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Synthesis, characterization and photocatalytic properties of nanostructured $CoFe_2O_4$ recycled from spent Li-ion batteries

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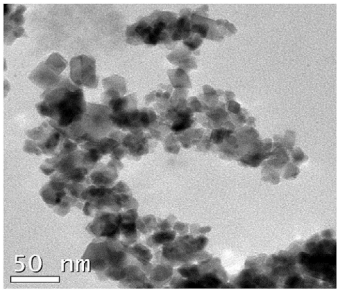
HIGHLIGHTS

- Cobalt was recycled from spent lithium ion batteries to synthesize $CoFe_2O_4$.
- Nanoparticles of $CoFe_2O_4$ with type spinel structures was synthesized.
- $CoFe_2O_4$ was applied as a catalyst in heterogeneous photo Fenton reactions.
- $CoFe_2O_4$ was characterized by XRD, SEM, TEM, and ICP OES techniques.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, cobalt (Co) was recycled from spent lithium ion batteries (LIBs) and used to synthesize cobalt ferrite ($CoFe_2O_4$-LIBs), which was applied as a catalyst for heterogeneous photo Fenton reactions that discolored methylene blue (MB) dye. The co-precipitation method was used to synthesize $CoFe_2O_4$-LIBs and $CoFe_2O_4$-R nanoparticles with spinel structures using as raw materials of the LIB cathodes and commercial reagents. X-ray diffraction (XRD) identified the formation of spinel-type $CoFe_2O_4$, which formed clusters that could be seen under scanning electron microscopy (SEM) analysis and nanometric particles seen under transmission electron microscopy (TEM). Inductively Coupled Plasma Optical Emission Spectrometer (ICP OES) analysis was used to determine the concentrations of metals present in the ferrite, which reached 6.5% (w/w) of Co. The optimal conditions for discoloring the dye were evaluated using a factorial design. Using $CoFe_2O_4$ as a catalyst, the best conditions for catalytic reaction were pH 3, 30.0 mg of catalyst, and 8.0 mL of H_2O_2 73% (v/v). Discoloration efficiencies of 87.3% and 87.7% were obtained from $CoFe_2O_4$-R and $CoFe_2O_4$-LIBs, respectively. Therefore, $CoFe_2O_4$-LIBs proved to be an efficient catalyst for discoloring MB dye using heterogeneous photo-Fenton reactions. This work is of scientific, social, economic, and environmental interest. It investigates the process of synthesizing,characterizing $CoFe_2O_4$LIBs and the efficiency of degrading MB dye, subjects that have economic and environmental, and therefore, social interest. The work has scientific interest particularly because of the correlation between the structure of the recycled material and its catalytic properties.

1. Introduction

Lithium ion batteries (LIBs) are used in cell phones, computers, digital cameras, and various electronic devices due to their high

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energy density, high voltage, and long charge and discharge cycles (Yao et al., 2016; Yu et al., 2012). It is estimated that by 2022, $46.21 billion of LIBs will have reached the global market (Natarajan and Bajaj, 2016). Cathodes in LIBs are generally mainly composed of lithiated cobalt oxide ($LiCoO_2$), lithiated cobalt, manganese and nickel oxide ($LiCoMnNiO_2$), and lithiated manganese oxide ($LiMnO_2$) (He et al., 2015; Lu et al., 2015). After their lifespans, LIBs form large quantities of hazardous solid waste (Yang et al., 2016; Yao et al., 2016; Yu et al., 2012). Therefore, recycling LIBs is environmentally necessary both to conserve natural resources and ensure sustainable development. LIBs recycling can be achieved by pyrometallurgical or hydrometallurgical processes (Chagnes and Pospiech, 2013; Kumar et al., 2015; Omar and Rohani, 2015). The pyrometallurgical process requires a great deal of thermal energy and releases polluting gases that require treatment (Ordoñez et al., 2016). The hydrometallurgical process uses inorganic or organic acids to leach spent LIBs, and both types of acids can be reused in subsequent leaching (Baba et al., 2009; Pegoretti et al., 2017; Tu et al., 2013). In addition, high-purity lithium (Li), cobalt (Co), nickel (Ni), and manganese (Mn) recycled from spent LIBs can be used as raw materials with which to synthesize ferrites, which are magnetic oxides that have the generic formula $M^{2+}Fe_2^{3+}O_4$, where M is a divalent metal (Lelis et al., 2004). Spinel-type ferrites can be classified as normal, inverted, or partially inverted and are represented by the formula $(M_{1-X}^{2+}Fe_X^{3+})_A(M_X^{2+}Fe_{2-X}^{3+})_BO_4^{2-}$. The tetrahedral sites are shown in (A) and the octahedral sites in (B), and the parameter X represents the fraction of divalent ions (Lelis et al., 2003). In the structure of spinel-type ferrites, substituting transition metals in the octahedral and tetrahedral sites increases surface area, which is desirable for catalytic activities (Carta et al., 2009). The amount of metal added and its distribution between the octahedral and tetrahedral coordination sites both depend on the preparation technique (Magalhães et al., 2007; Zhong et al., 2013). Because of their porous structures, which are effective at removing pollutants in aqueous solution, ferrites have been used as catalysts in the heterogeneous photo-Fenton process to degrade effluents (Al-Kahtani and Abou Taleb, 2016; Du et al., 2016; Hammouda et al., 2015; Khan et al., 2015; Ren et al., 2015; Wu et al., 2016), dyes (Al-Kahtani and Abou Taleb, 2016; Wu et al., 2016), drugs (Valcárcel et al., 2012), and estrogen (Zhao et al., 2010, 2008). Methylene blue (MB) is a dye typically used in the textile industry and difficult to degrade under natural conditions (Zhou et al., 2013). To reduce its harmful effects on the environment and living beings, MB must be degraded when present in aqueous solutions. When degrading dyes, special attention has been given to advanced oxidation processes (AOPs), which enable rapid degradation and complete decomposition of the dyes (Guimarães et al., 2012; Hisaindee et al., 2013). In the photo-Fenton process, hydroxyl radicals ($OH\cdot$), which are powerful oxidizing agents with a 2.8 V reduction potential, are formed by the oxidation of iron II to iron III and the catalytic decomposition of hydrogen peroxide (H_2O_2) into hydroxyl and ($OH\cdot$) (Esteves et al., 2016; Su et al., 2012). In the heterogeneous photo-Fenton process, the catalyst is solid, and the oxidation reaction occurs in the solid-liquid interface (Al-Kahtani and Abou Taleb, 2016). The immobilized iron on the solid matrix prevents the formation of sludge by the precipitation of iron hydroxide. This enables expanding the range of pH under study and increases the amount of ($OH\cdot$) formed (Al-Kahtani and Abou Taleb, 2016). One advantage of using cobalt ferrite ($CoFe_2O_4$) as an iron source in the heterogeneous photo-Fenton process is the formation of magnetic nanoparticles with good chemical stability and saturation magnetization (Zhou et al., 2014), which are easily separated from the aqueous medium by applying a magnetic field with a magnet (Sharma et al., 2015). Recent studies have used the sol-gel method to synthesize cobalt ferrite (Yang et al., 2016; Yao et al., 2016) from the cathodes of LIBs. However, these studies have not addressed the applications of the synthesized material.

The present study synthesized $CoFe_2O_4$-LIBs from the solution used to leach the cathodes of spent LIBs and then applied it to degrade MB, an organic pollutant from the textile industry, using the heterogeneous photo-Fenton process. In addition to recovering the Co from the spent LIBs, thus preventing environmental pollution, using the co-precipitation method to synthesize $CoFe_2O_4$-LIBs makes the recycling process practicable, low cost, and sustainable. This work is of scientific, social, economic, and environmental interest. It investigates the process of synthesizing, characterizing $CoFe_2O_4$LIBs and the efficiency of degrading MB dye, subjects that have economic and environmental, and therefore, social interest. The work has scientific interest particularly because of the correlation between the structure of the recycled material and its catalytic properties. The study characterized materials using thermal gravimetric analysis (TGA/DTG), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET specific surface area, atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP OES).

2. Experimental

2.1. Dismantling and separating active material from LIB cathodes and characterizing them using X-ray diffraction and ICP OES

First, spent LIBs were completely discharged to eliminate any remaining capacity and manually dismantled to physically separate the following main components: casing (plastic and metallic), separator, cathode, and anode. The active cathode material was separated from the current collector (aluminum foil) by scraping and then dried at room temperature and macerated to homogenize and reduce particle size. This material was characterized by XRD using D8 Discover equipment (Bruker; Madison, WI, USA). The sample was scanned from 2θ scan range between 10° and 90°, using an increment of 0.01° stepmin^{-1} and CuKα radiation. To determine metal concentrations, the sample was dissolved in 50.0 mL of HNO_3 (3 molL^{-1}) and 3.0 mL of H_2O_2 10% (v/v) under constant stirring at 80 °C for 2 h and then analyzed by ICP OES using an Optima 7000 DV spectrometer (PerkinElmer; Waltham, MA, USA).

2.2. Synthesizing ferrites doped with Co

Synthesizing cobalt ferrite from spent LIBs that were designated as $CoFe_2O_4$-LIBs was accomplished using the co-precipitation method as adapted from Lelis et al. (2003). First, a solution containing Co was prepared by dissolving 5.40 g of active cathode material from LIBs in 3 molL^{-1} of HNO_3 and H_2O_2 10% (v/v). The composition of Co in the cathodes was 47% w/w, as determined by ICP OES (section 3.1). The amount of matter relative to the Co was 0.043 mol. Then, 129 mmol (35.00 g) of hexahydrate ferric chloride P. A. (Vetec; Brazil) was added to this solution under constant stirring. In the $CoFe_2O_4$ designated as $CoFe_2O_4$-LIBs, the Co/Fe molar ratio was 1/3. Ammonium hydroxide P. A. (Vetec; Brazil) was added dropwise until the ferric hydroxide precipitated. Then, the solution was centrifuged (NT 810; Nova Técnica; Piracicaba, Brazil), and the precipitate was washed with 10% ammonium acetate solution P. A. (Synth; Brazil) 7 times to promote acetate sorption by the precipitate. The precipitate was dried (404/D; New Ethics) at 80 °C for 24 h, powdered, and homogenized. The precursor material of the cobalt ferrite was calcined at a temperature of 450 °C for 2 h, obtaining the $CoFe_2O_4$-LIBs.The same procedure was performed to