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# Application of electrocoagulation in sanitary landfill leachate treatment

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## Abstract

The application of electrocoagulation, as a post-treatment, in the removal of organic load from a leachate collected in an intermunicipal sanitary landfill was evaluated.

In order to understand the influence of the anode material in the electrocoagulation results, two different types of consumable anodes were used: iron and aluminum. Assays were run at constant applied potential, at natural initial pH.

Slightly better results in the COD removal were obtained in the electrocoagulation performed with the iron anodes. The assays run with iron anodes also present lower energetic consumptions per mass of COD removed. However, when COD removed by mass of metal consumed is compared, the best results were obtained when aluminum consumable anodes were used.

## Introduction

Leachate generation is an inevitable consequence of the deposition of solid wastes (MSW) in sanitary landfills, and is the result of water percolation through wastes, that extracts and brings with it several pollutant materials [1].

This way, sanitary landfill leachate composition is very complex and varied and depends primarily on: the type of solid wastes that are deposited, the climatic conditions and the age of the sanitary landfill [1]. Inadequate leachate management involves considerable risks, particularly contamination of water resources (at the surface and groundwater) and soil [2].

In Portugal, a common treatment for sanitary landfill leachates comprises biological reactors with nitrification / denitrification steps, followed by membrane technologies. However, due to variability in the quality and quantity of leachate throughout the life span of the treatment plant, these conventional treatments become ineffective, so it is necessary to implement technologies that can be adjusted to *in situ* needs [2].

Electrochemical technologies have shown high efficiency in the elimination of persistent pollutants. Several studies have described the application of electrochemical methods in wastewater treatment [3-5].

Electrocoagulation is an electrochemical technology that can be applied in pollution abatement from liquid effluents. Its application, characterized by its simple equipment, easy operation and decrease in the amount of sludge, has also been studied in the treatment of sanitary landfill leachates, with very promising results [6,7].

The aim of this work was to study the application of electrocoagulation as a post-treatment of sanitary landfill

leachates, using two different consumable anode materials: iron and aluminum. The leachate samples used in this study were collected from an intermunicipal sanitary landfill. The treatment performed at the sanitary landfill comprises a biological step, followed by an ultrafiltration operation. Since the ultrafiltration permeate still presents a high organic load, samples collected in this point of the treatment plant were used in this study.

## Materials and Methods

Electrocoagulation experiments were conducted in batch mode, without stirring and using 1L of leachate at natural pH. Two different anode materials were tested, aluminum and iron. All experiments were conducted with an applied voltage of 5.0 V, at room temperature (22-25 °C) and without addition of background electrolyte. Electrocoagulated samples started to precipitate after elapsed times between 60 and 80 minutes. At that time, current was turned off, the formed flocks were allowed to settle, and the suspension was decanted and subjected to filtration.

Assays run were followed by Chemical Oxygen Demand (COD) tests, using the closed reflux dichromate titrimetric method [8], and by suspended (SS) and dissolved solids (DS) measurements, performed according to standard procedures [8].

## Results and Discussion

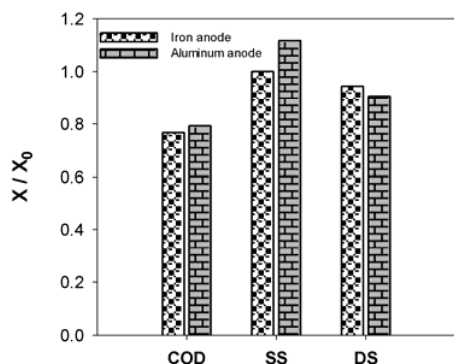
Table 1 presents the initial values for the parameters COD, SS and DS for the raw leachate collected at the sanitary landfill.

**Table 1.** COD, SS and DS for the raw sample collected at the ultrafiltration permeate.

COD / mg O <sub>2</sub> L <sup>-1</sup>	SS / g L <sup>-1</sup>	DS / g L <sup>-1</sup>
2605	0.43	11.33

Figure 1 presents the normalized COD, SS and DS variation for the electrocoagulation assays performed with both anode materials, iron and aluminium. It can be observed that electrocoagulation with iron promotes slightly higher removals of COD, but SS and DS are barely affected. With aluminium anodes, an increase in SS and a decrease in DS were obtained, which may lead to a more easy removal of the undesirable material.

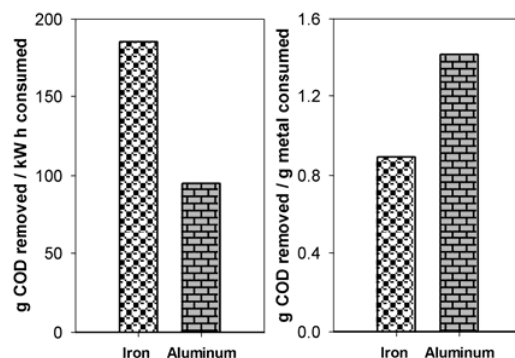
In Figure 2 the ratios of COD removed by energy consumed (a) and by mass of metal consumed (b) are presented. From an energetic point of view, the removal of COD can be favored by the use of iron electrodes, since the mass of organic load removed by unit of energy consumed when iron electrodes are used is twice the value obtained when aluminum anodes are used. However, higher removals of COD can be obtained with lower quantities of metallic ions when aluminum is the consumable anode material. These results must be related with the oxidation state of the different ions formed during the electrodegradation: On one hand, less energy is required to form the iron ions, which are divalent, while the aluminum ions are trivalent, but on the other hand, the trivalent ions promote flocculation of dissolved and suspended materials more easily, requiring lesser amount of material to perform similar reductions in the organic load.



**Figure 1.** Normalized COD, SS and DS variation for the electrocoagulation assays performed with two different anode materials, iron and aluminium, at an applied potential of 5.0 V, natural pH ( $\approx 8$ ) and without stirring.

## Conclusions

According to the obtained results, it seems feasible the application of electrocoagulation as a post-treatment of the ultrafiltration permeate from leachates of sanitary landfills to reduce the organic load. Between the two anode materials studied, iron presented the best energetic results, achieving a COD removal of 185.5 g per kW h of energy consumed. However, this result is obtained with higher consumption of metal ion than would be necessary if aluminum was used.



**Figure 2.** Ratios between COD removed and the energy consumption (a) or metal consumption (b) obtained in the electrocoagulation assays performed with two different anode materials, iron and aluminium, at an applied potential of 5.0 V, natural pH ( $\approx 8$ ) and without stirring.

## Acknowledgements

Financial support from FEDER, through Programa Operacional Factores de Competitividade – COMPETE, and FCT, for the project PTDC/AAC-AMB/103112/2008, and ICI-Santander Totta Investigação, for the grant awarded to A. Fernandes, are gratefully acknowledged.

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# Perovskite thin film electrodes for environmental applications produced by RF-Magnetron Sputtering

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## Abstract

In this work,  $\text{Ca}_{1-x}\text{Ho}_x\text{MnO}_3$  ( $0 \leq x \leq 0.4$ ) electrodes were prepared by RF-magnetron sputtering from nanosized powder targets previously prepared by self-combustion method using citric acid. The structural and morphological characterization was performed by XRD and AFM. The oxides electrochemical behaviour was studied by means of open circuit potential measurements and cyclic voltammetry. The oxide electrode's capacity has been estimated from the charging currents and the corresponding roughness factors evaluated. From the voltammograms features it was possible to identify the oxide redox couple  $\text{Mn}^{4+}/\text{Mn}^{3+}$  using the literature data. In addition, the stability potential range for these materials has been established. The electrodes performance was tested in photodegradation and photoelectrodegradation of ibuprofen, in aqueous  $0.035 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$  solution.

## Introduction

Electrochemical processes are among the polishing treatments that can be successfully applied to completely remove the residual organic load from wastewaters. However, it is critical to develop electrodes with a high activity for the oxidation of the pollutants and that have a long life and a low cost. Different materials can be used as electrodes, such as  $\text{A}_{1-x}\text{Ln}_x\text{MnO}_3$  ( $\text{A}$  = alkaline earth,  $\text{Ln}$  = rare earth) with perovskite-type structure, since they possess suitable electrical conductivity, electrochemical stability in basic solution in the negative potential range [1,2]. However, the implementation of the electrochemical processes has two main important issues to be addressed: the efficiency of the material as a catalyst in the electrochemical process, which is measured by the extension of the degradation reaction and the ability to promote total mineralization or just partial degradation with the formation of more oxidized compounds; the efficiency of the material as electrode, including its cost, electrochemical stability, durability and energetic consumption has to be taken into account. In fact, the electrodes when prepared by the conventional ways exhibit a poor mechanical resistance. To overcome these problems the electrodes preparation by DC-magnetron sputtering technique looks like a promising alternative. This technique presents several advantages [3] such as high deposition rates, high-purity films and extremely high adhesion of films.

In this context we have undertaken the preparation of oxide type electrodes by RF-magnetron sputtering. This work reports some preliminary results of the preparation and characterization of  $\text{Ca}_{1-x}\text{Ho}_x\text{MnO}_3$  ( $0 \leq x \leq 0.4$ ) electrodes by RF-magnetron sputtering from nanosized powder targets. The  $\text{Ca}_{1-x}\text{Ho}_x\text{MnO}_3$  thin films electrodes were tested in the photo and photoelectrodegradation of a "model" pharmaceutical compound, ibuprofen (IBU), in aqueous solutions.

## Materials and Methods

$\text{Ca}_{1-x}\text{Ho}_x\text{MnO}_3$  electrodes were deposited by RF-magnetron sputtering using  $\text{Ca}_{1-x}\text{Ho}_x\text{MnO}_3$  solid solutions ceramic targets. The polycrystalline  $(\text{Ca},\text{Ho})\text{MnO}_3$  ( $0 \leq x \leq 0.4$ ) samples, used as targets, were previously prepared by self-combustion method using citric acid as described in previous reports [4,5]. After the decomposition at  $600^\circ\text{C}$ , for 6 h, the resulting amorphous powder was grounded and heated in air at  $800^\circ\text{C}$  for 18 h in alumina crucibles (Alsint 99.7). The targets were prepared by mixing the synthesized powders with acetone. The mixture was placed on the cathode top and it was pressed and compacted until the acetone evaporation. The targets were sputtered in 99.999% pure argon at constant total sputtering gas pressure ( $P_{\text{Tot}}$ ) of 0.6 Pa and the deposition time was 90 min. It was used a RF power supply: Plasmaloc 2HF and all depositions were done using a sputtering power of 30 W, frequency = 200 KHz. The manganite films were deposited on ITO (Indium tin oxide) coated quartz glass substrates ( $20 \text{ mm} \times 10 \text{ mm}$  and 1 mm thick). In order to allow the crystalline growth, the films were annealed at  $800^\circ\text{C}$  in air during 6 h.

The structural characterization of the films was carried out by X-ray diffraction (XRD) on a Philips Analytical PW 3050/60 X'Pert PRO ( $\theta/2\theta$ ) equipped with X'Celerator detector and with automatic data acquisition (X'Pert Data Collector (v2.0b) software), using a monochromatized  $\text{CuK}\alpha$  radiation as incident beam, 40 kV–30 mA. Diffractograms were obtained by continuous scanning in a  $2\theta$ -range of  $20^\circ$  to  $90^\circ$  with a  $2\theta$ -step size of  $0.017^\circ$  and a scan step time of 20 s.

For a detailed study of the surface, an atomic force microscope (AFM) was used, AFM Topometrix TMX 2000 (Veeco Instruments), in contact mode. Silicon cantilevers were employed. All images were taken with  $400 \times 400$  pixels resolution and images with an area of  $1 \times 1 \mu\text{m}^2$  were obtained. A one step-leveling was applied for all images for accurate measurement of Z-height across a



sample without adding any erroneous tilt information to the data. The surface morphology of the films was characterized by the root mean square roughness ( $R_{\text{rms}}$ ) which was calculated by Topometrix software.

The oxides electrochemical behaviour was studied by means of open circuit potential measurements and cyclic voltammetry, in 1 mol L<sup>-1</sup> KOH solutions. Solutions were prepared from AnalAR reagents with Millipore Milli-Q water and degassed with nitrogen, 99.999% purity gas supplied by Air Liquide. The electrochemical experiments were performed in a two-compartment three-electrode glass cell at room temperature. The counter electrode was a graphite rod and, as reference, an Hg/HgO (0.099V vs. SHE) was used. Voltammetric studies were carried out using a low noise operational amplifier potentiostat incorporated with positive feedback IR compensation, programmed by a Bank VSG 83 waveform generator and a Kipp & Zonen Pr6-1 recorder and the chronopotentiometric studies with a Voltalab 32 Radiometer apparatus connected to an IMT 102 interface, controlled by a personal computer through the VoltaMaster 2 software.

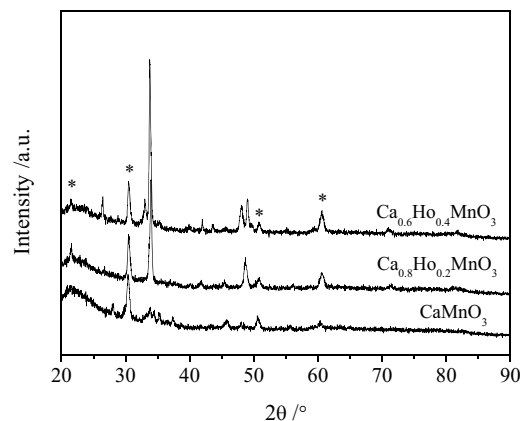
Preliminary studies of photodegradation and photoelectrodegradation were conducted using a 250 mL quartz photoreactor. The radiation source used was a Spectroline series Model ENF-280C/FE (230 V, 50 Hz, 0.17 A). In the photoelectrodegradation experiments the anode was  $\text{Ca}_{0.8}\text{Ho}_{0.2}\text{MnO}_3$  electrode and the cathode a stainless steel foil, both electrodes being 1 cm<sup>2</sup> in area and having a 1 cm gap between them. All anodic oxidation assays were performed under galvanostatic conditions with imposed current densities of 5 mA cm<sup>-2</sup>. The processed solution volume was 100 mL with a concentration of 100 ppm for IBU. Sodium sulfate aqueous solutions (5 g L<sup>-1</sup>) were used as the supporting electrolyte in all experiments. Assays were run for 24 h, and data points were collected at 2 h intervals during the first 8 h with a final one collected at 24 h. The degradation of the ibuprofen was followed by UV-Visible absorption spectrophotometry with absorbance measurements between 200 and 800 nm, using a UNICAM Hekios-a UV/VIS spectrophotometer.

Chemical Oxygen Demand (COD) determinations were made following the titrimetric method, according to standard methods [6]. Electrodegradation assays were also monitored by measurements of Total Organic Carbon (TOC), performed in a Shimadzu TOC-VCPH/CPN apparatus.

## Results and Discussion

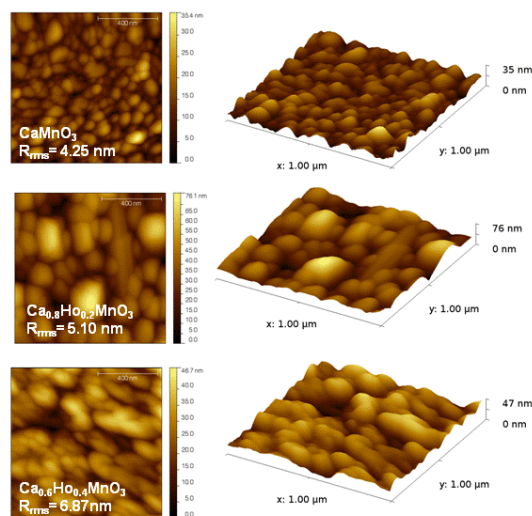
The structural characterization revealed that the as-sputtered manganite films were amorphous. To allow the crystalline growth the electrodes were annealed at 800 °C in tubular furnace for 6 h in air. The XRD data for the annealed manganites films are presented in Figure 1. The XRD results revealed the formation of perovskite-type phase for all the samples and the diffractograms are

characteristic of the orthorhombic symmetry, space group *Pnma*.



**Figure 1.** XRD patterns of the annealed manganite films deposited in ITO substrate (\* - corresponds to ITO substrate).

The surface morphologies of the electrodes were studied with AFM technique. Figure 2 shows the obtained AFM images (two- and three-dimensional images) for all films. All the films exhibit a rough surface texture and consist of particles fused together at the interparticle contact, building up high mountains and deep valleys. The analysis of AFM images show a slight increase in surface roughness with the increase in Ho content.

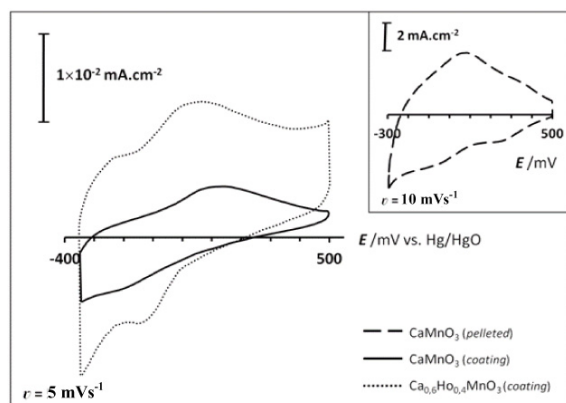


**Figure 2.** AFM images (two- and three-dimensional images) of the annealed manganite films.

The open circuit potential of the  $\text{Ca}_{1-x}\text{Ho}_x\text{MnO}_3$  ( $x = 0, 0.2$  and  $0.4$ ) oxide electrodes was measured in KOH 1 mol L<sup>-1</sup>. An average value of  $0.041 \pm 0.005$  V vs Hg/HgO has been obtained. No meaningful changes were observed by the presence of Ho-ions in the oxide. The value approaches the thermodynamic value calculated for the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  solid-state redox couple, 0.089V vs. Hg/HgO [7]. This result indicates that the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  redox couple

is the determinant on the surface equilibrium reaction, what is in accordance with previous studies on  $\text{CaMnO}_3$ -based electrodes [8,9].

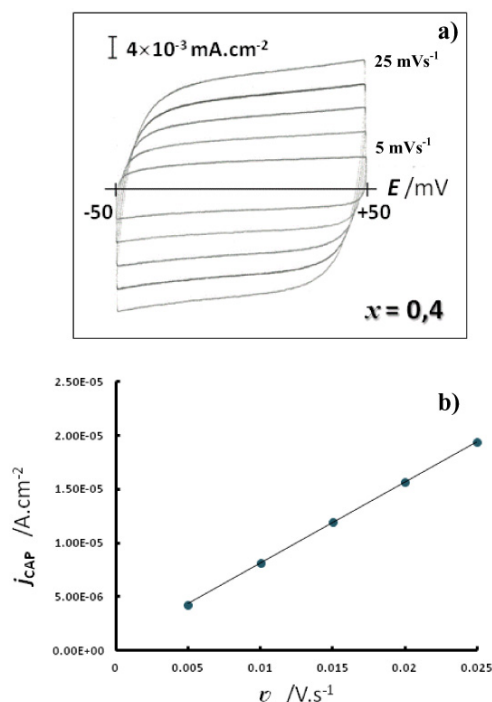
Cyclic voltammograms were recorded for the different oxides, in  $1 \text{ mol L}^{-1}$  KOH at a sweep rate of  $10 \text{ mV s}^{-1}$ , between the open circuit potential and different positive and negative limits. Figure 3 shows a representative family of voltammograms for the  $\text{CaMnO}_3$  and  $\text{Ca}_{0.6}\text{Ho}_{0.4}\text{MnO}_3$ . Comparing the different curves, it can be detected a similar behaviour with the one exhibited by the electrodes with the same composition but prepared in pellet [1] (see the inset in Figure 3) and also is observed an increase in the current density for the samples containing Ho. This result could be due to an increase of the oxide surface area promoted by the presence of Ho.



**Figure 3.** Cyclic voltammograms for the  $\text{Ca}_{1-x}\text{Ho}_x\text{MnO}_3$  ( $x = 0, 0.4$ ) electrodes prepared by RF- sputtering in  $1 \text{ mol L}^{-1}$  KOH. The inset shows the cyclic voltammogram for pelleted  $\text{CaMnO}_3$ .

Figure 4 presents a representative cyclic voltammograms obtained for  $\text{Ca}_{0.6}\text{Ho}_{0.4}\text{MnO}_3$  between  $-50$  and  $50 \text{ mV}$  vs.  $\text{Hg/HgO}$ . The shape of the voltammograms indicates a typical capacitive behaviour, where no faradaic currents were observed. The voltammetric profiles show the typical capacitor-like characteristics in the form of almost rectangular cyclic behaviour (Figure 4a). A linear variation between the current density, measured at  $E = 0 \text{ V}$  vs.  $\text{Hg/HgO}$ , and the sweep rate is observed for all the samples, as Figure 4b also displays for the  $\text{Ca}_{0.6}\text{Ho}_{0.4}\text{MnO}_3$  composition.

The capacitance was determined according to the equation  $C = dj/d(dV/dt)$ , where  $j$  is the current density and  $dV/dt$  the potential sweep rate. Assuming a value of  $60 \mu\text{F cm}^{-2}$  for the capacitance of the oxide/aqueous solution interface [10], the electrodes roughness factors have been also calculated. The calculated roughness factor increases with increasing the amount of Ho-ions in the samples (Table 1). This is consistent with the roughness factors obtained by AFM and indicates an enhancement of the oxides surface area.



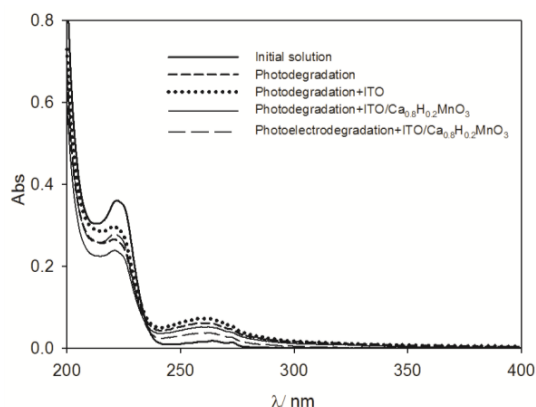
**Figure 4.** (a) Cyclic voltammograms obtained in the double-layer region for the  $\text{Ca}_{0.6}\text{Ho}_{0.4}\text{MnO}_3$  electrode in  $1 \text{ mol L}^{-1}$  KOH. (b) Charging current densities as a function of sweep rate for a  $\text{Ca}_{0.6}\text{Ho}_{0.4}\text{MnO}_3$  electrode in  $1 \text{ mol L}^{-1}$  KOH. Sweep rates of 5, 10, 15, 20,  $25 \text{ mV s}^{-1}$ .

**Table 1.** Roughness factor for the  $\text{Ca}_{1-x}\text{Ho}_x\text{MnO}_3$  oxide electrodes in  $1 \text{ mol L}^{-1}$  KOH solutions.

x	Electrode type	$R_f$
0	Pelleted	3725
0	Coating	5
0.2	Coating	**
0.4	Coating	13

\*\* - under progress

In Figure 5 results of the UV spectra for the degradation assays with ibuprofen, at 6 h, are depicted. Ibuprofen presents a characteristic band with a maximum of absorption at  $220 \text{ nm}$  and another weak band at  $264 \text{ nm}$ . We can observe that a decrease of the peak intensity of the band at  $220 \text{ nm}$  occurs in all the degradation assays and, simultaneously, the weak band at  $264 \text{ nm}$  increases. The same behaviour has already been reported in previous studies with ibuprofen [11,12].



**Figure 5.** UV spectra for the degradation assays performed at different experimental conditions: with radiation (254 nm), radiation+ITO, radiation+ITO/Ca<sub>0.8</sub>Ho<sub>0.2</sub>MnO<sub>3</sub> and radiation+current + ITO/Ca<sub>0.8</sub>Ho<sub>0.2</sub>MnO<sub>3</sub>.

In Table 2, the results for the removals in COD, TOC and absorbance (Abs), after 6 h assays, are presented and we can see that, the best absorption removal at 220 nm was obtained in the photocatalytic assay, i.e., when radiation and perovskite were present. However the best COD removal was obtained when current was simultaneously applied.

**Table 2** - Results of the Absorbance<sub>220nm</sub>, COD, and TOC removals for the degradation assays of ibuprofen, at 6 h.

Experimental technique	Removal at 6 h / %		
	Abs 220 nm	CQO	TOC
Photolysis (254 nm radiation)	24	19	21
Photolysis (254 nm radiation) + ITO	21	29	12
Photocatalysis (254 nm radiation) + ITO/Ca <sub>0.8</sub> Ho <sub>0.2</sub> MnO <sub>3</sub>	33	17	18
Photoelectrodegradation + ITO/Ca <sub>0.8</sub> Ho <sub>0.2</sub> MnO <sub>3</sub> (254 nm radiation + 5 mA cm <sup>-2</sup> )	20	34	9

## Conclusions

Ca<sub>1-x</sub>Ho<sub>x</sub>MnO<sub>3</sub> manganite electrodes in thin film form were prepared for the first time by magnetron sputtering technique using nanosized powder compacted targets. The electrodes exhibit good adherence to the substrates and high mechanic stability.

Sputtering technique seems a promising alternative for the development of this type of electrodes comparing with the conventional way.

The preliminary degradation tests run with Ca<sub>1-x</sub>Ho<sub>x</sub>MnO<sub>3</sub> manganite electrodes have shown promising results, mainly in photocatalytic assays.

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# Characterization of a leachate from a sanitary intermunicipal landfill. Analysis of the content in metals at several stages of the wastewater treatment plant.

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## Abstract

In this work the content in seven metals was analysed in samples from a leachate, collected in a sanitary intermunicipal landfill. Samples were collected in three stages of the wastewater treatment plant, just before the biological treatment, just after the biological treatment and from the ultrafiltration permeate. Pb, Cr, Cu, Fe, Mn, Cd, Zn content was determined. Fe was the most abundant of the analysed metals with 22.2 mgL<sup>-1</sup> in the samples before the, 41.3 mgL<sup>-1</sup> after the biological treatment and 4.0 mgL<sup>-1</sup> in the ultrafiltration permeate. Cd content was below detection limit of AAS. Zn, Cu, Cr, Mn and Pb contents are between those limits. The values obtained are in accordance with the range reported in the literature for the analyzed metals. The results obtained suggest that there is a higher concentration of metals in the fraction after the biological treatment, consistent with the fact that there is a recirculation of the ultrafiltration concentrate to this stage. The permeate of ultrafiltration presents the lowest metal content, which indicate an efficiency of the treatment stages so far in metal removal. From the point of view of metal recovery, the best stage to collect samples seem to be after the biological treatment.

## Introduction

Leachates from landfills constitute an environmental problem due to infiltration and contamination of soils and groundwaters. In their composition there are four main groups of pollutants designed in literature as dissolved organic matter, inorganic macrocomponents, xenobiotic organic compounds and heavy metals<sup>1,2</sup>.

Heavy metals are an environmental problem because they tend to accumulate in living organisms and are not biodegradable. On the other hand, some metals have economical interest and it is important to find ways to recover them. So, to remove metals may have both an environmental and an economical motivation<sup>3</sup>.

The design of wastewater treatment plants (WWTP) dedicated to leachates from landfills may have multiple approaches<sup>2</sup>. In this study the WWTP performs a treatment that comprises a biological step, followed by an ultrafiltration operation. The ultrafiltration concentrate is recirculated into the biological treatment.

In order to analyze the best point where to start an efficient metal recovery procedure in the leachate treatment process, we decided to collect samples from several stages in the leachate treatment process and analyse the content in several metals.

In this work we characterize a leachate from a sanitary intermunicipal landfill concerning seven metals (Pb, Cr, Cu, Fe, Mn, Cd, Zn) in three stages of the wastewater treatment plant: before the biological treatment, after the biological treatment, and from the ultrafiltration permeate.

## Materials and Methods

### 1. Sample collection

The leachate samples in the study were provided by a municipal sanitary landfill and collected in November of 2010. A single sample was collected at each point in containers of 5L. The first sample was collected, just before the biological treatment, the second was collected in the same way just after the biological treatment and a third sample was collected from the permeate of the ultrafiltration. The samples were placed at 4°C until processing and analysis.

### 2. Sample treatment

All material used in the experimental part was decontaminated using an acid solution with nitric acid and distilled H<sub>2</sub>O in the ratio of 1:5.

The samples studied had a heterogeneous appearance, dark color and high turbidity and so in order to obtain representative samples for analysis, the vessels containing the samples were intensively stirred to homogenize all of your content.

The pH was measured in the unit WTW pH Meter 526.

To prepare the samples for the analysis was followed a treatment process of acid digestion. Samples were placed in erlenmeyers with differential proportions of *aqua regia*. Appropriate volumes of *aqua regia* were added to different samples, since it is important to minimize the volume. The results obtain have shown that it was sufficient a ratio of 1:3 (3 parts of *aqua regia* for 1 part of sample in volume) in samples “before the biological treatment”, a ratio of 2:3 (3 parts of *aqua regia* for 2 parts of sample) for samples “after the biological treatment” and finally the ratio of 2:1 (half the volume of the sample in *aqua regia* was used in this case) for the samples of ultra-filtration permeate.

In order to improve the efficiency of sample digestion, the capped samples were subjected to magnetic stirring (Breda Scientific) about 30 min at 40-60°C making digestion and evaporation more efficient and faster. After this step, the samples were placed in a sand bath at 110±10 °C to total digestion of organic matter, i.e. the final solution it must be clear and transparent. Then, the samples were filtrated for flasks using filter paper, always at the lowest possible volume.

### 1. Analysis by Atomic Absorption Spectroscopy (AAS)

For the metals analysis an atomic absorption spectrometer Perkin-Elmer Model 3100 was used. Standard solutions of each metal were prepared from standard solutions by proper dilution with HNO<sub>3</sub> 0.01M. Three samples of each stage were measured and corresponding statistical treatment of the values was performed.

### Results and Discussion

Before any sample collection the pH of each one was measured. The sample “before the biological treatment” had a pH of 8.11, the sample “after the biological treatment” had a pH of 7.80 and the sample “ultrafiltration permeate” had a pH of 6.77. This is in accordance with the fact that before the ultrafiltration, an acidification process occurs.

The sample of first stage of the treatment process was more difficult to digest; requiring a larger volume of *aqua regia* and longer digestion followed by the sample after

biological treatment, and finally, the sample of the permeate of the ultrafiltration, which requires a lower volume of digestion solution and less time for digestion. These are consistent with the content in organic matter of each stage. The results obtained are presented in Table 1. Fe was the most abundant metal. Cr and Zn present also significant values. The metals content is within the range of values presented in literature<sup>2,5</sup> for leachates of landfills.

The stage after the biological treatment is where the leachate presents the highest metal content. This is probably due to the fact that there is a recirculation of the concentrate of the ultrafiltration back to the tanks where the biological treatment occurs. It is a result consistent with the evaluation made in literature<sup>1,6,7</sup> i.e. that metals in leachates are mostly associated with organic molecules and adsorbed on colloidal fractions.

**Table 1** – Metals content in each stage of collection of landfill leachate (mg L<sup>-1</sup>)

Stage of collection	Fe	Cr	Zn	Cu	Mn	Pb	Cd
Before biological treatment	22.34 ± 0.03	4.04 ± 0.30	1.76 ± 0.39	0.12 ± 0.00	0.40 ± 0.07	- *	- *
After biological treatment	41.27 ± 0.13	5.48 ± 0.00	2.36 ± 0.10	0.21 ± 0.00	0.66 ± 0.00	0.31 ± 0.10	- *
ultra-filtration Permeate	4.01 ± 0.18	0.79 ± 0.00	0.52 ± 0.03	0.01 ± 0.00	0.10 ± 0.01	0.09 ± 0.00	- *

\* values obtained are not within the limit of detection.

### Conclusions

The studied leachate presents low concentrations on the metals studied, namely on the heavy metals Pb and Cd.

The leachate samples just after the biological treatment present the highest metal content. This may be due to the recirculation of the ultrafiltration concentrate back to the lagoon where the biological treatment is done.

This study characterized the leachate from a intermunicipal landfill at several stages of the WWTP showing that the content in the analysed metals is within the ranges described in literature.

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