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Synthesis of polymetallic nanoparticles from spent lithium-ion batteries and application in the removal of reactive blue 4 dye

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ABSTRACT

In this study inedited polymetallic nanoparticles were synthesized from electronic wastes of spent lithium-ion batteries (PN-LIB) and applied in the removal of the dye reactive blue 4 (RB4). Initially, the extraction of metals from batteries was performed using HCl/HNO_3 (3:1 v/v). Subsequently, the PN-LIB were synthesized via chemical reduction with $NaBH_4$. The PN-LIB showed spherical shape and size smaller than 50 nm, being constituted by Cu, Co, Ni, and Mn. The surface area was estimated at 92.29 $m^2\,g^{-1}$ and the volume and average size of pores in 0.25 $cm^3\,g^{-1}$ and 5.84 nm, respectively. The X-Rays diffractogram presented characteristic peaks of the Cu^0. The PN-LIB were applied in the removal of the RB4 dye, in which the effects caused by the variables initial pH, dose of PN-LIB and initial concentration of dye in the removal process were evaluated. There was no significant effect of initial pH on the RB4 removal, since, a natural increase of this parameter occurred in the system and maintained at pH about 8.5. The rate of removal increases with the increase in the dose of PN-LIB and with the reduction of the initial concentration of dye. The experimental data were adjusted to the kinetic model of pseudo-second order and the Langmuir isotherm model, with a maximum capacity of removal, was calculated as being equal to 344.83 $mg\,g^{-1}$. The molecular absorption spectra in the UV/Vis region and the infrared spectra indicated that two phenomena happen, adsorption and degradation of the dye.

1. Introduction

Nowadays, with the advancement of technology, more innovative products are launched in the market, which leads the consumer to purchase new electronic products and discard the old ones, thus generating large amount of residue. In the 2017 year, it is estimated that the overall quantity of e-waste generated is around 47.8 million tons (Baldé et al., 2014).

Among the electronic wastes, there are several types of batteries such as Lithium-Ion Batteries (LIBs), Nickel-Cadmium (Ni-Cd) and Nickel Metal Hydride (Ni-MH) (Nayl et al., 2017). The LIBs are one of the most widely used, due to the advantages presented in relation to batteries Ni-Cd and Ni-MH, as higher energy density, longer life cycle, besides being more lightweight and do not have the memory effects (He et al., 2015). The LIBs can be used as a source of energy in mobile phones, laptops and electronic devices (Ferreira et al., 2009), and contain in their constitution various metals such as Al, Fe, Cu, Li, Co, Ni, and Mn (Georgi-Maschler et al., 2012).

There are some studies that aim to improve the performance of LIBs (Atar, Necip et al., 2015a; Atar, Necip. et al., 2015b). However, many works are directed at waste generated by improper disposal of batteries. This occurs because the amount of residues of LIBs generated is very large, since the lifetime of these batteries is approximately 2–3 years, depending on how they have used and their quality (Huang et al., 2016). The final disposal of this material requires care because the improper disposal of LIBs can cause environmental damage contaminating soil and water, once they are composed of various metals such as aluminum, iron, copper, lithium, cobalt, nickel, and manganese (He et al., 2015; Georgi-Maschler et al., 2012).

An alternative to discard consists of the recycling of these materials since they are potential sources of different metals. Therefore, technologies are necessary for the recycling of spend LIBs that generate new materials with added value. Several studies have focused on the recovery of metals present in LIBs (Chen et al., 2011;

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Ferreira et al., 2009; Huang et al., 2016; Leite et al., 2017; Nayl et al., 2017; Shin et al., 2005; Virolainen et al., 2017). However, works that reuse the LIBs metals for the production of new materials are scarce. (Santana et al., 2017) synthesized Co_3O_4 and $LiCoO_2$ from LIBs and (Yao et al., 2015) synthesized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ recycled metals of waste LIBs.

In this sense, a viable alternative would be the production of metallic nanoparticles, which are solid materials with nanometric size, which have distinct properties of conventional solids (Sharma et al., 2017a). Due to the reduced size, nanoparticles have high area/volume ratio which grants them the high strength of diffusion (Sharma et al., 2017b). The metallic nanoparticles have wide application in various fields, such as removal of organic pollutants and toxic metal ions in catalysis, in systems of deliveries of pharmaceuticals, semiconductors, magnetic materials, antimicrobial activity among others (Sharma et al., 2017b).

The metallic nanoparticles have also been widely used in the removal of dyes such as eosin Y (Xia et al., 2010), orange G (Bokare et al., 2008), methyl orange (Li et al., 2015; Meena Kumari et al., 2015; Sha et al., 2016), azo and anthraquinone dyes (Truskewycz et al., 2016) and scarlet 4BS (Lin et al., 2012).

Some studies involving the production of materials from waste for dye removal have also been carried out. Yola and collaborators synthesized a composite composed of silver nanoparticles and colemanite ore waste for removal of dyes Reactive Yellow 86 and Reactive Red 2 (Yola et al., 2014). Atar and Olgun used boron waste for sorption of dyes basic blue 41 and acid blue 225 (Atar and Olgun, 2009).

The dyes are substances that can be used for dying in several industrial sectors, including the textile industry (Nabil et al., 2014). The reactive dyes are among the most commonly used due to their high stability. However, because they are very soluble in water and make the low rate of fixation to the fibers, the reactive dyes can promote the generation of effluents with a high content of coloring (Vakili et al., 2015). Once present in water bodies, such substances may bring many problems to the aquatic flora and fauna. Among these, the change of color of water, which prevents the proper photosynthesis and reproduction of aquatic organisms, since it prevents the sunlight reaching the aquatic plants (Bouaziz et al., 2015). In addition, dyes can cause diseases and disorders in the health of living beings (Arshadi, 2015). One of the reactive dyes used by the textile industry is the Reactive Blue 4 (Table 1).

Then, the objective of this work was to synthesize polymetallic nanoparticles using as raw material residues of spent lithium-ion batteries. There are no reports in the literature of polymetallic nanoparticles synthesized from lithium-ion batteries used. This new value-added material will then be characterized and applied in the removal of a model molecule, the reactive blue dye 4, in aqueous system.

2. Material and methods

2.1. Reagents and solutions

All chemicals used were of analytical grade and all aqueous solutions were prepared using purified water from the Milli-Q system and stored at 4 °C. The Reactive blue 4 dye was purchased from Sigma-Aldrich (35% m/m), the sodium borohydride (minimum 98.0%), ethanol (99.5%), and the copper sulfate (II) pentahydrate were obtained from Vetec, sulfuric acid was purchased from Alphatec, sodium hydroxide, hydrochloric acid, and nitric acid were purchased from Neon, citric acid and cobalt acetate tetra hydrate was purchased from Dinâmica.

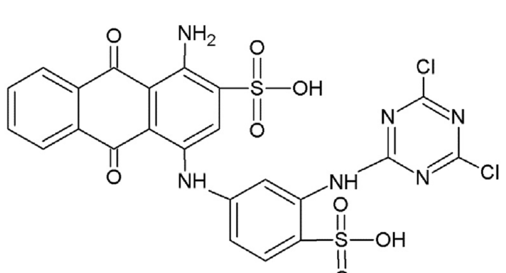
2.2. Extraction and characterization of metals present in spent lithium-ion batteries

The battery used was obtained from an obsolete computer. For the extraction of metals, first the spend lithium-ion batteries were discharged, dried in an oven at 60 °C for 24 h, and then the metal part was cut with the aid of a pair of scissors. 30 mL of aqua regia ($3HCl:1HNO_3$ v/v) were added to 10 g of the metal part. This material was maintained in a system of leaching in reflux, which remained under constant agitation and heating at 65 °C for approximately 60 min. The liquor obtained was cooled, filtered to vacuum and transferred to a 1000 mL flask where the volume was completed with distilled water. The quantification of the predominant metals in the liquor was carried out by Flame Atomic Absorption Spectrometry (Varian AA240 – Shimadzu).

2.3. Synthesis of PN-LIB, cupper nanoparticles (N-Cu) and cobalt nanoparticles (N-Co)

The synthesis of PN-LIB was performed via chemical reduction of metals present in the liquor, obtained in step of extraction. Therefore, it was added, slowly, 100 mL of a solution of sodium borohydride (1.06 mol L^{-1}) to 100 mL of the liquor of batteries, under constant agitation. The sodium borohydride solution was added in excess to ensure that all metals present in the liquor would be reduced. The nanoparticles obtained were vacuum filtered, washed with Milli-Q water and ethanol and subsequently dried and stored in a freezer.

Table 1
Structure and properties of RB 4 dye.



Name:	1-Amino-4-[3-(4,6-dichlorotriazin-2-ylamino)-4-sulfophenylamino]anthraquinone-2-sulfonic acid
Molecular Weight:	637.43 g mol^{-1}
Empirical Formula:	$C_{23}H_{14}Cl_2N_6O_8S_2$
Color Index Number:	61205

[*]Source: Sigma-Aldrich.