Journal of Hazardous Materials 361 (2019) 221–227

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Preparation of micro-electrolysis material from flotation waste of copper slag and its application for degradation of organic contaminants in water

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ARTICLE INFO

Keywords:
Copper slag
Carbothermal reduction
Micro-electrolysis
Organic contaminants

ABSTRACT

Flotation waste of copper slag (FWCS) was used as a raw material for the preparation of a micro-electrolysis material (MEM) through a carbothermal reduction process. The performance of MEM was evaluated for the degradation of organic contaminants in water. The effects of preparation conditions on the performance of MEM were investigated. Results showed that the MEM prepared under the conditions of calcination temperature of 1100 °C, calcination time of 60 min, and coal dosage of 25% presented the best performance for degrading methyl orange (MO). The decolorization process was enhanced by increasing the MEM dosage, decreasing the initial pH of the solution, and raising the solution temperature. Moreover, the MEM presented good capability for the degradation of methylene blue, eosin Y, and acid fuchsin. X-ray diffraction (XRD) analysis showed that increasing the roasting temperature was beneficial to the formation of zero-valent iron (ZVI). Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) showed that micro-sized ZVI particles were formed in the MEM, and they contained a small amount of copper element. Meanwhile, the mechanism analysis showed that a redox reaction of the MEM and MO occurred, the azo bond of MO was destroyed, and sulfanilic acid was generated.

1. Introduction

Copper slag is a solid waste produced during the pyrometallurgical production of copper from copper concentrates. For each ton of copper production, approximately 2.2 tons of slag is generated. The production of copper slag is calculated in millions of tons each year. The chemical composition of slag varies with the original properties of copper concentrates and process of treatment; in general, 30%–40% Fe and 0.5%–2.1% Cu are present in copper slag [1,2]. Flotation method has been widely used to recover copper minerals from copper slag [3]. However, the resulting FWCS, account for more than 90% of the weight of raw materials, cannot be used effectively. The FWCS has been piled up or sold to cement plants as iron source in small quantities [1,4]. Disposal of such huge amount of FWCS poses a threat to the environment because it contains heavy metals. Thus, considerable attentions have been devoted to the alternative uses of FWCS. Ozel et al. (2006) synthesized brown and black pigments from FWCS [5]. Karamanov et al. (2007) reported the production of glass–ceramic by using FWCS as raw material [6]. Moreover, few attempts have been conducted to use copper slag for wastewater treatment since it contains high content of iron. Gutiérreza et al. (2012) reported the use of copper slag to catalyze the removal of phenol in solution by H_2O_2 and H_2O_2/UV processes [7]. Kõyak et al. (1999) investigated the Cr(VI) reduction in aqueous by copper smelter slag [8]. It is generally agreed that the iron-bearing materials used in the advanced oxidation processes should contain mostly ferrous ion or ZVI which presented high reactivity [9–11]. However, the main iron-bearing mineral of copper slag is fayalite (Fe_2SiO_4) which is an insoluble ferrous mineral that hardly releases ferrous ion in a weak acidic solution [12]. Therefore, the application of copper slag in the environmental field was limited.

As a promising wastewater treatment technology, iron–carbon micro-electrolysis method is based on the electrochemical reactions of microscopic galvanic cells between ZVI and carbon in a solution. It has been proven to be a highly efficient technology for removing organic contaminants, arsenic, and Cr^{6+} from wastewaters [13–16]. The mechanism of MEM degrading contaminants have been summarized as follows: (1) precipitation of contaminants on the electrode surface due to electromigration and electrophoresis effect under micro-electric field; (2) reduction of contaminants by Fe° and Fe^{2+} formed from the oxidation of Fe°; (3) destruction of the carbon chains of organic contaminants by active hydrogen stems with H^+ reduction at cathode; (4) coagulation by ferrous and ferric hydroxides formed from precipitation

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https://doi.org/10.1016/j.jhazmat.2018.08.098
Received 17 June 2018; Received in revised form 28 July 2018; Accepted 31 August 2018
Available online 01 September 2018
0304-3894/

of Fe^{2+} and Fe^{3+}; and (5) adsorption of contaminants by carbon materials.

In previous studies, MEMs were mainly made of ZVI and activated carbon by physically mixing [3,17] or sintering them together under oxygen-free circumstance [16] or synthesis of MEM by solution reaction using iron salt and carbon as materials [18,19]. These production processes significantly increase the cost of producing MEM. Therefore, affordable processes using low-cost materials for preparing of MEMs are needed. In the present study, FWCS as an iron source and anthracite as carbon source were employed for the preparation of MEM through carbothermal reduction process. Several organic contaminants were used as model compounds to evaluate the performance of the prepared MEM. The effects of preparation conditions of MEM and the degradation parameters on contaminant degradation were studied. The degradation products and possible mechanism of the decolorization process were also investigated to some extent.

2. Experimental

2.1. Materials and chemicals

The FWCS used in this study was obtained from Guixi Smelting Plant, Jiangxi Copper Industry Co., Jiangxi Province, China. The particle size distributions and chemical compositions of the FWCS are presented in Tables 1 and 2, respectively. X-ray diffraction (XRD) analysis revealed that the main crystalline phases presented in the FWCS were fayalite ($FeSiO_4$) and magnetite (Fe_3O_4; Fig. 1). The reductant used in this work was anthracite. It contained 0.80% moisture, 81.11% fixed carbon, 10.91% ash, and 7.18% volatile. The coal was crushed to −0.1 mm for use.

All of the chemicals were purchased from Sinopharm (Shanghai, China), they were of analytical grade and used as received without further purification. The stock solutions were prepared by dissolving MO, methylene blue, eosin Y, and acid fuchsin in deionized water. Deionized water was used throughout this study.

2.2. Preparation of MEM

MEM was prepared as follows. FWCS (30 g) was mixed with coal (15 wt %-35 wt %), binder (sodium carboxymethyl, 0.5 wt%), and water (approximately 25 wt%) to produce materials that could be shaped manually to make ~10 mm diameter pellets. The dosages of coal, binder, and water were expressed as percentages that refer to their mass ratios to the FWCS. The wet pellets were oven dried at 105 °C for 2 h before roasting. The roasting experiments were performed in a muffle furnace under air atmosphere as follows. First, the pellets were placed in clay–graphite crucibles (70 mm in diameter and 75 mm in height) with a cap. Then, the crucibles were placed into the furnace and maintained for a certain time after the temperature reached the designated temperature. After heating, the crucibles were removed from the furnace and cooled to room temperature under air atmosphere. After cooling, the reduced pellets were grounded and sieved through 0.1 mm sieve and sealed storage for further use.

2.3. Batch experiments

Batch experiments were conducted to investigate the effects of roasting temperature, coal dosage, roasting time, initial solution pH, MEM dosage, and solution temperature on the decolorization of MO by MEM. The experiments were conducted in a 500 mL beaker with 400 mL solution (typically MO) with initial concentration of 100 mg/L. The desired initial pH value of solution was adjusted by diluted H_2SO_4 or NaOH and determined by a digital pH meter (pHS-25, Shanghai, China). In addition, all experiments were performed openly in the air, which was controlled with a water bath, and the slurry was mixed by a mechanical stirrer (400 rpm). After a preselected time of decolorization, the samples were collected by a syringe and filtered through a 0.45 μm membrane filter. All decolorization experiments were performed in triplicate.

Table 1
Particle size distributions of the FWCS.

Size (mm)	+0.104	−0.104 + 0.074	−0.074 + 0.048	−0.048
Content (wt%)	1.01	4.19	8.57	86.23

Table 2
Chemical compositions of the FWCS (wt%).

Fe	Cu	Al_2O_3	MgO	SiO_2	CaO	TiO_2
36.66	0.37	9.72	0.63	36.66	1.60	0.26

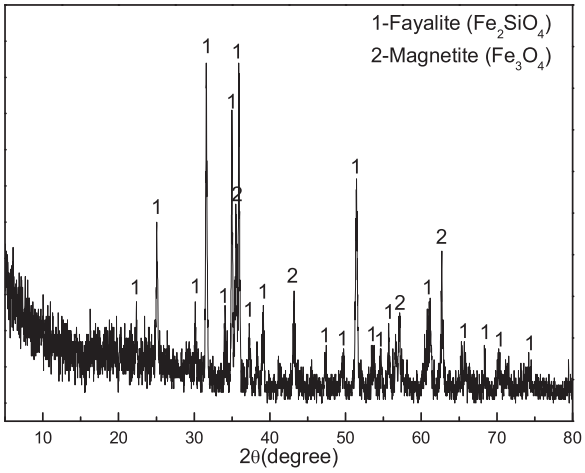

Fig. 1. XRD patterns of the FWCS.

2.4. Analytical methods

The residual concentration of the targeted contaminant in the solution was analyzed using a UV–vis (UV–vis) spectrophotometer (T6 New Century, Pgeneral, China). The detection wavelengths applied for MO, methylene blue, eosin Y, and acid fuchsin were 464, 664, 518, and 546 nm, respectively. Sample solution was diluted 10 times before measurement if needed.

The decolorization efficiency of the targeted contaminant is defined as follows:

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where R is the decolorization efficiency, C_0 is the initial concentration of the targeted contaminant in the solution, and C_t is the concentration of the targeted contaminant at time t (min).

2.5. Characterization

SEM and EDS analysis (MLA650 F, FEI, U.S.A.) were performed on the samples mounted in epoxy resin, and polished. The phases present in the samples were detected by XRD (DX-2700, HaoYuan Instrument Co., Ltd., China) under the following conditions: Cu-Kα radiation with a step of 0.02° and a scanning rate of 4.8°/min.