

Degradation of azo dye Acid Orange 7 in water by Fe⁰/granular activated carbon system in the presence of ultrasound

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Abstract

Degradation of azo dye Acid Orange 7 (AO7) was investigated using zero-valent iron/granular activated carbon (Fe⁰/GAC) in the absence and presence of ultrasound (US). The AO7 degradation efficiency by Fe⁰/GAC was dramatically enhanced by ultrasound, ultrasound alone had a little effect on the degradation. Effects of Fe⁰/GAC ratios and initial pH values on AO7 degradation were studied in the US–Fe⁰/GAC system. The degradation followed the pseudo-first-order kinetics model. The pseudo-first-order rate constant of AO7 degradation by Fe⁰/GAC was $8.74 \times 10^{-3} \text{ min}^{-1}$ while that by US–Fe⁰/GAC was $3.91 \times 10^{-2} \text{ min}^{-1}$. A significant synergetic effect was observed between US and Fe⁰/GAC. Ultrasound swept the reactive intermediates or products from Fe⁰ surface, and thereby the surface of Fe⁰ was cleaned and reactivated. Granular activated carbon was added as cathode to increase the unit of internal batteries and enhance the current efficiency of the internal electrolysis. The suitable Fe⁰/GAC ratio (v/v) for the degradation of AO7 in the presence of ultrasound was 1:1. The degradation was highly dependent on pH, and a decrease of the initial pH values from 12.0 to 4.0 led to the increase of degradation efficiencies. Sulfanilamide was proved as the main residual degradation product in the solution by the analysis of high-performance liquid chromatograms.

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1. Introduction

Wastewater from textile processing plants can be highly colored and difficult to be decolorized. Over 15% of the textile dyes are lost in wastewater stream during dyeing operation. Dye pollutants from the textile industry are an important source of environmental contamination. About a half of global production of synthetic textile dyes (7×10^5 t per year) are classified into azo compounds that have the chromophore of –N=N– unit in their molecular structure. These azo dyes are known to be largely non-biodegradable in aerobic conditions and to be reduced to more hazardous intermediates in anaerobic conditions [1]. Azo dyes are very difficult to be treated in environmental systems, because that the sulfonic acid groups in their chemicals make the dyes very water-soluble and polar [2–4]. The removal of

the recalcitrant was extensively studied by the processes such as electrocoagulation, photocatalytic oxidation, and ozonation [5–7]. The conventional treatment methods including coagulation, activated carbon adsorption, and biotreatment were also employed for the decontamination [8–10]. Nevertheless, these methods were insufficient to treat azo dye wastewater with high concentration and chroma.

Over the last decade, a great deal of interest was focused on the degradation of organic compounds and groundwater remediation with the new treatment methods by zero-valent iron metal (Fe⁰) [11,12]. The permeable reactive barriers (PRBs) containing Fe⁰ cuttings has been proved to be a cost-effective treatment approach for contaminated ground water. The addition of Fe⁰ has become a widely used technology in treating wastewaters, including chlorinated aliphatics, chlorinated aromatics, nitro aromatics and azo dyes. The destruction of azo bond N=N of azo dyes led to decolorization of dye solutions in visible region. High decolorization rates were observed in the reactions of nine azo dyes with granular Fe⁰ in batch systems by

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Nam and Tratnyek [13]. However, loss of reactivity over time, due to the corrosion products or other precipitates on the iron surface, is a great concern.

Ultrasonic irradiation has been applied in water treatment in recent years. The effects of ultrasound (US) result primarily from acoustic cavitations. The formation, growth, and implosive collapse of bubbles in liquids not only liberate considerable energy in a short time but also cause enhanced agitation of the liquid to speed up the mass transfer. It is thought that ultrasound serves to sweep reactive intermediates or products from metal surfaces thereby reactivating and cleaning the surfaces for subsequent reactions [14,15].

The type and the number of cathodes would influence the efficiency of the internal electrolysis by Fe^0 . Granular activated carbon (GAC) was added as cathode to enhance the current efficiency of the internal electrolysis. Meanwhile, GAC was chosen as cathode because of its low cost, high porosity and wide application in wastewater treatment. van der Zee et al. [16] used activated carbon as an immobilized redox mediator for the reaction of a recalcitrant azo dye during the anaerobic biotransformation. They indicated that activated carbon had accelerated the reduction by accepting electrons and transferring the electrons to azo dyes. Ma et al. [17] proposed Fe/Cu system to improve the reduction capacity.

In this study, degradation of Acid Orange 7 (AO7) by Fe^0/GAC in the absence and presence of ultrasound was investigated. Effects of Fe^0/GAC ratios and initial pH values were studied in the process of $\text{US}-\text{Fe}^0/\text{GAC}$ in detail. AO7 was chosen as a model of the hydrosoluble phenylazonaphthol dyes due to its wide application and resistance to biological degradation.

2. Materials and methods

2.1. Materials

Acid Orange 7 and sulfanilamide were purchased from Beijing Chemical Reagents Company and used without further purification. Other chemicals used in the experiment were of analytical grade. Deionized water was used throughout the whole experiment process.

Iron chippings was obtained from Hangzhou Jiali Metal Co., Ltd. (China). The particle size ranged from 1.25 to 2 mm (10–16 mesh). Granular activated carbon was obtained from Fujian Ningde Xinsen Chemical Industry Co., Ltd. (China). The particle size was 1.25–2.5 mm (8–16 mesh). In order to avoid the influence of GAC adsorption, GAC particles were added into 1000 mg l^{-1} AO7 solution and stirred in a rotary shaker for pre-adsorption, and then, the solution containing activated carbon particles was ultrasonically treated. The pretreatment was repeated several times till GAC had no adsorbability.

2.2. Experiments

The degradation of AO7 by Fe^0/GAC in the presence of ultrasound was carried out in an ultrasonic cleaning bath (KQ-100) at fixed frequency of 40 kHz and an output power of 100 W. The tank dimensions were $300 \text{ mm} \times 150 \text{ mm} \times 100 \text{ mm}$ with

liquid holding capacity of 4.0 l. A 250 ml conical flask with a plane bottom of thin glass was selected as the container in order to minimize sonic absorption and to ensure good heat exchange with the water bath. The conical flask containing 100 ml of AO7 solution was fixed at a constant position, and the surface of the solution in the conical flask was 5 mm under the water surface in the tank. The pH of the solution was adjusted with diluted NaOH or HCl solution using an Orion model 720Aplus Benchtop pH Meter (Thermo Orion Co., USA). Thermostating was conducted using coolant passed through $\Phi 6$ copper coils suspending in the bath connected with a thermostat, and the temperature of the bath was kept at about 22°C . GAC and iron particles were churned up to mix them completely, and then added into the solution. At different time intervals, 0.8 ml of suspension was drawn out with a syringe. The sample was diluted to 20 ml and filtrated through a $0.45 \mu\text{m}$ filter immediately. The initial concentration of AO7 was 1000 mg l^{-1} . Throughout the whole process, pH was not readjusted and no buffer solution was added.

2.3. Analysis

UV–vis spectra of the samples, from 190 to 600 nm, were recorded by a U-3010 UV–vis spectrophotometer (Hitachi Co., Japan) equipped with quartz cuvettes of 1 cm light path. The concentration of AO7 was achieved by measuring the absorbance of the diluted (typically 1:25 in water) samples at 484 nm, corresponding to the maximum absorption wavelength of AO7. Prior to the measurement, a calibration curve was obtained using standard AO7 solutions at 484 nm according to the Lambert–Beer's law. The curve showed a good linear relationship between the absorbance intensity and the concentration of AO7 in the range of 0– 1000 mg l^{-1} . The residual concentrations of dye in solution were calculated by the Lambert–Beer's law. Total organic carbon (TOC) concentration was measured with a Multi N/C 3000 (Analytik jena Co., Germany) total organic carbon analyzer. The morphologies of the iron chippings were characterized by a HITACHI S-3000N scanning electron microscope (SEM). Energy dispersive spectra were obtained simultaneously.

AO7 and its degradation products were analyzed by a high-performance liquid chromatography (HPLC) (Model-Organizer, Hitachi Co., Japan), with a DAD detector and the detection wavelength was fixed at 254 nm. An Allsphere ODS-2 5u column (Alltech, USA), $250 \text{ mm} \times 46 \text{ mm}$, was used, and the column temperature was 40°C . An acetonitrile/ammonium acetate (25/75) mixture solution was used as the eluent and was pumped at a rate of 1.0 ml min^{-1} . The concentration of ammonium acetate solution was 0.025 mol l^{-1} .

3. Results and discussion

3.1. Synergetic effect between Fe^0/GAC and ultrasound

The degradation of AO7 was carried out at three approaches as follows: (1) using the single US, (2) using Fe^0/GAC and (3) using $\text{US}-\text{Fe}^0/\text{GAC}$. As illustrated in Fig. 1, the degradation efficiency of AO7 was enhanced significantly by ultrasound. After 40 min reaction in the $\text{US}-\text{Fe}^0/\text{GAC}$ system, the removal

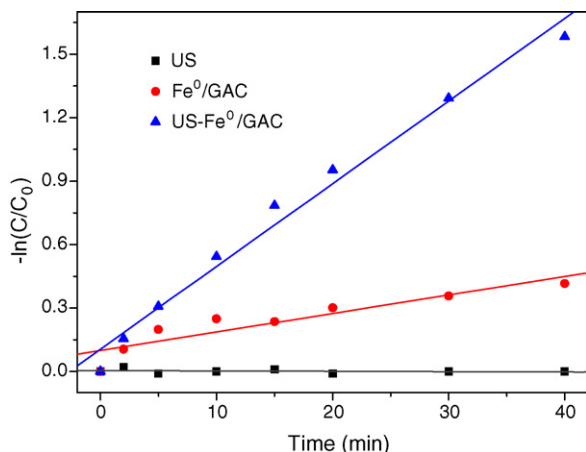


Fig. 1. Pseudo-first-order degradation of AO7 by US-Fe⁰/GAC. $C_0 = 1000 \text{ mg l}^{-1}$, pH 4.0, $[\text{Fe}^0]_0 = 12.0 \text{ g}$, $[\text{GAC}]_0 = 2.3 \text{ g}$ (Fe⁰ and GAC have the same volume).

of color and TOC was amounted to 80% and 57%, respectively. While the removal efficiency of color and TOC by Fe⁰/GAC were 34% and 28%, respectively. There was no concentration loss of AO7 occurring in the single ultrasound process.

The removal of color and TOC increased with the prolonged reaction time. The reaction was well followed by the pseudo-first-order model.

The correlation between $\ln C/C_0$ and the reaction time was linear. The kinetic expression can be presented as follows:

$$\ln \frac{C}{C_0} = -k_1 t \quad (1)$$

where C is the AO7 concentration at instant t , C_0 is the initial AO7 concentration, k_1 (min^{-1}) is the pseudo-first-order rate constant and t is the time of reaction. The pseudo-first-order rate constants for the degradation of AO7 by Fe⁰/GAC and US-Fe⁰/GAC were $8.74 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.9220$) and $3.91 \times 10^{-2} \text{ min}^{-1}$ ($R = 0.9920$), respectively. The reaction rate was increased by 3.5 times in the presence of ultrasound compared with that of absence of ultrasound. The degradation efficiency of AO7 by US-Fe⁰/GAC was much higher than the sum of the individual effects of Fe⁰/GAC and US, which might be due to a synergistic effect.

The same trend for TOC removal was obtained (Fig. 2). The pseudo-first-order rate constants for TOC removal by Fe⁰/GAC and US-Fe⁰/GAC were $6.79 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.8646$) and $2.02 \times 10^{-2} \text{ min}^{-1}$ ($R = 0.9530$), respectively. The TOC remove rate was increased by 2.0 times in the presence of ultrasound compared with that of the absence of ultrasound.

The process of Fe⁰/GAC was greatly enhanced by ultrasound. The reason may be that the transient cavitations, which were resulted from turbulent flow conditions within the reaction system, enhanced the overall mass transport in the presence of ultrasonic irradiation. In the process of the degradation, AO7 molecules transferred from the bulk solution to the vicinity of the Fe⁰ surface, and then were reduced by the reductive species. The degradation products of AO7 and the hydrolysates of iron oxides/hydroxides covered on the Fe⁰ surface, which inhibited

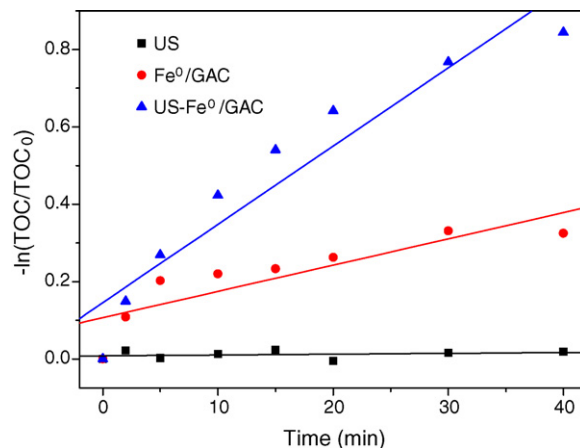


Fig. 2. Pseudo-first-order removal of TOC by US-Fe⁰/GAC. $\text{TOC}_0 = 340 \text{ mg l}^{-1}$, pH 4.0, $[\text{Fe}^0]_0 = 12.0 \text{ g}$, $[\text{GAC}]_0 = 2.3 \text{ g}$.

the contact between Fe⁰ and the azo dye, and thereby the activity of the Fe⁰ surface was decreased and the further decolorization rate of AO7 was decreased accordingly. The decolorization kinetics of azo dyes by Fe⁰ was limited by mass transfer of the substrates to the Fe⁰ surface [13,18]. In the presence of ultrasound, acoustic cavitations led to the cleaning of iron chippings, and accordingly more reactant surface area was formed for further surface reactions. Therefore, the US-Fe⁰/GAC system integrated utilized the actions of the physical effects associated with the continuous ultrasonic cleaning and activation of the Fe⁰ surface. Most of the sediments were separated and transferred into the bulk solution, the AO7 molecules continued to transfer to the vicinity of Fe⁰ surface and the subsequent degradation continued. In addition, the enhancement of mass transfer resulting from the turbulent effects of cavitations was integrated [19].

3.2. Effect of Fe⁰/GAC ratio

Chemical reduction with metallic iron in aqueous solutions is an electrochemical corrosion process. When the cast iron was immersed in aqueous solution, many internal batteries formed between the iron grains and the carbon particles. Anodic metal in Fe⁰-H₂O systems provided electrons for the reduction of AO7. Granular activated carbons were acted as cathodes to increase the unit of internal batteries and enhance the current efficiency of the internal electrolysis. The number of cathodes would affect the degradation. Fig. 3 illustrated the TOC removal of AO7 in the US-Fe⁰/GAC system at different Fe⁰/GAC ratios (v/v). The results showed that the removal efficiency of TOC was the highest with Fe⁰/GAC ratio of 1:1 (v/v). Because granular iron and GAC had similar particle size, the same volume means nearly the same particle number. Consequently, they had almost the same anode and cathode number in the internal electrolysis reaction. The less GAC cathode could not exert the best internal electrolysis efficiency while the more GAC cathode might inhabit much more space and cumbered the reaction. The ratio of 1:1 (v/v) for Fe⁰/GAC was selected in the following studies under otherwise identical experimental conditions. Song et al. [20] obtained the

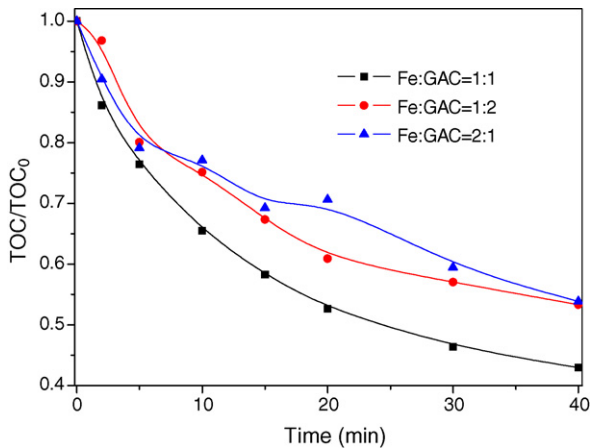
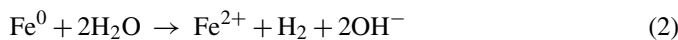


Fig. 3. TOC removal in the AO7 degradation with different Fe⁰/GAC ratio (v/v). TOC₀ = 340 mg l⁻¹, pH 4.0, [Fe⁰]₀ = 12.0 g.

same result that the optimum ratio was 1:1 in treating wastewater from dye-stuff production by internal electrolysis without ultrasound.

3.3. Effect of initial pH

The actual dye wastewater has a wide range of initial pH values, and the solution pH is an important parameter affecting the kinetics in the reduction process by Fe⁰ [21]. Different approaches are involved for the reaction of zero-valent iron in solutions with different pH values, which are presented as following equations:



According to Nernst Equation, the reduction potential for Fe²⁺/Fe increases with an increase of the H⁺ concentration and thus the initial pH values may affect the performance of the degradation of AO7. A series of AO7 solution with different initial pH values were treated in the US–Fe⁰/GAC system. Fig. 4 illustrated the TOC removal at 40 min reaction at different initial

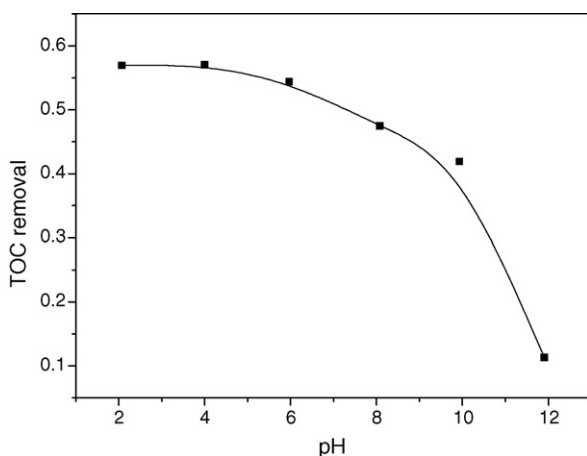


Fig. 4. TOC removal in the AO7 degradation with different pH. TOC₀ = 340 mg l⁻¹, [Fe⁰]₀ = 12.0 g, [GAC]₀ = 2.3 g.

pH values. The removal of TOC decreased with an increase of the initial pH values from 4.0 to 12.0. Similar removal rates were achieved at pH 2.0 and 4.0. The result was consistent with that from Cao et al. [11] in reductive degradation of azo dye by zero-valent iron in the absence of ultrasound.

The degradation of azo dyes using Fe⁰ occurs on the surface of metal iron [11]. When effective collision between dye molecules and elemental iron happens, elemental iron, as an electron donor, loses electrons. Meanwhile, the dye molecule, as an electron acceptor, gets electrons, and combines with H⁺ and turns into transitional products and finally terminal products. As a consequence, pH would strongly affect the degradation of AO7 and the removal of TOC. However, the TOC removal had no significant increase with the decrease of pH from 4.0 to 2.0, especially beyond 20 min treatment.

3.4. Analysis of the iron surface

The surface morphologies of the iron chippings before and after treatment were characterized by scanning electron microscope. Energy dispersive spectra (EDS) were also obtained (Fig. 5).

The raw surface of the iron chippings was clean and had many layers overlapping like scales. This coarse surface could augment reaction area and be favor of accreting sediments. Fe⁰ in Fe⁰–H₂O systems might potentially function as both a reactant

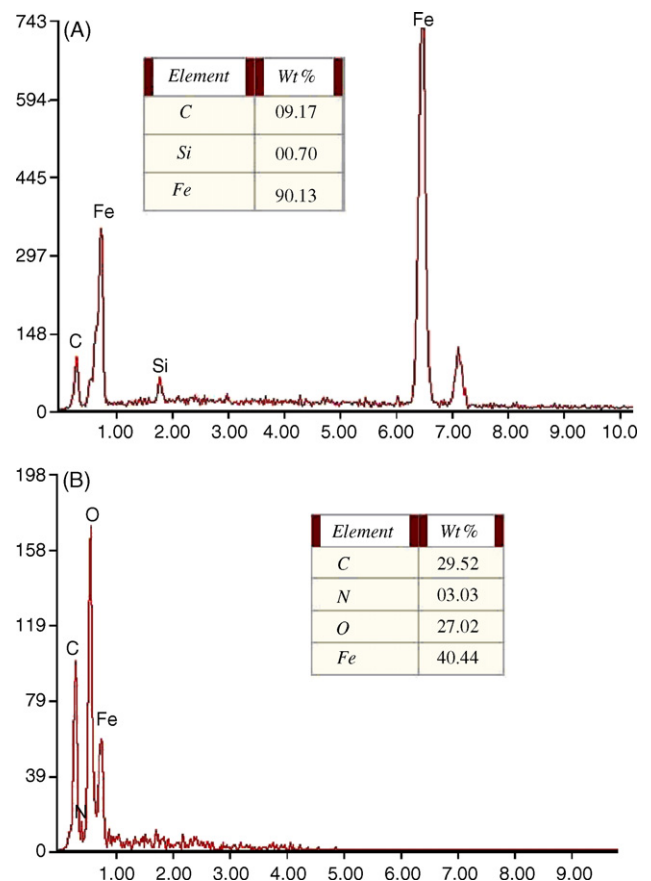


Fig. 5. Energy dispersive spectra of the iron surface before (A) and after (B) treatment.

and a catalyst during the reduction of contaminants [22]. The surface of iron and its defects could provide catalytic reaction sites. Some flock sediments were accreted on the interfaces or into cracks of the iron after reaction. Ultrasound could enhance the separation of the flock sediments from the interfaces or cracks, and the sonicated samples were visibly cleaner than nonsonicated samples. Activation of the metal surface was a basic step in organometallic chemistry [23]. The activated surface was essential for the reductive degradation of AO7. It could be seen that the sonicated samples were visibly cleaned due to the continuous ultrasonic cleaning [24]. Ultrasound had effectively removed the weakly absorbed ferrous hydroxide species, and thus the activity of zero-valent iron was increased.

A detailed EDS analysis was presented in Fig. 5. The major elements on the iron chippings such as Fe, C, O, N, and Si were examined. The content of iron element decreased while that of carbon element increased after the treatment. Meanwhile, a large amount of oxygen and nitrogen element appeared on the iron surface. This indicated that some of the organics, which may be resulted from the reductive degradation of AO7, were still adsorbed on the iron surface in spite of the influence of the ultrasound.

3.5. Analysis of the degradation products

HPLC chromatograms recorded the AO7 degradations at 0, 10 and 40 min were presented in Fig. 6. The figure of initial AO7 solution showed three chromatogram peaks with retention time (t_R) at 2.0, 2.8 and 7.7 min, respectively. After 10 min treatment by US-Fe⁰/GAC, the peaks at t_R 2.8 and 7.7 min reduced, while the peak at t_R 2.0 min raised quickly. After 40 min degradation, only the peak at t_R 2.0 min was remained.

The UV absorbance curves (200–300 nm) of AO7 and the final products with t_R at 2.0 and 2.8 min were presented in Fig. 7. The substance that with t_R 7.7 min was the same as that of AO7 (Fig. 7(A)). The strongest peak at t_R 7.7 min disappeared after reduction, which implied the total destruction of AO7. The other two peaks exhibited close intensity and they might be ascribed to the products resulted from the self-decomposition of AO7. Sulfanilamide and 1-amino-2-naphtol were the most probable

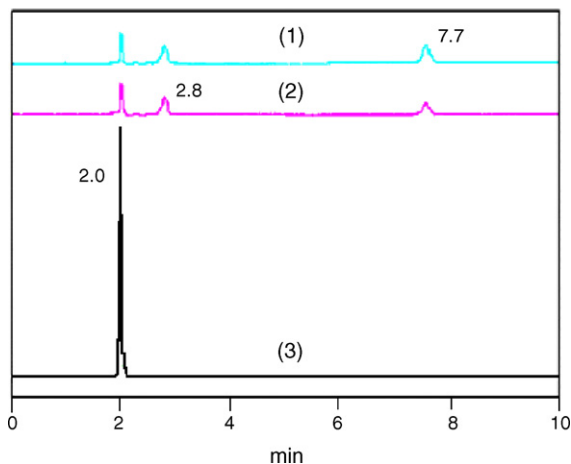


Fig. 6. HPLC chromatograms of the degradation of AO7 at (1) 0 min, (2) 10 min, and (3) 40 min.

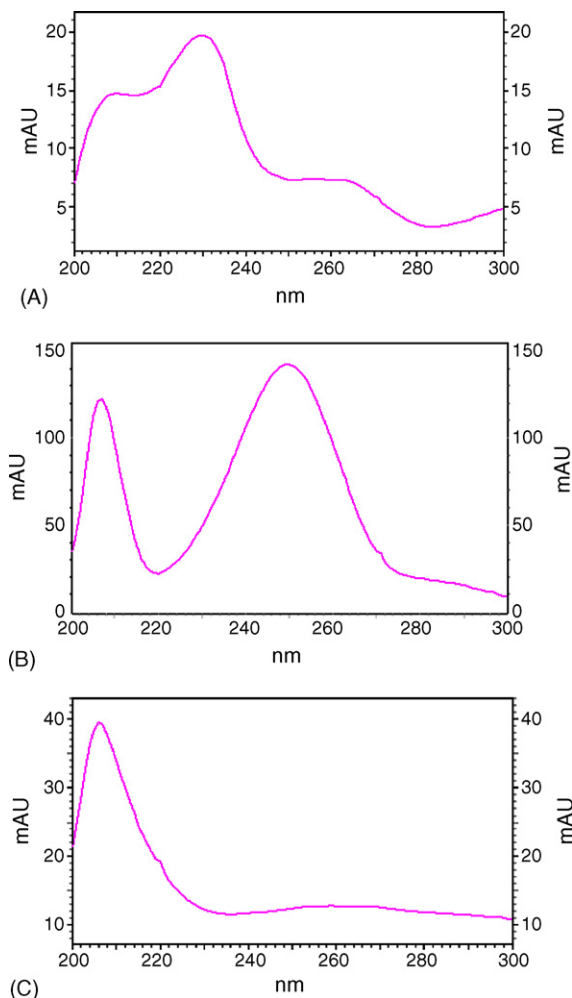
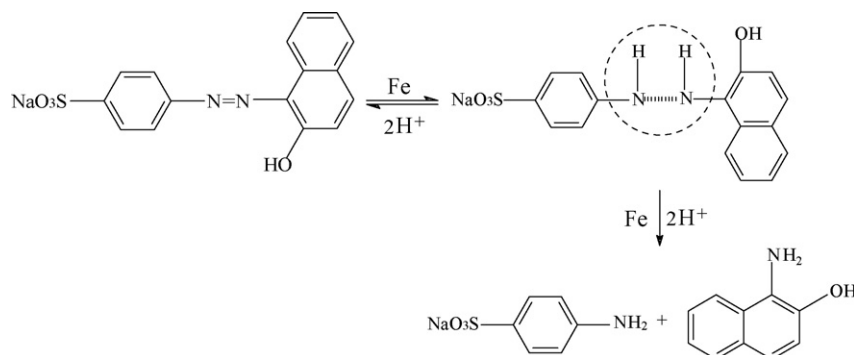


Fig. 7. UV absorbance curves (200–300 nm) of AO7 (A) and the final products with t_R at 2.0 min (B) and 2.8 min (C) obtained from HPLC.

products from metal iron reduction of AO7 [13,25]. The peak at t_R 2.0 min became the strongest one after reduction, which had the same UV spectrum and retention time as that of sulfanilamide in Fig. 7(B). This indicated that reductive cleavage of the azo group was the dominated stage in the process. Sulfanilamide had a high solubility and was very stable in acidic solution in the presence of metallic iron. The peak at t_R 2.8 min almost disappeared, which had the UV-vis spectrum showed in Fig. 7(C), but it could not be ascertained as 1-amino-2-naphtol due to its auto-oxidation [26].

The reduction of AO7 by zero-valent iron was regarded as a two-steps reaction [1,11]. The first step was reversible and the second step led to the cleavage of the azo conjugation between the aromatic rings. In the first step, the transitional compound (Ar-NH-NH-Ar') resulting from incomplete reduction of AO7, cumulated in the solution. Due to the increasing amount of reductive species, the reaction was driven toward the complete reduction cleavage of azo bond. The unstable transitional compound reduced into two degradation products (sulfanilamide and 1-amino-2-naphtol) at last. The proposed pathway for the reduction of AO7 by US-Fe⁰/GAC was presented in Scheme 1. When the internal electrolysis reaction stopped, the chemical balance

Scheme 1. Major degradation pathway by US-Fe⁰/GAC reduction for AO7.

was broken due to the loss of reductive species and some of the unstable transitional compounds returned into AO7. So the color of the solution partially reverted to its original orange color in the experiment [11]. The TOC removal mainly resulted from the sedimentation of iron ions [27], and a very small quantity of was due to the mineralization by the ultrasonication [28].

4. Conclusions

The degradation of azo dye AO7 by Fe⁰/GAC system in the absence and presence of ultrasonic irradiation was studied. The decolorization rate and TOC removal using Fe⁰/GAC were much higher in the presence of ultrasonic irradiation than those in the absence of ultrasound. A synergetic effect was found between US and Fe⁰/GAC. The highest degradation efficiency was obtained when the Fe⁰/GAC ratio was set at 1:1 (v/v). The degradation performance was strongly pH dependent and a decrease of the initial pH values resulted in the increase of degradation efficiencies from pH 4.0 to 12.0. The optimum pH value was found to be 4.0 for the reductive degradation of AO7 in the examined pH values. Azo groups were reduced into hydrogenated azo bond and even amino groups and the TOC removal was achieved by the sedimentation. It is feasible to couple ultrasonic irradiation with Fe⁰/GAC system for the degradation of azo dyes, both for decolorization and mineralization of the dye.

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