Degradation of trichloroethylene by activated persulfate using a reduced graphene oxide supported magnetite nanoparticle

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Abstract

A reduced graphene oxide (rGO) supported magnetite nanoparticle (nFe_3O_4) composite ($\text{nFe}_3\text{O}_4/\text{rGO}$) was synthesized and shown for the first time to be an efficient persulfate activator to generate $\text{SO}_4^{\bullet-}$ for trichloroethylene (TCE) degradation. The degradation efficiency of TCE (0.15 mmol L^{-1}) was 98.6% within 5 min in the presence of 6.94 g L^{-1} $\text{nFe}_3\text{O}_4/\text{rGO}$ with an optimum mass ratio of 1:4 and persulfate concentration of 3.0 mmol L^{-1} . By dispersing nFe_3O_4 on the rGO surface, nanoparticle agglomeration was prevented and the aggregation of the rGO sheets was disrupted. Both the redox effect coupled in nFe_3O_4 and the electron transfer by functional groups containing oxygen on the surface of rGO enhanced the $\text{SO}_4^{\bullet-}$ generation. Given the identified free radical species and the characterization of the $\text{nFe}_3\text{O}_4/\text{rGO}$, a persulfate activation mechanism by $\text{nFe}_3\text{O}_4/\text{rGO}$ for the degradation of TCE

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was interpreted.

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1. Introduction

Chlorinated solvents such as trichloroethylene (TCE) have been frequently detected in groundwater because of their use in industrial processes and for dry-cleaning purposes [1,2]. TCE is listed as a priority pollutant by the United States Environmental Protection Agency (USEPA) [3-5], and chronic exposure to TCE via inhalation of vapors released from groundwater may cause cancer and other adverse effects on human health. Various remediation processes such as adsorption, biodegradation, reduction and catalytic oxidation have been employed to remove TCE from groundwater [6,7]. Among these, advanced oxidation processes based on sulfate free radical ($\text{SO}_4^{\bullet-}$) have been proposed for the effective degradation and mineralization of TCE [8-10].

Transition metals such as Fe(II), Co(II), Mn(II), Ce(II), Cu(II) and Ag(I) can be introduced for persulfate ($\text{S}_2\text{O}_8^{2-}$) activation to generate $\text{SO}_4^{\bullet-}$ [11], and homogeneous Fe(II) is an effective reagent for the production of $\text{SO}_4^{\bullet-}$ in accordance with the following reaction:

In a previous study, Liang et al. [12] used the homogeneous $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$ system to remediate TCE in solution at pH 5.0, and found that the sulfate radical based system yielded the highest TCE degradation efficiency with a $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{TCE}$ molar ratio of 20/15/1. Higher Fe^{2+} concentrations did not result in more TCE degradation mainly due to the reaction

between excess Fe^{2+} and $\text{SO}_4^{\bullet-}$.

To minimize the competition of $\text{SO}_4^{\bullet-}$, attempt at using chelating agent of citric acid to manipulate the quantity of Fe^{2+} in solution was made [13]. Zero valent iron was also introduced as a heterogeneous persulfate activator to control the initial formation rate of $\text{SO}_4^{\bullet-}$ [14]. In our previous study, magnetite nanoparticle (nFe_3O_4) were developed as Fe(II) alternatives to activate persulfate for sulfamonomethoxine degradation [15]. However, due to the strong magnetic interaction and high surface energy, nFe_3O_4 particles tend to aggregate thereby partly diminishing their potency for persulfate activation.

Graphene is a promising material and has attracted tremendous attention in recent years. Due to its atom-thick, two-dimensional sheet structure, graphene has a large specific surface area and extraordinary electronic transport. It can therefore immobilize a large number of particles, such as nanoscale zero valent iron, manganese bioxide and iron oxides for environmental application [16-18].

In this study, a reduced graphene oxide (rGO) supported magnetite nanoparticle composite ($\text{nFe}_3\text{O}_4/\text{rGO}$) was synthesized and examined as an efficient persulfate activator for TCE degradation. nFe_3O_4 dispersed on rGO surface would prevent particle agglomeration whilst the superior conductivity of rGO enables efficient electron transfer between nFe_3O_4 and adsorbed hydrophobic pollutants [19]. In addition, the intrinsic atom arrangements of carbon hybridization, pore structure, defective sites, and proper amounts of functional groups (especially the carbonyl groups) of rGO were accounted for persulfate activation to produce radicals [20]. The objectives of this study are to (1) synthesize and characterize a novel

nFe₃O₄/rGO composite that prevents aggregation of the magnetite nFe₃O₄ particles by precipitating them uniformly onto rGO sheets; (2) to evaluate the persulfate activation potency of the nFe₃O₄/rGO composite to facilitate degradation of TCE in aqueous solution and (3) to understand the activation mechanism of persulfate in the presence of nFe₃O₄/rGO.

2. Materials and Methods

2.1. Materials

TCE standard solution (1000 µg mL⁻¹) was purchased from Amresco (Solon, OH, USA). FeSO₄·7H₂O, Fe(NO₃)₃·9H₂O, H₂O₂, Na₂S₂O₈, NH₃·H₂O, NaOH and KMnO₄ were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphite powder (SP1) purchased from Bay Carbon (Bay City, MI) was used to prepare rGO. 5,5-Dimethyl-1-Pyrroline-N-Oxide (DMPO) was obtained from Aladdin Industrial Corporation. All the chemicals were of analytical grade and used as received. Deionized water was used in the present work.

2.2. Preparation of nFe₃O₄/rGO composite

Graphene oxide (GO) was prepared from graphite according to a modified Hummers method [21], and rGO was synthesized by reduction of GO using sodium borohydride [22]. nFe₃O₄ was prepared through a reverse co-precipitation method using NH₃·H₂O [15]. The synthesis procedure of nFe₃O₄/rGO composite was described as follows: 0.10 g graphene was dispersed in 3.0 mol L⁻¹ of NH₃·H₂O with total volume of 50 mL, then placed in an ultrasound bath (25Hz, 100W). 0.12 g FeSO₄·7H₂O and 0.35 g Fe(NO₃)₃·9H₂O were completely dissolved in 10 mL water and added into the above solution at a rate of 10 mL min⁻¹. After 30 min reaction and cooling to room temperature, the nFe₃O₄/rGO composites

were collected by centrifuge, washed with deionized water until pH was neutral, and then dried under vacuum at 60 °C. The prepared composite was nFe₃O₄/rGO with a nFe₃O₄ to rGO mass ratio of 1:1 as measured by thermogravimetric analysis. nFe₃O₄/rGO composites with different nFe₃O₄ to rGO mass ratios were also prepared with the above synthesis process.

2.3. Characterization

The surface morphology of the materials was characterized using a Hitachi S-4800 scanning electron microscope (SEM) with 15 kV acceleration voltage. The X-ray diffraction (XRD) patterns of nFe₃O₄, rGO and nFe₃O₄/rGO composites were determined with a diffractometer (XRD-7000S/L, Shimadzu) with Cu K_α radiation. X-ray photoelectron spectra (XPS) were measured on Axis Ultra spectrometer (Kratos) using a Al K_α radiation excitation source. Fourier transform infrared spectroscopy (FT-IR) was conducted in the range from 400 to 4000 cm⁻¹ to identify the surface functional groups using the Nicolet iS50 (Thermo Fisher Scientific) spectrometer. Raman spectra ranging from 500 to 2500 cm⁻¹ were recorded on a Raman spectrometer (DXR, Thermo Fisher Scientific) with an excitation source of 532 nm, and the Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) analysis was performed with a Micromeritics ASAP 2020 accelerated surface area and porosimetry (ASAP) system .

2.4. Batch Reaction

Sacrificial batch experiments were carried out in a rotary shaker with 150 rpm at room temperature. Typically for TCE degradation, 0.15 mmol L⁻¹ TCE and 3.0 mmol L⁻¹ persulfate were in fully filled 20 mL borosilicate glass. The desired amounts of materials (i.e. nFe₃O₄, rGO and nFe₃O₄/rGO with different mass ratios) were added, and the glass vials were capped tightly. Control units were also set up under the same conditions with neither activators nor

persulfate. Solutions in the borosilicate glass were sampled and filtered through membranes for determination at desired time. The concentrations of TCE, dissolved iron and total organic carbon (TOC) were measured, respectively. Sacrificial batches were set up in triplicate, and the mean values were reported.

2.5. Analytical methods

The concentrations of TCE were measured by a headspace technique using an Agilent 7890A-5975C Gas Chromatograph-Mass Spectrometer (GC-MS) with a DB-624 (30 m $\times$ 0.25 mm $\times$ 1.40 μ m) chromatographic column. A 1,10-phenanthroline monohydrate spectrophotometry method was introduced to determine dissolved iron in aqueous solution on a Unico UV-2000 spectrophotometer. Total organic carbon (TOC) was calculated with an Analytik Jena AG TOC analyzer. The Electron Spin Resonance (ESR) spectra were received from a 10.00 mW microwave power Bruker ESR 300E spectrometer.

3. Results and discussion

3.1. Characterization of nFe₃O₄/rGO

The morphologies of the prepared materials were characterized by SEM. nFe₃O₄ particles were spherical with a diameter of about 20 nm and rGO had a morphology of crumpled sheet (Fig. 1(a) and (b) respectively). For the nFe₃O₄/rGO composite, nFe₃O₄ was dispersed on the surface of graphene homogeneously (Fig.1(c)). The phase structures of nFe₃O₄, rGO and nFe₃O₄/rGO were obtained from XRD spectrum (Fig. 1(d)). The XRD patterns of Fe₃O₄ diffraction peaks with 2θ values of 30.1, 35.4, 43.1, 53.6, 57.1 and 62.7° were observed. These can be indexed as typical Fe₃O₄ diffractions of (220), (311), (400), (422), (511) and (440) respectively (JCPDS 79-0419) [15]. The two representative peaks at

2 θ values of 25.1 and 43.0° were ascribed to (002) and (100) diffraction of rGO sheets [23]. In the XRD spectra of nFe₃O₄/rGO, both the nFe₃O₄ and the rGO diffraction peaks were observed, indicating that nFe₃O₄ was loaded onto the rGO surface.

Fig. 1(e) shows the Raman spectra of the composites. The D band (1350 cm⁻¹) is ascribed to disordered carbon and the G band (1596 cm⁻¹) corresponded to sp² hybridized carbon. The ratio values of I_D/I_G for rGO and nFe₃O₄/rGO composite were 1.15 and 1.17 respectively, which indicated that the synthesized material was nFe₃O₄/rGO as anticipated and in accordance with previous research [24]. The FT-IR spectra of rGO and nFe₃O₄/rGO are shown in Fig. 1(f). In the rGO spectrum, the peak at 1726 cm⁻¹ is assigned to the C=O vibration of rGO whilst the peak at 1585 cm⁻¹ is assigned to the carbon backbone of the rGO sheets [25]. The signal at 1132 cm⁻¹ indicated the presence of epoxy functional groups, and the peak at 1092 cm⁻¹ corresponds to the deformed C–O stretching vibrations [26]. After nFe₃O₄ is dispersed on the rGO surface, a new peak appears at 583 cm⁻¹, which can be assigned to the stretching vibration of Fe–O [19].

3.2. TCE degradation in the nFe₃O₄/graphene-persulfate system

TCE adsorption onto the prepared materials was tested before examining TCE degradation in the nFe₃O₄/RGO-persulfate system. After shaking for 1 h, equilibrium was established, and the data were shown in Fig. 2(a). TCE removal efficiencies were 5.2% and 19.7% with the addition of 1.39 g L⁻¹ nFe₃O₄ and 5.55 g L⁻¹ rGO, respectively. Adding nFe₃O₄/rGO composite with nFe₃O₄ to rGO mass ratios of 1:1, 1:2, 1:4 and 1:6 (with the same concentration of 1.39 g L⁻¹ nFe₃O₄), resulted in TCE removal efficiency of 13.1%, 16.1%, 24.6% and 18.4% , respectively.

The extent of TCE degradation with persulfate activated by nFe_3O_4 , rGO and various mass ratios of $\text{nFe}_3\text{O}_4/\text{rGO}$ composites were conducted, and the control tests in the absence of persulfate and activators was also set up which showed less than 2% TCE loss under the test conditions (curve 1 in Fig. 2(b)). From the data in Fig. 2(b), persulfate alone was unable to significantly degrade TCE in 5 min. Adding 1.39 g L^{-1} nFe_3O_4 , resulted in TCE degradation efficiency of 48.9% after 5 min reaction (curve 2 in Fig. 2(b)). Such a low TCE degradation efficiency might be due to aggregation of the nFe_3O_4 particles with a relative small S_{BET} value of $38.44 \text{ m}^2 \text{ g}^{-1}$. TCE degradation efficiency of 31.8% was obtained when 5.55 g L^{-1} graphene was added in the presence of 3.0 mmol L^{-1} persulfate (curve 3 in Fig. 2(b)). This was slightly higher than 24.6% by adsorption effect of rGO, suggesting its weak activation ability for persulfate [20]. TCE degradation efficiencies of 67.9%, 79.2%, 98.6%, and 89.3% were achieved for the $\text{nFe}_3\text{O}_4/\text{rGO}$ with mass ratios of 1:1, 1:2, 1:4 and 1:6, respectively. In comparison with nFe_3O_4 , $\text{nFe}_3\text{O}_4/\text{rGO}$ composite showed better efficiency for persulfate activation. rGO's layer structure gives S_{BET} value of $252.09 \text{ m}^2 \text{ g}^{-1}$, which is lower than the theoretical graphene S_{BET} value of $2620 \text{ m}^2 \text{ g}^{-1}$ [27]. The relative small S_{BET} value of rGO was potentially due to the agglomeration of the rGO layers during the reduction process [28]. nFe_3O_4 particles were well distributed on the rGO sheet surfaces, which could prevent their aggregation efficiently and disrupting the arrangement of the rGO sheets. Thus, TCE degradation efficiency was enhanced as the rGO mass ratio increased from 1:1 to 1:4 in $\text{nFe}_3\text{O}_4/\text{rGO}$ composites. However, further increases in rGO content of $\text{nFe}_3\text{O}_4/\text{rGO}$ mass ratio from 1:4 to 1:6 might result in an increased aggregation of the rGO sheets, as illustrated from the reduction of their S_{BET} value from $140.33 \text{ m}^2 \text{ g}^{-1}$ to $126.72 \text{ m}^2 \text{ g}^{-1}$. This led to a

decreased TCE removal efficiency of 89.3% (curve 7 in Fig. 2(b)). The phenomenon concurs with observations made for a MnO_2 /graphene composite used for the catalytic ozonation of gaseous toluene [29].

3.3. Effects of reaction parameters on the degradation of TCE

The effects of different concentrations of persulfate and $\text{nFe}_3\text{O}_4/\text{rGO}$ with a mass ratio of 1:4 on TCE degradation at pH 6.2 are shown in Fig. 2(c) and Fig. 2(d). It can be seen that TCE degradation efficiency increased rapidly from 34.5% to 84.1% and a maximum of 98.6% as persulfate concentration increased from 1.0 mmol L^{-1} to 2.5 mmol L^{-1} and 3.0 mmol L^{-1} respectively with a fixed $\text{nFe}_3\text{O}_4/\text{rGO}$ concentration of 6.94 g L^{-1} . This high TCE degradation efficiency demonstrates the excellent ability of the prepared $\text{nFe}_3\text{O}_4/\text{rGO}$ composite for persulfate activation.

It has been reported that $\text{SO}_4\bullet^-$ was the dominant radical species in Fe_3O_4 -persulfate system when the solution pH was less than 7.0 [15]. However, $\bullet\text{OH}$ was preferably produced in the presence of persulfate and 900°C heat reduced rGO [20]. At a persulfate concentration of 3.0 mmol L^{-1} in aqueous solution, the increase in the amount of $\text{nFe}_3\text{O}_4/\text{rGO}$ might yield more $\text{SO}_4\bullet^-$ and increased TCE degradation efficiency as $\text{nFe}_3\text{O}_4/\text{rGO}$ concentration increased from 0 to 6.94 g L^{-1} (Fig. 2(d)). However, above 6.94 g L^{-1} $\text{nFe}_3\text{O}_4/\text{rGO}$, TCE degradation efficiency decreased with increasing $\text{nFe}_3\text{O}_4/\text{rGO}$ concentration. When $\text{nFe}_3\text{O}_4/\text{rGO}$ was added in excess of 6.94 g L^{-1} , more $\text{SO}_4\bullet^-$ was generated but could not react fully with the TCE. The quenching reaction, according to Eq. (2), between excess Fe(II) on the nFe_3O_4 surface and $\text{SO}_4\bullet^-$ is rapid and leads to a large amount of $\text{SO}_4\bullet^-$ consumption [11]. Moreover, it is reported by Buxton et al. [30] that both scavenging between $\text{SO}_4\bullet^-$ species

themselves and competing interaction between $\text{SO}_4^{\bullet-}$ and persulfate would consume the abundant $\text{SO}_4^{\bullet-}$ in solution (Eq. (3) and Eq. (4)). Hence, the dosage of $\text{nFe}_3\text{O}_4/\text{rGO}$ was optimized at 6.94 g L^{-1} with 3.0 mmol L^{-1} persulfate.

The effect of pH on TCE degradation was also investigated in the presence of $\text{nFe}_3\text{O}_4/\text{rGO}$ and persulfate (Fig. 2(e)). In an acidic solution, additional $\text{SO}_4^{\bullet-}$ could be formed due to acid catalyzation [31]. Such higher radical concentrations result in increased TCE degradation, and nearly complete TCE degradation efficiency was achieved. Under alkaline conditions, comparatively more $\bullet\text{OH}$ might be formed (cf Eq. (6)). These $\bullet\text{OH}$ would be scavenged by sulfate ions in persulfate oxidation system, and result in a decreased TCE degradation efficiency as pH increased [32]. The reaction stoichiometric efficiencies (RSE) defined as the number of TCE moles degraded to the number of persulfate moles consumed at a specific time interval ($\Delta[\text{TCE}]/\Delta[\text{persulfate}]$) were calculated at pH values from 3.0 to 11.0, and the highest RSE for the pH 7.0 was observed (inset in Fig. 2(e)). It can be seen from Fig. 2(e) that though TCE degradation efficiency decreased as the solution pH increased, the efficiency was still 83.1% at pH 9.0 and 72.0% at pH 11.0. The relatively low drop in TCE degradation efficiency observed throughout the experimental range of pH (pH of 3.0 to 11.0) indicates that the $\text{nFe}_3\text{O}_4/\text{rGO}$ -persulfate system can remediate polluted water efficiently over a wide range of pH values.

3.4. Mineralization and dechlorination of TCE

To evaluate the mineralization of TCE in the presence of persulfate activated by

nFe₃O₄/rGO, the TOC removal of TCE was monitored with the TOC analyzer. The complete mineralization of one mole TCE will consume three moles S₂O₈²⁻ in accordance with Eq. (5).

In the investigated system of nFe₃O₄/rGO-persulfate, the initial concentration of TCE was 0.15 mmol L⁻¹, and the complete mineralization of TCE required 0.45 mmol L⁻¹ S₂O₈²⁻. It can be seen from Fig. 3(a) that with the addition of 0.45 mmol L⁻¹ S₂O₈²⁻, the TOC removal after 5 min was only 15.3%, corresponding to the TCE degradation efficiency of 18.8% by GC-MS results. The low TOC removal was owing to a small amount of SO₄•⁻ in aqueous solution with low concentration of persulfate. The increase in persulfate concentration to 3.0 mmol L⁻¹ caused TOC removal efficiency of 54.5% with TCE degradation efficiency of 98.6%. To enhance TCE mineralization further, 6.0 mmol L⁻¹ persulfate was added and resulted in TOC removal of 81.7%, with complete TCE degradation observed in 5 min. The results were in concordance with published data where mineralization extent improved when persulfate concentration is increased in solution [33,34].

For the three different persulfate concentrations used in this study, TCE dechlorination efficiency was also monitored (Fig. 3(b)). When 0.45 mmol L⁻¹ persulfate was added, Cl⁻ but no ClO₃⁻ was observed in the solution. After 5 min reaction, 0.062 mmol L⁻¹ Cl⁻ was detected, accounting for the TCE dechlorination efficiency of 13.7%, which was slightly lower than the TOC removal of 15.3%. When the persulfate concentration increased to 3.0 mmol L⁻¹, 0.19 mmol L⁻¹ Cl⁻ and 0.023 mmol L⁻¹ ClO₃⁻ were detected, indicating a TCE dechlorination efficiency of 47.3%. The appearance of ClO₃⁻ was mainly due to the oxidation of Cl⁻ by the generated radicals. For further increase in the persulfate concentration to 6.0

mmol L⁻¹, 0.29 mmol L⁻¹ Cl⁻ and 0.042 mmol L⁻¹ ClO₃⁻ were measured, and the total amount of Cl⁻ and ClO₃⁻ demonstrated a TCE dechlorination efficiency of 73.7%, corresponding to TOC removal of 81.7% obtained from TOC analyzer.

3.5. Identification of the free radical species in the nFe₃O₄/rGO-persulfate system

In the nFe₃O₄/rGO-persulfate system, free radical species are responsible for the degradation and mineralization of organic contaminants due to their high oxidation ability [13]. At different pH values, two main species of free radicals of SO₄•⁻ and •OH may be produced for the activation of persulfate. SO₄•⁻ can be generated with the decomposition of persulfate and •OH may be produced with the effect of OH⁻ under alkaline conditions (Eq. (6)). In addition the reaction between SO₄•⁻ and H₂O, presented in Eq. (7) [34], can also accounted for •OH generation.

To identify the dominant reactive free radical species in the presence of persulfate and nFe₃O₄/rGO at different pH values, radical quenching tests were performed. Alcohols with and without α-hydrogen, having different rate constants with radical species, were added to the reaction solution. Ethanol (EtOH, containing R-hydrogen) reacts with •OH and SO₄•⁻ at high rates: the rate constants are (1.2~2.8) × 10⁹ and (1.6~7.7) × 10⁷ mol L⁻¹ s⁻¹ with the reaction of SO₄•⁻ and •OH, respectively. Tert-butyl alcohol (TBA, without R-hydrogen) reacts with SO₄•⁻ and •OH at different rates: the rate constant for •OH is (3.8~7.6) × 10⁸ mol L⁻¹ s⁻¹, much greater than (4~9.1) × 10⁵ mol L⁻¹ s⁻¹ for the reaction with SO₄•⁻ [35]. Therefore, by adding the EtOH and TBA as quenching agents, the dominant free radicals from the

activation of persulfate can be clarified.

TCE was completely degraded in 5 min without quenching agents when pH ranged from 3.0 to 11.0 with addition of 6.0 mmol L⁻¹ of persulfate (curve 1 in Fig. 4). At pH value of 7.0 as illustrated in Fig. 4, 55.7% of TCE degradation efficiency and no TCE degradation were observed after the addition of 600.0 mmol L⁻¹ TBA and 600.0 mmol L⁻¹ EtOH (molar ratio of quenching agent/persulfate/TCE was 4000/40/1), respectively. The radical quenching effect for TBA was smaller than that for ethanol indicated that SO₄•⁻ was the main radical for TCE degradation (An approximate of 55.7% TCE was degraded by SO₄•⁻) [34,36]. As pH increased from 9.0 to 11.0 the radical quenching effect of TBA increased, indicating that •OH was produced, which was responsible for TCE degradation. In addition, the radical quenching effect of TBA at pH 11.0 was greater than that at pH 9.0, suggesting that more •OH radicals were being generated and played an increasingly significant role during the TCE degradation process.

To obtain direct evidence of the radical species during the activation process, ESR was utilized at different pH values. The spin trapping agent of DMPO could react with SO₄•⁻ or/and •OH to generate DMPO-SO₄•⁻ or/and DMPO-•OH adduct ($a_H = 15.6$ and $a_N = 14.9$ for DMPO-SO₄•⁻, $a_N = 13.2$ G, $a_H = 9.6$ G, $a_H = 1.48$ G, and $a_H = 0.78$ G for DMPO-•OH). The SO₄•⁻ and •OH can be identified from the different hyperfine splitting peaks from generated DMPO-SO₄•⁻ and DMPO-•OH respectively [20, 37]. From the results shown in Fig. 5(a), the predominant radical was SO₄•⁻ at pH 3.0 and 7.0. At pH 9.0, both SO₄•⁻ and •OH were detected, indicating the generation of •OH proceeded in accordance with Eq. (6). At pH 11.0, the reaction for •OH generation accelerated rapidly, and the dominant signal of •OH was

observed in ESR spectra.

3.6. Activation mechanism of persulfate in presence of nFe₃O₄/rGO

To explore the activation mechanism of persulfate in the presence of nFe₃O₄/rGO, the dissolved irons (Fe²⁺ and Fe³⁺) in the presence of 6.94 g L⁻¹ nFe₃O₄/rGO and 3.0 mmol L⁻¹ persulfate were detected, and 0.04 mmol L⁻¹ Fe²⁺ and 0.17 mmol L⁻¹ Fe³⁺ were measured after the reaction (Fig. 2(f)). In comparison with the amount of added iron in nFe₃O₄/rGO composite, the total dissolved iron could be ignored in the nFe₃O₄/rGO system, since the molar ratio of dissolved iron to added nFe₃O₄ was only 3.5%, and such an amount of dissolved iron only led to 5.0% TCE degradation in 5min. Similar to Fe²⁺ in solution, the surface lattice Fe(II) of nFe₃O₄ may be assumed to have a proper redox potential, and the transformation of Fe(II) to Fe(III) can induce the activation of persulfate to generate SO₄•⁻.

XPS spectra of nFe₃O₄/rGO were recorded in order to better understand the roles of Fe(II) and Fe(III) species of Fe₃O₄ in the activation of persulfate before and after the TCE degradation experiment. As shown in Fig. 5(b), the peaks of Fe(2p) were at 709.9 and 711.2 eV for the fresh nFe₃O₄/rGO, which were assigned to Fe(II) and Fe(III) [38]. Based on the deconvolution of Fe(2p) envelope and peak area, the percentages of Fe(II) and Fe(III) were 31.3% and 68.7% respectively. After 3 times cycle for TCE degradation, the percentage of Fe(III) increased to 100%, indicating that electron transfer had occurred from Fe(II) to persulfate on the surface of Fe₃O₄/graphene, accounting for persulfate activation and Fe(III) generation. In addition, to eliminate signal interferences of graphene, XRD patterns of pure nFe₃O₄ instead of nFe₃O₄/rGO before and after the reaction were examined (Fig. 5(d)). After reaction, a new peak at 22.3° of used nFe₃O₄ appeared, indicating the generation of γ-Fe₂O₃.

(JCPDS 4-0755) through the oxidation of $n\text{Fe}_3\text{O}_4$ in the presence of persulfate [39,40]. The XRD data also confirmed the transformation of Fe(II) to Fe(III) during activation, concurring with the XPS results.

C(1s) spectra of $n\text{Fe}_3\text{O}_4/\text{rGO}$ before and after the reaction were also measured. It can be seen from Fig. 5(c) that C–C (284.5 eV), C–OH (286.5 eV), C=O (288.1 eV) and COOH (289.0 eV) groups were detected, the contents of 54.8%, 35.1%, 1.1% and 9.0% for fresh $n\text{Fe}_3\text{O}_4/\text{rGO}$ [41]. After reaction, the contents of C–OH and COOH groups decreased to 31.7% and 5.9%, respectively, and no C=O group was observed for the used $n\text{Fe}_3\text{O}_4/\text{rGO}$. The decrease of functional groups containing oxygen on the surface of rGO before and after reaction indicated that rGO is acted as an electron transfer medium during persulfate activation. By proton release, C–OH and COOH groups were transformed to organic radicals of $\text{CO}\cdot$ and $\text{COO}\cdot$, while $\text{SO}_4^{\cdot-}$ and $\text{HSO}_4^{\cdot-}$ were generated after activation [42]. Though C=O group of 900°C heat reduced rGO were accounted for $\cdot\text{OH}$ production reported by Duan et al. [20], no obvious $\cdot\text{OH}$ signal was observed in the $n\text{Fe}_3\text{O}_4/\text{rGO}$ -persulfate system when pH values were less than 7.0.

On the basis of the above results, the mechanism of persulfate activation in the presence of $n\text{Fe}_3\text{O}_4/\text{rGO}$ and the TCE degradation process were proposed in Fig. 6. Firstly, $n\text{Fe}_3\text{O}_4$ was well dispersed on the surface of graphene through Fe–O bonding, $\text{SO}_4^{\cdot-}$ was then generated from persulfate by the unveiled activation sites of Fe(II) on $n\text{Fe}_3\text{O}_4/\text{rGO}$ surface. By transferring one electron to persulfate, Fe(II) was oxidized to Fe(III), and formed $\gamma\text{-Fe}_2\text{O}_3$ after activation. Secondly, C–OH and COOH groups on rGO surface would release organic radicals to produce $\text{SO}_4^{\cdot-}$, and the electron transferred from rGO to persulfate was

accelerated via the interface of the hydrophilic moiety of graphene. Once $\text{SO}_4^{\bullet-}$ was produced, it participated in the reaction through electron transfer process to form the TCE radical cation ($\text{TCE}^{\bullet+}$) that reacted rapidly with H_2O via hydroxyl abstraction or addition reaction to generate (hydroxyl) TCE radicals ((OH)TCE $\bullet$). In addition, if pH was above 7.0, the generated $\text{SO}_4^{\bullet-}$ would react with OH^- to produce $\bullet\text{OH}$, which reacted preferentially with the TCE molecule to generate (OH)TCE $\bullet$ through hydrogen abstraction or addition [15]. With the effect of $\text{SO}_4^{\bullet-}$ and the produced $\bullet\text{OH}$ at pH >7.0, efficient degradation and substantial mineralization of TCE was achieved.

4. Conclusions

nFe₃O₄/rGO was prepared and characterized as a persulfate activator for efficient TCE degradation in aqueous solution. Dispersion of nFe₃O₄ on rGO surface prevented its agglomeration and disrupted rGO sheets arrangement, accounting for TCE degradation efficiency of 98.6% in 5 min. The redox effect coupled in nFe₃O₄ and the electron transfer through functional groups containing oxygen on the surface of rGO promoted the generation of $\text{SO}_4^{\bullet-}$. The activation of persulfate in the presence of nFe₃O₄/rGO is shows promise for the remediation of TCE contaminated water.

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Figures Captions

Fig. 1. SEM images of (a) nFe_3O_4 ; (b) rGO; (c) $\text{nFe}_3\text{O}_4/\text{rGO}$; (d) XRD patterns of nFe_3O_4 , rGO and $\text{nFe}_3\text{O}_4/\text{rGO}$; (e) Raman spectra of rGO and $\text{nFe}_3\text{O}_4/\text{rGO}$ and (f) FT-IR spectra of rGO and $\text{nFe}_3\text{O}_4/\text{rGO}$.

Fig. 2. (a) Kinetic adsorption of TCE on (1) Fe_3O_4 , (2) rGO, (3) $\text{nFe}_3\text{O}_4/\text{rGO}$ with mass ratio of 1:1, (4) $\text{nFe}_3\text{O}_4/\text{rGO}$ with mass ratio of 1:2, (5) $\text{nFe}_3\text{O}_4/\text{rGO}$ with mass ratio of 1:4 and (6) $\text{nFe}_3\text{O}_4/\text{rGO}$ with mass ratio of 1:6; (b) kinetic data of TCE degradation in the systems of (1) $\text{Na}_2\text{S}_2\text{O}_8$, (2) $\text{nFe}_3\text{O}_4\text{-Na}_2\text{S}_2\text{O}_8$, (3) $\text{rGO-Na}_2\text{S}_2\text{O}_8$, (4) $\text{nFe}_3\text{O}_4/\text{rGO}$ (mass ratio of 1:1)- $\text{Na}_2\text{S}_2\text{O}_8$, (5) $\text{nFe}_3\text{O}_4/\text{rGO}$ (mass ratio of 1:2)- $\text{Na}_2\text{S}_2\text{O}_8$, (6) $\text{nFe}_3\text{O}_4/\text{rGO}$ (mass ratio of 1:4)- $\text{Na}_2\text{S}_2\text{O}_8$ and (7) $\text{nFe}_3\text{O}_4/\text{rGO}$ (mass ratio of 1:6)- $\text{Na}_2\text{S}_2\text{O}_8$; (c) effect of persulfate concentration on TCE degradation; (d) effect of $\text{nFe}_3\text{O}_4/\text{rGO}$ concentration on TCE degradation; (e) influence of initial solution pH on TCE degradation. (1) Square symbols represent TCE removal and (2) circles represent persulfate consumption; and (f) iron concentration in aqueous solution (1) before and (b) after reaction. Reaction conditions: the concentration of nFe_3O_4 itself or in $\text{nFe}_3\text{O}_4/\text{rGO}$ composite was 1.39 g L^{-1} , the concentration of rGO was 5.55 g L^{-1} , the concentration of $\text{Na}_2\text{S}_2\text{O}_8$ was 3.0 mmol L^{-1} , the concentration of TCE was 0.15 mmol L^{-1} , and the initial pH was 6.2.

Fig. 3. (a) Removal of TOC and (b) release of Cl^- and ClO_3^- in the presence of (1) 0.45 mmol L^{-1} , (2) 3.0 mmol L^{-1} and (3) 6.0 mmol L^{-1} persulfate during the degradation of TCE in the $\text{nFe}_3\text{O}_4/\text{rGO}$ -persulfate systems.

Fig. 4. TCE degradation (1) without EtOH and TBA, (2) with $600.0 \text{ mmol L}^{-1}$ TBA and (3) with $600.0 \text{ mmol L}^{-1}$ EtOH in the presence of $\text{nFe}_3\text{O}_4/\text{rGO}$ and $\text{Na}_2\text{S}_2\text{O}_8$ under different initial pH values within 5 min. Reaction conditions: the concentration of $\text{nFe}_3\text{O}_4/\text{rGO}$ was 13.88 g L^{-1} , the concentration of $\text{Na}_2\text{S}_2\text{O}_8$ was 6.0 mmol L^{-1} and the concentration of TCE was 0.15 mmol L^{-1} .

Fig. 5. (a) DMPO spin-trapping ESR spectra of $\text{SO}_4^{\bullet-}/\bullet\text{OH}$ radicals in the systems of $\text{nFe}_3\text{O}_4/\text{rGO}$ (mass

ratio of 1:4)- $\text{Na}_2\text{S}_2\text{O}_8$ -TCE at different pH values; (b) Fe 2p XPS spectra of $\text{nFe}_3\text{O}_4/\text{rGO}$ before and after the reaction; (c) C 1s XPS spectra of $\text{nFe}_3\text{O}_4/\text{rGO}$ before and after the reaction and (d) XRD patterns of nFe_3O_4 before and after reaction.

Fig. 6. A proposed mechanism for the degradation of TCE by $\text{nFe}_3\text{O}_4/\text{rGO}$ activation of persulfate.

Fig. 1

Fig. 2

Fig. 3

Fig.4

Fig. 5

Fig. 6

Graphical abstract