Copper metallurgical slag as a sustainable precursor of iron oxide photocatalysts to remove indigo carmine dye from water using the Photo-Fenton process

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Currently in this modern society with great population growth, it is necessary to develop sustainable strategies for the use of industrial raw materials by optimizing metal recovery rates during processing, developing capabilities to recover residual elements present in by-products, expanding the use of by-products and increasing the recycling of waste giving it added value. Which will ultimately reduce the waste footprint of resource extraction[1]. Copper slag, a waste material issued from the refining process of the metallurgical industry, due to its chemical composition can be a good candidate to recover several transition metals, which are used to produce catalysts for water treatment. For every ton of copper obtained, approximately 2.2 tons of pyrometallurgical slag are generated. It is estimated that 4.5 million tons of this waste are produced worldwide each year[23]. Copper slag is primarily composed of iron and silica oxides, with low amounts of Al, Ti, Ca and Mg and traces of Cu, Cr, Co, Zn and others[4]. The use of iron oxide present in copper slag has been studied as a photocatalyst in heterogeneous Photo-Fenton type reactions. The Slag/H_2O_2/Light-Uv system has been successfully studied in the elimination of organic waste such as: Textile Industrial Wastewater[4] , emerging contaminants particularly antibiotics [5], and pesticides such as thiabendazole [6]. However, it has been observed that the slag is composed of various semiconductors and these residues show a small surface area which produces very low degradation rates of pollutants.

In order to overcome this drawback, this work assesses the use of copper slag as a precursor material for the synthesis of Fe_3O_4 (magnetite), and its performance as catalyst in the Photo-Fenton process to degrade the indigo carmine dye in water. In the first stage of the work, for the synthesis of magnetite two amounts of citric acid and types of citric acid used (AC= commercial citric acid or AR= Reagent citric acid) for the extraction of Iron from the slag were evaluated. Briefly, 40g of copper slag was added to aqueous solutions containing two different concentrations of citric acid (0.2 and 0.4 M) and at room temperature or T= 45°C during the extraction for 2 h were applied. The leachates were dried and subjected to thermal treatment at 350°C for 2 h. The characterization of the prepared materials was carried out by XRD, FTIR, SEM, DRS, Z Potential, PZC, BET and the activity to degrade indigo carmine dye (*IC*) using the Photo-Fenton process was determined. The degradation reaction was carried out in 250 mL of an aqueous solution of IC at 10 ppm, 200 µL of peroxide (30 %), 20 mg of photocatalyst (Fe_3O_4), and UV irradiation at 365nm (9W lamp). The use of copper slag as a precursor material allowed to obtain Fe_3O_4 in all the experiments; the experimental conditions (0.2 M of AC and T=45°C) produced a catalyst (0.2ACT). The degradation of 90 % of the *IC* dye using this material was achieved in 60 minutes of reaction (Photo-Fenton) (Figure 1). The apparent kinetic rate constants (K_{app}) of the 0.2AC,0.4AC, 0.2ACT, 0.4ACT, 0.2AR and 0.4AR are 2.4, 4.2, 7.5, 6.1, 2.9 and 4.6 $\times10^{-2}$ min^{-1} respectively. We can observe that the temperature used to dissolve commercial citric acid directly impacts the photocatalytic activity.

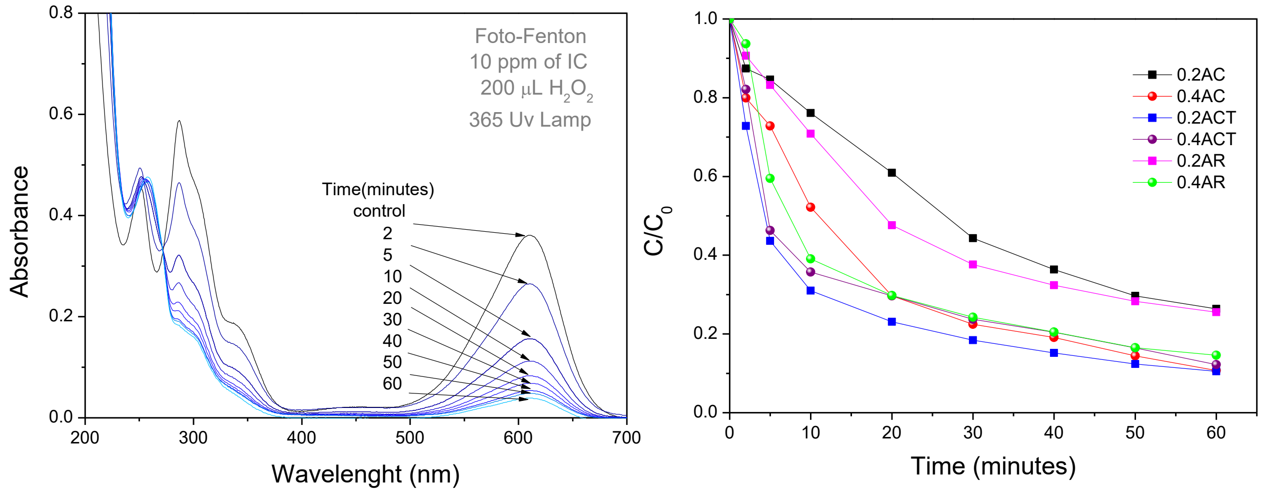

Figure 1. Absorbance spectra of 10 ppm of the *IC* dye as a function of Uv-light irradiation time and plot of C/C_0.

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