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Ozonation enhancement by Fe–Cu biometallic particles

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ABSTRACT

The aim of this work was to assess the effect of the bimetallic system Fe–Cu on the ozonation efficiency of indigo carmine and its main degradation product, isatin-5-sulfonic acid. As reference, experiments with single metal particles were also conducted. The metallic systems were synthesized by a chemical reduction method and characterized by EPR and HR-SEM/EDS. Cu and Fe oxidation states were found to be 2^{+}. The ozonation process was carried out in an up-flow bubble column. The organic compounds concentration was determined by UV–vis spectroscopy. The degree of oxidation and mineralization was determined by COD and TOC measurements, respectively. The effect of pH was also studied. It was found that the use of the bimetallic system not only considerably (by three times) improves the ozonation rate but also the mineralization degree of indigo carmine. The best results (97% indigo carmine removal and 92% of TOC removal) were obtained at pH 3 and with 1000 mg/l of Fe/Cu particles.

1. Introduction

A vast amount of water is employed by the textile industry. In the dyeing process, the produced wastewater contains strong color, which is reflected in a high chemical oxygen demand (COD). It has been estimated that 1–15% of the dye is lost during dyeing and finishing processes and it is released in the wastewater [1–3]. The discharge of effluents into the environment containing reactive dyes can interfere with sunlight transmission into flowing streams [4–7]. Available techniques for removing dyes have been studied as photodegradation [8], adsorption filtration [9], coagulation and biological treatments [10]. However, the stability of the organic molecules present in the dyes is high, and some of these methods are not completely effective. Therefore, recent progress on water treatment based on the chemical oxidation of organic compounds by advanced oxidation processes (AOPs) like ozonation have drawn attention [11]. Ozonation, which is effective, versatile, and environmentally sound, has been proved to be in recent years a good method for color removal. Ozone is a strong oxidant ($E^{\circ} = 2.07$ V) and reacts rapidly with most organic compounds degrading them [12,13]. In AOPs hydroxyl radicals ($^{\bullet}$OH) are used as oxidant, which is capable of oxidizing almost any organic substance. The fundamental feature of the radical is the existence of a single electron, instead of a free electron pair. This electron makes the $^{\bullet}$OH radical highly reactive. The oxidation of organic substances takes place in stages, with formation of intermediates, due to the high stability of organic molecules present in the dye-products. In the case of organics' complete oxidation, these are transformed into inorganic end products, water and carbon dioxide or mineralization of the molecule [14,15]. In spite of more efficient processes, the catalyzed ozonation has been successfully studied. In this sense, bimetallic systems have emerged as promising catalysts for environmental remediation. Their strong reducing ability can be used to remove numerous environmental pollutants (*e.g.*, heavy metals, halogenated organic compounds, nitro and azo compounds, and oxyanions) [16–19]. As a new class of materials comprising two different metals, bimetallic particles or metal oxides exhibit new functionalities because of synergy rather than merely additive effects of the metals [20–22]. In this work, the effect of adding metallic (Fe and Cu) and bimetallic particles (Fe–Cu) on the ozonation process efficiency is assessed. Indigo carmine and its main degradation product isatine-5-sulfonic acid [23–25], were elected as model molecules. The indigo carmine dye is widely and mainly used in the textile industry for denim dyeing.

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2. Materials and methods

2.1. Reagents

Sulfuric acid, sodium hydroxide, iron sulfate (II), copper sulphate (II), indigo carmine dye (IC), isatin5-sulfonic acid (ISA) and sodium borohydride analytical grade were purchased from Sigma-Aldrich Chemicals. 0.1 M solutions of the acid and the base were used without further purification to adjust the solutions pH to 3, 5 and 7. Ozone was generated *in situ* from dry air by an ozone generator (Pacific Ozone Technology), with an average production of 0.005 g/l.

2.2. Synthesis of Fe, Cu and Fe/Cu particles

In order to synthesize the binary Fe/Cu system, 250 ml of 0.01 M iron sulfate (II) solution and 250 ml of 0.01 M copper sulfate were mixed in a beaker at 300 rpm using glass stirrers. The solution pH was adjusted by the dropwise addition of 0.5 M NaOH solution. The pH was monitored with a potentiometer (15 Conductronic Digital pH–mV–pH–Meter °C). Subsequently and in concordance with reaction 1 [26] the chemical reduction of the particles was conducted by adding an excess (1.1 M, 100 ml) of sodium borohydride solution under a nitrogen atmosphere. The black colored precipitate was further stirred 15 min and this was followed by vacuum filtration through a 0.2 mm cellulose acetate filter paper. The borohydride in excess was removed with ethanol and acetone. The Fe and Cu particles were synthesized in a similar manner albeit separately under similar conditions.

$$2Fe^{2+} + 2Cu^{2+} + 2H_2O + BH_4^- + 4e^- \rightarrow 2Fe(Cu)_{(s)} + BO_2^- + 4H^+ + 2H_{2(g)} \quad \text{(reaction 1)}$$

2.3. Ozonation experiments

The ozonation experiments were conducted in a 1 l up-flow glass bubble column reactor. Ozone was continuously produced by an ozone generator and was fed through a 2 µm pore size gas diffuser at the lower part of the reactor. The effect of three materials (Cu, Fe and Fe/Cu particles) on the ozonation process efficiency was assessed. The effect of pH was also studied in the range of 3–7. At all experiments the indigo carmine (IC) initial concentration was 500 mg/l. As control experiments, IC concentration profiles were established by adsorption and by ozonation alone. For the adsorption experiment, only particles without any ozone supply were employed in order to discard the removal of IC by physical means. To avoid discharging ozone to the atmosphere, the unreacted ozone was trapped and destroyed in a heated catalytic ozone destroyer (Pacific Technology d41202). Samples were taken at specific time intervals to be analyzed by different techniques (UV–vis spectrophotometry, TOC and COD). All experiments were carried out at 288 K.

2.4. Characterization of Fe, Cu and Fe/Cu particles

2.4.1. High resolution scanning electron microscopy (HR-SEM/EDS)

Micrographs were obtained in a JEOL JSM 6510LV instrument at 15 kV with 10 mm WD using both secondary and backscattered electron signals. The metallic particles samples were coated with a 20 nm gold thin film using a Denton Vacuum DESK IV sputtering equipment with a gold target.

2.4.2. Electron paramagnetic resonance (EPR)

EPR measurements were conducted in a quartz tube at 77 K with a JES-TE300 JEOL spectrometer operating at X- band fashions at 100 KHz modulation frequencies and a cylindrical cavity in the TE_{011} mode. The external calibration of the magnetic field was made with a precision gauss meter JEOL ES-FC5. Spectral acquisition and manipulations were performed using the program ES-IPRITS/TE. The EPR spectrum was recorded as a first derivation and the main parameter such as *g*-factor values were calculated according to Wertz [27].

2.5. Chemical analysis

The concentration of indigo carmine was determined by UV–vis spectrophotometry by using a Perkin Elmer Model Lambda 25 UV–vis spectrophotometer with a wavelength range of 190–1000 nm. The samples were scanned at a rate of 960 nm/s in a quartz cell with 1 cm optical path. The samples absorbance was scanned at wavelengths from 200 to 900 nm. A maximum absorbance of IC at 610 nm was observed and for isatin5-sulfonic acid a maximum absorbance at 303 nm was determined. This was corroborated with the corresponding standards. All experiments were carried out at room temperature (19 °C ± 2). In addition, to determine the degree of mineralization of indigo carmine, total organic carbon (TOC) analyses were performed in a Shimadzu analyzer TOC-LCPH/CPN and chemical oxygen demand (COD) of the samples was determined using the American Public Health Association (APHA) standard procedures [28].

3. Results and discussion

3.1. Characterization

3.1.1. HR-SEM/EDS of Fe, Cu and Fe/Cu particles

Fig. 1 presents a SEM/EDS image of prepared Fe, Cu and Fe/Cu particles, before reaction with IC. It can be observed that Fe and Cu particles are spherical in nature (size 50–90 × 10^{-3} µm) and connected together forming cumulus, as shown in Fig. 1a and b. The SEM/EDS image of Fe/Cu (Fig. 1c) shows particles also forming a chain most probably due to the magnetic interaction between particles [29], which causes the rapid reduction rate of metal ions, in all cases.

3.1.2. Electron paramagnetic resonance (EPR)

In order to determine the oxidation state of Cu and Fe in the synthesized materials before and after their use in the ozonation process, X-band EPR spectra of Cu, Fe and bimetallic Cu/Fe particles were recorded at 77 K (Fig. 2). The presence and oxidation state of Cu(II) atoms could be easily identified because only Cu(II) (electronic configuration $3d^9$, $S = 1/2$) is active at this spectroscopy. The EPR spectra of Cu particles before and after their use in the ozonation process are almost symmetrical singlets (Fig. 2a) with isotropic *g* values of 2.394025 and 2.39001, respectively, which are typical of Cu(II) [27,28]. The absence of the superfine lines and a broad shape signal is explained by the fast rotation of particles in water and interparticle interactions, which results in an isotropic g tensor [28]. On the other hand, samples containing fresh Fe particles (before being used in the ozonation process) are EPR silent indicating a oxidation state +2. Interestingly, after degradation, these samples show a typical broad signal of Fe(III) with isotropic $g = 3.11152$ (electronic configuration $3d^5$, $S = 3/2$) (Fig. 2b). Fig. 2c shows the EPR spectra of bimetallic Fe/Cu samples. The spectrum of these particles prior their use in the ozonation process shows a signal with axial symmetry with two *g* values, the first high intensity band around $g = 2.18023$ and a less intense one at $g = 2.2034$. There are not observed signals that correspond to Fe(III) atoms in this spectrum. The *g* values follow the order $g_\perp > g_\parallel > 2.1823$ [30]. These values are rather characteristic of Cu(II) ions forming CuO clusters located in octahedral sites [38]. In contrast, the EPR spectrum of the used Fe/Cu particles shows two broad overlapping

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