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## Waste Management

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# Recovery of manganese oxides from spent alkaline and zinc–carbon batteries. An application as catalysts for VOCs elimination

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## ARTICLE INFO

## Article history:

Received 12 October 2012

Accepted 4 March 2013

Available online xxxxx

## Keywords:

Batteries

Biohydrometallurgy

Recycling

Manganese oxides

VOCs

## ABSTRACT

Manganese, in the form of oxide, was recovered from spent alkaline and zinc–carbon batteries employing a biohydrometallurgy process, using a pilot plant consisting in: an *air-lift* bioreactor (containing an acid-reducing medium produced by an *Acidithiobacillus thiooxidans* bacteria immobilized on elemental sulfur); a leaching reactor (where battery powder is mixed with the acid-reducing medium) and a recovery reactor. Two different manganese oxides were recovered from the leachate liquor: one of them by electrolysis (EMO) and the other by a chemical precipitation with  $\text{KMnO}_4$  solution (CMO). The non-leached solid residue was also studied (RMO). The solids were compared with a  $\text{MnO}_x$  synthesized in our laboratory.

The characterization by XRD, FTIR and XPS reveal the presence of  $\text{Mn}_2\text{O}_3$  in the EMO and the CMO samples, together with some  $\text{Mn}^{4+}$  cations. In the solid not extracted by acidic leaching (RMO) the main phase detected was  $\text{Mn}_3\text{O}_4$ .

The catalytic performance of the oxides was studied in the complete oxidation of ethanol and heptane. Complete conversion of ethanol occurs at 200 °C, while heptane requires more than 400 °C. The CMO has the highest oxide selectivity to  $\text{CO}_2$ .

The results show that manganese oxides obtained using spent alkaline and zinc–carbon batteries as raw materials, have an interesting performance as catalysts for elimination of VOCs.

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## 1. Introduction

The consumption of batteries has increased in the last 30 years because of their versatility, low maintenance, reduced cost and their requirements of the electronic industry (De Souza et al., 2001). Alkaline and zinc–carbon batteries are used in radios, recorders, toys, remote controls, watches, calculators, cameras, and in many other objects where small quantities of power are required (Sayilgan et al., 2009). Usually, they run out rapidly and are thrown away; they are a special residue because of their content in mercury, zinc, manganese and other heavy metals (Bartolozzi, 1990). This fact presents a major environmental and health threat (Kierkegaard, 2007). The waste batteries cause a serious concern due to their toxicity, abundance and permanence in the environment (Li and Xi, 2005).

The benefits of recycling materials from an economic, environmental and technical point of view depend on many factors, including transport, recycling processes and materials to be treated (Rydh and Karlstrom, 2002).

Each year, approximately 160,000 tonnes of portable batteries are placed on the Community market. In 2002, for example, 45% of the portable batteries sold in the European Union that year went to final disposal (incineration or landfill), instead of being collected and recycled.

In terms of tonnage, the following estimated amount of metals would not go to landfills/incineration, but could be recovered: Manganese: 20,000 tonnes/year; Zinc: 20,000 tonnes/year; Iron: 15,000 tonnes/year; Lead: 7500 tonnes/year; Nickel: 2000 tonnes/year; Cadmium: 1500 tonnes/year; Mercury: 28 tonnes/year. Additionally, a range of substances such as various acids, salts and plastics which are also contained in the batteries will be captured by the system and diverted from municipal waste to specific installations equipped to deal with waste batteries. The use of recycled metals in battery production instead of virgin metals has positive environmental impacts through reduced energy use and reduced pollution related to the mining of the virgin source. As an example, using recycled cadmium and nickel require respectively 46% and 75% less primary energy compared with the extraction and refining of virgin metal. For zinc, the relation between the energy needed for recycling and the energy needed for extraction from primary resources is 2.2 to 8. These figures are particularly important given the fact that the primary production of metals is the source of approximately 10% of global  $\text{CO}_2$  emissions (Commission of the European Communities, 2003).

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Due to new environmental legislation regulating batteries' disposal in several countries, some processes were developed for the recycling of such products.

The recycling of batteries for metal recovery involves hydrometallurgical or pyrometallurgical processes. In the mining industry, the bio-hydrometallurgical process (bioleaching) has been gradually replacing hydrometallurgical ones due to their environmental and economic benefits (Das et al., 2011; Liu et al., 2011; Rossi, 1990). Some of the advantages of bio-hydrometallurgical processes are: less energy consumption, less atmospheric emissions, small, safe and versatile plants, simplicity and low cost of the process, applicability to low grade sources, low costs of installation and possibility of on-site treatment. On-site sulfuric acid production has multiple advantages, since it eliminates the manipulation of concentrated sulfuric acid, the pollution of its industrial production and the transport costs (Brierley and Brierley, 2001; Brierley, 2010; Morin et al., 2006).

Bioleaching generally allows efficient release of metals from solid phase into aqueous solution under mild conditions such as room temperature and pressure in the presence of sulfur-oxidizing bacteria (Cui and Zhang, 2008; Rohwerder et al., 2003;). The aim of this work is to study the applicability of one final product of a bio-hydrometallurgical process for the recovery of metals from spent alkaline and Zn–C batteries: manganese oxide.

Manganese oxides such as  $\text{Mn}_3\text{O}_4$  (Baldi et al., 1998a),  $\text{Mn}_2\text{O}_3$  (Baldi et al., 1998b) and  $\text{MnO}_2$  (Lahousse et al., 1998) are known for exhibiting high activity in the oxidation of volatile organic compounds (VOCs), a class of contaminants produced in various industrial processes. The catalytic application of manganese oxides is due to their high efficiency in the reaction/oxidation cycles, the presence of  $\text{Mn}^{4+}/\text{Mn}^{3+}$  and  $\text{Mn}^{3+}/\text{Mn}^{2+}$  type redox couples and facile lattice oxygen (Bastos et al., 2009; Figueroa et al., 2005; Gandhe et al., 2007; Lamaita et al., 2005a; Peluso et al., 2003).

The aim of this work is to analyze the use of manganese oxides, which were obtained from a biohydrometallurgical process, in the catalytic abatement of two different VOC such as ethanol and heptane.

## 2. Experimental

### 2.1. Batteries pre-treatment

Spent alkaline and zinc–carbon batteries were collected from CICPBA Campus in the City of La Plata, Argentina. Most of these spent batteries were AA size. Spent alkaline and zinc–carbon batteries were first separated and then manually dismantled. Dismantling products such as plastic films, ferrous scraps and paper pieces were discarded. The powders, which were about 40–64% of the total weights of dismantling batteries, were mixed, dried, ground by milling and sieved to obtain a mesh size of less than 200  $\mu\text{m}$ . The resulting powder was used for leaching experiment. Prior to leaching, the contents of both Zn and Mn in the powder were determined as 47% and 25% in mass, respectively, using atomic absorption spectrophotometry after digestion by  $\text{HNO}_3$ –HCl (1:3) method.

### 2.2. Catalysts preparation

All catalysts, except for the reference  $\text{MnO}_x$ , were prepared in a biohydrometallurgical process for the recovery of metals from spent batteries as described below.

#### 2.2.1. Description of the biohydrometallurgical process for the treatment of spent batteries

The biohydrometallurgical process for the recycling of metals from spent alkaline and zinc–carbon batteries consists in three steps occurring in three different reactors:

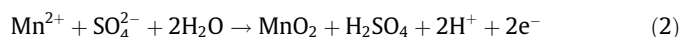
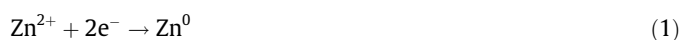
**2.2.1.1. Bioreactor.** The bacteria used were an *Acidithiobacillus thiooxidans* (At) (DSM 11478). The organism was propagated in a 0 K (Silverman and Lundgren, 1959) medium at initial pH of 2.5 with powdered sulfur (2 wt%) as energy source, at 30 °C.

The bioreactor was an *air-lift* reactor containing 0 K liquid medium with a sulfur-packed bed. Sulfur (particles < 5 mesh) was obtained from YPF (Yacimientos Petrolíferos Fiscales), an Argentine energy company. It was the residue of a petrochemical process.

Cultures of At were used as inoculums. Temperature of the bioreactor was kept at 30 °C. Air was continuously fed to the solution at a flow of 300  $\text{L h}^{-1}$ . At is a chemoautotrophic microorganism, it means that it uses the  $\text{CO}_2$  from the air as its carbon source and an inorganic reduced compound (sulfur in this work) as its energy source. Sulfur is oxidized by At and sulfuric acid and reducing compounds are produced as a result of its metabolism. This is the acid-reducing media used in the leaching reactor. The resultant acid media has an  $\text{H}^+$  concentration of 0.30 M.

**2.2.1.2. Leaching reactor.** The leaching reactor was a stirred tank where the acid reducing medium produced in the bioreactor is mixed with the batteries powder. In a typical procedure, 2000 g of batteries powder were subjected to three consecutive extractions with acid. Each extraction was carried out with 28 L of sulfuric acid and during 3 h. In this reactor, zinc and part of the manganese contained in the batteries were leached. As a result of this step a solution of manganese sulfate and zinc sulfate was produced. The solid remaining after leaching was the manganese oxide that does not react with the acid reducing media; we named this manganese oxide *Residual Manganese Oxide*, RMO for its study as a catalyst. RMO was washed several times with deionized water to remove the sulfates, dried at 120 °C, and finally calcined in air at 500 °C for 2 h.

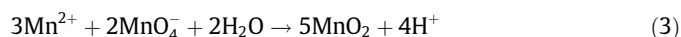
**2.2.1.3. Recovery reactor.** In the recovery reactor, zinc and manganese were separated from the solution and recovered. Two alternatives were studied for this reactor, electrolysis and selective precipitation. In the electrolysis of the leaching solution, the reactor was an electrolytic cube with stainless steel electrodes connected to a DC source. Metallic zinc was deposited in the cathode and manganese oxide in the anode, according to the following reactions:



Experiments were carried out at room temperature and an average current of 3 A  $\text{dm}^{-2}$ . The pH of the medium varied from 5 to 1.5 during the 60 h of the electrolytic process. This electrolytic manganese oxide, named EMO, was washed several times with deionized water to remove the sulfates, dried at 120 °C, and finally calcined in air at 500 °C for 2 h, to study its catalytic activity.

For the precipitation, potassium permanganate was used to obtain manganese oxide named *Chemical Manganese Oxide*, CMO from the leaching solution.

It was prepared by reaction of the  $\text{Mn}^{2+}$  present in the leachate liquor with  $\text{KMnO}_4$  solution, according to the following equation:



Then 100 mL of  $\text{KMnO}_4$  0.100 M (Anhydrous 99%), was added dropwise to 100 mL of the leachate liquor and the suspension was stirred at 30 °C for 1 h. The product was filtered, washed with distilled water and dried at 120 °C for 24 h. Finally, the solid was calcined in air at 500 °C for 2 h.

### 2.2.2. Reference $MnO_x$

A manganese oxide prepared in our laboratory, which presented a great activity towards VOCs oxidation (Lamaita et al., 2005b), was also evaluated as comparison. In a typical procedure, 10 g of  $MnCO_3$  were decomposed at 350 °C under flowing oxygen saturated with water (50 cm<sup>3</sup> min<sup>-1</sup>) for 1 h, with a heat rate of 20 °C min<sup>-1</sup> and finally calcined in air at 500 °C for 2 h.

### 2.3. Catalysts characterization

The X Ray diffraction (XRD) patterns were carried out at room temperature with a Philips PW1390 instrument by using Ni filter and Cu K $\alpha$  radiation ( $\lambda = 1.540589 \text{ \AA}$ ) in the  $2\theta$  range between 5° and 60°.

The BET specific areas were measured by N<sub>2</sub> adsorption at the liquid nitrogen temperature (77 K) in a Micromeritics Accusorb 2100 D sorptometer.

Surface morphology and quantitative analysis of the composition of the samples were carried out with a scanning electron microscope provided with energy dispersive X-ray analysis (SEM-EDS) using a Philips SEM 505 microscope.

The metal content in solution was measured in a Varian AA 240 spectrophotometer.

FTIR spectra were obtained in a Bruker IFS66 infrared spectrometer with a KBr optics and DTGS detector in the 400–4000 cm<sup>-1</sup> range. The spectra were obtained by co-adding 200 scans collected at 4 cm<sup>-1</sup>.

X-ray photoelectron spectra (XPS) of the compounds were obtained using a multi-technique system, equipped with a hemispherical PHOIBOS 100 MCD analyzer using unmonochromatized Al K $\alpha$  radiation (1486.6 eV). Binding energies (BE:  $\pm 0.1 \text{ eV}$ ) were calculated using adventitious hydrocarbon (C 1s = 284.6 eV) as the internal reference.

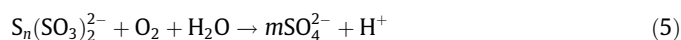
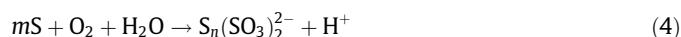
### 2.4. Catalytic activity

Ethanol and heptane were the VOC chosen for this study. The catalytic oxidation of VOC was performed at atmospheric pressure in a continuous flow tubular glass reactor filled with 0.100 g of catalysts. An air stream saturated with the VOC was created by using a saturator equipped with temperature and pressure controls, and then diluted with pure air resulting in a feed composition of 1 vol% of VOC. The total gas flow was 100 cm<sup>3</sup> min<sup>-1</sup>. Catalytic tests were performed at temperature range of 100–500 °C, which was measured using a thermocouple projecting into the center of the bed. The VOC conversion was analyzed by gas chromatography using a Shimadzu A9 GC, equipped with a flame ionization detector. The CO<sub>2</sub> production was analyzed on-line using a TELAIRE CO<sub>2</sub> sensor.

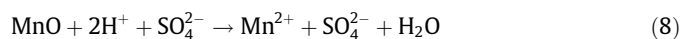
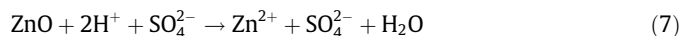
## 3. Results and discussion

### 3.1. Leaching process

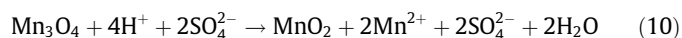
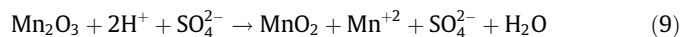
*A. thiooxidans* (At) bacteria obtains their energy by the oxidation of reduced sulfur compounds. The products of this metabolism are oxidant, reducing and acid chemical species:



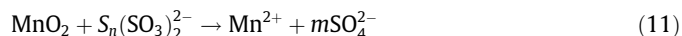
Metallic zinc, zinc oxide and manganese oxide can be fully leached by sulfuric acid media according to the following equations:



However, the dissolution of  $Mn_2O_3$  and  $Mn_3O_4$  is partial due to the formation of  $MnO_2$  according to the following equations:



Therefore, to improve the leaching efficiency of  $MnO_2$ , a reducing agent is required:



In addition to a solution rich in manganese and zinc, the leaching process generates a solid residue which was not leached. In the liquor, the values observed for extraction yields were 44% of manganese and 96% of zinc from the battery powder. The electrolytic method produced a manganese oxide (EMO) in the anode and metallic zinc in the cathode. The recovery of manganese and zinc from the lixiviated solution was 40% and 60% respectively. By the precipitation method it was recovered the 90% of Mn cations (CMO), whereas the  $Zn^{2+}$  cations remain in the solution.

### 3.2. Solid characterization

The oxides obtained from the batteries (RMO, EMO and CMO), were washed with distilled water and afterwards the sulfate concentration was measured in the residual water. After ten successive washings of 1 g of sample with 50 ml of distilled water, there were removed about 140, 100 and 50 mg of sulfate for the EMO, CMO and RMO solids, respectively. EDS analyses confirmed the presence of sulfur in the samples without washing and there were not detected sulfur in the washed samples.

After calcination at 500 °C, the specific area of the samples was 7, 44, 49 and 19 m<sup>2</sup> g<sup>-1</sup> for the RMO, EMO, CMO and  $MnO_x$  samples, respectively. The higher specific area of the EMO and CMO samples compared to RMO is attributed to the open structure of the formed oxides in the electrode (EMO) and in the reaction of  $Mn^{2+}$  cations with  $KMnO_4$  (Figueroa et al., 2005).

Scanning electron microscopy (SEM) micrograph of the manganese oxides are shown in Fig. 1. RMO and EMO present a similar laminar morphology, whereas the CMO sample presents a different morphology, with small globular particles, characteristics of manganese oxides prepared with  $KMnO_4$  precursor (Jothiramalingam et al., 2006). The reference manganese oxide presents a completely different morphology, with globular structure.

The XRD patterns of the manganese oxides are shown in Fig. 2. The XRD spectrum of RMO sample reproduces the spectrum of  $Mn_3O_4$  (Hausmannite JCPDS 89-4837). Additionally, a peak at  $2\theta = 26^\circ$  corresponding to C graphite was detected (De Souza and Tenorio, 2004; Krekeler, 2008). The spectrum of  $MnO_x$  presents diffraction lines corresponding to a mixture of oxides, eg.  $Mn_2O_3$  (Bixbyite JCPDS 89-4836) and a  $MnO_2$  phase (JCPDS 004-0779). The spectra of EMO and CMO are characterized with broad and low intensity peaks, which is indicative of poorly crystalline materials. In both oxides, diffraction lines corresponding to  $Mn_2O_3$  were detected. The presence of the  $Mn_2O_3$  phase in the EMO sample is coincident with the results of Malloy et al. (2005), who have detected  $Mn_2O_3$  after calcination at 500 °C of an oxide prepared via electrolysis of manganese sulfate in acid medium.

The presence of a more reducible phase in the RMO sample could be due to the presence of carbon in the residual solid. During the calcination, the carbon oxidized to CO<sub>2</sub> produced in the



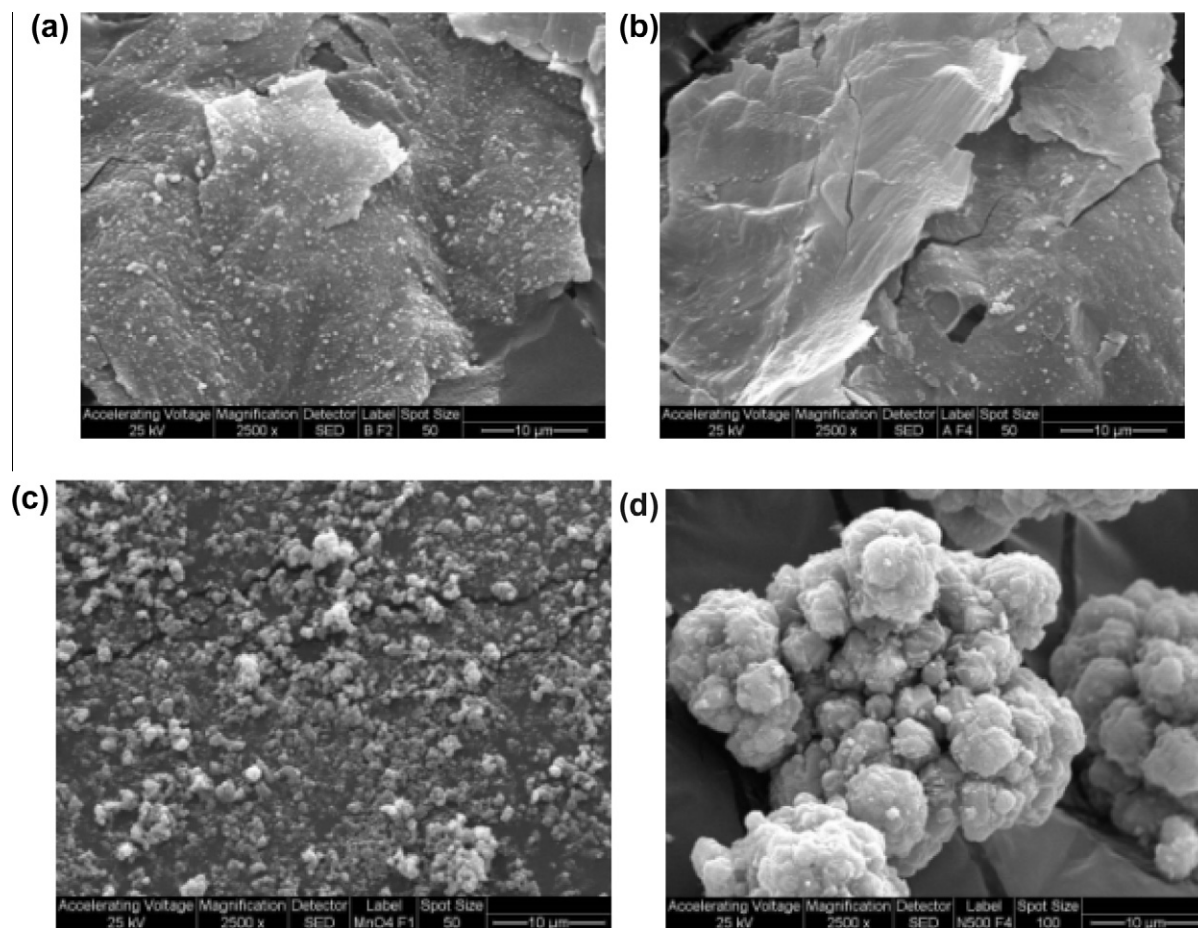


Fig. 1. SEM micrographs. (a) RMO, (b) EMO, (c) CMO and (d) MnO<sub>x</sub>.

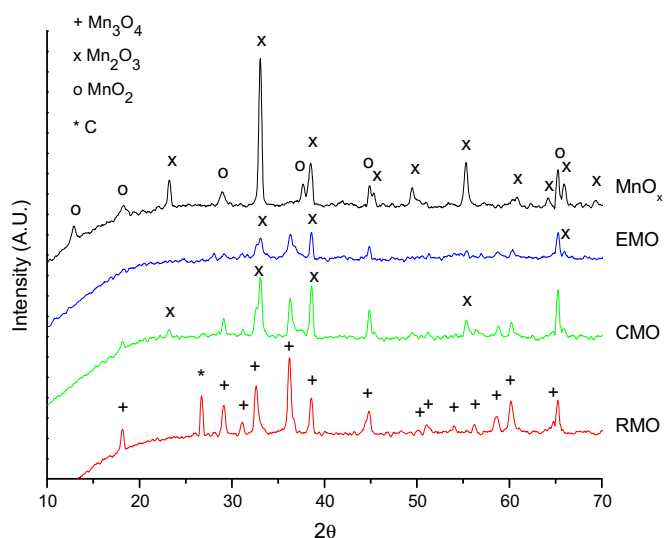


Fig. 2. X-Ray diffraction patterns of manganese oxides.

oxidation of C could react with more C to produce CO, which could act as a reducing agent.

The results of FTIR spectroscopy of the studied manganese oxides are shown in Fig. 3. IR spectroscopy has proven to be useful for

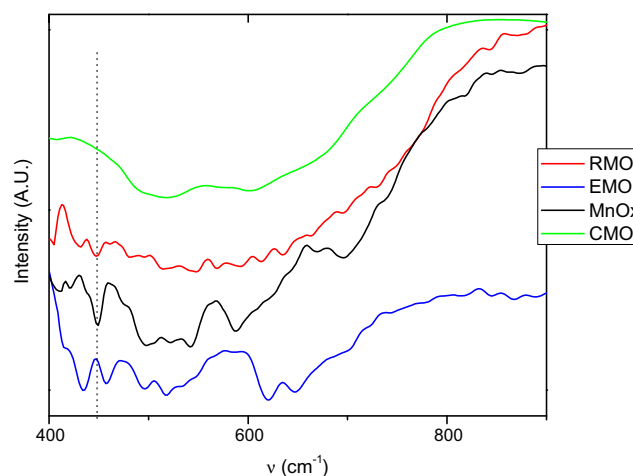


Fig. 3. FTIR spectra of manganese oxides.

the identification of the manganese oxide phases (Julien and Massot, 2003), and yields more reliable information than the X-ray diffraction technique. The IR bands in the region 1000–400 cm<sup>−1</sup> reveal information about MnO<sub>6</sub> octahedral. In the RMO sample, it can be distinguished a band at 447 cm<sup>−1</sup> assigned to Mn<sub>2</sub>O<sub>3</sub> (Nohman et al., 1992). The EMO bands at 495 and 517 cm<sup>−1</sup> are assigned to α-Mn<sub>2</sub>O<sub>3</sub> (Julien et al., 2004), whereas

the bands at 430, 620 and 650  $\text{cm}^{-1}$  could be assigned to  $\text{MnO}_2$  (Petit et al., 1993). The bands at 517 and 600  $\text{cm}^{-1}$  in CMO could be associated with a cryptomelane phase. In the case of  $\text{MnO}_x$  sample, bands at 447 and 495  $\text{cm}^{-1}$  are associated with  $\text{Mn}_2\text{O}_3$  (Julien et al., 2004; Nohman et al., 1992), whereas bands at 541, 587 and 698  $\text{cm}^{-1}$  could be assigned to nsutite or  $\gamma\text{-MnO}_2$  phase (Petit et al., 1993).

The average oxidation state (AOS) of Mn was examined by X-ray photoelectron spectroscopy. Generally, the binding energy of Mn 2p peaks is used to define the average oxidation state of Mn. Nevertheless, the interpretation of the Mn 2p spectrum is complicated due to the multiple splitting of the Mn 2p spectra of  $\text{Mn}^{4+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions (Fan et al., 2008).

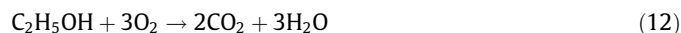
It has been reported that the analysis of Mn valence states is more precise using the Mn 3s peak separation energies. Results of the Mn 3s peak separation energies are listed in Table 1. According to the relationship between Mn 3s splitting and formal valence of Mn ions, (Fan et al., 2008; Grbic et al., 2006; Nagarajan et al., 2007) the results suggest that the AOS of RMO, EMO, CMO and  $\text{MnO}_x$  are 2.4, 3.5, 3.4 and 3.2, respectively.

According to the results of the different characterization techniques, the manganese oxide samples have the following characteristics: (a) RMO catalyst is constituted by  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$  and C impurities, (b) EMO and CMO are a mixture of crystalline  $\text{Mn}_2\text{O}_3$  and an amorphous  $\text{MnO}_2$  phase; (c)  $\text{MnO}_x$  is a mixture of  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  phases.

According to Gandhe et al. (2007), Peluso et al. (2008) and Shaheen and Selim (1998), the presence of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  and the formation of an amorphous phase are a necessary conditions to obtain catalysts for VOCs elimination.

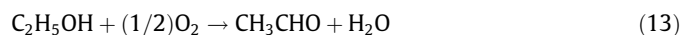
### 3.3. Catalytic activity

The complete oxidation of ethanol proceeds according to the equation:



The catalytic performance for the ethanol oxidative destruction on manganese oxide catalysts is shown as a function of temperature in Fig. 4. The oxides obtained from the lixiviation of spent batteries (EMO and CMO) present an activity comparable to the reference  $\text{MnO}_x$ , with a  $T_{50}$  almost 10 °C higher than that of  $\text{MnO}_x$  sample. Total conversion occurs at near 200 °C for the CMO and  $\text{MnO}_x$  catalyst, and needs more temperature for the EMO catalysts. RMO presents the lowest conversion, with a  $T_{50}$  of 276 °C.

The conversion of ethanol to  $\text{CO}_2$  over catalyst (Fig. 4b), is lower than the total conversion of ethanol. The discrepancy is due to the formation of an ethanol partial oxidation product, namely acetaldehyde, formed according to the equation:



No other partial oxidation products were detected.

Fig. 5a and b shows the formation of acetaldehyde as a function of the reaction temperature and the ethanol conversion, respec-

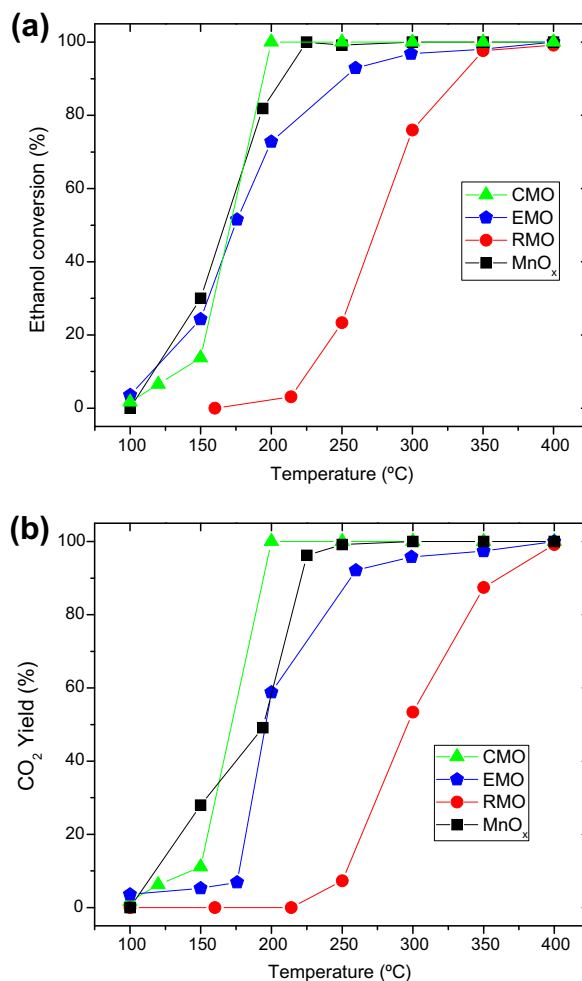


Fig. 4. (a) Ethanol conversion and (b)  $\text{CO}_2$  yield over manganese oxides.

tively. The production of acetaldehyde reaches a maximum at approximately 180 and 190 °C for the  $\text{MnO}_x$  and EMO respectively, and at higher temperatures, 300 °C, for the RMO sample. CMO catalyst presents a negligible amount of acetaldehyde production, producing total conversion to  $\text{CO}_2$  at near 180 °C.

The complete oxidation of heptane proceeds according to the equation:



The catalytic performance for heptane oxidation is shown as a function of temperature in Fig. 6. The manganese oxide catalysts activity order was  $\text{MnO}_x > \text{CMO} > \text{EMO} > \text{RMO}$ . The conversion of heptanes to  $\text{CO}_2$  (Fig. 6b) is again lower than the total conversion of heptanes, due to the production of partial oxidation products. There were detected three by-products, which have not yet been identified.

In general, the capacity of manganese oxides to oxidize VOCs is attributed to the existence of the redox pair  $\text{Mn}^{3+}/\text{Mn}^{4+}$ , and to the poor crystallinity of the oxides.

Additionally, it was reported generally that the activity of the different manganese oxide phases was  $\text{MnO}_2 > \text{Mn}_2\text{O}_3 > \text{Mn}_3\text{O}_4$  (Lamaita et al., 2005b; Spinicci et al., 2003).

CMO and EMO catalysts present a mixture of  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  phases, and their specific areas are similar. The conversion of VOCs on the reference  $\text{MnO}_x$  catalyst is higher than that of CMO and EMO

**Table 1**  
Specific area and manganese average oxidation state of manganese of manganese oxides.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$\Delta E$ Mn 3s (eV)	Mn AOS
CMO	49	5.02	3.4
EMO	44	4.94	3.5
$\text{MnO}_x$	20	5.16	3.2
RMO	7	5.82	2.4

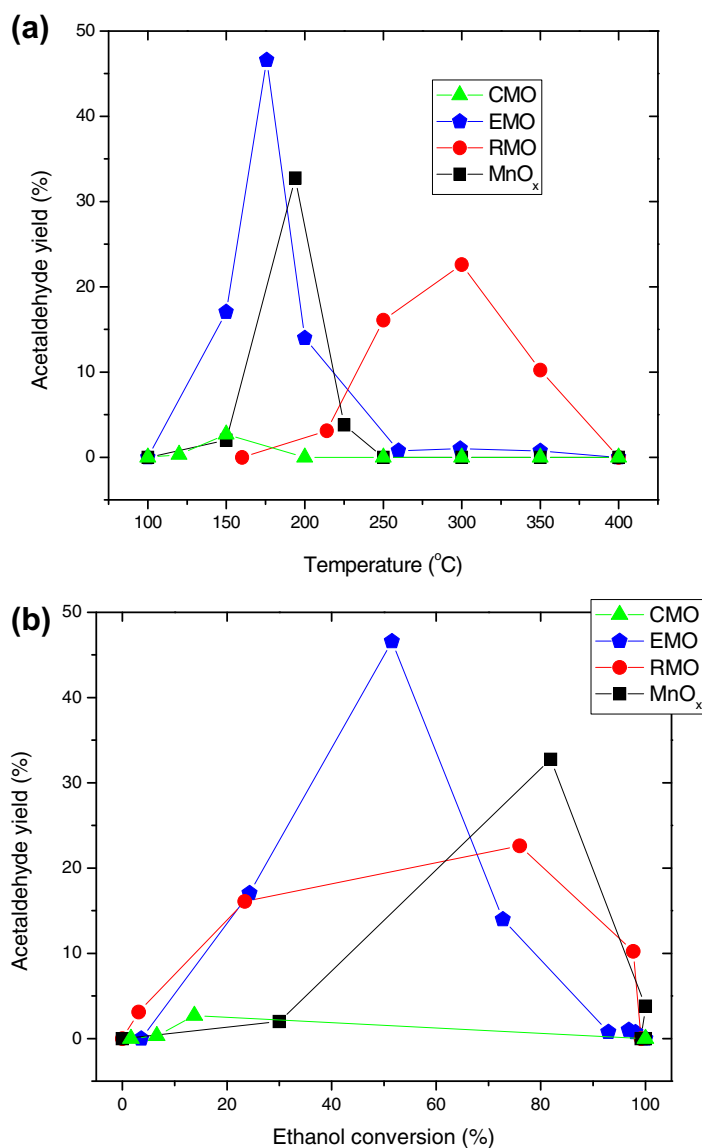


Fig. 5. Acetaldehyde yield in ethanol oxidation: (a) as a function of temperature and (b) as a function of ethanol conversion.

catalysts, although its specific area is lower than the oxides obtained from the lixiviation process.

On the other hand, RMO catalyst is the leaching residue, containing other components than manganese oxide, namely carbon (as it was found in XRD analysis). Carbon plays a detrimental role in the oxidation of VOCs, maybe by blocking active sites of the catalysts (Arena et al., 2008; ÁAlessandro et al., 2012).

Additionally, the lower specific area and the presence of the Mn<sub>3</sub>O<sub>4</sub> phase contribute to the low activity of the RMO material.

In all the catalysts studied, ethanol was easily oxidized than heptane, in coincidence with other authors (Blasin-Aubé et al., 2003; Huang et al., 2008). Reasonable correlation have been found showing that the lower the C–H bond dissociation enthalpy the easier the complete oxidation of the corresponding organic molecule (Blasin-Aubé et al., 2003; ÓMalley and Hodnett, 1999). Regarding the two organic compounds studied in this work, ethanol and heptanes, the dissociation enthalpies of the weakest C–H bonds are 389 kJ mol<sup>−1</sup> for ethanol and 400 kJ mol<sup>−1</sup> for heptane.

Other factors could also contribute to the difference in reactivity of the VOCs, namely the adsorption of the VOC molecule on the catalyst surface, which could be related to the polarity of the VOCs. Alcohols are more probably adsorbed stronger on the manganese oxides surface than heptane (ÓMalley and Hodnett, 1999; Santos et al., 2010), with the consequent increment in the VOC conversion.

Manganese present in spent alkaline and zinc–carbon batteries can be recovered and according on the treatment could be reutilized. Our results show that manganese oxides obtained using spent alkaline and zinc–carbon batteries as raw materials, can be used as effective catalysts for the elimination of gaseous emissions of VOCs.

In fact, the pollution produced for the emission of VOCs can be minimized by the use of a dangerous solid waste such as spent alkaline and zinc–carbon batteries.

Further investigations in our laboratory are carried out to improve the recuperation process and to recover the Zn from the

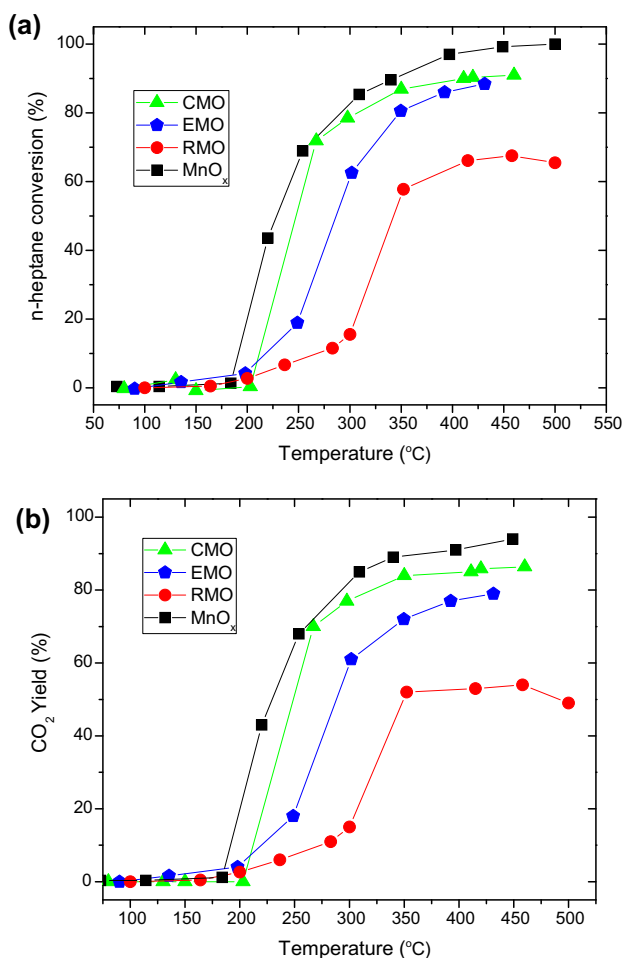


Fig. 6. (a) n-Heptane conversion and (b) CO<sub>2</sub> yield over manganese oxides.

solution, which could be used as catalysts support or a catalyst itself.

#### 4. Conclusions

Spent alkaline and zinc-carbon batteries were subjected to a biohydrometallurgical process in order to recover manganese in form of manganese oxides. Different manganese oxide phases were obtained depending on the method used to recover the manganese. The oxide obtained by calcination of the bio-lixiviation residue presented the lowest specific area and the Mn<sub>3</sub>O<sub>4</sub> phase. The oxides obtained by precipitation with KMnO<sub>4</sub> and electrolysis of the batteries leachate (CMO and EMO) present similar specific areas and a structure characterized by the presence of Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>.

The catalytic combustion of two VOC (ethanol and heptanes) was carried out over the obtained manganese oxides. Ethanol was more easily oxidized than heptane in all catalysts. The activity of the oxides in ethanol combustion decrease in the order: MnO<sub>x</sub> = CMO = EMO > RMO and in heptanes oxidation decrease in the order: MnO<sub>x</sub> > CMO > EMO > RMO.

This work shows that spent alkaline and zinc-carbon batteries can be used as raw materials to prepared different manganese oxides, which can be used as efficient catalysts for the total oxidation of volatile organic compounds emissions.

#### Acknowledgments

The authors thank CICPBA and CONICET (PIP 519) for financial support and Mariela Theiller for the SEM analyses.

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