Decolorization of azo dyes in a heterogeneous persulfate system using FeS as the activator

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ABSTRACT

Textile effluents containing synthetic refractory azo dyes are one of the most important sources of water pollution. However, these kinds of refractory organic pollutants did not resist a persulfate (PS) oxidation process which was correctly activated. In this study, PS was activated by ferrous sulfide (FeS) in a heterogeneous system to break down azo dyes wastewater. The results showed that all five selected azo dyes were efficiently broken down using the PS/FeS system, except for DY 12, and more than 95% of azo dyes were decolorized within 60 minutes. The decolorization efficiency of DR 81 in the PS/FeS system was comparable to PS activated with heat (60 °C) or Fe2⁺, and was slightly superior to Fe⁰ powders under the same conditions. Quenching studies indicated that both SO₄⁻• and •OH were formed in the FeS surface and diffused into the solution to facilitate the successive transformation of DR 81, the •OH reaction with DR 81 might the crucial reaction. The coexisting chelating agents in real azo dye effluents at high concentrations had a negative influence on azo dye decolorization by PS/FeS. However, the superior factor of the PS/FeS system was the regenerability and reusability of the heterogeneous catalyst.

Key words | azo dyes, decolorization, ferrous sulfide (FeS), heterogeneous system, persulfate (PS)

HIGHLIGHTS

- Five selected azo dyes were efficiently broken down using the PS/FeS system.
- DR 81 decolorization by PS activated with FeS was comparable to other activators.
- •OH might play a crucial role on DR 81 decolorization by PS/FeS system.
- DR 81 decolorization proceeded by PS/FeS with correct coexisting chelating agents.
- FeS was regenerable and recyclable in the heterogeneous PS/FeS system.

GRAPHICAL ABSTRACT

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INTRODUCTION

The synthetic dye industry has synthesized millions of different colored dyes since 1865, and about half of these synthetic dyes are azo dyes, which are characterized by the presence of one or more azo groups (–N=N–) bound to aromatic rings (Papic et al. 2014). These azo dyes of various natures are synthesized in different forms such as Direct, acid, base, reactive, dispersive, metal complexed, mordant and sulfur dyes, because of their chemical stability and versatility; they are the major colorants widely used in textile dyeing and printing industries (Papic et al. 2014; Dontsova et al. 2018; Weng & Tao 2018). The effluents inextricably released from these industries are problematic since more than 15% of the residual dyes end up in wastewater (Ay et al. 2009). Direct discharge of this highly colored raw sewage into the environment is a source of considerable pollution, in addition aquatic organism are inevitable disturbed due to the toxic, carcinogenic, mutagenic or allergenic nature of most dyes molecules (Ay et al. 2009; Tarkwa et al. 2019).

Most azo dyes are intentionally designed to resist degradation, treatment of these azo dye effluents to meet effluent discharge criteria therefore is a challenge (Weng & Tao 2018). The conventional biological treatment methods are designed for dyestuff decontamination (Tarkwa et al. 2019). Advanced oxidation processes (AOPs) have proven to be alternative techniques for efficient oxidation and mineralization of a wide range of refractory organic pollutants like azo dyes (Ivanets et al. 2019; Zhang et al. 2020). As one of the AOPs, the persulfate (PS) oxidation process has gained extensively increased attention from current research fields (Fan et al. 2017; Fang et al. 2017). Generally, PS alone only achieves a negligible treatment result (Ike et al. 2018; A et al. 2020). This process destroys contaminants mainly through sulfate radicals (SO₄⁻), which can be generated by the cleavage of O–O bond of PS (E° = 2.01 V vs. standard hydrogen electrode (SHE)) in which the bond length corresponds to 1.497 Å (Ding et al. 2019). PS was selected as the source of sulfate radicals mainly due to its bargain price, high stability, aqueous solubility, and outstanding mobility. It is a solid at ambient temperature, which facilitates its transport and storage is also a factor to be taken into account (Ding et al. 2019). The oxidation potential of SO₄⁻ (E° = 2.6 V vs. SHE) is comparable with another frequently used radical, -OH (E° = 2.8 V vs. SHE), which is typically produced in Fenton or Fenton-like oxidation processes using hydrogen peroxide (H₂O₂, E° = 1.77 V vs. SHE) (Suehnholz et al. 2020). In addition, SO₄⁻ is also characterized by a longer half-life, as well as higher reactivity over a relatively wide pH range (Ding et al. 2019; Lyu et al. 2019). Activation of PS is necessary to induce the production of SO₄⁻, through heat, UV radiation, ultrasound, and base as well as transition metals (Meⁿ⁺) are all reported effective approaches, as shown in Equations (1)–(5) (Weng & Tao 2018):

\[
\begin{align*}
S₂O₅²⁻ & \xrightarrow{\text{heat}} 2SO₄⁻ \quad (1) \\
S₂O₅²⁻ & \xrightarrow{\text{hv}} 2SO₄⁻ \quad (2) \\
S₂O₅²⁻ & \xrightarrow{\text{uv}} 2SO₄⁻ \quad (3) \\
2S₂O₅²⁻ + 2H₂O & \xrightarrow{\text{OH}} SO₄⁻ + O₂⁻ + 3SO₂⁻ + 4H⁺ \quad (4) \\
S₂O₅²⁻ + Meⁿ⁺ & \xrightarrow{} SO₄⁻ + Meⁿ⁺⁻ + SO₂⁻ \quad (5)
\end{align*}
\]

where \(\xrightarrow{\text{uv}}\) refers to the application of ultrasound.

Among them, environmental friendly iron-based materials are identified as one of the most widely used activators to induce the rapid decomposition of PS to generate SO₄⁻ (Chen et al. 2017). Although large amounts of free Fe(II) ions can be generated from the dissolution of FeSO₄ or FeCl₂ which is favorable for SO₄⁻ release, PS activation in a completely homogenous system is not recommended by researchers since these excess Fe²⁺ ions simultaneously act as quenching agents which quickly scavenge the radicals, as shown in Equation (6), resulting in serious competition for any pollutant to be degraded and eventually the poor utilization of PS and iron (Chen et al. 2017; Balpreet et al. 2019). Therefore, scientists have turned to concentrate on Fe²⁺ slow-release iron for heterogeneous activation of PS. Zero-valent iron (ZVI) at this time is deemed as an ideal option to exhibit excellent performance when assisting PS oxidation, but the reported inactivation problem, high cost and thermodynamic instability limit the wide application of this material (Fan et al. 2017; Huang et al. 2019). Other kinds of iron-contained minerals like hematite, goethite, ferrilydrite, and magnetite have also been developed as heterogeneous PS activators to facilitate SO₄⁻ generation, unfortunately, most of these iron-containing materials have insufficient Fe(II) content, thus hindering their applications (Wang et al. 2019). Therefore, the search for other desirable iron minerals with abundant Fe(II) content for the heterogeneous activation of PS is of
great environmental significance:

\[ \text{SO}_4^{2-} + \text{Fe}^{2+} \rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+} \]  

(6)

Ferrous sulfide (FeS), commonly called mackinawite and found in the subsurface environment, is a ubiquitous innocuous metastable mineral formed by the dissimilatory bacterial reduction of sulfate (Fan et al. 2017; Cheng et al. 2020). Fe(II) and S(II) species within FeS both have the ability to act as electron donors, and their reducibility to remedy environmental contamination has been extensively assessed (Chen et al. 2019). Research results have shown that FeS is effective in mediating transformation of many environmental contaminants such as inorganic heavy metals, as well as organic contaminants, for example chlorinated and aromatic compounds (Chen et al. 2019). Recently, some research groups have paid attention to using FeS as a potential PS catalyst in a heterogeneous system to initiate sulfate radical formation, and the results indicated that PS activation is mainly achieved by Fe(II) at the FeS surface, the generated radical then diffuses into the aqueous phase to promote the transformation of target contamination, moreover, Fe(II) is regenerated from Fe(III) by S(II) at the FeS surface, thus eventually resulting in a continuous oxidation process (Fan et al. 2017). Trichloroethene, dinitrodiazophenol, 2,4-dichlorophenoxycetic acid and p-chloroaniline decontamination using this kind of AOP has been reported to be effective and feasible (Chen et al. 2017; Fan et al. 2017; Suehnholz et al. 2020; Wang et al. 2020). At present, azo dye is still one of the most widely troubling contaminants and is probably a threat to the environment if it has been incorrectly disposed of, application of the PS oxidation process based on FeS as the activator (PS/FeS) for azo dye decomposition therefore is of great environmental significance. The oxidation efficiency of this technique on different azo dyes has been rarely discussed.

The purpose of this paper was to focus on the heterogeneous decoloration of azo dyes in aqueous solution using PS activated with FeS. The goals of this study were to: 1) compare the degradation behavior of PS/FeS in a heterogeneous system to various azo dyes and the characteristics of utilizing FeS as a heterogeneous PS activator compared with other activation approaches on azo dyes degradation; 2) study the influence of chelating agents, which probably coexist in real azo dye effluents on azo dye decolorization by PS/FeS and the recyclability of the heterogeneous catalyst; 3) elucidate the reactive species responsible for the degradation of azo dyes in the PS/FeS system and the speculated decomposition pathways of azo dyes by PS/FeS.

### MATERIALS AND METHODS

#### Materials

All chemicals used in this study were at least of analytical grade and employed without further purification. As shown in Figure 1, Five azo dyes, namely Direct Red 81 (abbreviated as DR 81, C29H10N5Na2O8S2), Direct Blue 15 (abbreviated as DB 15, C34H27N6NaO14S6), Direct Yellow 12 (abbreviated as DY 12, C30H26N4Na2O4S2), Allura Red AC (abbreviated as AR AC, C13H14N2Na2O6S2), and Sirius Red (abbreviated as SR 80, C45H26N10Na6O21S6) respectively coupled to monoazo, disazo and polyazo dyes were purchased from Titan Technology Co., Ltd (Shanghai, China). PS, methanol (MeOH, CH3OH), ethyl alcohol (EtOH, C2H5OH) and tert-butyl alcohol (TBA, C3H7OH) were obtained from the Sinopharm Group Chemical Reagent Co., Ltd (Shanghai, China). All other reagents such as FeSO4·7H2O and phenanthroline used in this study were acquired from Kelong Chemical Factory (Chengdu, China). Manufactured iron powder (Fe0) and FeS powder purchased from Xilong Scientific Co., Ltd (Guangdong, China) were further ground and filtered through a 100 mesh sieve, and the as-prepared Fe0 and FeS powders were respectively stored before further use. All solutions were prepared with ultrapure water from a Milli-Q System.

#### Experimental procedure

Unless specified, all batch experiments were conducted in 150 mL conical flasks under visible light conditions using a reaction solution volume of 100 mL. The effect of visible light on azo dyes degradation by PS/FeS was negligible in this study as shown in Figure S1 in Supplementary Information. Stock solutions of five azo dyes (5 mM) and PS (200 mM) were prepared using ultrapure water and a magnetic stirrer (DF-101S, YUHUA, China). For each batch experiment, specific volumes of azo dyes and PS stock solutions were successively added into ultrapure water, the initial concentrations of azo dyes and PS were 0.03 and 5 mM respectively. The experiments were started immediately after a defined amount of FeS was finally dosed under uncontrollable pH conditions. The mixture was then placed in a shaker (ZCY-103B, ZHICHENG, China) and was shaken at 150 rpm at ambient temperature (25 ± 2 °C). At predetermined time intervals, a 3.5 mL sample was withdrawn and passed through a 0.45 μm membrane filter, according to...
specific conditions, then 0.5 mL of pure methanol or 0.5 mL of 1 M sodium thiosulfate, which are effective quenching agents for sulfate radicals, were added in excess to the filtered samples immediately to quench the reaction before analysis (Olmez-Hanci et al. 2014; Yuan et al. 2015; Fan et al. 2017).

All the batch experiments selected DR 81 as the target contaminant unless to study decomposition efficiency of different azo dyes by PS/FeS. To compare DR 81 decolorization by PS activated with FeS, as well as by PS activated with the other approaches, the heat activation process was conducted by placing conical flasks containing certain amounts of mixed DR 81 and PS in a water bath with the temperature set to 40 °C or 60 °C, the same mole concentration of Fe$^0$ powders or FeSO$_4$ was dosed instead of FeS to evaluate activation of PS by Fe$^0$ and Fe$^{2+}$. Quenching experiments were performed by adding a certain dose of ethyl alcohol (EtOH) and TBA to the reaction solution before the reaction started. Real azo dye wastewater often contains other substances such as chloride ions, chelating agents and dyeing auxiliaries, to investigate the influence of these substances on azo dyes decolorization, three commonly used chelating agents, namely sodium citrate, sodium EDTA, and sodium oxalate were chosen as coexisting substances and separately added into the reaction solution simultaneously with DR 81 at different pre-set concentrations. To test the sustainable capacity of the PS/FeS reaction system, every 60 minutes FeS particles were retained by centrifuging the reaction solution at 8,000 rpm for two minutes. The precipitated FeS was then washed three times with ultrapure water before the next run without any other treatments. For each continuous cycle, fresh DR 81 and PS were added to the same concentration as in the first run.

In addition, a mixed azo dye solution and containing 0.03 mM DR 81, DY 12 and DB 15, was also decolorized using the heterogeneous PS/FeS system containing the same PS and FeS as the previous experiments. The reusability test was completed by repeatedly recycling the used FeS particles using a centrifuge at 8,000 rpm for two minutes, the precipitated FeS was then washed three times with ultrapure water and dried at 80 °C for 12 h before the next run. Furthermore, when necessary, blind experiments without either FeS or PS were performed in order to determine the contribution of these two compounds to azo dye degradation. Each batch experiment was performed at least in triplicate and all data were plotted as the mean of triplicates.
the error bars in the figures of the following contents represent the deviation from the mean.

**Analytical methods**

The concentrations of five azo dyes, namely DR 81, DB 15, DY 12, AR AC, and SR 80, were separately analyzed by measuring the absorbance at 500 nm, 595 nm, 390, 500 and 530 nm using a spectrophotometer (Evolution 201, Thermo Scientific, USA) (Weng et al. 2015; Marson et al. 2017; Campos et al. 2019; Hernández-Zamora & Martínez-Jerónimo 2019; Streit et al. 2019). Three milliliters of filtered and quenched samples at different elapsed times were used for full absorbance spectrum scan analysis with wavelengths ranged from 200 to 800 nm with 1 nm intervals. The absorbance of each sample at wavelengths of 436, 525, and 620 nm was simultaneously measured to calculate the color number (CN) according to Equation (7) (Wang et al. 2020). The concentration of total organic carbon (TOC) was acquired using a TOC analyzer (Vario TOC Select, Elementar, Germany). The concentrations of total iron and Fe(II) in the solution were analyzed by measuring the absorption at 510 nm using o-phenanthroline photometry. Other parameters like pH and temperature were directly measured and were considered to be constant (R²). Decolorization of all five selected azo dyes by PS/FeS fitted pseudo-first-order kinetics well. The kobs values of 0.243 min⁻¹ and 0.405 min⁻¹ were obtained by fitting the sharp degradation phase of DB 15 and SR 80 between 0 and 5 minutes. By comparing degradation efficiency of three red dyes, i.e. AR AC, DR 81 and SR 80 separately affiliated to monoazo, disazo, and polyazo dye in this study, the degradation capability of PS/FeS to azo dyes was apparently negatively correlated to the number of azo groups. It is

\[
CN = \frac{A^2_{436} + A^2_{525} + A^2_{620}}{A_{436} + A_{525} + A_{620}}
\]

where \(A_{436}, A_{525}, \text{ and } A_{620}\) are the absorbance values of the samples at wavelengths of 436, 525, and 620 nm, respectively:

\[
\ln \frac{C_t}{C_0} = -k_{obs}^1 t
\]

where \(C_t\) and \(C_0\) refers to the concentration of the specific azo dyes at times \(t\) and 0 (min). The \(k_{obs}^1\) are the rate constants of the pseudo-first-order reaction kinetics models.

**RESULTS AND DISCUSSION**

**Degradation of different azo dyes by PS/FeS**

Five kinds of azo dyes distributed in three principal colors of dyestuff were tested for their ability to be degraded by PS/FeS. As shown in Figure 2, PS/FeS was an efficient system by which to break down the azo dye molecules, and more than half of the feeding azo dyes could be degraded within 60 minutes. Except for DY 12, the other four dyes exhibited similar degradation patterns, most of the degradation was quickly completed in about ten minutes during the reaction process, the degradation rates in the 60th minute reached 95.53 ± 1.33%, 96.24 ± 0.71%, 97.70 ± 1.14%, and 97.94 ± 0.92% for DR 81, DB 15, SR 80, and AR AC by PS/FeS, respectively. DY 12 seemed to be the most difficult dyes among them, and the degradation rate of DY 12 was calculated to be only 19.78 ± 1.00% in the first 10 minutes. A sharp decline in the concentration of DY 12 was not observed in the following reaction time, and the degradation rate was 56.40 ± 2.01% in the 60th minute. The rate constants (kobs) of azo dye decolorization as shown in Figure 2 were analyzed using pseudo-first-order kinetics and were confirmed by the square of the correlation coefficient (R²). Decolorization of all five selected azo dyes by PS/FeS fitted pseudo-first-order kinetics well. The kobs values of 0.243 min⁻¹ and 0.405 min⁻¹ were obtained by fitting the sharp degradation phase of DB 15 and SR 80 between 0 and 5 minutes. By comparing degradation efficiency of three red dyes, i.e. AR AC, DR 81 and SR 80 separately affiliated to monoazo, disazo, and polyazo dye in this study, the degradation capability of PS/FeS to azo dyes was apparently negatively correlated to the number of azo groups. It is

![Figure 2](https://example.com/figure2.png)

**Figure 2** Decolorization performance of five azo dyes by PS/FeS. (DR 81): [DB 15], [DY 12]; [AR AC]; [SR 80] = 0.03 mM, [FeS] = 2 mM, [PS] = 3 mM; temperature = 25 ± 2 °C, pH = 7.14 ± 0.24. The results of degradation kinetics and prolonged degradation of DY 12 by PS/FeS are shown in the inset in Figure 2.
speculated that more azo groups within azo dyes could improve the probability of radicals produced by PS/FeS to attack and break down the dyes. Moreover, DY 12 was the most tenacious dye and resistant to degradation among the three disazo dyes, while DR 81 and DB 15 were broken down quickly and apparently exhibited almost indistinguishable decomposition rates, which meant that DY 12 was a restriction factor if these three disazo dyes were present in combined pollution (Fig. S2).

Decolorization of DR 81 by a PS oxidation process based on different activators

Decolorization of DR 81 by utilizing FeS as a PS catalyst in an heterogeneous system to initiate sulfate radical formation was compared with the other common approaches applied for PS activation. The results are shown in Figure 3. FeS alone barely hardly or adsorbed DR 81, the concentration of DR 81 remained unchanged throughout the 60 minutes. Although possessing strong oxidizing properties, PS alone was also unable to break down DR 81, and a negligible removal ratio (9.51 ± 2.00%) was achieved during this period. FeS, Fe$^{2+}$, Fe$^{0}$ and heat in this study all were capable of activating PS to facilitate degradation of DR 81. Fe$^{2+}$ should be one of the most effectively activators ($k_{obs}^{1} = 0.536$ min$^{-1}$ from 0 to 5 minutes) compared with the other methods, replenishment with fresh Fe$^{2+}$ was recommended to be necessary once to restart the homogenous system and to initiate another sulfate radical formation process (Zhang et al. 2020). The activation efficiency obviously was increased by using a higher temperature, for instance, 60 °C ($k_{obs}^{1} = 0.284$ min$^{-1}$ from 0 to 10 minutes) compared with 40 °C ($k_{obs}^{1} = 0.03$ min$^{-1}$ from 0 to 60 minutes) when implementing the PS activation process by taking heat into consideration. By coincidence, newly produced azo dye effluents generally had a relative high temperature. Utilizing PS oxidation with heat as the activation approach to decolor these azo dyes wastewater was economically feasible. However this technique lost its appeal and it became unfeasible to treat azo dyes that were at normal temperature or which even had already been released into the environment. FeS as a PS activator for DR 81 decomposition performed noticeably well ($k_{obs}^{1} = 0.233$ min$^{-1}$ from 0 to 10 minutes) and was superior to Fe$^{0}$ ($k_{obs}^{1} = 0.132$ min$^{-1}$ from 0 to 30 minutes), another commonly applied PS activator to initiate sulfate radical formation. As well as sodium PS used in this research, potassium and ammonium PS activated by FeS were also an effective means to decontaminate azo dyes (Fig. S3). Therefore, after comprehensive consideration, the application of PS oxidation processes based on FeS as the activator (PS/FeS) for azo dyes decomposition is a realistic prospect.

The influence of quenching agents on DR 81 decomposition by PS/FeS

Radical quenching experiments were performed by adding EtOH and TBA to determine the radical species formed in PS/FeS and their contributions to removal of DR 81. The decolorization performance of PS/FeS within either EtOH or TBA as well as PS/FeS alone on DR 81 are shown in Figure 4.

![Figure 3](image-url) | Decolorization of DR 81 by PS activated with different activators. ([DR 81]$_{0}$ = 0.03 mM, [FeS]$_{0}$ = [Fe$^{0}$]$_{0}$ = [FeSO$_{4}$]$_{0}$ = 2 mM, [PS]$_{0}$ = 5 mM, temperature = 25 ± 2 °C, pH$_{0}$ = 7.04 ± 0.13). The results of degradation kinetics are shown in the inset in Figure 3.

![Figure 4](image-url) | The influence of quenching agents on DR 81 decomposition by PS/FeS. ([DR 81]$_{0}$ = 0.03 mM, [FeS]$_{0}$ = 2 mM, [PS]$_{0}$ = 5 mM, [EtOH]$_{0}$ = 1 M, [TBA]$_{0}$ = 1 M, temperature = 25 ± 2 °C, pH$_{0}$ = 7.24 ± 0.22).
Degradation efficiencies were both greatly suppressed by adding EtOH or TBA into the heterogeneous reaction system. Although degradation rates increased with time elapsed, 6.15 ± 0.10% and 43.14 ± 2.87% of DR 81 were separately removed by extra feeding with EtOH or TBA throughout the 60 minutes, and was 88.17% and 51.16% lower than the control with PS/FeS alone. Generally, EtOH is regarded as scavenger for both •OH and SO$_4$$^\bullet$ at reaction rates of 1.2–2.8 × 10$^9$ M$^{-1}$s$^{-1}$ and 1.6–7.7 × 10$^7$ M$^{-1}$s$^{-1}$, respectively (Deng et al. 2014; Chen et al. 2017). TBA, meanwhile, is mainly considered as an •OH scavenger due to its much higher reaction rate with •OH (3.8–7.6 × 10$^9$ M$^{-1}$s$^{-1}$) compared with SO$_4$$^\bullet$ (4.0–9.1 × 10$^5$ M$^{-1}$s$^{-1}$) (Chen et al. 2017; Fan et al. 2017). In the heterogeneous reaction system, both •OH and SO$_4$$^\bullet$ were responsible for breaking down DR 81. In addition, the dosage of EtOH did not thoroughly stop the reaction, which meant some other unidentified radical species might exist and participate in degrading DR 81. The specific proportions of •OH, SO$_4$$^\bullet$ and other unidentified radical species in DR 81 decomposition are listed in Figure 4 in the form of a cumulative column chart and the computational process is shown in Figure S1. The proportion of •OH in DR 81 decomposition gradually decreased and changed from 93.13% in the second minute to 54.25% in the 60th minute. Its contribution was replaced by SO$_4$$^\bullet$; the proportion of SO$_4$$^\bullet$ in DR 81 decomposition reached up to 39.25% in the 60th minute. By contrast, the proportion was only 4.95% in the second minute. The removal efficiency of DR 81 by the other unidentified radical species accounted for less than 10% throughout the 60 minutes. Contrary to expectations, the DR 81 reaction with •OH might play a crucial role throughout the 60 minutes, and indicated that SO$_4$$^\bullet$ formed through the PS reaction with FeS was capable of conversion into •OH according to Equations (9) and (10), a phenomenon commonly observed in other studies (Yuan et al. 2015; Chen et al. 2017; Fan et al. 2017; Suehnholz et al. 2020):

\[
SO_4^{\bullet} + H_2O \rightarrow HSO_4^{-} + OH^\bullet
\]  
\[
SO_4^{\bullet} + OH^- \rightarrow SO_4^{2-} + OH
\]

**Decolorization process of DR 81 by PS/FeS**

During DR 81 decolorization by PS/FeS, the spectra of samples at specific time intervals were captured and the results are presented in Figure 5. Before the reaction initiated, the spectra of DR 81 were characterized by one main band in the visible region and a narrow band in the ultraviolet region with absorbance peaks at approximately 500 and 295 nm, which respectively corresponded to the conjugate chromophore structure (–N=N–) of DR 81 and benzene rings bonding to the –N=N– groups (Weng & Tao 2018). After the reaction, the characteristic peak at 500 nm decreased quickly within 10 minutes and the peaks reduced to the minimum as the reaction proceeded. The destruction of the conjugate structure within DR 81 through the PS/FeS system was visible to the naked eye by color variation, as shown in inset graph in Figure 5. In addition, the change of CN with time also provided more evidence and confirmed the decomposition of the chromophore structure. Moreover, the disappearance of DR 81 in the first two minutes of the reaction was closely related to the strength of absorbance at 295 nm, probably related to the formation of aromatic fragments. The characteristic peaks of these aromatic intermediates then similarly decreased with time, which implied that these aromatic intermediates were further oxidized to cleave the benzene rings and form other intermittent products. Comparing the concentration and CN data, the description of the DR 81 oxidation process by TOC variation with time obtained differing results as exhibited in the inset graph in Figure 5. The whole decoloration process could be divide into two stages. TOC values in the first stage were relative stable in the first 5 minutes of the reaction, then it began to decline until a minimum value was observed at the end of the reaction, the TOC removal efficiency throughout the AOP finally in the 60th minute was calculated to be 72.38 ± 2.81%. For
comparison, the removal efficiency under the same conditions separately reached 94.30 ± 0.28% and 92.25 ± 1.85% calculated by the concentration and CN values. The change in the TOC values indicated that the breakdown of the conjugate structure and benzene rings within DR 81 was first completed within a fraction of the time by radicals present in the PS/FeS system. These intermediates then continue oxidation to form organic small molecular substances and eventually were mineralized to non-toxic products such as carbon dioxide and water. To acquire a better TOC removal efficiency, a prolonged reaction time was recommended to be necessary.

The whole AOP was performed under acidic conditions mainly ascribed to the acidic properties of PS (Nie et al. 2014; Wang et al. 2019). An initial pH of 7.00 ± 0.19 was linearly decreased to 3.26 ± 0.11 once PS was added, the pH of the system then became stable and the variation was limited to within 10% subsequently. Acidic conditions had a minor effect on dissolution of FeS, iron ions in the solution were maintained at a relatively low level throughout the 60 minutes. It is well known that Fe Fe(N) plays a crucial role in the continuous reaction with PS to stimulate the production of SO4(N), at the same time Fe Fe(N) was oxidized to Fe Fe(N), which meant Fe Fe(N) was constantly consumed during the reaction (Chen et al. 2017). The constant low concentration of ions in the solution meant that SO4(N) formed by PS reacting with Fe Fe(N) dissolved in the solution was theoretically impossible. Considering the crucial role of -OH on DR 81 breakdown and the constant acidic conditions of the PS/FeS system in this study, -OH produced in the solution according to Equation (9) (first-order kinetic constant of kobs < 3 × 10 s ) and Equation (10) (conducted under alkaline conditions) was also unfeasible (Neta et al. 1988; Suehnholz et al. 2020). Fan et al. (2017) proposed a heterogeneous activation mechanism in which surface Fe (II) species activated PS to simultaneously produce -OH and SO4(N); these radicals then diffused from the FeS surface into the solution to degrade the target contaminant. Most importantly, as shown in Equation (11), S(N) within FeS was responsible for regeneration of Fe(II) from Fe(III) at the FeS surface. It was therefore capable of mediating cycling of iron species, which resulted in less FeS breakdown throughout the reaction. The results of this study were probably another proof of this hypothesis:

\[ S^{2-} + 8Fe^{3+} + 4H_2O \rightarrow SO_4^{2-} + 8Fe^{2+} + 8H^+ \]  

The influence of coexisting substances on DR 81 breakdown by PS/FeS

Real azo dye effluents always coexist with other substances such as chloride ions, chelating agents and dyeing auxiliaries (Aleboyeh et al. 2012; Ding et al. 2017, 2019). In this study, sodium citrate, sodium EDTA, and sodium oxalate, three commonly used chelating agents in the printing and dyeing industries were selected as coexisting substances. The influence of these substances on azo dye decolorization by PS/FeS is presented in Figure 6. The three chelating agents had no influence on DR 81 decolorization with a molar ratio (chelating agent/DR 81) less than 2. A distinct consequence arose when the molar ratio was increased to 5, the influence of sodium citrate on azo dye oxidation is still negligible, the degradation rate reached 94.5% in 60 minutes, sodium oxalate at a concentration of 0.15 mM has a minor effect on azo dyes degradation. In total, 73.59% of DR 81 was removed during this period of time, however DR 81 decoloration by PS/FeS was almost completely inhibited when sodium EDTA was set at the same concentration. A higher concentration of these three chelating agents all had a negative influence on azo dye decolorization by PS/FeS, and the inhibition effect was the positive correlation with the concentration of chelating agents. As shown in Figure 6(d), the decoloration rates with concentration of chelating agents at 3 mM were 12.96%, 5.66%, and 1.82% in the 60th minute for sodium citrate, sodium EDTA, and sodium oxalate, respectively. Citrate, EDTA, as well as oxalate, all were effective chelating agents and play a crucial role in printing and dyeing industries. When attempting to purify azo dye effluents, these substances likewise became inhibitory. Fe(N) ions released from FeS, which was essential for PS activation, would immediately combine with these chelating agents, and azo dye decolorization by PS/FeS eventually was terminated.

Sustainable capacity of the heterogeneous PS/FeS system

For practical application of FeS as an activator in the PS/FeS system to conduct an AOP, the reusability of FeS is one of the most crucial issues that need to be considered. In this study, after DR 81 was depleted in the first cycle, the used FeS served as a PS activator for another six consecutive cycles and the results are shown in Figure 7. The DR 81 decolorization process of each cycle fitted pseudo-first-order kinetics well. DR 81 degraded the fastest in the first cycle by dosing fresh FeS as activator with a maximum
$k_\text{obs}^1$ of 0.198 min$^{-1}$ obtained. The $k_\text{obs}^1$ irregularly reduced in the following cycles with a minimum value of 0.024 min$^{-1}$ acquired in the last cycles. The decolorization rate of DR 81 was negatively correlated with the number of cycles, a phenomenon that probably could be attributed to inevitably loss of FeS in each cycle. DR 81, as well as the oxidation products, binding to the FeS surface in the previous cycle, and eventually resulting in inactivation of FeS in the following cycle, was also a reasonable explanation (Weng et al. 2018; Chen et al. 2011; Fan et al. 2017). However, the decolorization in each cycle initiated quickly without any delay, even when FeS was repeatedly used for seven consecutive cycles, and the decolorization efficiency of DR 81 in the seventh cycle still reached 77.68 ± 1.28% within 60 minutes, indicated that using recycled FeS as a PS activator for the successive removal of contaminates was feasible (Chen et al. 2017). In addition, the residual FeS solution, whether
or not exposed to oxygen atmosphere for 30 days, also exhibited a nearly indiscriminate catalytic performance on PS for the oxidative decomposition of DR 81 (Fig. S4), which further convinced us that it was an optimal option to select FeS as an activator for a PS oxidation process.

**CONCLUSIONS**

Most azo dyes are intentionally designed to resist degradation. Currently, AOPs, especially the PS oxidation process has proven to be effective in oxidation and mineralization of these kinds of refractory organic pollutants. Although PS alone only achieves a negligible treatment result, an extra dosing of appropriate amounts of activator, which promotes the formation of radicals, would improve the reaction activity of this approach. This study investigated the degradation of azo dyes by PS activated with FeS. The PS/FeS system exhibited a satisfactory catalytic activity on the breakdown of five selected azo dyes, which come in three principal colors of dyestuff and separately affiliated to monoazo, disazo, and polyazo dyes. Compared to degradation of DR 81 by PS or single FeS alone, the decolorization of DR 81 in the PS/FeS system was significantly accelerated by PS activated with FeS, which was comparable to another commonly applied PS activation measures such as heat at 60 °C or utilizing dissolved Fe(II) and was slightly superior to Fe0 powders under the same conditions. Quenching studies indicated that both SO4⁻ and -OH were formed and were responsible for the breakdown of DR 81 in the PS/FeS system, and that the -OH reaction with DR 81 -OH might be the crucial reaction. The decolorization of DR 81 in the PS/FeS system in this study was appropriately explained by a heterogeneous activation mechanism, which proposed that -OH and SO4⁻ were initially formed on the surface of FeS and then diffused from the FeS surface into the solution to facilitate the successive transformation of DR 81 from aromatic intermediates to finally mineralized products, such as carbon dioxide and water. It was speculated that S2²⁻ at the FeS surface had the potential to regenerate Fe(II) from Fe(III) and therefore was capable of mediating cycling of iron species. Although coexisting chelating agents at high concentrations had a negative influence on azo dye decolorization by PS/FeS, it was still an attractive AOP to be applied for azo dye degradation in real-world situations, considering the nearly indiscriminate decolorization performance in several consecutive cycles of using recycled FeS as a PS activator.

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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