



Research Paper

Degradation of atrazine by $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ nanomaterial-catalyzed sulfite under UV–vis light irradiation: Green strategy to generate $\text{SO}_4\cdot^-$



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ABSTRACT

Degradation of atrazine, a widely-used herbicide, by a novel advanced oxidation process was investigated through photo-catalyzing sulfite, the precursor of sulfate radical ($\text{SO}_4\cdot^-$) in this study, by zinc-copper ferrites ($\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$) under UV–vis light irradiation. The $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ with different ratios of Zn to Cu was synthesized through a facile sol-gel combustion method, and characterized by X-ray powder diffractometry, scanning electron microscopy, transmission electron microscopy, porosimetry, and UV–vis diffuse reflectance spectroscopy, and by a vibrating sample magnetometer and Mössbauer spectrometer. The $\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ demonstrated the highest photocatalytic ability to activate sulfite for the degradation of atrazine under current experimental conditions. The sulfate radical generated in the UV–vis light/ $\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ /sulfite system was identified as the main reactive species through radical quenching experiments and measuring two important byproducts (atrazine-desethyl and atrazine-desisopropyl). The XPS spectra of fresh and used catalysts were analyzed to further elucidate the reaction mechanisms. There are two possible approaches to produce $\text{SO}_4\cdot^-$: the oxidation of sulfite by photo-generated holes and the accelerated decomposition of metal-sulfite complexes (Fe(III)-sulfite and Cu(II)-sulfite) on the surface of $\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$. Based on the detected byproducts, the transformation pathways of atrazine by UV–vis light/ $\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ /sulfite were proposed as well. After the complete decomposition of atrazine, the used catalysts could be magnetically recovered using a magnet and no sulfite remained in the system. The results suggest that the UV–vis light/ $\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ /sulfite system is a “green” advanced oxidation technology for future application in wastewater treatment.

1. Introduction

Sulfate radical ($\text{SO}_4\cdot^-$) based advanced oxidation processes (AOPs) are gaining increasing attention [1,2] because $\text{SO}_4\cdot^-$ has a high oxidation potential (2.5–3.1 V) and can react with various recalcitrant organic contaminants [3,4]. $\text{SO}_4\cdot^-$ is usually produced from the activation of peroxymonosulfate (PMS) or peroxydisulfate (PDS) by UV [3,5,6], heat [5], ultrasound [7], electro-chemical methods [8], and transition metals [9]. However, after complete decomposition of substrate contaminants, the treated solutions still contain a large fraction of PMS or PDS [4,10], which may cause secondary pollution. Therefore, sulfite is considered as a substitutive precursor for the generation of $\text{SO}_4\cdot^-$ in AOPs and it can be simultaneously decomposed along with

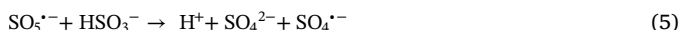
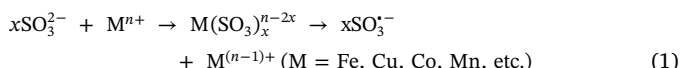
the organic contaminants [1].

In general, to produce $\text{SO}_4\cdot^-$, sulfite is activated homogeneously by transition metals, as shown in Eqs. (1) – (5) [11–13]. Nonetheless, homogeneous activation of sulfite has similar drawbacks to the Fenton reaction, such as: (1) narrow reaction pH ranges due to the hydrolysis of transition metal ions, and (2) precipitation of the formed iron-hydroxyl complexes, which may cause other issues to the follow up treatment processes. To overcome these drawbacks, firstly, photo irradiation is utilized to promote the efficiency of homogeneous activation of sulfite at a wider range of pH, including UV [14], UV–vis light [15] and sunlight [15]. Photo-irradiation accelerates the rate of the decomposition of the metal-sulfite complexes in Eq. (1), which is the rate-limiting step [16,17]. Also, sulfite can be catalyzed heterogeneously to avoid

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precipitation. For example, sulfite was activated by CoFe_2O_4 to remove metoprolol effectively, whereas the optimum reaction pH was up to 10 [2]. Consequently, a novel photocatalysis technology is needed for the activation of sulfite to generate $\text{SO}_4^{\cdot-}$ effectively at the neutral pH condition without any precipitation of metal-hydroxyl species in wastewater treatment applications.



Zinc ferrite (ZnFe_2O_4) is a promising photocatalyst for the activation of sulfite because of its narrow band gap and high photochemical stability. ZnFe_2O_4 was used to photo-catalyze oxidants (i.e., hydrogen peroxide (H_2O_2) [18,19], PMS [20] and PDS [10]) and reductants (i.e., oxalic acid [21]) for the effective decomposition of organic dyes under visible light irradiation. Nevertheless, ZnFe_2O_4 is not an environmentally friendly material due to its difficulty to recycle. The weak magnetic property of ZnFe_2O_4 makes it hard to be removed from the reaction solution by an external magnetic field; however, it can be improved by doping another transition metal into ZnFe_2O_4 , such as copper [22]. It is also worth mentioning that Cu(II) and Fe(III) have a positive synergistic effect on the homogeneous activation of sulfite [23], providing potential solutions for the heterogeneous catalysis of sulfite. Thus, zinc-copper ferrite nanocomposites ($\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$) will be used as the photocatalyst to activate sulfite, and such a process as reported herein has not yet been studied.

Our goal in this study is twofold. Firstly, it is important to find out whether the UV-vis light/ $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ /sulfite technology is both efficient and environmentally friendly to remove organic contaminants. Specifically, $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ was synthesized via a sol-gel combustion method and used to catalyze sulfite under UV-vis light irradiation to degrade atrazine ($\text{C}_8\text{H}_{14}\text{ClN}_5$), which is a widely-used and frequently detected herbicide in wastewater. To the best of our knowledge, it is the first study to apply heterogeneous photocatalysis to activate sulfite in the degradation of organic chemicals. The physical, optical, and magnetic properties of as-synthesized materials were characterized, operation parameters were optimized, and the residual concentration of sulfite after reaction was measured. Secondly, we predicted that the produced $\text{SO}_4^{\cdot-}$ mainly contributed to the degradation of atrazine. Therefore, possible mechanisms for the activation of sulfite by $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ /UV-vis light and potential degradation pathways of atrazine were proposed based on XPS analysis, quenching experiments, and detected reaction byproducts. This study provides a fundamental understanding and theoretical support for the applications of UV-vis light/ $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ /sulfite technology in wastewater treatment.

2. Experimental methods

2.1. Preparation of $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles

Magnetic ferrites of $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.33, 0.5, 0.67, 0.8$, and 1) were synthesized by a sol-gel combustion process with citric acid, as previously reported [24,25]. Typically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper nitrate hemi(pentahydrate) ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$), and ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in Milli-Q water at a specified stoichiometric ratio, followed by adding citric acid solution (25 mM) dropwise until the molar ratio of citric acid to Fe cations reached 3:2. After adjusting the pH of the resulting mixture with ammonium hydroxide to around 5, it was stirred rigorously at 60 °C towards the formation of a gel-like network, dried in

an oven at 90 °C for 6 h, and calcined at 400 °C for 2 h. Finally, the calcined particles were ground, washed with ethanol, 0.1 M H_2SO_4 and Milli-Q water, and dried at 100 °C for 12 h.

2.2. Characterization

The surface morphology of the as-prepared samples was observed with a scanning electron microscope (SEM, FEI SCIOS) and a high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010). The structure and crystal phase of the as-prepared samples were analyzed using X-ray powder diffraction (XRD, PANalytical). The Brunauer–Emmett–Teller (BET) surface area and optical property of the samples were measured by TriStar 3000 surface area analyzer (Micromeritics) and UV-vis spectrophotometer (Shimadzu 2501 PC) mounted with an integrating sphere accessory (ISR1200), respectively. The transmission ^{57}Fe Mössbauer spectra were collected at room temperature using a Mössbauer spectrometer in a constant acceleration mode with a $^{57}\text{Co}(\text{Rh})$ source. The isomer shift values were related to metallic $\alpha\text{-Fe}$ at room temperature. The spectra were evaluated by the software MossWinn 4.0. The magnetic data were measured on powder samples using a Quantum Design physical properties measurement system (PPMS Dynacool system) with the VSM option. The experimental data were corrected for the diamagnetism and signal of the sample holder. The hysteresis loops were recorded at a temperature of 300 K in externally magnetic fields ranging from -9 to $+9$ T. The changes of chemical oxidation states of elements on the surface of fresh and used catalysts were recorded by high-resolution X-ray photoelectron spectroscopy (XPS) employing a PHI 5000 VersaProbe II XPS system (Physical Electronics) using a monochromatic Al-K_α source (15 kV, 50 W) with photon energy of 1486.7 eV. Dual beam charge compensation was used for all the measurements. All spectra were measured in a vacuum of 1.4×10^{-7} Pa and at room temperature of 22 °C. For the high-resolution spectra, pass energy of 23.500 eV and step size of 0.200 eV were used. The XPS patterns were evaluated with the MultiPak (Ulvac-PHI, Inc.) software. All binding energy values were referenced to the C1 s peak at 284.80 eV. The surface charges of as-prepared catalysts in solutions with different pH values were characterized using Zeta potential analyzer (NanoBrook Omni).

2.3. Catalytic degradation experiments

Photocatalytic experiments were conducted using a 500 W Xenon lamp (Newport 67005) for UV-vis light irradiation. The light was filtered by Air Mass 1.5 global filter (Newport Corporation) and FSQ-KG5 heat absorbing glass filter (Newport Corporation), and the filtered light spectrum was in the range of 350–700 nm, as shown in Fig. S1 in Supporting Information.

Unless stated otherwise, degradation experiments were carried out in a 50-mL crystallizing dish, covered with a round quartz cover, and shaken by a basic shaker (IKA KS 130). $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles were firstly dispersed into 20 mL atrazine solution (4.4 μM), and the mixture was shaken for 15 min to achieve the adsorption/desorption equilibrium between the catalyst and the target compound. Then, 0.1 mL of sulfite stock solution (100 mM) was added into the solution followed by adjusting the initial pH to 7.2 with 0.1 M H_2SO_4 as quickly as possible. The sulfite stock solution was always freshly prepared. Once the photo-degradation was initiated, 200 μL samples were taken at given time intervals of 2, 5, 10, 15, 20, and 30 min, immediately quenched by 200 μL methanol (34.7 M), filtered by 0.2 μm PTFE syringeless filter (Whatman, GE Healthcare Life Sciences), and then analyzed by high-performance liquid chromatography (HPLC). All experiments were conducted in triplicate at room temperature.

2.4. Analysis methods

The concentration of atrazine was determined by an Agilent 1100

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