Heterogeneous activation of Oxone by substituted magnetites Fe$_{3-x}$M$_x$O$_4$ (Cr, Mn, Co, Ni) for degradation of Acid Orange II at neutral pH

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**A B S T R A C T**

In this study, the effect of incorporation of transition metals (i.e., Co, Mn, Cr, and Ni) into the magnetite on the reactivity towards Oxone activation was investigated at neutral pH. The magnetite samples were characterized by XRD and EXAFS. Co, Cr, and Ni were in the valences of +2, +3, and +2, respectively, while Mn was in the valences of +2 and +3. These cations occupied the octahedral sites of magnetite, but the distribution of Mn and Ni on the octahedral sites of magnetite surface increased with an increase of substitution extent. The activity of magnetites in Oxone activation was investigated through Acid Orange II (AOII) degradation at an initial pH of 7.0 with or without phosphate-buffered solution. In neutral medium, the AOII degradation by Mn, Cr, and Ni substituting magnetites followed pseudo-first-order kinetics. The incorporation of Co, Mn, and Ni improved the catalytic activity of magnetite in the order Mn < Ni < Co, while Cr showed an inert effect. The dominant reactive radicals were indicated through the scavenging effect of ethanol and tert-butyl alcohols. The different effects of studied substitutions on the reactivity of magnetite were discussed in views of reactive radical species and microstructural environment.

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**1. Introduction**

The contamination of toxic and biorefractory organic pollutants in subsurface soil and groundwater has been a critical environmental concern in recent years. In situ chemical oxidation (ISCO) has been developed as a promising technology for the remediation of contaminated soils and groundwater [1]. ISCO is usually performed by injecting chemical oxidants (e.g., hydrogen peroxide (H$_2$O$_2$), potassium permanganate (KMnO$_4$), ozone (O$_3$), and persulfate salts (Na$_2$S$_2$O$_8$, K$_2$S$_2$O$_8$, and KHSO$_5$)) into the subsurface [2]. Among the various oxidants used in the ISCO process, persulfate is the newest and least studied, but has received increasing attention [3]. Persulfate has comparable oxidation capacity to that of O$_3$, but is more stable and easier to acquire than O$_3$ [4]. Persulfate has the advantages of higher solubility, longer residence time in subsurface than H$_2$O$_2$, and wide operative pH range [5]. With the presence of UV-light, heat, bases, microwave, and ultrasonic irradiation, persulfate can be activated to generate the intermediate sulfate radical (SO$_4$•–) with high redox potential ($E_0 = +2.6$ V) [6,7].

The transition metal cations (e.g., Fe$^{2+}$, Mn$^{2+}$, etc.) are another alternative for persulfate activation (Eqs. (1)–(2)), due to their abundance in soil and sediment and excellent environmental harmony. This homogeneous process requires large quantities of acid and high metal dosage, which would raise the complexity and costs [8]. Thus, the development of heterogeneous technology for persulfate activation is of considerable interest. In fact, some minerals such as pyrite (FeS$_2$) [1], birnessite (α-MnO$_2$) [9], and goethite (α-FeOOH) [2,10], which contain active transition metals and commonly occur in soil, have been proved as effective activators in persulfate activation.

$$S_2O_8^{2–} + M^{n+} \rightarrow SO_4^{–•} + SO_4^{2–} + M^{(n+1)+} \quad (1)$$

$$HSO_5^- + M^{n+} \rightarrow SO_4^{–•} + OH^- + M^{(n+1)+} \quad (2)$$

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Among the iron oxide minerals, magnetite (Fe₃O₄) has some unique structural features, which makes it of promising application in persulfate activation. Magnetite contains both Fe²⁺ and Fe³⁺ in inverse spinel structure, with Fe²⁺ occupying the octahedral site and Fe³⁺ being distributed in both octahedral and tetrahedral sites. Fe²⁺-bearing minerals have been found to be more effective than the only Fe³⁺-bearing ones in heterogeneous catalytic oxidation of organic pollutants [11–13]. The simultaneous occupation of Fe²⁺ and Fe³⁺ in the octahedral sites allows the Fe species to be reversibly oxidized and reduced while the structure remains unchanged [14].

In most natural magnetites, iron cations are isomorphously substituted by divalent (Co, Ni, Mn, etc.), trivalent (V, Cr, etc.), and tetravalent (Ti) cations [15]. The introduction of Cr [16], Mn [17], Co [14], and V [18] remarkably improved the catalytic activity of magnetite in heterogeneous Fenton reaction. Recently, Su et al. [19] reported an improvement effect of Co substitution on the catalytic activity of magnetite in Oxone activation for the degradation of rhodamine B (RhB). Some transition metal ferrites, e.g., MnFe₂O₄ [20] and CoFe₂O₄ [21] have also been found as active heterogeneous catalysts of Oxone oxidation. These experimental evidences are benefit for the application of transition metal substituted magnetites in Oxone activation for ISCO process. However, to the best of our knowledge, except for Co and Mn, the effect of other substituting transition metals, e.g., Cr and Ni, on the activity of magnetite in Oxone activation has not been reported. These metals have been verified to change the heterogeneous Fenton activity of magnetite [14.16–18]. Furthermore, ascribed to the distinct sample preparation and reaction conditions of Oxone activation adopted [14,16–18], the effects of common substituting metals on the activity of magnetite have been difficult to compare.

In this study, four series of magnetites with substitutions of different transition metals (Fe₃₋ₓMₓO₄, M = Cr, Mn, Co, and Ni) were used as heterogeneous catalysts towards the degradation of Acid Orange II (AOII) by Oxone at neutral pH. The main objective of this study was to compare the effects of the studied substitutions on the activity of magnetite in Oxone activation at neutral pH. Through structural characterization and dominant reactive radical investigation, the restriction mechanism of substitutions on the reactivity of magnetite in Oxone activation was discussed. The obtained results are of great significance for the application of magnetite-group minerals for persulfate activation in ISCO process.

2. Experimental

2.1. Magnetite preparation

All the chemicals and reagents used in this study were of analytical grade and used as received. The substituted magnetite samples were synthesized by a precipitation–oxidation method as described in our previous publication [22,23]. For the synthesis of Fe₃O₄, suitable amount of FeSO₄·7H₂O was dissolved in an HCl solution (total metal cation concentration ≈ 0.90 mol L⁻¹). 1.0 mL of hydrazine was added to prevent the oxidation of ferrous cations, and the pH was set low enough (pH < 1) to prevent iron oxidation and hydroxide precipitation. This solution was heated to 90–100 ºC. Equal volume of a solution containing 4.0 mol L⁻¹ NaOH and 0.90 mol L⁻¹ NaNO₂ was added dropwise (10 mL min⁻¹) into the heated iron solution and the reaction was maintained at 90 ºC for 2 h, while stirring at a rate of 500 rpm. Then the solution was cooled to room temperature. It is necessary to emphasize that during the reaction, a N₂ flux was passed through to prevent the oxidation of ferrous cations by air. The particles were then separated by centrifugation at 3500 rpm for 5 min and washed with boiling distilled water, followed by an additional centrifugation. After 3 and 4 washings, the particles were collected and dried in a vacuum oven at 100 ºC for 24 h. The Fe₃₋ₓCrₓO₄, Fe₃₋ₓMnₓO₄, Fe₃₋ₓCoₓO₄, and Fe₃₋ₓNiₓO₄ samples were prepared by following the above-mentioned steps except dissolving a pre-calculated amount of Cr₂(SO₄)₃·9H₂O, MnSO₄·H₂O, CoSO₄·7H₂O, and NiSO₄·6H₂O with FeSO₄·7H₂O, respectively, while preparing the initial acid solution. For the synthesis of each substituted series, the mole ratio of M/Fe was controlled at 1:1, 1:5, 1:3, and 1:2. The concentration of metal cation M and Fe was kept at about 0.90 mol L⁻¹. All the samples were ground and passed through a 200 mesh screen.

2.2. Magnetite characterization

The contents of Fe and substituting metals in the synthetic samples were determined on ICP-AES (Varian VISTA-PRO AX). The synthetic magnetite samples were labeled as (Fe₃₋ₓMₓO₄, M = Cr, Mn, Co, and Ni). The value x was determined by comparing the content proportion of M/Fe obtained from chemical analysis to the theoretical value of Fe₃₋ₓMₓO₄. Powder X-ray diffraction (PXRD) patterns were recorded between 10° and 80° (2θ) at a step of 1° min⁻¹ on a Bruker D8 advance diffractometer with Cu Kα radiation (40 kV and 40 mA). BET specific surface area (SSA) was measured on a PE AAnalyst 400 Flame Atomic Absorption Spectrophotometer (FAAS). Total organic carbon (TOC) concentration was analyzed in a PE AAnalyst 400 Flame Atomic Absorption Spectrophotometer (FAAS). Total organic carbon (TOC) concentration was analyzed in an ASAP 2020 instrument. Before measurement, the samples were degassed at 433 K for 12 h.

X-ray absorption fine structure (XAFS) spectra of the synthetic samples and reference compounds were measured on the beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF). The storage ring is operated at the electron energy of 2.2 GeV with beam current of 250 mA. The 1W1B is a focused X-ray beamline, using a Si (1 1 1) double crystal monochromator. The spectra were acquired at room temperature in transmission mode. The obtained XAFS data was analyzed with IFEFFIT software package.

2.3. Degradation experiment

The degradation experiments were performed in 300 mL conical flask under magnetic stirring at room temperature about 20 ºC. Firstly, the solution of 250 mL containing dye (0.1 mmol L⁻¹) and magnetite (0.2 g L⁻¹) was stirred for 1 h to achieve adsorption equilibrium. The initial pH (7.0) of solution was adjusted using 0.05 mmol L⁻¹ H₂SO₄ and 0.1 mmol L⁻¹ NaOH or phosphate–buffered solution (10% by volume). The buffered solution used to control the reaction pH was prepared by mixing 0.122 mol L⁻¹ Na₂HPO₄ and 0.078 mol L⁻¹ NaH₂PO₄. Then the degradation was initiated by adding the oxidant Oxone (2H₂SO₅·KHSO₅·K₂SO₅·FMS, obtained from J&K Scientific Ltd.) into the system at the 0.2 mmol L⁻¹. At given intervals, the reaction solution was sampled and filtered through 0.22 μm membrane for AOII concentration analysis by UV–vis spectroscopy (PE Lambda 850) at a wavelength of 484 nm. The pH of reaction system was monitored by a pH3-3C pH meter. The concentrations of leaching Fe and substituting cations during the degradation were determined on a PE AAnalyst 400 Flame Atomic Absorption Spectrophotometer (FAAS). Total organic carbon (TOC) concentration was analyzed in a Shimadzu TOC-VCPH analyzer to evaluate the mineralization of dyes.

After the degradation in buffered system was completed, the reaction solution was filtered through a Millipore filter (pore size 0.22 μm) to remove the solid catalysts. Then Oxone (0.2 mmol L⁻¹) and Acid Orange II (0.1 mmol L⁻¹) were added to the filtrate, to build a homogeneous reaction system catalyzed by dissolved iron and
substituting cations [24]. The operation of homogeneous reaction was similar to that of heterogeneous reaction mentioned above.

3. Results and discussion

3.1. Magnetite characterization

3.1.1. Chemical analysis and XRD characterization

From the chemical analysis of prepared magnetite samples (Table A.1), the content proportion between substituting metal and iron increases with the increment of Cr, Mn, Co, and Ni content, respectively, indicating an increase of substitution extent of these metals for iron.

X-ray diffraction patterns of Co (Fig. 1), and Ni (Fig. A.1) substituted magnetite series well correspond to the standard card of magnetite (JCPDS: 19-0629) [25], indicating that transition metal doped magnetite has been successfully synthesized and the introduction of metal cations exerts little effect on the inverse spinel structure of magnetite. The Cr substituted magnetites also have spinel structure, and the detail discussion on XRD characterization has been presented elsewhere [26]. For the Mn series samples, Mn substituted magnetite is the only phase in the samples at a certain Mn content (Fe2.77Mn0.23O4 and Fe2.53Mn0.47O4 in Table A.2), the detailed discussion on the SSA variation of magnetite by substitution has been presented Text A.1.

3.1.2. XAFS characterization

XAFS characterization was carried out to probe the valence and coordinated environment of substituting cations in the magnetite. For cations with the nearest neighbors of the same chemical species, the edge shift is positively related to the valence [28]. The K edge position of substituting cations in synthetic samples and their reference samples are summarized in Table A.2. For Cr0 in Cr foil (5989.2 eV), Cr3+ in Cr2O3 (5998.5 eV) and Cr6+ in CrO3 (6007.2 eV), their energy positions of absorption edge shift to higher energy with the increase of valence. For octahedral Cr3+ in normal spinel FeCr2O4, its absorption edge (6000.5 eV) is close to that of Cr2O3. K edge positions (6000.7 eV) of Fe2−xCrxO4 are also close to those of Cr3+ in Cr2O3 and FeCr2O4, but far from those of Cr2O3 and Cr metal, indicating that Cr in Fe2−xCrxO4 is mainly Cr3+. By comparing the K edge positions of Co and Ni in magnetites to those of their reference samples, both Co and Ni are in the valence of +2. The absorption edge of Mn in Fe3−xMnxO4 is more complicated, and is between MnO (6544.0 eV) and Mn2O3 (6548.4 eV). The absorption edge gradually shifts to higher energy with the increase of Mn content, and finally becomes close to MnFe2O4 (6546.8 eV) (Table A.2), in which the Mn cations are in the valences of +2 and +3 [26]. This suggests that Mn cations in magnetite have a mixed valence of +2 and +3.

The extend X-ray absorption fine structure (EXAFS) spectra and the corresponding Fourier-transform (FT) curves for Fe2−xCoxO4 are shown in Fig. 2a and b. On the FT curves, the position of the first peak in the range of 1.5–2.0 Å presents the length of the Fe–O bond. The second peak is a doublet, corresponding to the two different distances of Fe–O bond. The peak positions and profile related to the Cr–O bond are shown in Fig. A.2. With an increase of Mn content (i.e., Fe2.33Mn0.67O4 and Fe2.58Mn0.42O4 in Fig. A.2), a new phase of feitknechtite (β-MnOOH) with the reflections 2θ around 19° and 34° (JCPDS: 18-0804) appears [27], besides the dominant phase of Mn substituted magnetite.

The substitution of Cr and Ni gradually increases the SSA of magnetite, while the Co and Mn substitution decreases the SSA (Table A.1). The detailed discussion on the SSA variation of magnetite by substitution has been presented Text A.1.
The position of the first peak on the FT curves of Mn K-edge is around 1.6 Å for Fe2.77Mn0.23O4 and Fe2.53Mn0.47O4 and 1.4 Å for Fe2.33Mn0.67O4 and Fe2.09Mn0.91O4 (Fig. 4). The intensity of second peak around 3 Å, corresponds to the Mn/O shells. For Fe2.77Mn0.23O4 and Fe2.53Mn0.47O4, the Mn–O distance is about 2.08 ± 0.01 Å, and the coordination numbers are 5.3 and 5.4 (Table A.5). The Mn–Mn/Fe shells distances are close to the theoretical distances of the corresponding ones in magnetite structure[29], indicating that the Mn cations occupy the octahedral sites (Fig. 3b). The peak at 3.49 Å on FT curves shows obvious difference between these two samples. For Fe2.77Mn0.23O4, the coordination number for this peak is 6.2, consistent with the theoretical value of Feoct/Fetet subshell in the bulk structure of magnetite. This indicates that Mn cations in Fe2.77Mn0.23O4 mainly exist in the bulk of magnetite by substituting octahedral Fe. However, for Fe2.53Mn0.47O4, the coordination number is just 3.9. Such obvious decrease in coordination number implies that partial Mn cations occupy the octahedral sites on magnetite surface. For Fe2.33Mn0.67O4 and Fe2.09Mn0.91O4, the Mn–O and Mn–Mn/Fe distances, and their coordination number are even lower than those of Fe2.53Mn0.47O4 (Table A.5), indicating the octahedral occupation on magnetite surface increases (Fig. 3b). To keep the charge balance, some surface Mn cations with unoccupied atomic orbitals are bonded to the hydroxyls in the aqueous solution and even form a new phase feitknechtite β-MnOOH, which is consistent with the observation from XRD. In the structure of feitknechtite, Mn cations are also octahedrally coordinated (Fig. A.2).

The EXAFS results (Fig. A.4 and Table A.6) of Fe3−xNi2xO4 is similar to those of Fe3−xMn2xO4. This indicates that the occupation of Ni on the octahedral sites on magnetite surface increases with the increase of Ni substitution (Fig. 3b). The detailed discussion of the EXAFS results of Fe3−xNi2xO4 has been presented Text A.2.

3.2. AOII degradation by Fe3−xMxO4 catalyzed Oxone oxidation

3.2.1. AOII degradation at initial pH 7.0 without buffered solution

From previous studies, the neutral pH for the degradation of organic pollutants by Oxone, was set in two ways. One way was that the initial pH was adjusted at 7.0, but not maintained with the degradation proceed[4,7,10,19]. The other way was to add buffered solution into the reaction system to keep the pH constant[3,21,30]. In this study, to fully compare the catalytic activity of the studied magnetites at neutral pH, the AOII degradation was carried out in both ways.

The AOII degradation by Fe3−xCo2xO4 and Oxone at initial pH 7.0 without readjustment are shown in Fig. 5. Before adding Oxone, the AOII removal only relied on the adsorption on Fe3−xCo2xO4. The adsorption efficiency was quite low (<1%). The AOII degradation was initiated by Oxone addition. Compared with the only Oxone system and Oxone/Fe3O4 combined system, in which no obvious AOII degradation took place in 40 min, the presence of Oxone and Fe3−xCo2xO4 accelerated the AOII degradation significantly. As AOII was not adsorbed onto magnetite surface, the kinetic study of AOII degradation could be performed by assuming that the reaction between the sulfate radicals and the AOII molecules was the rate determining step. Thus, by assuming that SO4− instantaneous concentration was a constant, AOII degradation was described by the pseudo-first-order kinetic equation (Eq. (3)):

\[ -dC/dt = k \times C_{SO4} \times C = k_{app} \times C \rightarrow -\ln C_t/C_0 = k_{app} \times t \]  

(3)

where C0 and Ct are the AOII concentrations (mmol L−1) at the initial time and reaction time t, k_app is apparent pseudo-first-order
appear constant (min⁻¹), and t is degradation time (min). The AOII degradation in Fe₃₋ₓCoₓO₄/Oxone combined system was well fitted in the form of Eq. (3) (Fig. 5, R² > 0.99). The kₚₑ₄ values were 1.92 × 10⁻⁴, 0.0286, 0.0337, 0.0996, and 0.127 min⁻¹ for the systems catalyzed by Fe₃O₄, Fe₂.₈₀Co₀.₂₀O₄, Fe₂.₅₇Co₀.₄₃O₄, Fe₂.₃₃Co₀.₆₇O₄, and Fe₂.₁₀Co₀.₉₀O₄ (Table A.7), respectively. The kₚₑ₄ gradually increased with the increase of Co substitution in magnetite.

For the other metal (i.e., Cr, Mn, and Ni) substituting magnetites, the degradation processes were well fitted with the pseudo-first-order kinetic equation (Fig. 6). For Mn and Ni series, kₚₑ₄ was lower than those of Co series, but gradually increased with the increment of the substitution extent. However, for all the Fe₃₋ₓCrₓO₄ samples, the kₚₑ₄ was about 4 × 10⁻⁴ min⁻¹ and slightly larger than that of Fe₃O₄. Among the four series samples (Table A.7), Fe₃₋ₓCoₓO₄ displayed the best catalytic performance.

Although the pH was initially set at 7.0, it varied obviously (Fig. 7). After the addition of Oxone, the pH quickly decreased to ca. 4.5 with a slight decrease during the degradation process. Such phenomenon about the obvious decrease of pH has also been reported previously [5,8]. Two factors, most possibly, were involved in the significant decrease of pH. Since Oxone was an acidic immediate products were generated during the degradation [31,32], which also lead to a decrease of reaction pH. As shown in Fig. 7, the decrease of final pH enhanced in the order blank system < Fe₂.₃₃Cr₀.₆₇O₄ < Fe₂.₃₃Ni₀.₆₇O₄ < Fe₂.₀₉Mn₀.₉₁O₄ < Fe₂.₁₀Co₀.₉₀O₄, which was consistent with the order of the degradation efficiency.

The great decrease of pH inevitably influenced on the degradation process. From previous studies [33,34], the degradation efficiency increased with reaction pH decrease. As the pHₚₑ₄ of magnetite and substituted magnetites was about 6.8 [22,35], the decrease of system pH to acid stage promoted the protonation of surface hydroxyls. For AOII (pKₐ₁ is 1.0, pKₐ₂ is 11.4), most of the dye existed as anions at the studied pH range. The increase of positive charges over magnetite surface improved the AOII adsorption through electrostatic interaction, which also accelerated the degradation. Furthermore, the great decrease of pH to acid stage increased the dissolution of iron and substituting cations from magnetite surface (Fig. 8) and improved the homogeneous reaction by leaching cations [36]. Most of cations in the studied magnetites, e.g., Fe²⁺ [37], Co²⁺ [38], Ni²⁺ [39], and Mn²⁺ [40], have displayed activity in Oxone activation. Therefore, based on the great decrease of reaction pH during the reaction, the AOII degradation at initial pH of 7.0 without readjustment (Figs. 5 and 6) could not absolutely reflect the heterogeneous activity of substituted magnetites in Oxone activation.

### 3.2.2. AOII degradation at pH 7.0 with buffered solution

In order to exclude the influence of pH decrease, the AOII degradation was conducted at pH 7.0 with phosphate-buffered solution (Fig. 9) [41,42]. During the degradation, the pH maintained by buffered solution was decreased by up to 0.5. During the degradation, the concentration of iron and substituting cations dissolved from the magnetite surface was below 1.0 mg L⁻¹ (Fig. 8), indicating the heterogeneous process of AOII degradation. Without the presence of magnetite, 10% of AOII were degraded by Oxone in 8.0 h. The degradation efficiency by Fe₃₋ₓO₄/Oxone combined system was quite close to that by only Oxone.

For Fe₃₋ₓCoₓO₄, the degradation efficiency increased quickly in the first 20 min, but did not change significantly in the following reaction time. The final degradation efficiency was in the range of 70–80%, with a slight increase with the increment of Co substitution (Fig. 9a). The AOII degradation by Mn, Ni, and Cr substituted magnetites was much slower. The degradation character by Fe₃₋ₓNiₓO₄ were identical to those by Fe₃₋ₓCoₓO₄. The degradation efficiency gradually increased in the first 240 min, and no obvious change was observed in the following procedure. The
removal efficiency (53–78%) increased with Ni substitution in magnetite (Fig. 9b). Different from Co and Ni substituted magnetites, the degradation efficiency by Mn substituted magnetite increased in the whole studied process. The final efficiency (20–65%) also increased with the enhancement of Mn substitution (Fig. 9c). However, the Cr substitution did not show distinct positive effect. The removal efficiency was quite close to those by Fe3O4/Oxone and Oxone systems (Fig. 9d).

In terms of reaction kinetics, although Co substitution obviously improved the A0II degradation, both initial stage and the whole process could not be fitted by the zero-order or pseudo-first-order kinetics (Fig. 9a). For the Cr, Mn, and Ni series, their catalyzing processes were well fitted with the pseudo-first-order kinetics (Fig. 9 and Table 1). For Mn and Ni series, the rate constants $k_{\text{app}}$ were in the range of $5.96 \times 10^{-4}$–$2.07 \times 10^{-3}$ min$^{-1}$, and $2.26 \times 10^{-3}$–$5.04 \times 10^{-3}$ min$^{-1}$, respectively. The $k_{\text{app}}$ for both series increased with the increase of substitution. All $k_{\text{app}}$ of Cr series were about $4.0 \times 10^{-4}$ min$^{-1}$, without obvious variation (Table 1). From the kinetics results, the introduction of Co, Mn, and Ni improved catalytic activity of magnetite in Oxone activation for A0II degradation at natural pH, while Cr showed an inert effect.

To further confirm that the Oxone activation by substituted magnetites was heterogeneous process, the homogeneous Oxone activation catalyzed by leaching iron and substituting cations for A0II was investigated (Fig. A.5). For the homogeneous reaction catalyzed by the leaching cations from Fe$_{2.10}$Co$_{0.90}$O$_4$, the degradation efficiency at 40 min was below 10%, much lower than that in the heterogeneous degradation catalyzed by Fe$_{2.10}$Co$_{0.90}$O$_4$ (81%) the same reaction time. For the other homogeneous reaction catalyzed by the leaching cations from Fe$_{2.09}$Mn$_{0.91}$O$_4$, Fe$_{2.06}$Ni$_{0.94}$O$_4$, and Fe$_{2.33}$Cr$_{0.67}$O$_4$, the degradation efficiency is quite close to that of blank system containing A0II and Oxone. Thus, the effect of homogeneous Oxone activation on the degradation process can be neglected. The A0II decomposition through Oxone activation by substituted magnetites was dominated by heterogeneous reaction.

3.3. Radical mechanism of Oxone activation by Fe$_{3-x}$M$_x$O$_4$

During the Oxone activation, two types of radicals (i.e., sulfate (SO$_4^{•-}$) and hydroxyl (•OH)) are possibly responsible for the destruction of organic contaminants, depending on the reaction pH [5,43]. SO$_4^{•-}$ are the predominant radicals at acidic condition (Eq. (2)), whereas •OH are the dominant radicals under alkaline condition (Eq. (4)) [44]. SO$_4^{•-}$ can facilitate the generation of •OH (Eq. (5)), with higher oxidation potential (2.73 V) than that of SO$_4^{•-}$ (2.6 V) [45]. So it is necessary to confirm the dominant radical species in the Oxone/Fe$_{3-x}$M$_x$O$_4$ combined system at neutral pH.

$$\text{SO}_4^{•-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + •\text{OH} \quad (4)$$

$$4\text{SO}_4^{•-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + •\text{OH} + \text{H}^+ \quad (5)$$

In this study, alcohols were selected as the radical scavengers. Alcohols with and without α-hydrogen display different reactivity towards radical species. Ethanol (EtOH, containing α-hydrogen) reacts with •OH and SO$_4^{•-}$ at high and comparable rates, with rate constants of $(1.2–2.8) \times 10^9$ and $(1.6–7.7) \times 10^7$ mol L$^{-1}$ s$^{-1}$, respectively. However, tert-butyl alcohol (TBA, without α-hydrogen) has different reaction rate constants, and the rate constant for •OH ($(3.8–7.6) \times 10^6$ mol L$^{-1}$ s$^{-1}$) is 418–1900 times greater than that for SO$_4^{•-}$ ($(4–9.1) \times 10^5$ mol L$^{-1}$ s$^{-1}$) [44]. The changes in the degradation efficiency of A0II by the TBA addition allowed us to differentiate between sulfate and hydroxyl radicals. The effect of EtOH served as supplemental data to the information...
derived from the effect of TBA and allowed us to differentiate the formation of freely diffusible or bound to the magnetite free radicals [30].

To confirm the dominant radical species in the degradation at neutral pH, radical scavenging experiment was conducted in buffered systems, which contained magnetites with the highest substitution in each series. The addition of radical scavengers somehow decelerated the degradation to a certain extent. For the system catalyzed by Fe$_{2.09}$Co$_{0.90}$O$_4$, the presence of TBA and ethanol decreased the degradation by about 7% and 100%, respectively (Table A.8), indicating that the freely diffusible sulfate radicals were exclusively generated. But for the systems containing Fe$_{2.09}$Mn$_{0.91}$O$_4$, Fe$_{2.33}$Cr$_{0.67}$O$_4$, and Fe$_{2.06}$Ni$_{0.94}$O$_4$, the degradation efficiency decreased by about 26%, 20%, and 7%, due to the addition of TBA, indicating the dominating roles of sulfate radicals. But in the presence of EtOH, the degradation efficiency decreased by about 66%, 64%, and 72%, respectively, suggesting that sulfate radicals were freely diffusible or caged to the magnetite.

3.4. Reaction mechanism

For the Oxone activation at neutral pH, the substitutions of Co, Mn, and Ni improved the catalytic activity of magnetite, while Cr substitution showed no obvious effect. Co series displayed the best catalytic activity. The activity of Mn and Ni series was comparable. The SSA and activation capability of magnetite samples did not show obvious relationship, probably due to the fact that SSA is mainly related to the adsorption property of magnetite and AOII was not adsorbed on the substituted magnetite surface.

The effect of studied cations on the catalytic activity of magnetite in H$_2$O$_2$ decomposition has been investigated in previous studies [14,16,22]. The introduction of Cr, Mn, and Co remarkably improved the catalytic activity of magnetite in H$_2$O$_2$ decomposition to produce $^•$OH radicals, while Ni showed an inhibitory effect. Persulfate (e.g., Oxone and Na$_2$S$_2$O$_8$) is similar to H$_2$O$_2$ in the structure, as both have the O–O bond. However, in this study of Oxone activation, though Co and Mn substitution also improved the activity of magnetite, the effect of both Cr and Ni was reverse to that in H$_2$O$_2$ decomposition.

The strong catalytic activity of Fe$_{3-x}$Co$_x$O$_4$ in Oxone activation has been reported in previous study [19]. Among the common transition metals, Co(II) is the best metal catalyst for the activation of peroxymonosulfate [30]. At neutral pH, Co(II)/KHSO$_5$ generated almost exclusively freely diffusible sulfate radicals via Eq. (6):

$$\text{Co}^{2+} + \text{HSO}_5^- \rightarrow \text{Co}^{3+} + \text{OH}^- + \text{SO}_4^{\cdot -}$$  \hspace{1cm} (6)

<table>
<thead>
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<th>Samples</th>
<th>$k_{app}$/min$^{-1}$</th>
<th>$R^2$</th>
<th>Samples</th>
<th>$k_{app}$/min$^{-1}$</th>
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<th>Samples</th>
<th>$k_{app}$/min$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{2.77}$Mn$</em>{0.23}$O$_4$</td>
<td>$5.96 \times 10^{-4}$</td>
<td>0.996</td>
<td>Fe$<em>{2.05}$Co$</em>{0.95}$O$_4$</td>
<td>$4.84 \times 10^{-4}$</td>
<td>0.989</td>
<td>Fe$<em>{2.79}$Ni$</em>{0.24}$O$_4$</td>
<td>$2.26 \times 10^{-3}$</td>
<td>0.993</td>
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<tr>
<td>Fe$<em>{2.82}$Cr$</em>{0.18}$O$_4$</td>
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<td>Fe$<em>{2.06}$Co$</em>{1.04}$O$_4$</td>
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<td>$3.59 \times 10^{-3}$</td>
<td>0.999</td>
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<td>0.993</td>
<td>Fe$<em>{2.06}$Ni$</em>{0.08}$O$_4$</td>
<td>$4.61 \times 10^{-4}$</td>
<td>0.997</td>
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<td>$4.52 \times 10^{-3}$</td>
<td>0.990</td>
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<td>Fe$<em>{2.53}$Mn$</em>{0.47}$O$_4$</td>
<td>$8.64 \times 10^{-4}$</td>
<td>0.996</td>
<td>Fe$<em>{2.53}$Cr$</em>{0.47}$O$_4$</td>
<td>$4.14 \times 10^{-4}$</td>
<td>0.990</td>
<td>Fe$<em>{2.28}$Ni$</em>{0.48}$O$_4$</td>
<td>$5.04 \times 10^{-3}$</td>
<td>0.986</td>
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<tr>
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<td>0.998</td>
<td>Fe$<em>{2.53}$Cr$</em>{0.47}$O$_4$</td>
<td>$4.14 \times 10^{-4}$</td>
<td>0.990</td>
<td>Fe$<em>{2.28}$Ni$</em>{0.48}$O$_4$</td>
<td>$5.04 \times 10^{-3}$</td>
<td>0.986</td>
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<td>Fe$<em>{2.09}$Mn$</em>{0.91}$O$_4$</td>
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<td>0.997</td>
<td>Fe$<em>{2.53}$Cr$</em>{0.47}$O$_4$</td>
<td>$4.14 \times 10^{-4}$</td>
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<td>Fe$<em>{2.28}$Ni$</em>{0.48}$O$_4$</td>
<td>$5.04 \times 10^{-3}$</td>
<td>0.986</td>
</tr>
</tbody>
</table>

Table 1

The rate constant (min$^{-1}$) for the Acid Orange II degradation through heterogeneous activation of Oxone by Fe$_{3-x}$M$_x$O$_4$ (M = Cr, Mn, and Ni) at pH 7.0.
From the radical investigation in this study, the system catalyzed by Fe$_{2.09}$Co$_{0.90}$O$_4$ also exclusively generated freely diffusible sulfate radicals. From the XAFS characterization, Co was in the valence of +2 and occupied the octahedral sites in the spinel structure. Based on higher reduction potential of Co(II) (Eq. (7)) than Fe(II) (Eq. (8)), the reduction of Co(III) by Fe(II) on the octahedral sites was thermodynamically favorable (Eq. (9)). Thus, the efficient regeneration of surface Co(II) was responsible for the remarkable improvement of the catalytic activity towards Oxone activation.

$$\begin{align*}
\text{Co}^{3+} + e^- & \rightarrow \text{Co}^{2+}, E^0 = 1.81 \text{ V} \\
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+}, E^0 = 0.77 \text{ V} \\
\text{Fe}^{2+} + \text{Co}^{3+} & \rightarrow \text{Fe}^{3+} + \text{Co}^{2+}, \Delta E = 1.04 \text{ V}
\end{align*}$$

For Mn and Ni, their substituted magnetites displayed lower reactivity than Co series. This is probably ascribed to the fact that from the radical investigation, Fe$_{3-x}$Mn$_x$O$_4$ and Fe$_{3-x}$Co$_x$O$_4$ generated partial SO$_4^{•−}$ bound to the magnetite surface, which decreased the contact between SO$_4^{•−}$ and AOII. The similar way of SO$_4^{•−}$ generation by Mn$^{2+}$ and Ni$^{2+}$ cations has been reported in previous studies (Eqs. (10) and (11)) [30]. For Mn$^{2+}$, its reduction potential was also higher than that of Fe(II) (Eq. (12)). So the reduction of Mn$^{3+}$ by Fe$^{2+}$, allowing the regeneration of Mn$^{2+}$, was also thermodynamically favorable (Eq. (13)). Although Ni$^{2+}$ inhibited Fenton activity of magnetite, it indeed improved the reactivity of magnetite towards Oxone activation. This was due to the active role of Ni$^{2+}$ in KHSO$_5$ decomposition, and inert performance in H$_2$O$_2$ decomposition [30]. But it was uncertain whether Ni$^{3+}$ or Ni$^{4+}$ prevailed after the oxidation of Ni$^{2+}$. From the XAFS results, both Mn and Ni concentrated on the octahedral sites of magnetite surface with the substitution increase. The increase of active sites on the magnetite surface leads to an improvement of the activity towards Oxone activation.

$$\begin{align*}
\text{Mn}^{2+} + \text{HSO}_4^- & \rightarrow [\text{Mn}^{3+}(\text{SO}_4^{•−})]^2+ + \text{OH}^- \\
\text{Ni}^{2+} + \text{HSO}_4^- & \rightarrow [\text{Ni}^{3+}(\text{SO}_4^{•−})]^2+ + \text{OH}^- \\
\text{Mn}^{3+} + e^- & \rightarrow \text{Mn}^{2+}, E^0 = 1.51 \text{ V} \\
\text{Fe}^{2+} + \text{Mn}^{3+} & \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+}, \Delta E = 0.74 \text{ V}
\end{align*}$$

It was interesting that the Cr substitution improved the Fenton activity of magnetite, but showed an inert effect on the reactivity of magnetite towards Oxone activation. In the Fenton reaction, the role of Cr$^{3+}$ was to regenerate Fe$^{2+}$ on magnetite surface through the reduction of Fe$^{3+}$ by Cr$^{2+}$ (Eqs. (14) and (15)), where Cr$^{2+}$ was produced by the reduction of Cr$^{3+}$ with H$_2$O$_2$ or HO$_2^−$ [16,22]. Fe$^{2+}$ is the most active cation in Fenton reaction [30]. However, for the Oxone activation at acidic or neutral pH, the oxidation of Cr$^{3+}$ to Cr$^{4+}$ was not thermodynamically favorable [16], while the oxidation of Cr$^{3+}$–Cr$^{4+}$ was not tolerated in the magnetite structure, due to the high valence and small radius of Cr$^{4+}$. So Cr$^{3+}$ in magnetite did not initialize the Oxone decomposition. Although Fe$^{2+}$ for Oxone activation could be regenerated through the reduction of Fe$^{3+}$ by Cr$^{2+}$ and Cr$^{2+}$ was hard to generate by Oxone. Accordingly, Cr$^{3+}$ did not show obvious effect on the catalytic activity of magnetite in Oxone oxidation.

$$\begin{align*}
\text{Cr}^{3+} + e^- & \rightarrow \text{Cr}^{2+}, E^0 = −0.408 \text{ V} \\
\text{Fe}^{2+} + \text{Cr}^{2+} & \rightarrow \text{Fe}^{3+} + \text{Cr}^{3+}, \Delta E = 1.179 \text{ V}
\end{align*}$$

3.5. Catalysis stability and TOC removal

Stability is an important property for effective catalyst. The stability of Fe$_{2.10}$Co$_{0.90}$O$_4$ (the most active catalyst in this study) was investigated in three run test after the catalyst recycled from the buffered system. After each recycling, the catalyst was treated by centrifugation, dried and reused. As shown in Fig. A.6, the catalyst presented strong stability in three run tests. The degradation rates of the dye were 81%, 79%, and 76% after 40 min reaction in cycle 1–3, respectively. It indicates that the substituted magnetite is a promising catalyst with high stability and activity. The small decrease of catalytic activity was due to dissolution of iron and substituting cation from magnetite.

To investigate the AOII mineralization during its degradation by substituted magnetite in the presence of Oxone, the mineralization process catalyzed by Fe$_{2.10}$Co$_{0.90}$O$_4$ and Oxone in the buffered system was investigated (Fig. A.7). Mineralization efficiency is the percentage of organic compound transformed to inorganic compound, calculated as below:

$$\text{Mineralization efficiency} = \left(1 - \frac{T_t}{T_0}\right) \times 100\%$$

where $T_0$ and $T_t$ are the initial TOC concentration and instantaneous TOC concentration, respectively.

With the presence of Fe$_{2.10}$Co$_{0.90}$O$_4$ (1.0 g L$^{-1}$) and Oxone (0.20 mmol L$^{-1}$), though AOII (0.1 mmol L$^{-1}$) was quickly degraded by about 81% in 40 min (Fig. 9a), AOII was not obviously mineralized (Fig. A.7). According to Eq. (16), 21 mol of Oxone are theoretically needed for the complete mineralization of 1 mol of AOII. The necessary amount of Oxone in the present study for complete mineralization of 0.1 mmol L$^{-1}$ of AOII is 2.1 mmol L$^{-1}$. Thus, the ineffective mineralization was ascribed to the low Oxone dosage. When the Oxone dosage was increased to 2.1 mmol L$^{-1}$, the AOII degradation was greatly improved (Fig. A.7). The AOII degradation efficiency achieved nearly 100% in 2 min (data not shown), and the mineralization was also fast. The mineralization efficiency was about 50% in 5 min, while no obvious mineralization was observed in the blank system containing AOII (0.1 mmol L$^{-1}$) and Oxone (2.1 mmol L$^{-1}$), which indicated the strong activity of substituted magnetite in activation of Oxone for AOII mineralization. But the mineralization efficiency did not increase in 1.0 h degradation, probably ascribed to the presence of some achronamic medium products during the degradation process. Further study was needed to investigate the species of the medium products.

$$\begin{align*}
21(2\text{HKSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4) & + 2\text{C}_16\text{H}_11\text{N}_2\text{NaO}_4\text{S} \\
& \rightarrow 16\text{CO}_2 + 4\text{H}_2\text{O} + 2\text{HNO}_3 + \text{NaHSO}_4 \\
& + 63\text{KHSO}_4 + 21\text{K}_2\text{SO}_4
\end{align*}$$

4. Conclusions

In the present study, four series of substituted magnetites Fe$_{3-x}$Mn$_x$O$_4$ (M = Cr, Mn, Co, and Ni) was used to catalyzing the degradation of Acid Orange II (AOII) through the heterogeneous Oxone activation at neutral pH. The degradation by Mn, Cr, and Ni series was fitted with pseudo-first-order kinetics. Co, Mn, and Ni substitution improved the reactivity of magnetite, while Cr substitution showed an inert effect. Co series displayed the best catalytic activity, which generated freely diffusible SO$_4^{•−}$ radicals. The activity of Mn and Ni series was lower but comparable, ascribed to the production of partial SO$_4^{•−}$ bound to the magnetite surface. The improvement effect was related to the strong activity of Cr$^{2+}$, Mn$^{2+}$, and Ni$^{3+}$ in initializing Oxone oxidation, and their efficient regeneration on the magnetite surface through Fe$^{3+}$ reduction with an electron transfer in the magnetite structure. The above results are of great significance for the application of magnetite-group minerals for persulfate activation in ISCO process.
Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.11.024.

References