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Insight into reactive oxygen species in persulfate activation with copper oxide: Activated persulfate and trace radicals

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HIGHLIGHTS

- Copper oxide showed an excellent performance on persulfate activation to eliminate *p*-chloroaniline.
- Chloride and bicarbonate ions had no negative effect on *p*-chloroaniline degradation by copper oxide activated persulfate.
- Partially activated persulfate was dominant reactive oxygen species in persulfate activation by copper oxide.
- Trace sulfate and hydroxyl radicals were generated in copper oxide-persulfate system.

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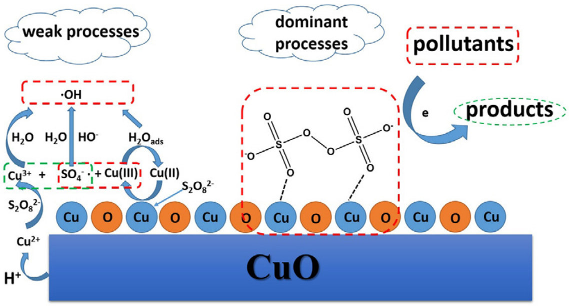
GRAPHICAL ABSTRACT



ABSTRACT

Activated persulfate along with trace sulfate and hydroxyl radicals were found to be reactive oxygen species in copper oxide activated persulfate system in this study. Persulfate decomposition study revealed that activated persulfate was predominant instead of sulfate and hydroxyl radicals. The radical scavenger investigation supported this point and led to the surface activation mechanism of persulfate. The *p*-chloroaniline (PCA) degradation in copper oxide activated persulfate system in neutral and acidic condition provided the evidence of prime heterogeneous persulfate activation and minor homogeneous persulfate activation caused by dissolved copper ion. Electron Paramagnetic Resonance study indicated the generation of sulfate and hydroxyl radicals. Integrating all the experiment facts, it is proposed that activated persulfate was main reactive oxygen species generated on copper oxide surface, along with minor sulfate and hydroxyl radicals produced. Chloride ions showed no effect on PCA degradation in copper oxide activated persulfate system. While bicarbonate ions improved PCA degradation without pH adjustment (initial pH is about 3) and performed an inhibition effect when the initial pH was adjusted to neutral. These findings indicated the potential applicability of copper oxide for in situ chemical oxidation for two reasons: (1) ubiquitous chloride and bicarbonate ions showed no negative effect and (2) the slight radical generation avoid the persulfate consumption by non-pollutant reductive materials.

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1. Introduction

Persulfate-based advanced oxidation is a promising technique for destructive removal of organic pollutants from water and soils [1–4]. The process involves generation of sulfate and hydroxyl radicals that are highly reactive and nonspecific selectivity for oxidation of organic molecules [1,5,6]. Heat [7,8], UV and visible light [9–11], alkali [12,13], transition metal ions [14–16] and heterogeneous activators [17–20] are efficient for activating persulfate to produce sulfate and hydroxyl radicals. Persulfate tends to obtain an electron to form a sulfate radical which may further react with water and hydroxyl ions to produce hydroxyl radicals [12]. In the persulfate oxidation systems, sulfate radicals are the main species in acid and neutral conditions, but hydroxyl radicals may dominate in basic solutions when persulfate is activated by base [21] or heterogeneous activators [22].

Heterogeneous activators are ideal activators for persulfate activation which show considerable efficiency, less chemicals or energy requirement and continuous activation performance. Zero valent iron works well in persulfate activation by continuously providing ferrous ions which activate persulfate to form sulfate radicals [19,23–26]. Minerals such as pyrite, clay and other tested species successfully activate persulfate to degrade organic pollutants [27–29], which demonstrates the feasibility of in situ chemical oxidation (ISCO). Transition metal oxides have received great attention since both the forms of oxides and relevant transition metal ions activate persulfate efficiently. Researchers have tried iron oxides [30–32], zinc oxides [33], manganese oxides [34] and titanium dioxide [35,36] to activate persulfate and received effective pollutants degradation. In the field of metal-absent materials, carbon with kinds of morphological features like nanotubes [37], granular [38], diamond crystal [39], biochar [40] and so on were also applied to activate persulfate. Without exception, these catalysts activate persulfate by generating sulfate radicals.

Recently, copper oxide has been paid attention into as a suitable heterogeneous activator for activating persulfate because of its little energy input, lower cost of pH adjustment and evitable heavy metals contamination and high treatment efficiency at neutral condition [41,42]. There are two different mechanisms proposed recently [42,43]. Zhang [42] reported the non-radical surface activation mechanism of persulfate with copper oxide. They found sulfate and hydroxyl radical scavengers—ethanol had no negative effect on 2,4-DCP degradation in copper oxide activated persulfate system, which was opposite to radical oxidation process. Furthermore, the Attenuated Total Reflection Fourier Transform Infrared spectrum (ATR-FTIR) and Confocal Raman applications on mixture of persulfate and copper oxide implied no persulfate decomposition and no chemical bond formed on surface, which supported the non-radical generation process. However, Lei [43] reported that the persulfate activation by copper oxides followed a radical mechanism and the main oxidative species were hydroxyl and sulfate radicals absorbed on CuO-Fe_3O_4 surface in CuO-Fe_3O_4 activated persulfate system. They proposed that surface Cu(II) went through a Fenton-like reaction with persulfate to form Cu(III) and sulfate radicals, both of which could subsequently reacted with water to produce hydroxyl radicals. It should be noticed that iron species such as zero valent iron (ZVI), pyrite, iron oxide and ferrous ion are efficient persulfate activators to promote radical generation. So in Lei's system [43], Fe_3O_4 was also responsible for activating persulfate. The activation mechanism in CuO-Fe_3O_4/PS system might be affected by iron species. Thus, apparently, the mechanism of copper oxide activated PS process is still disputable.

The objectives of this work were to further explore the mechanism and applicability of copper oxide activated persulfate system for refractory pollutants degradation. PCA (*p*-chloroaniline) was chosen as target pollutant. PCA is suspicious carcinogenic, high toxic and persistent. In addition, it is one of the wide used intermediates and raw materials of dyes, pesticides, plastics, cosmetics and pharmaceutical production, which can be released to environment from producing, processing and utilizing, forming pollution and resulting in the risk of ecology and human health welfare losses [44]. More physiochemical properties could be refer to Text S1.

To rule out the influence of iron, pure copper oxide was selected as catalyst. The main reaction oxidation species, PCA degradation efficiency and copper oxide recycle use stability were investigated.

2. Materials and methods

2.1. Chemicals

Methanol (HPLC, 99.9%) and *p*-chloroaniline (AR, 98%) were purchased from Sigma-Aldrich Chemical Company (Shanghai, China). Phenol, ethanol, 5, 5-Dimethyl-1-pyrroline N-oxide (DMPO, AR, ⩾96.0%) were purchased from Tianjin Nuoke Science and Technology Development Ltd (Tianjin, China), Shanghai Titan Company (Shanghai, China) and Shanghai Aladdin Company (Shanghai, China), respectively. $Na_2S_2O_8$, KI, $Cu(NO_3)_2\ 3H_2O$ and NaCl at their highest grades were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). NaOH was purchased from Tianjin Baishi Chemical Ltd (Tianjin, China). $Na_2S_2O_3$, $NaHCO_3$ and H_2SO_4 were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Water used in the experiment was deionized distilled water produced by a Millipore Milli-Q system (America).

Copper oxide preparation. Copper oxide was obtained following a thermal treatment procedure described in Liang's paper [41]. In brief, 5 g of $Cu(NO_3)_2\ 3H_2O$ in a ceramic crucible was placed in a muffle furnace. The temperature was elevated to 150 °C in 10 min, and retained there for 1 h. It was increased to 300 °C in 10 min, and retained there for 4 h. The final product was collected after the furnace was cooled to room temperature and stored in a desiccator before use.

2.2. Experimental procedure

The oxidation reaction was conducted at 20 °C using a completely mixed batch reactor system. An initial aqueous solution was prepared by diluting 5 mL 10 mmol L^{-1} PCA solution with 90 mL deionized water. The reactor was closed and shaken at 125 rpm for 10 min. An aliquot of 0.5 mL mixture was sampled and filtered through 0.45 μm filters. Then the mixture was further mixed with 0.5 mL sodium thiosulfate solution (2 mol L^{-1}, to keep the same sampling and test condition with calibration curve and samples with persulfate) for analyzing the initial PCA concentration. Then 0.05 g copper oxide was added, the reaction was initiated by adding 5 mL 50 mmol L^{-1} sodium persulfate to the reactor. The content of the reactor was continuously mixed on a shaker. An aliquot of 0.5 mL reaction solution was sampled and filtered through 0.45 μm filters at specific time interval, mixed with 0.5 mL sodium thiosulfate solution (2 mol L^{-1}) for quenching the reaction, and analyzed for residual PCA concentrations. To void the volume dilution effect, the calibration curve was made at the same condition. To quantify the effect of bicarbonate and chloride ions on the rates, a certain amount of bicarbonate, sodium chloride were respectively added into CuO/PS/PCA system (bicarbonate and chloride ions concentration were both three gradient: 2.5, 5 and 10 mmol L^{-1}). To identify the radical species, ethanol and phenol were respectively added into CuO/PS/PCA system (the ethanol and phenol concentration was both 500 mmol L^{-1}). 1 mL 0.1 mol L^{-1} DMPO was added into 10 mL reaction mixture (the mixture had been reacting for 5 min before the addition) to react for 1 min before EPR analysis. The initial pH of reaction mixtures were adjusted by sulfuric acid and sodium hydroxide solution.