



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



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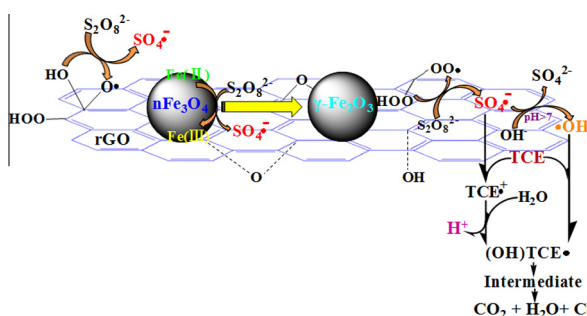
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HIGHLIGHTS

- $n\text{Fe}_3\text{O}_4/\text{rGO}$ was successfully prepared and characterized as persulfate activator.
- TCE was efficiently degraded at a wide range of pH from 3.0 to 11.0.
- High TOC removal and dechlorination efficiency were achieved.
- The possible mechanism of persulfate activation by $n\text{Fe}_3\text{O}_4/\text{rGO}$ was interpreted.

GRAPHICAL ABSTRACT



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ABSTRACT

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

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1. Introduction

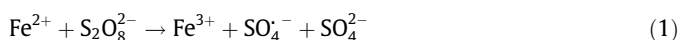
Chlorinated solvents such as trichloroethylene (TCE) have been frequently detected in groundwater because of their use in industrial processes and for dry-cleaning purposes [1,2]. TCE is listed as

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 ($\text{SO}_4^{\cdot-}$) have been proposed for the effective degradation and mineralization of TCE [8–10].

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Transition metals such as Fe(II), Co(II), Mn(II), Ce(II), Cu(II) and Ag(I) can be introduced for persulfate ($S_2O_8^{2-}$) activation to generate $SO_4^{\cdot-}$ [11], and homogeneous Fe(II) is an effective reagent for the production of $SO_4^{\cdot-}$ in accordance with the following reaction:



In a previous study, Liang et al. [12] used the homogeneous $Fe^{2+}/S_2O_8^{2-}$ 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 $Fe^{2+}/S_2O_8^{2-}/TCE$ 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 $SO_4^{\cdot-}$.



To minimize the competition of $SO_4^{\cdot-}$, 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 $SO_4^{\cdot-}$ [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 dioxide and iron oxides for environmental application [16–18].

In this study, a reduced graphene oxide (rGO) supported magnetite nanoparticle composite (nFe_3O_4/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 nFe_3O_4/rGO composite that prevents aggregation of the magnetite nFe_3O_4 particles by precipitating them uniformly onto rGO sheets; (2) to evaluate the persulfate activation potency of the nFe_3O_4/rGO composite to facilitate degradation of TCE in aqueous solution and (3) to understand the activation mechanism of persulfate in the presence of nFe_3O_4/rGO .

2. Materials and methods

2.1. Materials

TCE standard solution ($1000 \mu\text{g mL}^{-1}$) was purchased from Amresco (Solon, OH, USA). $FeSO_4 \cdot 7H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, H_2O_2 , $Na_2S_2O_8$, $NH_3 \cdot H_2O$, NaOH and $KMnO_4$ were obtained from Sino-pharm 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 nFe_3O_4/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]. nFe_3O_4 was prepared through a reverse co-precipitation method using $NH_3 \cdot H_2O$ [15]. The synthesis procedure of nFe_3O_4/rGO composite was described as follows: 0.10 g graphene was dispersed in 3.0 mol L^{-1} of $NH_3 \cdot H_2O$ with total volume of 50 mL, then placed in an ultrasound bath (25 Hz, 100 W). 0.12 g $FeSO_4 \cdot 7H_2O$ and 0.35 g $Fe(NO_3)_3 \cdot 9H_2O$ 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 nFe_3O_4/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 nFe_3O_4/rGO with a nFe_3O_4 to rGO mass ratio of 1:1 as measured by thermogravimetric analysis. nFe_3O_4/rGO composites with different nFe_3O_4 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 nFe_3O_4 , rGO and nFe_3O_4/rGO composites were determined with a diffractometer (XRD-7000S/L, Shimadzu) with $Cu K\alpha$ radiation. X-ray photoelectron spectra (XPS) were measured on Axis Ultra spectrometer (Kratos) using a $Al K\alpha$ 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. nFe_3O_4 , rGO and nFe_3O_4/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 ($30 \text{ m} \times 0.25 \text{ mm} \times 1.40 \mu\text{m}$) chromatographic column. A 1,10-phenanthroline monohydrate spectrophotometry method was introduced to determine dissolved iron in aqueous solution on a Unicou 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.

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