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Rapid decoloration of Reactive Black 5 by an advanced Fenton process in conjunction with ultrasound

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ABSTRACT

The decoloration of reactive azo dye, Reactive Black 5 (RB5), by an advanced Fenton process in conjunction with ultrasound (Fenton/US) was investigated. The Fenton/US process using zero-valent iron (ZVI) aggregates as catalyst could achieve synergistic degradation of RB5, as compared to Fe(0)/US and Fenton systems. A synergy factor of 22.9 based on the first-order rate constant (k) was found. The decoloration efficiency was strongly influenced by initial pH, ZVI dose, H_2O_2 dose, ultrasonic input power, and the presence of salts in reaction solution. Experimental results showed that the optimum conditions for the decoloration of RB5 were ZVI 1 g/L, initial pH 3.0, and H_2O_2 1.03×10^{-2} mol/L with acoustic power of 120 W/L at 60 kHz. These conditions yielded 99% decoloration of 5.0×10^{-4} M RB5 (ADMI 5605) solution within 10 min treatment and the operation cost was only 2.25 USD/m^3. The dye solutions containing inorganic anions could retard the decoloration. The inhibitory effect of various inorganic anions on decoloration of RB5 followed the sequence of $H_2PO_4^- \gg Cl^- > ClO_4^- \approx NO_3^- \approx SO_4^{2-}$. High acoustic power accelerated the reaction rate and increased decoloration efficiency. ZVI aggregates were reusable and the decoloration efficiency did not decrease substantially with repeated use of ZVI. Findings showed that the Fenton/US process could effectively decolor the reactive azo dye RB5 in wastewater.

1. Introduction

Azo dyes are the largest category of synthetic dyes used in textile and printing industries. They are characterized by the bearing of azo-bonds (N=N—) in association of aromatic rings (benzene and/or naphthalene), which may carry sulfonic group [1]. The effluents containing azo dyes can cause adverse effects to aquatic and human life if the effluents are not properly treated. Most of azo dyes are non-biodegradable; conventional biological treatment process may no longer be considered as a satisfactory decoloration process. Literature revealed that the use of a novel bacterial consortium in an aerobic sequencing batch reactor (SBR) could effectively decolorize the reconstituted reactive dye effluents [2]. However, the microorganisms in SBR have to be acclimated to real textile effluent for a period of 30 days before inoculation.

The non-destructed decoloration methods, such as membrane separation, coagulation, electrocoagulation, and adsorption are currently available. However, the degradation of dyes could not be achieved in above treatment processes. Besides, maintenance of fouled membranes, chemical sludge generation, and adsorbent regeneration may raise serious concerns. Therefore, the subject of developing destructive processes, such as advanced oxidation processes (AOPs), has received significant attention. AOPs have been proven to be effective technologies for degradation of dye laden wastewaters [3–11]. Amongst AOPs, Fenton's reaction is a relatively cost-effective process in terms of operation and maintenance.

Fenton process is the use of ferrous iron (Fe^{2+}) and hydrogen peroxide (H_2O_2) mixture to degrade organic compounds via generation of hydroxyl radicals ($\cdot OH$) within catalytic process. The process was first discovered by Fenton [12]. The successful application of the Fenton process for destruction a wide range of organic contaminants depends on the production of $\cdot OH$ under acidic condition when ferrous ion reacts with H_2O_2. The production of ferrous and ferric ions (Fe^{3+}) will perform coagulation to remove suspended substances. The revised Fenton mechanism was proposed [13]:

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + \cdot OH + Fe^{3+} \quad (1)$$

$$\cdot OH + \text{organics} \rightarrow \text{products or intermediates} \quad (2)$$

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

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad (4)$$

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2^{\cdot} \quad (5)$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe - OOH^{2+} + H^+ \quad (6)$$

$$Fe\text{-}OOH^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot} \quad (7)$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \quad (8)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad (9)$$

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Because Fenton's reaction can easily break down double bonds and hydrogen bond, Fenton-based technologies (electro-Fenton, photo-Fenton, and sono-Fenton) have been developed. These technologies have been proven to treat dye waste effectively [1,7,8,14–19]. In the Fenton process, because Fe^{2+} is consumed more rapidly than being reproduced [20], a sufficient amounts of the catalyst, Fe^{2+}, are required to ensure the continuous production of ·OH. Most recently, the use of zero-valent iron (ZVI) in Fenton process, namely advanced Fenton process (AFP), for the degradation of pollutants has received attention. Some studies have shown that Fenton process in conjunction with ultrasound (Fenton/US) could effectively degrade organic pollutants and dyes [21–23]. The effect of ultrasound is the cavitation allowing the formation of ·OH and enhances the Fenton's degradation rate.

The Fenton process coupled with ultrasonic irradiation process can produce synergistic effects and accelerate the oxidation reaction. Therefore, it is considerably more efficient than Fenton's reaction alone [4,15,21,23,24]. This process enables further degradation of recalcitrant organic substances. In the AFP system, the reaction mechanisms are described as follows (Eqs. (4), (6), (10)–(17)) [25]:

$$H_2O_2 \xrightarrow{)))} 2{\cdot}OH \quad (10)$$

$$O_2 \xrightarrow{)))} 2O{\cdot} \quad (11)$$

$$O{\cdot} + H_2O \rightarrow 2{\cdot}OH \quad (12)$$

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

$$Fe^0 \xrightarrow{)))} Fe^{2+} + 2e^- \quad (13)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\cdot}OH + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+ \quad (6)$$

$$Fe\text{-}OOH^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot} \quad (14)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+ \quad (15)$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \quad (16)$$

where "))))" represents ultrasound wave.

To our knowledge, only a few papers have been published on the use of ZVI aggregates as the catalyst for decoloration of reactive azo dyes by Fenton/US process. In this study, we systemically investigated the decoloration efficiency of the ZVI-aggregates-activated Fenton/US process for oxidation of Reactive Black 5 (RB5). The ZVI aggregates were chosen as catalyst mediator due to: (1) ultrasound can enhance the corrosion of ZVI under acidic conditions, resulting in the continuous release of large quantities of in situ Fe^{2+}, which in turn triggers a more effective Fenton's reaction; (2) it is a low-cost catalyst compared with nano-sized ZVI particles; (3) the aggregate is reusable. The objectives of the study were to: (1) compare the effectiveness of sonolysis, US/H_2O_2, Fe(0)/US, Fenton, and Fenton/US processes on the decoloration of RB5; (2) determine the operational parameters (initial solution pH, ZVI dose, H_2O_2 dose, and ultrasonic power) affecting the Fenton/US process and identify suitable decoloration conditions; (3) study the effects of some common inorganic anions ($H_2PO_4^-$, Cl^-, ClO_4^-, NO_3^-, and SO_4^{2-}) on decoloration efficiency of Fenton/US for practical consideration; (4) test the reusability of ZVI aggregates in the Fenton/US process; and (5) evaluate the cost-effectiveness of treating RB5 with Fenton/US process.

2. Materials and methods

2.1. Materials

C.I. RB5 ($C_{26}H_{25}N_5O_{19}S_6{\cdot}4Na$, CAS No. 17095-24-8) was purchased from Sigma–Aldrich and used as received. RB5 concentration was analyzed by measuring the absorption at 596 nm using a spectrophotometer (DR2800™, Hach, USA). The catalyst, ZVI aggregates, with particle size 0.297–2.380 mm and specific weight 2240–2560 kg/m^3 were obtained from Connelly-GPM Inc., USA. H_2O_2 (analytical grade, 35% w/w) was purchased from J.T. Baker (USA). The concentrations of total Fe and Fe^{2+} in the solution without dye were analyzed by measuring absorption at 510 nm using Hach FerroVer® iron reagent [26]. Fe^{3+} was determined from the difference between total dissolved Fe and Fe^{2+}.

2.2. Experimental procedures

Sonication of the RB5 dye solution was conducted in air atmosphere with a fixed frequency of 60 kHz generated by an ultrasonic generator (S-450A, Brason, USA) equipped with a titanium probe transducer (Fig. 1). The tip of the probe was 1.2 cm in diameter; 6-cm length was submersed in the dye solution. The sonication was administered in pulses with a 60% duty cycle. The applied electrical power was manually adjusted to achieve an actual power density in the liquid phase between 80 and 120 W/L. The ultrasonic generator provides direct sonication, which will not cause energy loss because the reaction matrix is in direct contact with the mechanical vibration. The step-wise sonication of the experimental run was as follows: (1) Fenton/US experiments were conducted for a 1000 mL RB5 dye solution placed in a glass beaker; (2) the pH was adjusted to a predetermined value using a solution of either HNO_3 or NaOH; (3) the experimental solution was placed in a beaker and irradiated with an ultrasonic horn and an appropriate amount of ZVI and H_2O_2 were added; and (4) at desired time intervals, a 5-mL sample was drawn from the beaker and immediately filtered using a 0.45-μm membrane filter to collect the supernatant, which was then analyzed to determine the residual concentration.

3. Results and discussion

3.1. Decoloration of RB5 in different comparable systems

As reported previously, sonolysis applied alone could not lead to any decoloration of RB5 [27]. In this study, under the acidic condition (pH 3.0), several systems (US, US/H_2O_2, Fe(0)/US, Fenton, and Fenton/US) were compared for the effectiveness of RB5

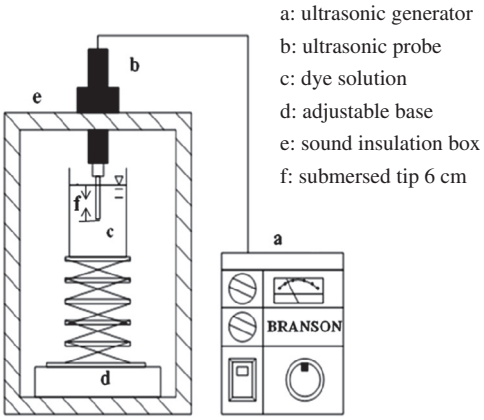

Fig. 1. Experimental set-up of Fenton/US apparatus.