

Article

Zero-Valent Copper-Mediated Peroxymonosulfate Activation for Efficient Degradation of Azo Dye Orange G

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Abstract: Zero-valent metal (ZVMs)-based persulfate activation systems are extensively applied for the elimination of organic pollutants in aqueous environments. In this study, for the first time, zero-valent copper (ZVC) was employed as the peroxydisulfate (PMS) activator for the efficient degradation of Orange G (OG). The physicochemical properties of ZVC were systematically characterized by FESEM, EDX, TEM, XRD and XPS measurements. Furthermore, the effects of catalyst loading, PMS dosage, OG concentration and inorganic anions on the ZVC/PMS system were, respectively, investigated and explicated. The formation of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ in the system was verified by quenching experiments and then the possible reaction mechanism was proposed. This work can provide insight into water treatment technology based on ZVMs.

Keywords: heterogeneous catalyst; ZVC; PMS; OG



Citation: Yu, B.; Li, Z.; Zhang, S. Zero-Valent Copper-Mediated Peroxymonosulfate Activation for Efficient Degradation of Azo Dye Orange G. *Catalysts* **2022**, *12*, 700. <https://doi.org/10.3390/catal12070700>

Academic Editor: Antonio Eduardo Palomares

Received: 19 May 2022

Accepted: 24 June 2022

Published: 26 June 2022

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1. Introduction

The ever-growing nature of mankind's activities vastly threatens the ecological environment, and the water pollution caused by refractory organic pollutants is particularly serious. Azo dyes, one of the most used synthetic dyes in the printing and dyeing process, have attracted much attention for their toxicity, carcinogenicity and biodegradability [1]. Unfortunately, conventional water treatment technologies are ineffective in degrading azo dyes in wastewater, creating barriers to meeting the discharge standard [2,3].

In recent years, persulfate-based advanced oxidation processes have been extensively used to decompose and mineralize refractory organic pollutants in water [4,5]. Many persulfate activation methods were applied, such as ultraviolet light (UV) activation [6], thermal activation [7], ultrasonic (US) activation [8], transition metal ion activation [9], carbon material activation [10], etc. The energy-based activation processes suffer from the high energy consumption in long-term operation. Transition metal ions are commonly active but difficult for recycling, restricting the large-scale application. Therefore, it is imperative to develop low-cost, green and efficient activation tactics. In this regard, zero-valent metals (ZVMs), as highly efficient and recyclable catalysts, serve as a promising option for persulfate activation. The ZVMs can efficiently activate persulfate to generate reactive species with strong oxidation ability via direct or indirect activation (low-valent metal ions) [11,12]. Among them, zero-valent copper (ZVC) is widely used to catalyze persulfate to remove various organic contaminants [13–16]. However, to our best knowledge, there is no report about OG degradation by the ZVC/persulfate system. It is noteworthy that OG as a common azo dye in textile wastewater is often used for dyeing synthetic fiber, wool, etc. Moreover, wastewater containing OG is a significant threat to human beings and aquatic organisms. For instance, studies have discovered that OG is teratogenic and genotoxic to organisms [17]. Therefore, more efforts should be devoted to the degradation of OG.

In this paper, ZVC, for the first time, was used to activate peroxymonosulfate (PMS) for OG degradation. Firstly, the physicochemical properties of commercial ZVC were characterized by field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The effects of ZVC loading, PMS dosage, OG concentration and inorganic anions on the degradation reaction were investigated. The dominant reactive species were identified and then the reaction mechanism was proposed. This study provides insights into water purification technology based on zero-valent metals.

2. Materials and Methods

2.1. Materials and Instruments

The main materials and reagents include: KHSO_5 (PMS), Acid Orange G (OG), zero-valent copper (ZVC), NaCl , NaHCO_3 , Na_3PO_4 , methanol (MeOH), and tert-Butanol (TBA). All reagents were analytically pure and the solutions were prepared with deionized water. The main instruments include: ultraviolet-visible spectrophotometer (DR-5000, Hach Company, Loveland, CO, USA), electronic analytical balance (AUY120, Shimadzu, Japan), and magnetic stirrer (JOAN LAB SH-2).

2.2. Analytical Method

OG was determined by spectrophotometry from their maximum absorbance at 478 nm. The morphological characteristics of the samples were obtained by field emission scanning electron microscopy (FESEM, Thermo Scientific Apreo 2C, Waltham, MA, USA) and transmission electron microscope (TEM, Talos F200S G2). X-ray diffraction (XRD, X-D6, PUXI) was used to study the structural information of the materials. The elemental compositions of samples were obtained from energy-dispersive X-ray spectroscopy (EDX) equipped with Oxford Instruments Ultim Max 65 detector. X-ray photoelectron spectra (XPS, AXI Sultra DLD) were further performed to illustrate the chemical compositions and the elemental valence states of materials.

2.3. Degradation Experiment

The batch experiments were carried out in a 150 mL beaker at room temperature. The reaction was initiated by adding a certain amount of ZVC and PMS into OG solution with magnetic stirring at 400 rpm. At predetermined intervals, the water samples were taken out and filtered through a 0.22 μm filter membrane, followed by adding a trace amount of MeOH (reaction terminator) for further analyses.

3. Results and Analysis

3.1. Characterization

Figure 1a,b depicted the SEM images of the catalyst sample. It is evident that the catalyst consists of irregular agglomerates with smooth surfaces, and no obvious porous structure is observed. The TEM micrograph also confirmed the apparent aggregation of the catalyst particles (Figure 1c). As indicated by EDX measurement (Figure 1d), the catalyst sample is mostly composed of the Cu element, while the detected C and O elements can be ascribed to the presence of conducting resin used for investigation. By means of the XPS test, the zero oxidation state of the catalyst was further revealed (Figure 1e).

The XRD pattern of the catalyst is shown in Figure 1f. Three characteristic diffraction peaks of the sample located at around $2\theta = 43.3^\circ$, 50.4° and 74.1° , corresponded to the (111), (200) and (220) planes of metal Cu (PDF #04-0836). Meanwhile, no impurity peak was detected, indicating that the catalyst is indeed pure ZVC material [18].

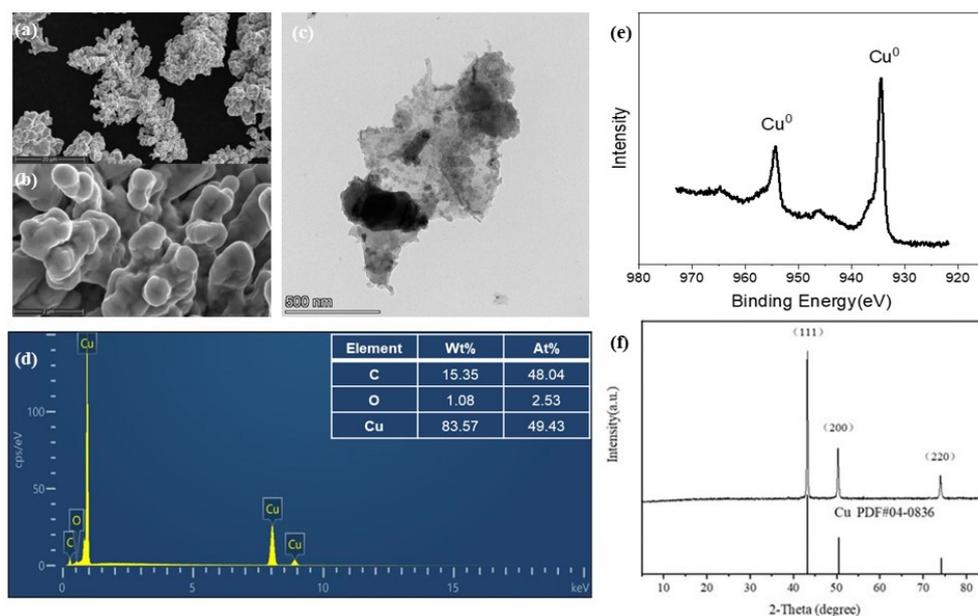


Figure 1. SEM (a,b), TEM (c), EDX (d), XPS (e) and XRD (f) of the catalyst.

3.2. Catalytic Performance of ZVC

To evaluate the activity of ZVC, several degradation experiments were conducted in different systems. As shown in Figure 2, the concentration of OG barely changed with the addition of sole PMS. Similarly, slight removal of OG (only ~1.2%) was obtained with ZVC alone, which is attributed to the adsorption of OG molecules onto ZVC. In contrast, once binary PMS and ZVC were mixed in the solution, the removal efficiency of OG reached 99.6% only after 10 min, and OG was completely removed within 20 min. It is preliminarily speculated that owing to the high reactivity of copper element [19–21], ZVC could effectively activate PMS to produce highly oxidative reactive species for rapid decomposition of OG.

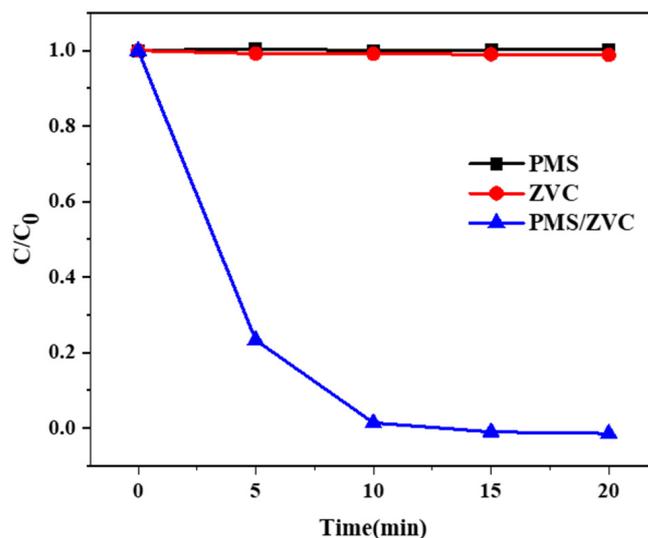


Figure 2. The OG degradation in different systems. Condition: [OG] = 50 mg/L, [PMS] = 3 mM, [ZVC] = 0.3 g/L.

3.3. Quenching Experiment

A series of quenching experiments were carried out to probe the reactive species formed in the ZVC/PMS system. Methanol (MeOH) can effectively quench $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, while tert-butyl alcohol (TBA) can quench $\bullet\text{OH}$ more quickly [22–24]. As shown in Figure 3,

3.4. Effect of Initial OG Concentration

The effects of the initial OG concentration were investigated and described in Figure 5. As OG concentration changed from 30 mg/L to 50 mg/L, the decay efficiency of OG elevated from 43.7% to 76.7% within 5 min, and then the final removal efficiency increased from 96.8% to nearly 100%. This enhancement may be ascribed to the increase in OG molecules, which could generate more organic radicals to accelerate the regeneration of Cu^+ . However, once the concentration of OG was up to 70 mg/L, its degradation efficiency immediately diminished to 94.6%. The reason is that the steady-state concentration of radicals is constant, thus the limited radicals were incapable of decomposing excessive substrate.

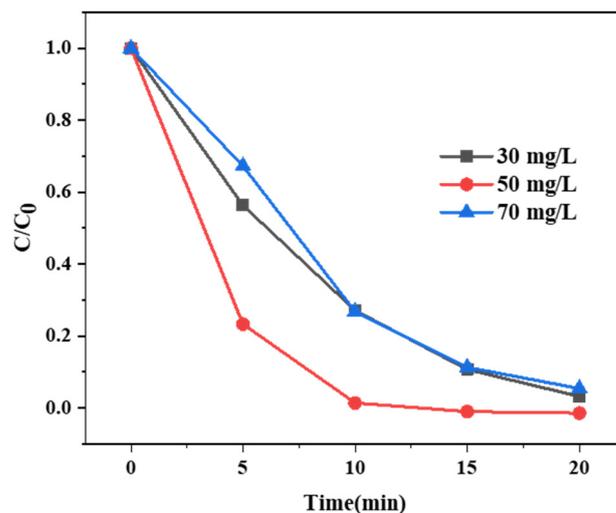


Figure 5. Effect of initial OG concentration on OG degradation. Condition: [PMS] = 3 mM, [ZVC] = 0.3 g/L.

3.5. Effect of PMS Concentration

The effects of PMS concentration on OG degradation are displayed in Figure 6. When PMS concentration increased from 1 mM to 3 mM, the OG elimination process was significantly enhanced (removal efficiency increased from 86.4% to 100.0%). With the addition of 5 mM PMS, the reaction was further accelerated to achieve the complete removal of OG in only 10 min. The reason for this phenomenon may be that adding more PMS can appropriately improve the yield of radicals and speed up the oxidation process [25].

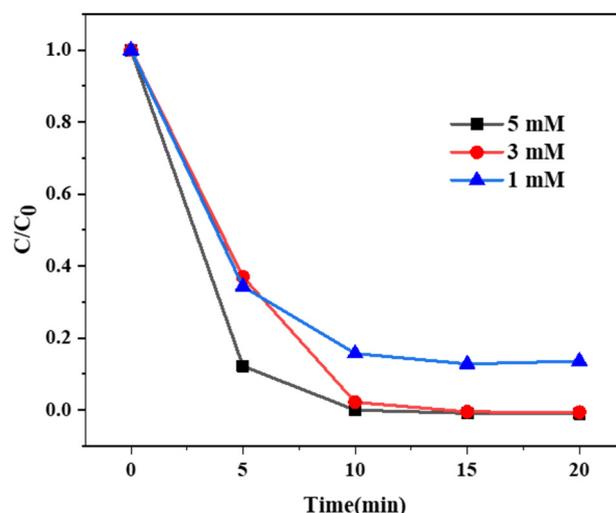


Figure 6. Effect of PMS concentration on OG degradation. Condition: [OG] = 50 mg/L, [ZVC] = 0.3 g/L.

3.6. Effect of Catalyst Dosage

Since the catalyst is recognized as providing active sites for a catalytic reaction, its dosage variation can generally affect the reaction rate to a large extent [4,26]. As presented in Figure 7, the OG removal efficiency raised from 92.4% to 100.0% with ZVC dosage switching from 0.1 g/L to 0.3 g/L. However, with further dosing of 0.5 g/L ZVC, the reaction rate slowed down slightly despite fulfilling the complete removal of OG. The corresponding reason may be that an excessive amount of catalyst would result in excessive radical species, simultaneously raising the self-quenching rate of radicals and weakening the degradation ability of the ZVC/PMS system [27,28].

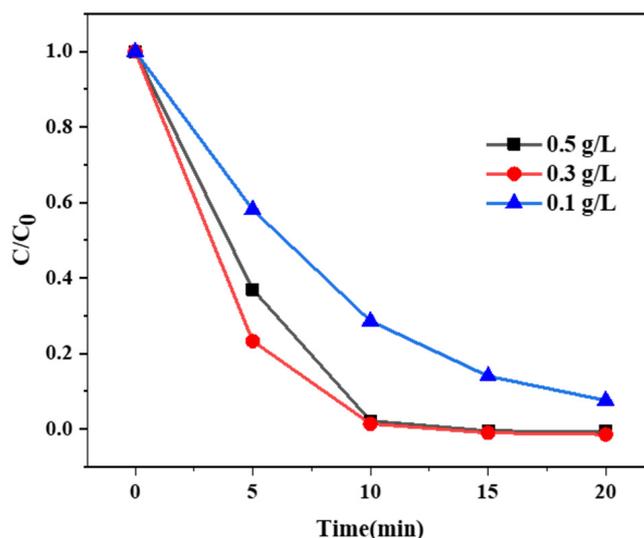


Figure 7. Effect of catalyst dosage on OG degradation. Condition: [OG] = 50 g/L, [PMS] = 3 mM.

3.7. Effect of Co-existing Ions

The actual wastewater usually contains various inorganic anions, which can interfere with the activation of PMS. In this study, the effects of Cl^- , HCO_3^- , PO_4^{3-} on OG degradation were investigated, respectively. Figure 8a indicates that chloride ions posed dual influences on OG degradation. When the concentration of Cl^- increased from 0 mM to 10 mM, OG degradation was significantly inhibited, which may be ascribed to the reaction between coexistent Cl^- and $\cdot\text{OH}/\text{SO}_4^{\cdot-}$ to generate $\text{Cl}\cdot$ and $\text{Cl}_2^{\cdot-}$ with lower redox potential, thus diminishing the oxidation capability of the ZVC/PMS system [29,30]. However, as the Cl^- concentration further changed from 10 mM to 50 mM, the removal performance of the system was clearly intensified (even better than the result obtained with 0 mM Cl^-), which may be owing to the reaction of excessive Cl^- with PMS to form HClO and Cl_2 for accelerating the reaction [31]. According to previous studies, the coexistence of HCO_3^- can scavenge free radicals to impede the degradation process [32]. As expected, apparent repression of OG decay was observed with 10 mM HCO_3^- (Figure 8b). In contrast, 50 mM HCO_3^- promoted the removal process to some extent compared with 10 mM HCO_3^- , which may be because excessive HCO_3^- increased the alkalinity of the solution, inducing the base activation of PMS. As exhibited in Figure 8c, the addition of either 10 mM or 50 mM PO_4^{3-} facilitated the degradation reaction, which may be due to the hydrolysis of PO_4^{3-} for increasing the solution's pH to initiate the base activation of PMS.

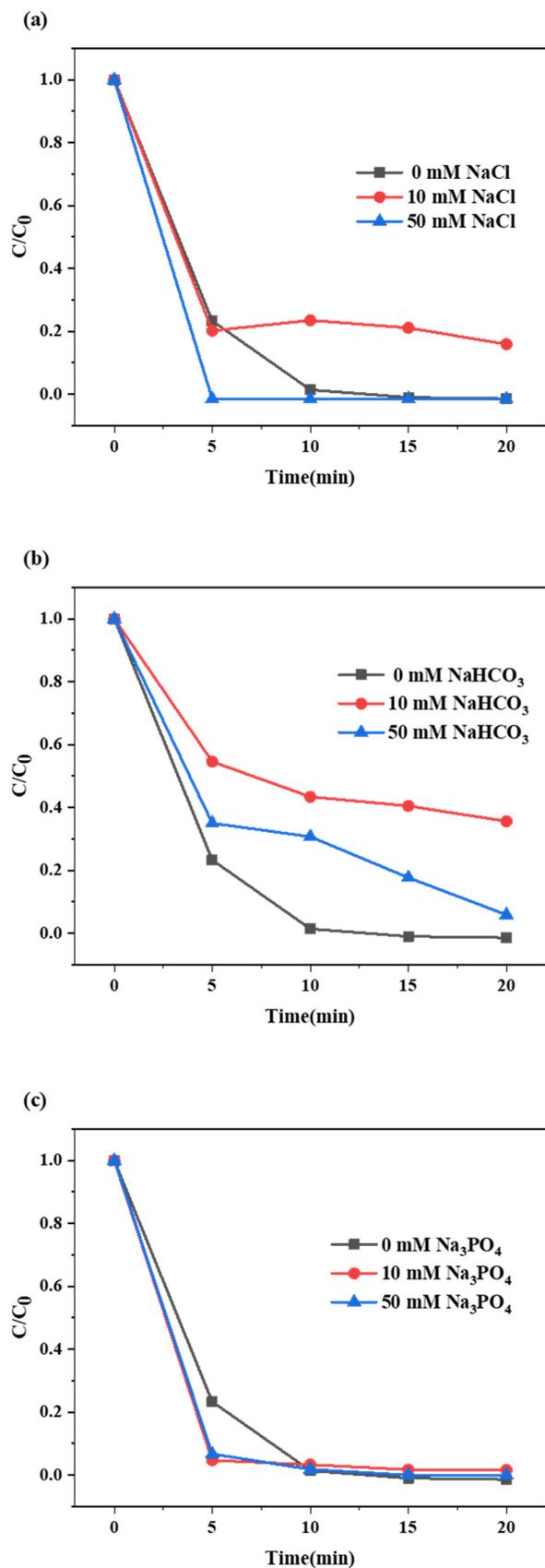


Figure 8. Effect of co-existing Cl^- (a), HCO_3^- (b), and PO_4^{3-} (c) on OG degradation. Condition: $[\text{OG}] = 50 \text{ g/L}$, $[\text{PMS}] = 3 \text{ mM}$, $[\text{ZVC}] = 0.3 \text{ g/L}$.

4. Conclusions

In this paper, a ZVC/PMS system was proposed that showed excellent degradation performance on azo dye OG. When 3 mM PMS and 0.3 g/L ZVC were simultaneously added to the OG solution, 50 mg/L of OG could be completely removed within 20 min. The radical quenching experiments indicated that $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ were responsible for the degradation process. With the increase in OG concentration, the OG degradation was firstly accelerated and then retarded gradually. The production of radicals can be increased for the intensified oxidation process by reasonably manipulating the PMS concentration and the ZVC dosage. Cl^- and HCO_3^- possessed dual effects on OG elimination, while PO_4^{3-} accelerated the degradation process. This study provides insights into water treatment technology based on ZVMs.

Author Contributions: Investigation, Visualization, Methodology, Formal analysis, Data curation, Writing—original draft and Writing—review and editing, B.Y.; Conceptualization, Resources, Visualization, Methodology, Validation, Data curation and Writing—review and editing, Z.L. Investigation, Writing—review and editing, S.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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