinc, which were already present in the leachate samples used in this study.

2. Experimental

2.1. Analytical methods

Degradation tests were followed by chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), dissolved organic carbon (DOC), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and ammonia nitrogen (AN) determinations, which were performed according to the standard methods [32]. COD determinations were made using the closed reflux titrimetric method. The BOD_5 was evaluated by determining the oxygen consumption after 5 days of incubation. The DOC and TN were measured in a Shimadzu TOC-V_{CPH} analyzer combined with a TNM-1 unit. Before DOC and TN determinations, samples were filtered through 1.2 μm glass microfiber filters. The TKN and AN were determined according to standard procedures using a Kjeldatherm block-digestion-system and a Vapodest 20 s distillation system, both from Gerhardt. The evolution of the concentration of iron, chromium and zinc during EC and AO was determined by flame atomic absorption spectrometry using a Perkin Elmer Apparatus. The sample preparation followed a standard procedure that includes an HCl–HNO_3 acid digestion [32].

2.2. Leachate characterization

The leachate samples used in this study were collected at a Portuguese intermunicipal sanitary landfill site. This site serves a population of over 220,000 and has an onsite facility capable of treating up to 50 m^3/day of leachate. The treatment applied at this landfill site comprises a biological step followed by an ultrafiltration operation. The raw leachate samples used in this study were collected in the equalization tank before the biological treatment, and their physicochemical characteristics are presented in Table 1.

2.3. Electrochemical experiments

The electrocoagulation experiments were conducted in batch mode, without stirring and using 500 mL of leachate. Iron consumable electrodes with an immersed area of 40 cm^2 were used as the anode and the cathode, with a gap between them of 1.0 cm. The experiments were conducted at an applied current intensity of 2.5 A, at room temperature (22–25 °C) and without addition of a background electrolyte. The two initial pH conditions studied were the natural pH (8.5) and a pH of 6. The influence of the EC assay

Table 1
Physicochemical characteristics of the raw leachate.

Property	Medium value (±SD[a])
COD/g L^{-1}	21.7 ± 0.5
BOD_5/g L^{-1}	6.5 ± 0.5
BOD_5/COD	0.30 ± 0.03
DOC/g L^{-1}	8.5 ± 0.2
TN/g L^{-1}	2.1 ± 0.1
TKN/g L^{-1}	2.0 ± 0.1
AN/g L^{-1}	1.2 ± 0.1
Chloride/g L^{-1}	4.4 ± 0.1
pH	8.5 ± 0.1
Conductivity/mS cm^{-1}	36.1 ± 0.4

[a] SD – standard deviation.