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New insights on abatement of organic matter and reduction of toxicity from landfill leachate treated by the electrocoagulation process

Aline Roberta de Pauli[a], Fernando Rodolfo Espinoza-Quiñones[a,*], Isabella Cristina Dall'Oglio[a], Daniela Estelita Goes Trigueros[a], Aparecido Nivaldo Módenes[a], Caroline Ribeiro[a], Fernando Henrique Borba[b], Alexander Dimitrov Kroumov[c]

[a] *Postgraduate Program of Chemical Engineering, West Paraná State University, Rua da Faculdade 645, Jd. Santa Maria, 85903-000, Toledo, PR, Brazil*
[b] *Postgraduate Program of Environment and Sustainable Technologies, Federal University of Fronteira Sul, Rua Major Antônio Cardoso 1580, 97900-00, Cerro Largo, RS, Brazil*
[c] *The "Stephan Angeloff" Institute of Microbiology – Bulgarian Academy of Sciences, Acad. G. Bonchev str., Bl. 26, Sofia 1113, Bulgaria*

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ABSTRACT

In this work, new insights on organic matter (OM) removal performance along with the assessment of the toxicity of landfill leachate (LL) treated by Electrocoagulation (EC) method were investigated. In the context of response surface methodology (RSM), the optimal EC experimental conditions were sought by applying a 3^3 complete factorial design, regarding pH, current density and electrolysis time as operational parameters. The sum of dissolved organic and inorganic carbon, namely as dissolved total carbon (DTC), was chosen as a global response parameter. Other EC experiments were performed, keeping fixed pH and current density at local optimal values and varying the electrolysis time. Determination of the median lethal concentration (LC_{50}) from bioassays based on *Artemia salina* and *Lactuca sativa* indicators was performed. A second-order polynomial function was statistically validated with good predictions of the DTC data, indicating best removals by setting values of pH, current density, and electrolysis time at 5, 128.57 Am^{-2} and 120 min, respectively. Additionally, removals above 90% were achieved for color, turbidity, iron concentration and dissolved inorganic carbon, whereas reductions on related-to-organic matter parameter values were around 60%. Although the EC treatment reduced the LL effluent toxicity, as verified by toxicity bioassays, 90 min treatment times showed best results on LC_{50}, but higher toxicity was persistent in electrolysis times below 40 min. Thus, a second stage of treatment based on a biological process could be suitably included in order to abate recalcitrant OM and decrease remaining toxicity in a more efficient integrated treatment system.

1. Introduction

Nowadays, there are many environmental problems in our technological societies being, in great part, caused by their strong interferences and contributions with discharging of any type of wastes in the environment. In this context, one of the main environmental issues that resulted from urbanization was urban solid waste disposal [1]. To reduce the anthropic impact on environmental compartments, landfills have been used to minimize the contamination of water and soils by any type of organic or inorganic pollutant, being a common practice to dispose of solid waste in large and medium-sized cities [2].

Although the correct disposal of solid wastes was apparently solved, another environmental problem has originated from the natural degradation of solid wastes along with rainwater percolation, which allows for the formation of landfill leachate (LL) effluents in large amounts. In addition, LL effluents are mainly characterized by containing a great variety of pollutants based on recalcitrant substances and other inorganic and organic pollutants, such as aromatic hydrocarbons, acids, esters, alcohols, amides, ammonia nitrogen, and heavy metals [3,4] – all of which produce an usually strong dark color and an unpleasant odor. Due to their complex compositions and their high potential for contamination, if these pollutants were directly discharged into groundwater and surface waters, then LL wastewaters would be a serious environmental concern. The simplest way to reduce their impact is to keep LL effluents in aerobic lakes. Likewise, other more sophisticated treatment methods could be applied to solve this environmental problem, such as trying to drive the removal of high pollutant charges so that they reach the recommended environmental

* Corresponding author:
E-mail addresses: f.espinoza@terra.com.br, fernando.espinoza@unioeste.br (F.R. Espinoza-Quiñones).

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requirements before being discharged into bodies of water as proposed by the authors [5,6].

To remove the pollutants from LL effluents, many unconventional technologies have been proposed; examples include the advanced oxidation processes, the membrane filtration process, a biologic process, and coagulation-flocculation methods [7]. Among these methods or processes, few have exhibited good performance in treating LL effluents by reducing their environmental impacts, but unfortunately, their costs were higher than other methods due to the complexity and different natures of the LL pollutants. Hence, new approaches were introduced for increasing the treatment method's performance and reducing costs − among them, the electrocoagulation (EC) method [8,9] is highlighted. In the framework of the EC method, organic and inorganic compounds undergo electrochemical reactions, which are supported by the addition of coagulants via oxidation of the electrodes along with the water hydrolysis, to form long chains of metallic hydroxides, where the electrically modified pollutants are confined so that they are quickly separated from the aqueous medium in a simple way [10].

Although the EC technique had a high performance and reliability as an LL treatment alternative [11], experimental results showed that some recalcitrant pollutants remained after the EC treatment, which demonstrated the requirement for further purification activities. As an environmentally responsible way to elucidate the possible impact of treated effluents on living organisms found in freshwater bodies, toxicity assessments are usually demanded. In this context, the toxicity assessments for LL effluents are traditionally based on physico-chemical analyses as reported by Klauck et al. [12]. These analyses reveal low sensitivity and are unable to represent the real toxic effects of the remaining pollutants on biota and fauna. Hence, another approach, which uses bioassays for the toxicity assessments [13], should be performed to evaluate the real environmental risks, such as the method reported by Sobrero and Ronco [14]. In the framework of bioassay testing, it was possible to evaluate the biological effects and other factors, such as the bioavailability and interactions with toxicants in an integrated way [15]. As an evaluation criterion, the median lethal concentration (LC_{50}) is usually employed, which provides an integrated response in time to all the toxicological effects [13]. Two special living organisms, *Lactuca sativa* and *Artemia salina*, have usually been recommend and employed for assessing the toxicological effects of wastewaters [16–18,12]. This is because the *Artemia-salina*-based toxicity tests show precision and reliability in assessing the toxicological effects of EC treated LL effluents [19].

In this work, the minimum environmental impact of LL effluents treated using the EC method was investigated. This study was performed by applying a two-stage strategy. First, an evaluation of the best operational conditions for the EC process was investigated based on the response surface methodology, which involved applying a 3^3 experimental design. Second, the removal performance of organic and inorganic pollutants was evaluated by examining the main components of the LL effluents for the dissolved total carbon (DTC), the chemical oxygen demand (COD), the biochemical oxygen demand (BOD), the ammonia nitrogen concentration ($N\text{-}NH_3$), the turbidity, and the color, as well as, for the concentration of a series of chemical elements. The toxicity index for raw and treated LL effluents was statistically inferred from the LC_{50} determination.

2. Materials and methods

2.1. Collection, monitoring, and preservation of LL samples

In the Cascavel municipality, which is located in the western region of Brazil's Parana state, almost all the solid waste collected from urban residences are often disposed of in a modern municipal sanitary landfill. Since this practice began, this landfill has generated a huge amount of gases that were generated by the degradation of organic matter, which enables the production of enough electricity to be used as a source of power generation. Additionally, a large amount of landfill leachate was produced and stored in aerobic lakes for pretreatment. For the purposes of employing and studying the EC method as a part of the LL treatment system in this landfill, about 100 liters of leachate effluent were collected in plastic cylindrical containers and then preserved using refrigeration at 4 °C in a laboratory, which is as the methodology described in the Standard Methods [20]. A few physico-chemical parameters, such as temperature, pH, the dissolved oxygen, and the electrical conductivity, were measured *in situ* using a multi-parameter meter (Hanna, HI 9828 model), whereas other parameters were measured under lab conditions. Throughout one year, the main physico-chemical and pluviometric parameters were monitored monthly; the pluviometric data was provided for research purposes by the Meteorological System in the Brazilian state of Paraná.

2.2. Chemicals and stock solutions

All stock solutions and dilutions were prepared by using chemicals of analytical grade and ultra-pure water obtained from a reverse osmosis filtration system (Millipore® Direct-Q-Model). According to the Standard Methods [20], chemical solutions were prepared and stored for analysis of the chemical oxygen demand (COD), the biochemical oxygen demand (BOD), the ammoniacal nitrogen, and the color. Additionally, a certified standard solution of Gallium, with a $1.0\,gL^{-1}$ concentration in a 5% nitric acid medium, and ICP grade (Sigma-Aldrich®, CAS 16639) were used to analyze the total reflection X-ray fluorescence (TXRF) by applying the internal standard method to determine the concentrations of chemical elements in aqueous samples.

According to the protocol proposed by Meyer et al. [16], a nutrient solution consisting of 23.0 g of NaCl, 11.0 g of $MgCl_2{\cdot}6H_2O$, 4.0 g of Na_2SO_4, 1.3 g of $CaCl_2{\cdot}2H_2O$, and 0.7 g of KCl were placed in 1.0 L of Milli-Q water, which was prepared for all the toxicity tests using *A. salina*. The pH of the nutrient solution was adjusted to 9.0 by adding aliquots of Na_2CO_3 solution. The nutrient solution, with pH = 9.0, was used as a diluent and as a negative control for the bioassays with *A. salina*. Likewise, as proposed by Sobrero and Ronco [14], reconstituted hard water, which consists of 1.01 g of $MgSO_4{\cdot}7H_2O$, 0.72 g of $NaHCO_3$, 0.30 g of KCl, and 0.48 g of $CaSO_4$ in 4.0 L of Milli-Q water, was prepared for the *Lactuca-sativa*-based toxicity tests. The hard water was used as a diluent and as a negative control in the bioassays with *Lactuca sativa*.

2.3. Characterization of the LL effluents

To follow the performance of the EC process and its improvement, a series of physico-chemical indicators, which were mainly associated with the content of organic and inorganic matter, were used. Reductions in the COD, the BOD, the color, the turbidity, the ammoniacal nitrogen, the dissolved organic carbon (DOC), and the dissolved inorganic carbon (DIC) were related to the raw effluent used as a response parameter for the evaluation of the EC process performance, whereas concentrations of iron and other chemical elements were associated with inorganic origins.

The amounts of organic and inorganic carbon in the raw LL effluent were estimated to have a concentration range above $100\,mgL^{-1}$, and different sized particulates were noticed in the raw LL effluent, which probably introduced undesirable interference that prevented a reliable analysis of the DOC and the DIC concentrations. Therefore, diluted and filtered samples of raw LL effluent were prepared and analyzed. The concentration of the DTC (DOC + DIC), the DOC, and the DIC were measured using a TOC analyzer (Shimadzu, model TOC-L), which was equipped with an OCT-L sampler.

Following the analysis described by the Standard Methods [20], the COD was determined using the closed reflux method. The BOD was measured using the respirometric method. The ammoniacal nitrogen analysis was performed using the phenate method, and the phosphate