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Efficient activation of ozone by zero-valent copper for the degradation of aniline in aqueous solution

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ABSTRACT

A series batch experiments were performed to explore the catalytic role of zero-valent metals, including Fe(0), Co(0), Al(0) and Cu(0), in ozonation degradation of aniline in aqueous solution. It was found that Cu(0) exhibited the best catalytic activity of ozonation. Approximately 98% of the initial aniline (10 mg/L) was destructed by ozone assisted with Cu(0) within 24 min. The dosage of Cu(0) and solution pH were two critical factors affecting aniline degradation. The increase of Cu(0) dosage promoted aniline degradation. And aniline could be effectively removed in an initial pH range of 4–10, whereas a lower or higher solution pH was not favorable for the degradation of aniline. Free radicals were investigated by electron paramagnetic resonance technique, which confirmed that ·OH was the primary active oxidant responsible for the degradation of aniline. The further mechanism investigation revealed that the generation of ·OH is ascribed to Fenton-like reaction between Cu(I) and H_2O_2, both of which are *in situ* yielded through a series subsequent of reactions starting with oxidation–reduction reaction between ozone and Cu(0). Based on the results obtained in this study, it can be inferred that ozone activated with Cu(0) is a promising approach to degrade organic pollutants.

1. Introduction

Ozone poses high oxidation potential and is widely applied for the disinfection of drinking water and for the treatment of wastewater [1,2]. However, because the ozonation of organic pollutants is relatively selective and slow, only a partial mineralization is achieved when organics react with ozone [2,3]. Thus, heterogeneous catalytic ozonation attracts a lot of attention due to its high potential in degradation and mineralization of refractory organic contaminants. It has been generally recognized that metal oxides, such as MnO_2 [4], MgO [5], ZnO [6], Fe_2O_3 [7], TiO_2 [8], CuO [9], Υ-Al_2O_3 [10], are promising catalysts for ozonation of refractory organic pollutants.

Zero-valent metals as heterogeneous catalysts for activating chemical oxidants including hydrogen peroxide [11], persulfate [12,13], oxygen [14] have also been widely used in dealing with organic contaminants. This is because some active oxygen species, such as hydroxyl radical (·OH), sulfate radical (SO_4^{-}·) and superoxide anion radical (O_2^{-}·), resulting from the metal catalytic process, have much higher activity for the oxidation of organics than these common oxidants (H_2O_2, $Na_2S_2O_8$ and O_3). For example, Li and Zhu [15] found that *p*-chloronitrobenzene from contaminated groundwater was effectively degraded in the system of both H_2O_2 and Fe(0), in which ·OH responsible for the degradation of *p*-chloronitrobenzene was resulted from Fe(0) induced Fenton process. Compared with homogeneous Fenton system (H_2O_2/Fe^{2+}), H_2O_2/Fe(0) system could be applied in a wider pH range and reduce the generation of iron sludge [16]. Persulfate could be efficiently activated by Zn(0) or Fe(0) to generate SO_4^{-}· or ·OH, leading to the degradation of methyl orange [17], dibutyl phthalate [18], alachlor [12], and bentazon [13]. Fe(0), Al(0) and Cu(0) also possess the capacity to activate oxygen in acidic condition, in which the transfer of electrons from zero-valent metals to oxygen occurs and active oxygen species are generated [14,19–22]. Ozone has higher oxidation capacity than oxygen, resulting in an efficient transfer of electrons from zero-valent metals to ozone and the generation of active oxygen species. Indeed, there have been several reports on the activation of ozone by Fe(0) for removal of organic contaminants [23,24]. Our previous studies have demonstrated that Zn(0) exhibits a significantly synergistic role with ozone in the degradation of aniline and *p*-chloronitrobenzene, respectively [25,26]. But, to the best of our knowledge, the activation of ozone with other zero-valent metals as the catalysts to degrade organic pollutants has been rarely reported.

Aniline is an important organic chemical raw material and widely used in dyes, pesticides, pharmaceuticals and other

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industries. Aniline, a highly toxic organic contaminant and very difficult for biodegradation, has been frequently detected in environment owing to improper discharge. Thus, aniline was selected as a target pollutant to explore the catalytic efficiency of zero-valent metals including Fe(0), Co(0), Al(0) and Cu(0) for ozonation degradation of aniline. And then, the major interest of this study focused on the degradation of aniline in the coexistence of ozone and Cu(0) since Cu(0) exhibited the highest catalytic performance among these zero-valent metals. The effect of the dosage of Cu(0) and solution pH on the degradation efficiency of aniline was also investigated. And the potential mechanism of the activation of ozone by Cu(0) was proposed. It is expected that the results from the present study could offer insight into the degradation of organic contaminants by ozone in the present of Cu(0).

2. Materials and methods

2.1. Materials

Aniline was purchased from Kelong Chemical Reagent (Chengdu, China) and dissolved in deionized water to the required concentration as the stock solution. *N*-(1-naphthyl) ethylenediamine dihydrochloride, as a chromogenic agent for determining the concentration of aniline, was provided by Sinopharm Chemical Reagent, China and its stock solution was also prepared with deionized water and stored in the brown bottle at 277 K prior to use. Fe(0) was obtained from the Development Center of Kemiou Chemical Reagent (Tianjin, China), Co(0) from Macklin Biochemical Limited Company (Shanghai, China), Al(0) from Xiya Reagent and Cu(0) from Aladdin Inc. All these zero-valent metals were directly used without any pretreatments. The spin trapping agent, 5,5-dimethyl-1-pyrolin-*N*-oxide (DMPO), was bought from Aladdin Inc. The other chemical reagents employed in this study were at least of analytical grade.

2.2. Ozonation process

The experiments were carried out in a 150 mL flask, which was placed at an apparatus with thermostatic bath and magnetic stirring. First, 50 mL of 10 mg/L aniline solution and the required amount of zero-valent metal powders were successively added into the flask. Then, ozone produced from an ordinary grade air by WH-H-Y ozone generator (Nanjing Wohuan) was immediately bubbled into the flask. During the experiment, a sufficient mixture was achieved by using the magnetic stirring and the reaction temperature was kept constant by the thermostatic bath. The initial pH of the solution was not controlled except for discussing the effect of pH on aniline degradation, in which the diluted NaOH and HNO_3 solution were adopted to adjust the initial pH of the solution to the desired value. Approximately 3 mL of the sample was withdrawn with a 5 mL plastic syringe at the predetermined time intervals and then filtrated through 0.45 μm membrane filter to a clean and dry glass tube for the further analysis of aniline. All experiments in the section were performed in triplicate and the mean values were described in the results with error bars.

2.3. Analytic methods

The concentration of aniline was measured at 545 nm on an Alpha-1502 UV–vis spectrometer (Shanghai Puyuan, China) using *N*-(1-naphthyl) ethylenediamine as the chromogenic agent. The concentration of ozone in the gas phase was analyzed according to the method reported by Rakness et al. [27]. The solution pH was detected with a CyberScan pH2100 Bench Meter (Eutech Instruments, USA) after three-point calibration. The concentration of copper ions yielded from the reaction was determined with a flame atomic adsorption spectroscopy (HITACHI Z-2000, Japan). The concentration of H_2O_2 generated from the ozonation process was measured at 551 nm on an Alpha-1502 UV–vis spectrometer (Shanghai Puyuan, China) using a photometric method in which *N*,*N*-diethyl-*p*-phenylenediamine was oxidized by a peroxidase catalyzed reaction [28].

The products of aniline degradation were determined on Agilent 1200 series LC equipped with Agilent 6410 Triple Quad mass spectrometer. The separation was performed with a ZORBAX Eclipse Plus C18 column (2.1 × 150 mm) (Agilent, USA). The mobile phase consisted of 50% methanol and 50% water and the flow rate was set at 0.2 mL/min. The mass spectrometer was operated under the positive and negative ion mode through an electrospray ionization source.

In order to identify the free radicals engendered from the activation of ozone by Cu(0) through electron paramagnetic resonance (EPR) technique, DMPO was utilized as a commonly spin trapping agent of free radicals to generate stable paramagnetic adducts, which are more stable and relatively longer life than free radicals [29]. The EPR experiments were conducted on a Bruker EMX10/12 EPR spectrometer (Bruker Instruments Inc., Germany). The sample was taken at the designed time and placed in capillary tube, which was fixed at the cavity of the EPR spectrometer. The EPR parameters were: microwave frequency = 9.722 GHz; microwave power = 19.873 mW; modulation amplitude = 1 G; modulation frequency = 100 kHz. EPR spectra were simulated using WIN-EPR *SimFonia* (Bruker Instruments Inc., Germany).

3. Results and discussion

3.1. Degradation of aniline by ozone in the presence of different zero-valent metals

In the section, the catalytic performances of different zero-valent metals for the degradation of aniline by ozone were investigated and the results are illustrated in Fig. 1. As compared with the removal of aniline by ozone alone (almost no decrease in aniline concentration within 40 min), it is found that these zero-valent metals exhibited different catalytic performances, following the order of Cu(0) > Co(0) >> Fe(0) > Al(0).

It has been reported that Fe(0) plays a significant role in promoting the removal of COD, color and turbidity in the ozonation process of wastewater treatment [30]. And the reaction between ozone and Fe(0) happens as depicted in reaction (1) [30]:

$$2H^+ + Fe^0 + O_3 \rightarrow Fe^{2+} + O_2 + H_2O \quad (1)$$

Subsequently, ferrous ion could further react with ozone, leading to the generation of ·OH responsible for the removal of organics (reactions (2) and (3)) [30]. Moreover, ferrous ion could also react with H_2O_2 from the self-decomposition of ozone, yielding ·OH according to Fenton reaction (reaction (4)) [23].

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \quad (2)$$

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (3)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \quad (4)$$

In this study, however, the degradation efficiency of aniline by ozone combined with Fe(0) was not satisfactory. Only 42% of the initial aniline was removed within 40 min (see Fig. 1). This is possibly ascribed to the fact that generated ferric ion easily formed hydroxide precipitation in the near-neutral solution (Fe(0) consumed H^+), coating the surface of Fe(0) to block the further access of ozone to Fe(0). A similar phenomenon was observed by Keenan

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