

Copper slag as a source of iron for the synthesis of a magnetically recoverable catalyst used to degrade organic pollutants in water

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Introduction

The importance of waste processing has grown within the mining and metallurgical sector. The scarcity of mineral raw materials has shifted focus towards recycling, while environmental regulations have prompted researchers to explore new alternatives to minimize or eliminate waste generation. This work aims to revalorize a waste material with high iron content, such as copper metallurgical slag, and produce useful materials for treating wastewater contaminated with dyes such as methylene blue, which is one of the most commonly used dyes in the textile industry (Oladoye *et al.*, 2022). Material synthesis typically requires controlled conditions, pure reagents, and aggressive agents such as reducers or organic solvents which limit the scalability of the process. Therefore, it is important to develop new approaches that allow material synthesis from mineral-rich waste and the utilization of easily obtainable and low-toxicity complexing agents such as citric acid. Through XRF, it was determined that 58% of the iron was successfully extracted from a copper slag when subjected to leaching with citric acid, generating a citrate-iron complex. Subsequently, by solid-state thermal decomposition of the iron-citrate complex, a brown-colored magnetic material was produced. The calcined material was characterized by various techniques; FT-IR spectra and XRD patterns revealed that the phase obtained was magnetite Fe₃O₄. The surface area of the magnetite was 123.3 m²/g, showing a type IV isotherm, characteristic of mesoporous materials. The magnetic iron oxide obtained was evaluated through different removal systems to determine its potential as a photocatalyst and adsorbent, with the latter property having the greatest impact on the removal of MB.

Material and Methods

Commercial citric acid was purchased from Taste & Joy, technical-grade sodium hypochlorite (6% w/w) from Meyer, hydrogen peroxide (30% w/w) from J.T Baker, and methylene blue chloride from Hycel. The copper slag (CS) originated from a smelting industry in northern Mexico, with an approximate particle size of 74 μm (200 mesh) used. The chemical composition was determined through X-ray fluorescence (XRF) using a Rigaku Primus II X-ray spectrometer. Phase identification of the slag was determined via X-ray diffraction (XRD) on an Empyrean diffractometer.

Synthesis and characterization of Fe₃O₄

To obtain the iron-citrate complex, the copper slag underwent a hydrometallurgical extraction method which involved agitating 40 g of slag with 0.267 M citric acid in 1 L of distilled water for 2 hours. The mixture was vacuum-filtered, and the supernatant, which exhibited a green coloration, was heated to 80°C until the volume reduced. Subsequently, the product was placed in 100 mL porcelain capsules and dried at 100°C for 12 hours. The sample was identified as CSL. The identification of functional groups confirming the formation of the iron-citrate complex was determined through Fourier-transform infrared spectroscopy (FT-IR) using a Thermo Scientific Nicolet 6700 instrument. To determine the decomposition temperature of the precursor complex, thermogravimetric analysis (TGA) was conducted using a Labsys Evo TG thermobalance from Setaram.

Approximately 5 g of the obtained powder was taken in a 50 mL ceramic crucible and heated to 300°C for 2 hours. After calcination, the furnace was allowed to cool naturally to room temperature. The resulting material was ground in an agate mortar, yielding a brown-colored magnetic powder identified as CSL300. The determination of phases obtained was conducted using FT-IR and XRD. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and nitrogen adsorption/desorption isotherms at 77.4 K were measured using the Bel Japan Minisorp II equipment. Prior to the analyses, the sample was degassed at 200°C in a nitrogen flow for 12 hours.

Removal of methylene blue dye

In this study, methylene blue (MB) was used as the model contaminant because its decolorization can be easily monitored using UV-Vis spectroscopy. The reaction vessel consisted of a borosilicate glass cylinder with a capacity of 250 mL. In all experiments, a solution with a concentration of 10 mg/L of MB, 125 mg of catalyst, and 1 mM of H₂O₂ and NaClO were used, as appropriate. In all experiments, a reaction time of 60 minutes was set, and no pH adjustment was made at the beginning of the reactions, resulting in a pH close to neutrality (6.5-7.5). For photo-assisted tests, a 9 W UV lamp (365 nm) was used. The decolorization of MB was monitored using a Shimadzu UV-Vis 2600 spectrophotometer, and the wavelength of maximum absorbance at 664 nm was selected.

Results and discussion

Initially, the CSL precursor underwent TGA analysis to determine the calcination temperature required to decompose the iron citrate complex and produce iron oxide. The decomposition of CSL was observed at a temperature of 260°C, where the formation of magnetic iron oxides has been reported upon calcination of iron citrate for two hours within a temperature range of 300 to 350°C. Therefore, 300°C was selected for this material. (Patra *et al.*, 2019). In the XRF analyses, the major components were iron oxide (Fe₂O₃ with 35% and 20%), silicon (SiO₂ with 23% and 12%), and calcium (CaO with 23% and 11%) for the CS and CSL samples, respectively. This indicates that the extraction process employed was sufficient to leach approximately 58% of the iron present in the copper slag. The formation of the iron citrate complex was identified through FT-IR spectra, where Fe-O stretching at peaks 843, 450, and 578 cm⁻¹ indicates coordination between citric acid and iron for CSL (Dodge and Francis, 2003). In CSL300, bands located at 585, 440-444 cm⁻¹ for the Fe-O bond have been observed in iron oxides such as magnetite, ferrite, and hematite (Dey *et al.*, 2019). In Figure 1 a) the XRD patterns for CS and CSL300 are shown. In CSL300, a phase of magnetite Fe₃O₄ with low crystallinity was identified, which may be attributed to the non-use of pure precursors in this study. The surface area of CSL300 was 123.3 m²/g compared to CS with an area of 0.541 m²/g. The isotherm for CSL300 was of type IV with an H3 hysteresis loop, indicative of a mesoporous material, showing promise for evaluation as an adsorbent.

CSL300 was evaluated to determine its potential as an adsorbent and photocatalyst for advanced oxidation processes. In Figure 1 b) the graph illustrates the removal of MB under different reaction systems. In photocatalysis, the MB removal was 56%, representing a 10% increase compared to adsorption alone. A comparison of oxidants (H₂O₂ y NaClO) in the presence and absence of light was conducted. In the Fenton and heterogeneous photo-Fenton reactions (H₂O₂-CSL300, H₂O₂-CSL300-UV), MB removals of 42% and 45% were achieved, respectively. When NaClO is used as the oxidant, 50% of MB is removed in Cl-CSL300 and 62% in Cl-CSL300-UV. These results demonstrate that, even when reaction systems are photo-assisted or accompanied by an oxidant, the most remarkable property of this material is its adsorption capacity. CSL300 exhibited a 46% removal of MB when used solely as an adsorbent, which can be attributed to its mesoporous nature as observed in the BET analysis.

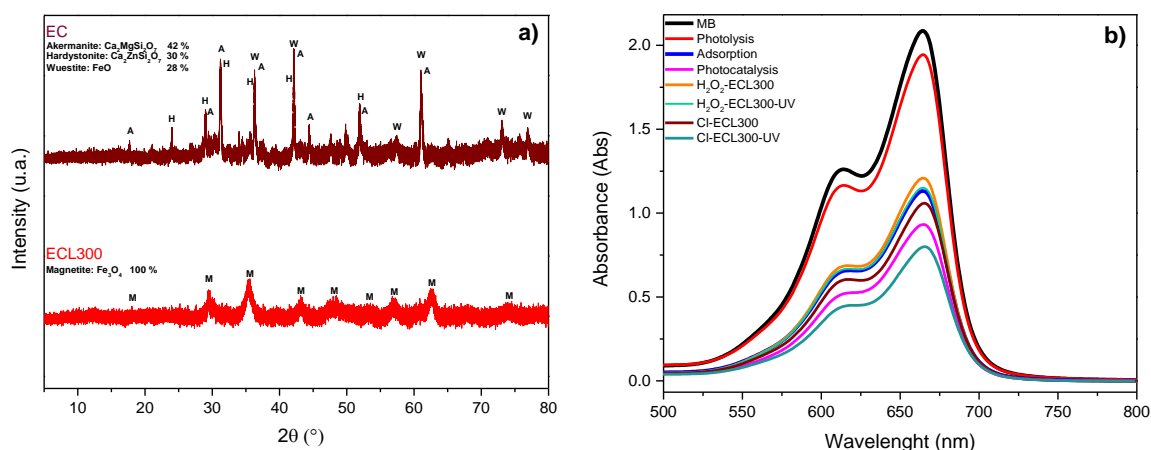


Figure 1. a) XRD patterns of EC and ECL300 and b) Absorption spectra of the MB aqueous solution in different removal systems, fixed conditions: 10 mg/L MB, 125 mg ECL300, 1 mM H₂O₂ y NaClO, 60 min reaction.

Conclusions

Copper slag was evaluated as a source of iron, along with commercial citric acid, to form an iron citrate complex through a hydrometallurgical process. Subsequently, solid-state thermal decomposition of ferric citrate was performed to obtain magnetite with suitable properties for use in MB removal from aqueous solution. BET surface analysis showed an area of 123.3 m²/g, successfully demonstrating the material's adsorbent capacity by removing 46% of MB within 1 hour. This capacity can be further enhanced by adding an oxidizing agent or by photo-assistance.

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