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Degradation of nitrobenzene by sodium persulfate activated with zero-valent zinc in the presence of low frequency ultrasound

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ABSTRACT

In the presence of low frequency ultrasound (US) generated from an ultrasonic cleaning bath, the degradation efficiency of nitrobenzene ($C_6H_5NO_2$, NB) by Zn^0 -activated persulfate (PS) reached 96% within 2 h, which is much higher than that by PS or Zn^0 alone in the presence of US or that by Zn^0 -activated PS in the absence of US. The synergistic effect in the US/ Zn^0 /PS system and the optimum degradation conditions was investigated by batch experiments. The variations of pH and concentrations of Zn^{2+} and SO_4^{2-} over time and the removal of chemical oxygen demand (COD) and total organic carbon (TOC) in different systems were analyzed, which agreed well with the degradation pattern of NB in different systems. The formation of free radicals was measured using electron paramagnetic resonance (EPR) spectroscopy to further investigate the possible mechanism of the enhanced degradation of NB by Zn^0 -activated PS in the presence of low frequency US.

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1. Introduction

Nitrobenzene ($C_6H_5NO_2$, NB) has been claimed as a priority contaminant by United States of Environmental Protection Agency (USEPA) due to its carcinogenicity, mutagenicity and the tendency to accumulate in environment. NB is widely used for the production of explosives, plastics, metal polishes, insecticides, herbicides, pharmaceuticals and dyes. The acceptable limit of NB in water is 2 mg/L, so when a certain amount of NB released from these chemical industries to the water exceeds from this level then the water can be declared as hazardous [1–3]. So NB is of environmental concern because the presence of small amount of NB in water can create many problems to human and other living organisms. However, the strong electron-withdrawing character of the nitro-group prevents the oxidation of NB by conventional chemical oxidation. The mineralization of NB by conventional biological treatment is also ineffective due to the effect of toxic and mutagenic deriving from NB and its transformation on biological systems, such as nitrosobenzene, hydroxylaminobenzene and aniline [1].

During the last two decades, various chemical reduction methods and advanced oxidation processes (AOPs) have been studied for the degradation of NB in aqueous solution, such as Fe^0 reduction [1,3–6], ozonation [7], photocatalysis [8] and other catalytic oxidation methods [9].

In recent years, persulfate anions (PS, $E^0 = 2.01$ V) have received much attention for treatment of hazardous compounds due to its stable and reliable performance in aqueous solution [10,11]. PS is activated to cause generation of stronger oxidant, sulfate radicals ($SO_4^{\cdot-}$, $E^0 = 2.50$ – 3.10 V) and/or hydroxyl radicals ($\cdot OH$, $E^0 = 2.70$ V) in sufficient quantities for contaminant degradation [10]. Some activation methods including heat energy, UV radiation, ultrasound (US), and electron transfer of transition metal ions [12–14] have been investigated to activate PS. Among which, Fe^0 serves as a very capable activator not only because of the long-term supply capacity associated with its solid-phase form, but also due to an apparent synergistic interaction with PS [15,16]. However, Fe^{2+} released from Fe^0 consumes $SO_4^{\cdot-}$, leading to a waste of the oxidant [13], which is a disadvantage of Fe^0 -activated PS. Unlike Fe^{2+} , Zn^{2+} produced from zero-valent zinc (Zn^0 , ZVZ) does not consume $SO_4^{\cdot-}$, since there is no other oxidation state. Thus, it is presumed that Zn^0 might be a better activator of PS than Fe^0 .



The activation of PS by zero-valent metal (M^0 , ZVM) is a surface-mediated electron transfer process (Eq. (1)). The properties of surface coating will affect the reactivity of M^0 particles [5,17]. According to previous studies [10,15,16], the degradation of organic contaminants by M^0 -activated PS lead to an increase in pH, which may be attributed to M^0 (including Fe^0 and Zn^0) corrosion. The formation of precipitates such as $Zn(II)$ (hydr)oxides on the Zn^0 surface inhibits electron transfer by masking the reactive sites on Zn^0

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surface where electron transfer occurs, resulting in a diminished lifespan of Zn^0 .

Environmental sonochemistry is a rapidly growing area, and the cavitation of US is an effective tool for degrading different organic pollutants, these compounds are indirectly decomposed mainly through the reaction with $\cdot OH$ that is produced during cavitation process [18]. But the mechanical effects of US including dispersing and cleaning cannot be ignored. The mechanical effects even play a major role under certain conditions with US as a basic or auxiliary process [18–22].

In this study, the use of low frequency US as synergistic effect to disperse and clean the Zn^0 particle surfaces was investigated for the first time in the Zn^0 -activated PS system. NB was selected as the model organic contaminant. The low frequency US was generated from an ultrasonic cleaning bath which is the most widely used and cheapest source of US [23]. With our interest focusing on the possible synergistic mechanism of US and Zn^0 in PS activation, the synergistic effect in the US/ Zn^0 /PS system was studied by batch experiments. The effects of the initial solution pH and the dosages of PS and Zn^0 were investigated. The variations of pH and concentrations of Zn^{2+} and SO_4^{2-} over time, the chemical oxygen demand (COD) and the total organic carbon (TOC) in different systems were analyzed. And the formation of free radicals was measured using electron paramagnetic resonance (EPR) spectroscopy.

2. Materials and methods

2.1. Materials

Nitrobenzene was obtained from Chengdu Kelong Chemical Reagent Factory (Chengdu, China), and its stock solution (5000 mg/L) was prepared in acetonitrile. The stock solution of PS (Shanghai Chemical Reagent Co., Ltd, Shanghai, China) with a concentration of 1000 mg/L was prepared in deionized water. Micro-scale Zn^0 particles and barium chloride ($BaCl_2$) which was served as the precipitant to analyze the concentration of sulfate ion were purchased from the Development Center of Kemiou Chemical Reagent (Tianjin, China). Hydroxyapatite (HA) which was adopted to remove the residual Zn^{2+} from the final treated solution to avoid secondary pollution was obtained from Shanghai Aladdin Biochemical Technology Co. Ltd (Shanghai, China). 5,5-Dimethyl-1-pyrrolin-*N*-oxide (DMPO), which was applied to produce stable paramagnetic adducts for EPR characterization to determine free radicals generated from the degradation process, was purchased from Adamas Reagent Co. Ltd (Shanghai, China).

All of the chemicals used in this study were at least analytical grade and used without further purification. All of the stock solutions used in this study were stored in a refrigerator at 4 °C in the dark.

All of the glassware used in the experiments were cleaned by soaking in 1 mol/L HCl for more than 12 h, and thoroughly rinsed first with tap water, then with deionized water.

2.2. Pretreatment of Zn^0 particles

Zn^0 particles were pretreated with approximately 0.1 M NaOH and 0.1 M H_2SO_4 , respectively, and then washed by deionized water for several times to remove residual H_2SO_4 . The cleaned Zn^0 particles were dried in a vacuum-drying oven at 60 °C for 2 h and then stored in a desiccator prior to use. The specific surface area of Zn^0 particles was 2.5 m²/g. It was measured by Brunauer–Emmett–Teller (BET) gas adsorption isotherm with N_2 gas on a V-Sorb 2800P surface area and porosity analyzer (Beijing Gold App Instrument Corporation, Beijing, China).

2.3. Experiments for NB degradation

Experiments on the degradation of NB were carried out in 100 mL glass bottles with the required amounts of the stock solutions of NB and persulfate. The solution was adjusted with diluted NaOH and HNO_3 to the desired initial pH, and the final volume was 50 mL. Then, the desired amount of pre-cleaned Zn^0 particles was introduced into the reaction solution. These bottles were sealed with rubber stoppers and polytetrafluoroethylene membranes and placed in low-frequency US field generated by an ultrasonic cleaning instrument (KH-500, Qunshan Hechuang Ultrasonic Instrument Co., Ltd, Kunshan, China) immediately. The working frequency of the ultrasonic cleaning instrument was 40 KHz, and the reaction temperature was 45 °C. For comparison, the degradation of NB was also conducted in a shaking water bath (BS-31, SIM Company) at 45 °C and 180 rpm. All the experiments in this section were performed in triplicate.

2.4. Analytic methods

The degradation of NB was monitored by determining the residual concentration remaining after certain periods of reaction. At regular time intervals, a 2 mL aliquot of sample was withdrawn, filtered through a 0.45 μm syringe-driven filter, and then analyzed using HPLC (Waters 2489) equipped with an Agilent TC-C₁₈ column (5 μm , 4.6 mm \times 250 mm) and a diode array ultraviolet detector. The mixture of methanol/water in the proportion of 70/30 was the mobile phase at a flow rate of 1 mL/min. The injection volume was 20 μL and the detection absorbance was monitored at 254 nm, similar analytic methods were reported by some researchers [6,24].

The concentration of Zn^{2+} released into the reaction solution was measured by an atomic absorption spectroscopy (AAS, Hitachi Z-2000). Turbidimetry which is a well-known procedure for sulfate determination is adopted to determine the concentration of sulfate ion using $BaCl_2$ as the precipitant [25]. And the samples were analyzed by the UV–vis spectrometer (Beijing Ruili Corp, UV-9100) at the characteristic λ_{max} of 420 nm.

Within the course of NB degradation experiments, the mimic wastewater was periodically sampled and measured using a COD rapid detection analyzer (SQ-SCA, Technology Electronics Co., Ltd, Shangqing, Hebei, China), which was equipped with an intelligent temperature digestion device (SQ-PXJ-12). The digestion was carried out at 165 °C for 15 min, and the COD measurement wavelength was set to 440 nm. In the end of the degradation reaction, samples from different reaction systems were extracted to determine the removal of TOC by Shimadzu TOC-L analyzer (Japan), with 200 kPa oxygen as carrier gas at a following velocity of 150 mL/min.

The formation of radicals during the degradation process was examined by employing an EPR spectrometer. The mixed solution of reaction sample and the spin trapping agent DMPO was immediately placed in capillaries, and analyzed by a Bruker EMX10/12 EPR spectrometer (Bruker Instruments, Inc., Germany). The spectra were recorded at room temperature, at the microwave frequency of 9.852 GHz, microwave power of 19.540 mW, and magnetic field modulation amplitude of 2.00 G. The EPR spectra were simulated using WIN-EPR *SimFonia* (Bruker Instruments, Inc., Germany).

3. Results and discussion

3.1. The degradation of NB under different conditions

To compare the individual and combined NB degradation efficiency of Zn^0 -activated PS and ultrasonic irradiation, the NB degradation experiments were conducted in the presence of only ultrasonic irradiation, single Zn^0 in the presence of US, single PS in the

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