

Discarded Carbon-Zinc Batteries as Source of an Efficient Heterogeneous Fenton-Like Catalyst Employed to Degrade Organic Molecules in an Aqueous Medium

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Abstract

The present work evaluates the feasibility of using the raw material collected from discarded zinc-carbon batteries as heterogeneous catalyst to degrade the dye Indigo Carmine in an aqueous solution. Besides the evident environmental application, this work also presents an economic alternative for the production of new catalysts used to remediate polluted waters. For this, discarded carbon-zinc batteries were gathered, disassembled and their anodic paste collected. After acidic treatment and calcination at 500°C, characterization measurements, *i.e.* flame atomic absorption spectroscopy (FAAS), nitrogen sorption, X-ray diffraction (XRD) and scanning electron microscopy (SEM), revealed that the so-obtained material consisted mainly of $ZnMn_2O_4$. This material acts as a heterogeneous catalyst in a Fenton-like process that degrades the dye Indigo Carmine in water. That is probably due to the presence of Mn(III) (manganese in the +3 oxidation state) in this material that triggers the decomposition of hydrogen peroxide (H_2O_2) to yield hydroxyl radicals (HO^\bullet). Moreover, direct infusion electrospray ionization coupled to high resolution mass spectrometry (ESI-HRMS) was employed to characterize the main by-products resulting from such degradation process. These initial results thus indicate that raw materials from waste batteries can therefore be potentially employed as efficient Fenton-like catalysts to degrade organic pollutants in an aqueous solution.

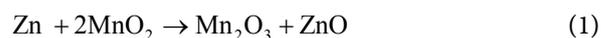
Keywords

Electronic Waste, Zinc-Carbon Batteries, $ZnMn_2O_4$, Fenton-Like Degradation, Indigo Carmine, Direct Infusion Electrospray Ionization High

1. Introduction

The use of electronic devices has been growing continuously worldwide, with increasing consumption of primary (non-rechargeable) and secondary (rechargeable) batteries [1] [2]. The annual consumption of batteries was estimated to be 8 billion units per year in the USA and Europe, 6 billion in Japan, and 1 billion in Brazil [3] [4]. Alkaline and zinc-carbon batteries are primary disposable batteries and one of their main usage is the powering of day-to-day gadgets [5]. After their use, most batteries are discarded as waste. An immediate consequence of the incorrect disposal of e-wastes in the environment is the contamination of the environment by heavy metals, mainly lead, mercury, cadmium and nickel [6]. The recycle of spent batteries is therefore essential not only for environmental safety and human health issues but also for an economic point of view [7] [8]. Thus, many works have been carried out aiming at recovering the metals from these residues, obtaining alloys, nanoparticles with magnetic, adsorbents or catalytic applications [2] [7] [9].

The zinc-carbon battery uses zinc as anode, manganese dioxide as cathode, and an electrolyte of ammonium chloride and/or zinc chloride dissolved in water [10]. As the cell is discharged, the zinc is oxidized and the manganese dioxide is reduced according to a simplified overall cell reaction Equation (1):



Robinson and coworkers [11] compared various manganese oxides, such as Mn_2O_3 , Mn_3O_4 and MnO_2 , in the catalytic photochemical oxidation of water to evolve oxygen. They found that the catalytic activities followed the order: $\text{Mn}_2\text{O}_3 > \text{Mn}_3\text{O}_4 \gg \text{MnO}_2$. Qiu and coworkers [12] synthesized ZnMn_2O_4 nanorods by a co-precipitation process. The ZnMn_2O_4 nanorods were used as a Fenton-like heterogeneous catalyst for the degradation of methyl violet and its catalytic performances were systematically compared to those of ZnMnO_3 nanorods. The results indicated that ZnMn_2O_4 nanorods exhibited significantly higher catalytic activity towards the degradation of methyl violet. However, to the best of our knowledge, a detailed study on the reuse of battery residues to obtain ZnMn_2O_4 catalysts applied to Fenton-like processes is unprecedented.

This paper aims to collect the anodic paste (comprised mainly by manganese oxides) of discarded zinc-carbon batteries and, after proper treatment and characterization, to test the so-obtained material as a Fenton-like catalyst to degrade organic pollutants in an aqueous medium. Indigo Carmine was chosen as a prototype analyte because of its low cost and easy degradation monitoring (via UV-Vis spectrophotometry). Finally, direct infusion electrospray ionization coupled to high resolution mass spectrometry (ESI-HRMS) is employed to cha-

racterize the main by-products and, as a consequence, to propose a plausible degradation route for Indigo Carmine under these conditions.

2. Materials and Methods

2.1. Materials and Reagents

All chemicals were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used without further purification. Ultrapure water ($18 \text{ M}\Omega\cdot\text{cm}^{-1}$, Milli-Q system, Millipore, Burlington, Massachusetts, EUA) was used to prepare the solutions.

2.2. Battery Dismantling

Discarded batteries were manually dismantled by removing the metallic external cover to access the internal anodic paste. The raw anodic material, a black petrified solid, was grated and triturated in grail and pestle to obtain fine black powder rich in manganese oxides, carbon, zinc, zinc oxides and other trace substances.

2.3. Anodic Material: Acid Leaching and Calcination

The black powder anodic material was leached with a sulfuric acid aqueous solution. The purpose of this step was to decrease the content of zinc and other trace substances from the raw anodic material aiming at the attainment of a catalyst with a superior activity. The leaching conditions employed was: sulfuric acid concentration ($0.01 \text{ mol}\cdot\text{L}^{-1}$); temperature (60°C); time (20 min); ratio of the volume of sulfuric acid solution (mL) per weight (1 g) of the anodic material = 200. These leaching conditions were employed based on a previous work by Velloso and coworkers [13]. The solid material was isolated upon filtration and dried for 15 min in an oven and then calcined at 500°C for 5 h in a muffle. After calcination, the material obtained, named CBR (calcined battery residue), possessed a brown color.

2.4. Characterization

Analyses by flame atomic absorption spectroscopy (FAAS) were conducted in a Varian Fast AA-240 instrument (Trenton, NJ, USA). A mixture of air/acetylene was employed in all analyses at the following flow rates: air ($13.50 \text{ L}\cdot\text{min}^{-1}$) and acetylene ($2.00 \text{ L}\cdot\text{min}^{-1}$). For the analyses of zinc and manganese an electrical current of 5 A was used. For manganese, the reading range was 0 to $4 \mu\text{g}\cdot\text{mL}^{-1}$ with the wavelength set to 279.5 nm and with a slit of 0.2 nm. For zinc, the reading range, wavelength and slit were set to 0 to $2 \mu\text{g}\cdot\text{mL}^{-1}$, 213.9 nm and 1.0 nm, respectively. Powder X-Ray Diffraction (XRD) experiments were carried out on a ShimadzuXRD-7000 diffractometer (Tokyo, Japan), using Cu $K\alpha$ radiation and operating at 40 kV and 40 mA. XRD patterns were collected in the 2θ range of 10° to 90° , using a scan velocity of $2.0 \text{ degrees min}^{-1}$. The identification of the crystalline phases was performed using the library Crystallographica Search-Match, software version 3.0 and the JCPDS (International Centre for Diffraction

Data[®]), file numbers 24-1133 for ZnMn₂O₄. Scanning electron microscopy (SEM) analyses were performed in a FEG-Quanta 200 FEI microscope, using an electron voltage of 15.0 kV. Samples were sputter-coated with a gold layer of about 5 nm thickness before the SEM tests. Sorption tests were conducted on a Micromeritics ASAP 2020 apparatus using nitrogen as adsorbate at 77 K. The sample analyzed was previously degassed at 130°C for up to 48 h under vacuum. The specific surface area (SSA) and pore size distribution were assessed by employing the multipoint Brunauer, Emmett and Teller (BET) and the density functional theory (DFT), respectively.

2.5. Degradation Experiments

Degradation tests were carried out in order to check out the activity of the CBR material as a Fenton-like catalyst to degrade Indigo Carmine. Hence, to 50 mL of an aqueous Indigo Carmine solution (at 30 mg·L⁻¹), 50 mg of CBRcatalyst and 0.5 mL of H₂O₂ (CBR/H₂O₂ system) were added. The reaction vessel was maintained under magnetic stirring with no heating and pH control for 120 min. Aliquots of 8 mL were collected at times of 0, 15, 30, 60 and 120 min. The resulting suspension was centrifuged for 10 minutes at 4000 rpm in a centrifuge Centribio model 80-2B. The supernatant was then collected and the absorbance of the solution immediately measured at 610 nm (λ_{\max} for Indigo Carmine) on a UV-VIS spectrophotometer model CARY 50 Conc, Varian. The measurements were made in a quartz cell with an optical length of 1 cm. Adsorption (with the CBR material) and tests with pure hydrogen peroxide (H₂O₂) were also performed as controls.

2.6. Direct Infusion ESI-HRMS Analysis

ESI-HRMS analyses were performed on a hybrid (ion trap-time of flight—IT-ToF) mass spectrometer (Shimadzu Corporation) that provides high sensitivity and accuracy with a resolving power over 10.000. The mass spectrometer was equipped with an electrospray ionization (ESI) source operating in the negative (-3.5 kV) mode and with a nebulizer gas (N₂) at a flow rate of 1.5 L·min⁻¹. The interface and CDL (curved desolvation line) were operated at a constant temperature of 200°C. A mass-to-charge (m/z) range of 50 - 500 was recorded for each aliquot. The samples (10 µL) were directly infused into the ESI source via an autosampler model SIL 20AC (Shimadzu Corporation).

3. Results and Discussion

3.1. Characterization of the CBR Material

Atomic absorption analyses revealed that the CBR material has high contents of Mn (44% w/w) and Zn (23% w/w). These data are in agreement with results previously reported in the literature [9] [10]. Such metals are present as oxides, as will be discussed later in this paper. Other components at trace level could also be present in this sample.

Figure 1 shows the XRD patterns for (a) CBR and (b) hetaerolite, a mineral with a chemical formula of ZnMn_2O_4 . These data clearly reveal an excellent correlation between the peaks observed in both diffractograms. This finding therefore indicates that the chemical composition of the CBR material is essentially ZnMn_2O_4 , in which manganese is found in an unstable oxidation state, *i.e.* Mn(III). Similar results were previously described in the literature [5] [14]. **Figure 1** also reveals that these peaks have a thickness close to that of hetaerolite, indicating that CBR is a material with a remarkable crystallinity.

The image by scanning electron microscopy (SEM) shows that the CBR material is quite heterogeneous (**Figure 2**). Note the presence of grains with varied sizes and shapes. This feature is probably due to the conditions employed in the preparation procedure, which favors the particles coalescence.

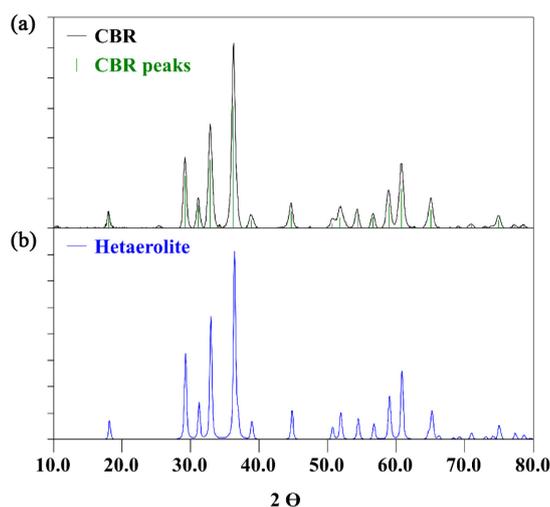


Figure 1. X-ray diffractograms of the (a) CBR material and (b) hetaerolite mineral (chemical formula: ZnMn_2O_4).

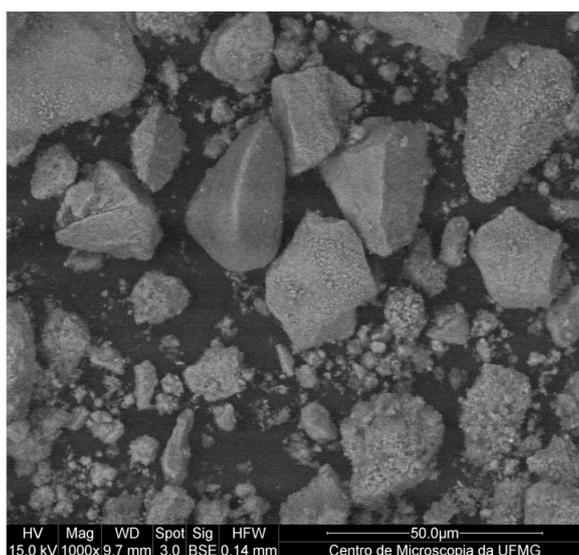


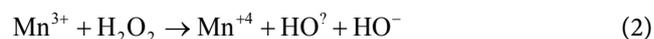
Figure 2. Scanning electron microscopy (SEM) image of the CBR material.

The CBR material presented negligible specific surface area (SSA) and the isotherms (not shown) are classified as type II, according to IUPAC (International Union of Pure and Applied Chemistry) [15]. This isotherm is characteristic of a non-porous or macroporous adsorbent material. The low SSA is certainly a consequence of the conditions employed in its preparation [16] [17] [18].

3.2. Fenton-Like Degradation Experiments

Degradation tests were conducted in order to determine the catalytic efficiency of the CBR material towards the degradation of Indigo Carmine in an aqueous solution. **Figure 3** shows the degradation rates produced by the Fenton-like (CBR/H₂O₂) and controls (CBR and H₂O₂) systems.

Firstly, results from the control experiments (CBR and H₂O₂) clearly indicated that the dye Indigo Carmine was removed at very small rates. After 120 min of exposure, the CBR material removed about 20% of the dye via adsorption, whereas H₂O₂ removed only 10%, probably due to the H₂O₂ decomposition that yields hydroxyl radicals. The small adsorption capacity of the CBR material was expected indeed because of its low SSA. The Fenton-like system (CBR/H₂O₂), on the other hand, yielded a much higher degradation rate (93% after 120 min of exposure). These data therefore indicate that the dye degradation is directly induced by the CBR material, which probably acts as a Fenton-like catalyst in the presence of H₂O₂. Although the CBR material possesses a too small specific surface area (SSA), the prominent presence of unstable Mn(III) in its structure favors the formation of hydroxyl radicals (HO[•]), according to Equation (2) [11] [12]. These extremely-reactive species promptly cause the oxidation of Indigo Carmine, as reported several times elsewhere [19] [20] [21].



3.3. By-Products Characterization by ESI-HRMS

Analyzes by direct infusion electrospray ionization mass spectrometry (ESI-MS) was conducted aiming at detecting at least the most abundant by-products resulting from the degradation promoted by the CBR/H₂O₂ system. ESI-MS is a

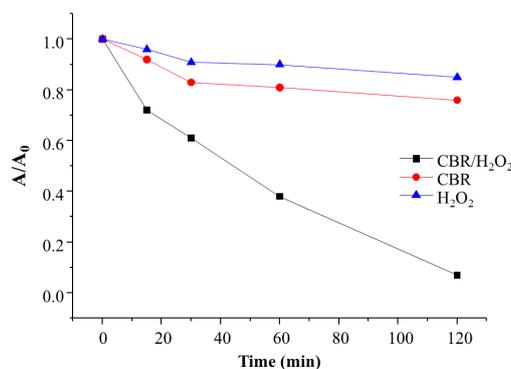


Figure 3. Relative absorbance (A/A_0) of Indigo Carmine solutions monitored during exposure to Fenton-like (CBR/H₂O₂) and controls (CBR and H₂O₂) systems.

key technique for the identification of by-products resulting from the degradation of water contaminants, and therefore has played an important role in elucidating possible degradation pathways [20] [21]. This technique gently transfers species from the condensed to the gas phase without inducing undesirable side reactions. Because of that, ESI-MS has been successfully applied to monitor an increasing number of environmental processes [19].

Figure 4 shows the mass spectra of aliquots collected after 0 and 120 min of exposure of an aqueous solution of Indigo Carmine to the CBR/H₂O₂ system. Note that in the mass spectrum of the initial solution (**Figure 4(a)**) only the ion of *m/z* of 209.9829, which corresponds to [Indigo Carmine-2H]²⁻ (Indigo Carmine in its doubly-deprotonated form), can be detected. After 120 min, however, the mass spectrum (**Figure 4(b)**) reveals the absence of this ion, which indicates that Indigo Carmine was fully degraded. This mass spectrum (**Figure 4(b)**) also displays a number of other ions, some of them ascribed to be the deprotonated forms of degradation products possibly formed under these conditions. Molecular formula for each one of these ions were proposed based on the high-resolution mass spectrometry data, which presented small differences between the experimental and theoretical accurate masses (**Table 1**).

Other ions, besides the ones displayed in **Table 1**, are also detected in **Figure 4(b)** (for instance, *m/z* of 260.8643 and 189.9011). However, reasonable molecular formula with an acceptable error could not be proposed for any of them. These compounds probably leached from the heterogeneous catalyst during the degradation process.

Based on these results as well as on the well-known reactivity of hydroxyl radical towards organic molecules in aqueous medium, a route for the degradation of Indigo Carmine by the CBR/H₂O₂ system could thus be proposed, as outlined in **Figure 5**. The formation of by-products **2** and **3** arising from the oxidation and desulfonation of Indigo Carmine, respectively, has been reported in the literature [19] [20] [21]. It is important to state that in both pathways the determinant participation of hydroxyl radicals is noticeable.

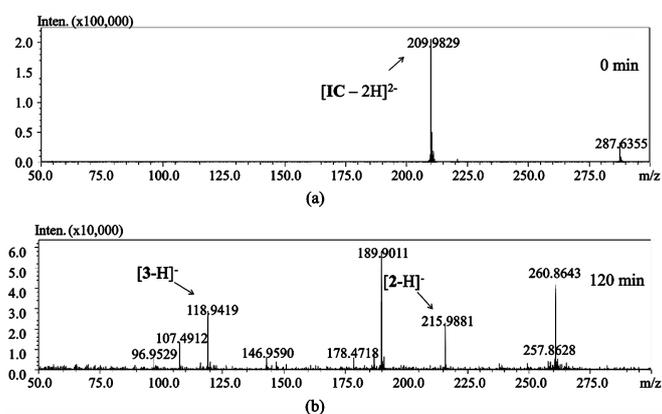


Figure 4. Mass spectra of two aliquots collected at the following reaction times: (a) 0 min; (b) 120 min. The reaction process refers to the degradation of Indigo Carmine induced by the CBR/H₂O₂ system in an aqueous solution.

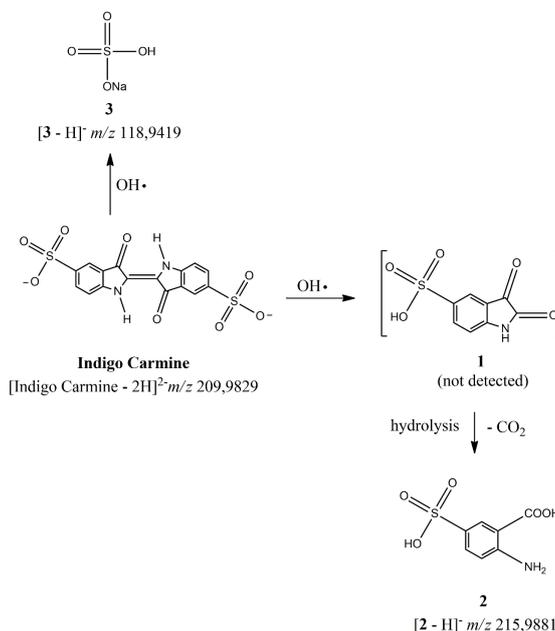


Figure 5. Proposed route for the degradation of Indigo Carmine induced by the CBR/ H_2O_2 system in an aqueous solution.

Table 1. High resolution mass spectrometry data used to determine the molecular formula of the degradation products resulting from the exposure of Indigo Carmine to the CBR/ H_2O_2 system in an aqueous medium.

Compound	Deprotonated Form		
	Molecular formula	m/z (theoretical)	m/z (experimental)
Indigo Carmine	$[\text{C}_{16}\text{H}_8\text{N}_2\text{O}_8\text{S}_2]^{2-}$	209.9861	209.9829
2	$[\text{C}_7\text{H}_6\text{NO}_5\text{S}]^-$	215.9967	215.9881
3	$[\text{NaSO}_4]^-$	118.9415	118.9419

4. Conclusion

This work demonstrates that the ZnMn_2O_4 catalyst can be obtained from discarded batteries (anodic paste). It acts as an efficient Fenton-like catalyst in the degradation of Indigo Carmine in an aqueous solution. The high efficiency of this catalyst is probably due to the presence of Mn(III), a quite unstable and reactive species. The interaction of Mn(III) with H_2O_2 generates hydroxyl radicals that are responsible for the high removal of the Indigo Carmine dye from an aqueous medium. It is important to mention that the catalyst was obtained from electronic waste (discarded zinc-carbon batteries). Therefore, in addition to avoiding that such electronic waste becomes a potential source of environmental contamination, this work proposes its use as an efficient remediation agent for water bodies containing organic pollutants. Hence, besides the evident environmental application, this work also presents an economic alternative for the production of new catalysts used in Fenton-like processes. It is noteworthy that this is the first report regarding the attainment of an effective Fenton-like catalyst,

i.e. ZnMn₂O₄ from battery residues. Finally, other possible remediation processes making use of such a promising material are underway in our laboratory.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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