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pH-dependent degradation of acid orange II by zero-valent iron in presence of oxygen

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ABSTRACT

In this study, zero-valent iron (ZVI)-mediated advanced oxidation was applied to degrade the acid orange II (AOII) in the presence of oxygen. The effect of pH value, ZVI dosage, O_2 concentration and added Fe^{2+} ions on the degradation efficiency was investigated. It was found that the increases of acidity in aqueous solution, ZVI dosage and O_2 concentration were favorable to the oxidation reaction of AOII in ZVI-mediated advanced oxidation processes. The lower pH value in aqueous medium was favorable for AOII degradation in ZVI/O_2 system. The AOII degradation efficiency and COD removal efficiency system could achieve more than 95% and 65% within 3 h in the ZVI/O_2 at initial pH 3.0, respectively. The AOII degradation in ZVI/O_2 system followed the first-order reaction kinetics at pH range of 3.0–7.0, while AOII degradation followed the zero-order reaction kinetics at pH range of 9.0–11.0. The measurements of H_2O_2 and Fe^{2+} in ZVI/O_2 system, and the characterization for used ZVI particles demonstrated the role of Fenton reaction in the ZVI/O_2 system, which occurred favorably at low pH to generate H_2O_2 and Fe^{2+}, followed by a likely species $^{\cdot}OH$ to degrade AOII. The involvement of $^{\cdot}OH$ in oxidizing AOII was examined by determining the degradation rates using $^{\cdot}OH$ scavenger. Moreover, the coexistence ions had no significantly influence the oxidation process, indicating the true application process. Finally, organic compounds as intermediates of the degradation process were identified by LC/MS.

1. Introduction

Azo dyes constitute a recalcitrant pollutant in industrial dyestuffs representing an increasing environmental danger widely. Therefore, the removal of azo dyes from wastewater has attracted critical attention [1,2]. A variety of treatments have been employed to remove azo dyes from industrial wastewater, such as physical adsorption, oxidation or reduction methods, biological degradation, and the integrative treatments of various methods [1,3,4]. Among them, the degradation of azo dyes using zero-valent iron (ZVI or Fe^0) has been receiving much interest due to its low cost and environmentally benign properties [5,6]. In the ZVI-mediated process, the direct electron transfer from ZVI to organic pollutants has been recognized as the main mechanism of pollutants transformation by ZVI in the subsurface [5]. However, such a process cannot reach a satisfactory degree to completely oxidize aromatic compounds and other recalcitrant contaminants [7–10].

Recently, there has been a growing interest in ZVI-mediated advanced oxidation processes (AOPs) using small-sized ZVI particles to oxidize pesticides, aromatic compounds and chelating agents in the presence of oxygen [11–15]. So far, the proposed mechanisms of the ZVI-mediated advanced oxidation (ZVI/O_2) process have been classified into two different pathways. The first pathway is a two-electron transfer between ZVI and oxygen to produce hydrogen peroxide [16,17]. The second pathway is through a series of one-electron transfers to produce hydrogen peroxide via the reaction of oxygen with ferrous iron produces by Fe^0 [18–20]. Subsequently, the hydrogen peroxide generated through the above-mentioned two pathways converted to the reactive oxygen species (ROS), such as hydroxyl radical ($^{\cdot}OH$). These reactive oxygen species produced in the ZVI-mediated advanced oxidation processes are effectively capable of oxidizing arsenic(III) [18] and recalcitrant organic compounds such as 4-chlorophenol, pentachlorophenol [19], molinate [16] and EDTA [12,20].

The hydrogen peroxide produced in ZVI-mediated advanced oxidation process, via the two-electron transfer between ZVI and

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oxygen, and/or a series of one-electron transfers, leading to the generation of ROS which is the key factor to determine the oxidation reaction rate in the ZVI-mediated advanced oxidation process. Thus, the parameters affected the formation of ROS was investigated by many researchers, and pH value was shown to be one of crucial factors in the ZVI/O_2 system. Pioneer studies demonstrated that the hydroxyl radical was involved during ZVI oxidation under acidic conditions [21,22]. For example, Keenan et al. investigated the oxidation of organic compounds by the reaction of ZVI with oxygen under different pH and found that acidic conditions would be beneficial to the formation of hydroxyl radical [22]. Katsoyiannis et al. investigated As(III) oxidation by ZVI in aerated water under different pH and demonstrated that As(III) was oxidized through hydroxyl radical during ZVI oxidation under acidic conditions [23]. Thus, the nature and overall efficiency in ZVI-mediated advanced oxidation processes can be affected by the parameters of pH, ZVI dosage, and O_2 concentration in a ZVI/O_2 system.

Herein, the ZVI-mediated advanced oxidation process was applied to degrade the acid orange II (AOII) in the presence of oxygen. The effect of initial pH value in aqueous medium, initial concentration of AOII, ZVI dosage, O_2 concentration, coexisting inorganic ions and added Fe(II) ions on the degradation efficiency was investigated. The concentrations of Fe(II) and H_2O_2 in the ZVI/O_2 system were determined as well as to elucidate the reaction mechanism. Furthermore, the organic compounds as intermediates of the degradation process in ZVI-mediated advanced oxidation process were identified by HPLC/MS.

2. Experimental section

2.1. Materials

The zerovalent iron (ZVI) powder with the particle size of 100 mesh and 99.9% purity, containing no trace elements at toxic concentrations, was purchased from Tianjin Kermel Chemical Co., Ltd. in China. The specific surface area of ZVI powder measured with Brunauer–Emmett–Teller (BET) analysis by N_2 adsorption at 77.3 K was 7.5 $m^2\ g^{-1}$. Acid orange II (AOII) was purchased from Aldrich. Other chemicals including $K_2TiO(C_2O_4)_2$, $C_{12}H_8N_2{\cdot}H_2O$, NH_4F, CH_3COONH_4, $FeCl_2{\cdot}4H_2O$, K_2SO_4, KNO_3, KCl, NH_4Cl, $CuCl_2{\cdot}2H_2O$, $CaCl_2$, $MgCl_2$ with analytical grade were obtained as reagents and used without further purification. Deionized water was used throughout this study.

2.2. Characterization

X-ray diffraction (XRD) analysis was analyzed using a diffractometer (D-MAX 2200 VPC Japan) with radiation of Cu target (Kα, λ = 1.54059 Å). The morphologies of fresh and used ZVI were analyzed with a JSM-6330F field emission scanning electron microscope (JEOL, Japan) using an acceleration voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) data was recorded with the Al Kα line at 150 W using a X-ray photoelectron spectroscopy/ESCA (ESCALAB 250).

2.3. Experimental procedure

All experiments were carried out at room temperature (25 ± 2 °C) in 400 mL cylindrical Pyrex reactor. In each reaction process, an O_2 flow was employed to 300 mL of AOII solution continuously to maintain the fully aerobic conditions as well as to produce a well-dispersed suspension of ZVI in the solution during the oxidation reaction process. The desired initial pH value in aqueous solution was adjusted with 0.1 M HCl or 0.1 M NaOH. The pH of solutions was buffered with sodium dihydrogen phosphate for pH 5.0–7.0, and 0.001 M borate for pH 9.0–11.0. The solutions of initial pH value of 2.0 and 3.0 were un-buffered. The pH value of the solution was measured by a digital pH meter (pHS-3C, Shanghai, China). Before measurement, the digital pH meter was calibrated with three standard buffers (pH 4.00, 6.86 and 9.18) at 25 °C. The reaction was timed starting when ZVI was added into the reactor containing 300 mL of AOII solution. Samples were taken periodically using a syringe and subjected to filtration using a 0.22 μm Millipore membrane filter before measuring UV–vis absorption spectra of solution. Each batch experiment was repeatedly performed in duplicates. To investigate the effect of pH value, ZVI dosage and O_2 concentration on AOII degradation efficiency in ZVI/O_2 system, three sets of experiments were conducted to degrade AOII in aqueous solution. The first set was conducted in AOII aqueous solution with ZVI dosage of 3.0 $g\ L^{-1}$ and O_2 flow rate of 24 $mL\ min^{-1}$ at different pH value (3.0, 5.0, 7.0, 9.0, 11.0). The second set was conducted in AOII aqueous solution at pH 3.0 with ZVI dosage of 3.0 $g\ L^{-1}$ under different O_2 flow rate (8, 16, 24, 32 $mL\ min^{-1}$). The third set was conducted in AOII aqueous solution at pH 3.0 with O_2 flow rate of 24 $mL\ min^{-1}$ under different ZVI dosage (1.0, 3.0 and 5.0 $g\ L^{-1}$). The procedure for the experiments of coexisting inorganic anions (Cl^-, NO_3^-, SO_4^{2-} with concentration of 50 $mmol\ L^{-1}$) and cation (NH_4^+, Mg^{2+}, Cu^{2+}, Ca^{2+}, Fe^{2+} with concentration of 10 $mmol\ L^{-1}$) on the degradation efficiency was identical except for the addition of coexisting ions into AOII solution prior to pH adjustment.

2.4. Analytical methods

The concentration of AOII solution was analyzed by UV–vis spectroscopy (UV-2501PC, Shimadzu) at a maximum wavelength of 484 nm. The degradation efficiency for AOII was calculated as follows:

$$\text{Degradation efficiency } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

where C_0 is the initial AOII concentration in the solution ($mg\ L^{-1}$), and C_t is the AOII concentration at reaction time t in the solution ($mg\ L^{-1}$).

Chemical oxygen demand (COD) was measured with potassium dichromate after samples were digested with a MS-3 COD microwave digestion system according to the APHA standard method.

The intermediates of AOII oxidation were analyzed by liquid chromatography–mass spectrometry (LC-MS, Agilent 1100 LC, equipped with a Model 486 variable wave wavelength UV detector set at 256 nm). A zorbax eclipse XDB C8 column 150 mm × 4.6 mm was used for separating product intermediates. The mobile phase was a filtered mixture of acetonitrile and 0.1 M ammonium acetate. The flow rate was 1 $mL\ min^{-1}$. From 0 to 5 min, the ratio of acetonitrile: ammonium acetate was 1:1; from 5 to 10 min the ratio was 2:1. The injection volume was 10 μL. MS analysis in the positive and negative ion mode was performed using a mass spectrometer equipped with an ESI ion source. The ESI probe tip and capillary potentials were set at 3.0 kV and 18 V, respectively. The mass range was 120–500 m/z. The heated capillary was set to 250 °C.

The concentration of dissolved Fe(II) was determined according to the standard phenanthroline colorimetric method [24,25]. Briefly, 2 mL of 6.0 M HCl, 2 mL of sample containing Fe(II), 2 mL of 2.0 M NH_4F, 2 mL of wt. 0.2% phenanthroline hydrate and 2 mL of ammonium acetate buffer (pH 4.2) were added individually, the obtained mixed solution was analyzed by an UV–vis spectroscopy (UV-2501PC, Shimadzu) at a maximum wavelength of 512 nm. The standard curve of Fe(II) was linear with a regression coefficient of 0.993 in the range of 0.05–1.0 mM. The concentration of H_2O_2 was determined using potassium titanium (IV) oxalate