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Degradation of Acid Orange 7 in aqueous solution by zero-valent aluminum under ultrasonic irradiation

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ABSTRACT

Degradation of azo dye Acid Orange 7 (AO7) by zero-valent aluminum (ZVAl) in combination with ultrasonic irradiation was investigated. The preliminary studies of optimal degradation methodology were conducted with sole ultrasonic, sole ZVAl/air system, ultrasonication + ZVAl/air system (US-ZVAl). In ZVAl/air system, the degradation of AO7 could almost not be observed within 30 min. The degradation of AO7 by ZVAl/air system was obviously enhanced under ultrasound irradiation, and the enhancement is mainly attributed to that the production of hydroxyl radicals in ultrasound-ZVAl process was much higher than that in sole ultrasonic or in sole ZVAl/air system. The variables considered for the effect of degradation were the power of ultrasound, the initial concentration of AO7, as well as the initial pH value and the dosage of zero-valent aluminum. The results showed that the decolorization rate increased with the increase of power density and the dosage of ZVAl, but decreased with the increase of initial pH value and initial concentration of AO7. More than 96% of AO7 removal was achieved within 30 min under optimum operational conditions (AO7: 20 mg/L, ZVAl: 2 g/L, pH: 2.5, ultrasound: 20 kHz, 300 W). This study demonstrates that ultrasound-ZVAl process can effectively decolorize the azo dye AO7 in wastewater.

1. Introduction

Zero-valent aluminum (ZVAl) is a strong reducing agent ($E^o = -1.662$ V) that has a standard reduction potential more negative than zero-valent iron ($E^o = -0.43$ V) [1]. The electron transfer capacity of ZVAl has already been exploited for the degradation of organic compounds through aluminum corrosion [2,3]. However, the reductive degradation of organic compounds with ZVAl suffers from time-consuming and incomplete mineralization in some cases [1].

Like the widely known zero-valent iron, ZVAl could also activate molecular oxygen in air to produce reactive oxygen species (ROS), including hydrogen peroxide (H_2O_2), superoxide radical ($O_2^{\cdot -}$), and hydroxyl radical (.OH), which are capable of oxidizing contaminants that cannot be removed by ZVAl reductively. For example, Lien and Wilkin showed that ZVAl treated by surface modification with sulfate groups could easily eliminate methyl tert-butyl ether [4]. Bokare and Choi demonstrated that in an aerated environment, ZVAl was capable of degrading organic pollutants (e.g., 4-chlorophenol, sodium dichloroacetate, phenol, and nitrobenzene) through the production of $^{\cdot}$OH radicals with a concurrent oxidation corrosion of ZVAl surfaces [5]. Liu et al. found that ZVAl demonstrated an excellent capacity to remove bisphenol A [6]. Although ZVAl/air system has been proved to be feasible for removal of organic pollutants, the formation of an oxide layer on Al surface inhibits the reducibility of Al at near neutral pH. So more acid should be added into the solution [1,7].

Sonolysis has proven to be an effective method for degrading organic effluents into less toxic compounds and, in many cases, completely mineralize the compounds [8,9]. The organic pollutants in water can undergo high-temperature pyrolysis in the gas phase inside the bubbles, and the non-volatile, hydrophilic species can be degraded by $^{\cdot}$OH at the bubble surface or in bulk solution. Although most of the organic pollutants can be degraded by ultrasonic irradiation, the degradation rates are rather slow in practical applications [10].

Over the last few years, ultrasound coupled with advanced oxidation processes (AOPs) as a potential treatment for the degradation of organic pollutants in water have gained considerable interest and have been proved to greatly enhance the degradation efficiency of pollutants [10-14]. As ZVAl effectively degrades hazardous compounds, the combination of sonication and ZVAl should be a suitable method to increase the efficiency of degradation process.

The ZVAl with ultrasonic irradiation (US-ZVAl) to destroy recalcitrant organic substances is of interest because it enables further degradation and is considerably more efficient than ZVAl/air system alone. The mechanism could be described as follows

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$$Al^0 + O_2 + H^+ \rightarrow Al^{3+} + H_2O_2 \quad (1)$$

$$Al^0 + H_2O_2 + H^+ \rightarrow Al^{3+} + {}^{\cdot}OH + H_2O \quad (2)$$

$$H_20 +))) \rightarrow {}^{\cdot}OH + {}^{\cdot}H \quad (3)$$

$$^{\cdot}OH + {}^{\cdot}OH \rightarrow +H_2O_2 \quad (4)$$

$$O_2 +))) \rightarrow 2{}^{\cdot}O \quad (5)$$

$$^{\cdot}O + H_2O \rightarrow 2{}^{\cdot}OH \quad (6)$$

First, ·OH was formed according to Eqs. (1) and (2) in the sole ZVAl process without ultrasonic, however, oxide layer and aluminum hydroxide wrapped in the surface of ZVAl could inhibit the reaction after a period of reaction, and this phenomenon would be avoided when ZVAl combined with the US. Second, more ·OH radicals which had excellent oxidative power were directly generated in US-ZVAl system (Eqs. (3) and (6)). Third, partial recombination of hydroxyl radicals produced from ultrasonic of water would result in the formation of hydrogen peroxide in ultrasound system, the ZVAl would react with the hydrogen peroxide and produced ·OH again, then a cycle mechanism was established (Eqs. (1)–(6)). From the above, more ·OH can be formed rapidly in the process of US-ZVAl system and so the best degradation result of organic compound was achieved [4–6,10,15,16].

To our knowledge, there was no research to investigate the degradation of azo dyes by the oxidation via ZVAl/air system under ultrasound irradiation. Therefore, in this study, Acid Orange 7 (AO7), as a model azo dye, was treated by ZVAl in combination with ultrasound irradiation. The purposes of this study were: (1) to compare the effectiveness of US process, sole ZVAl/air system, and US-ZVAl process; (2) to characterize the key parameters (ZVAl dose, AO7 concentration, pH, ultrasound power) affecting the US-ZVAl process and identify optimal decolorization conditions.

2. Experimental

Acid Orange 7 (Formula: $C_{16}H_{11}N_2NaO_4S$, Formula weight: 350.32) was purchased from Shanghai Chemical Reagent Company, China. All the other chemicals were of analytical grade and were provided from Tianjin, China, including HCl, NaOH, aluminum powder (purity >99%, particle size 38–48 μm, surface covered with native aluminum oxide layer). The aluminum powder were washed thrice for 5 min in 0.1 M HCl in order to remove surface oxidation layers, rinsed with deoxygenated deionized H_2O, and dried at 30 °C in a stainless steel vacuum glove box under an Ar atmosphere. The water used in all experiments was purified by a Milli-Q system.

The experimental set-up was similar to that in our previous study [17]. Sonication was performed with a 20 kHz ultrasonic generator (Model JY92-IIN, NingBo Xinzhi-Technology Co., China) which was equipped with a titanium probe (10 mm of diameter), a water-circulating unit and a temperature controller. Typically, the degradation experiments were conducted in a jacketed reactor of 50 mL capacity. The depth of titanium probe immersed into solution was about 1 cm. Prior to each experiment, appropriate amounts of AO7 and ZVAl were transferred into the jacketed reactor to achieve the predefined molar ratios of contaminant, the initial volume of reaction solution was 50 mL. At different time intervals, 5 mL of sample was withdrawn from the reactor by syringe and centrifuged at 8000 rpm for 2 minutes with a TGL-16C centrifuge (Shanghai, China) to remove the catalyst immediately. The concentrations of the residual AO7 were determined by monitoring decrease in absorbance at the maximum wavelength (484 nm) with UV–Vis spectroscopy (Shanghai, China). The pH was determined at room temperature using a S-25 pH-meter (Shanghai, China), which was calibrated with pH 4.0, 6.86 and 9.18 reference buffer solutions. Diluted hydrochloric acid or sodium hydroxide was used to adjust the initial pH of the dye solution.

3. Results and discussion

3.1. Degradation characteristics of AO7 under different processes

The different processes, sole ZVAl, sole US, and US-ZVAl, were carried out as the control experiments for the degradation of AO7 when aluminum powder addition is 2 g/L, ultrasound power is 300 W, and the initial pH value is 2.5. Due to a positive synergistic effect, the coupled US-ZVAl process was much more effective than ZVAl reaction or ultrasound irradiation alone. As shown in Fig. 1, the degradation of AO7 by US only could almost not be observed within 30 min, although ·OH could be formed during water sonolysis. The same situation was also observed in the processes of ZVAl only, although ·OH was generated in ZVAl process over a 30 min period, oxide layer and aluminum hydroxide wrapped in the surface of ZVAl would inhibit the reaction after a period of reaction, and the concentration of ·OH remained low compared with that in US-ZVAL systems. However, in the same period, nearly 96% removal of AO7 was achieved with US-ZVAl (Fig. 1). The synergistic mechanism of the US-ZVAl process is generally attributed to the increase in ·OH radicals concentration, resulting from the influence of ultrasound [11,16].

3.2. Effect of zero-valent aluminum addition

In order to investigate the effect of aluminum powder addition, five different ZVAl additions between 0 and 6 g/L in 50 mL dye aqueous solution were tested when AO7 concentration is 20 mg/L, ultrasonic power is 300 W, and the initial pH value is 2.5. It was found that the degradation rate of AO7 increased with the increasing of ZVAl dosage, varying from 2.7% to 96.5% within 30 min (Fig. 2). As described above, hydroxyl radicals, the actual oxidant for the decomposition of AO7, were generated via direct electron transfer from the ZVAl surface to H_2O_2 (Eq. (2)). Therefore, the enhanced AO7 removal with higher aluminum loadings may be attributable to both the increase of hydrogen peroxide produced

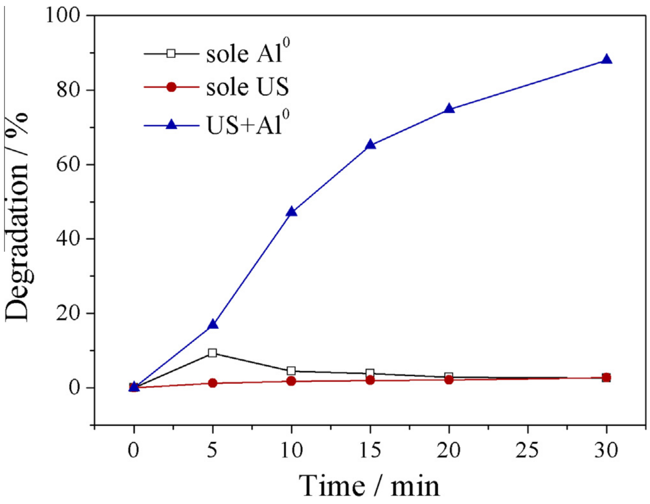

Fig. 1. Degradation of AO7 treated with different processes (Experimental conditions: [AO7] = 20 mg/L, [ZVAl] = 2 g/L, pH 2.5, ultrasound: 20 kHz, 300 W).