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Visible Light-Driven Selective Organic Degradation by FeTiO₃/Persulfate System: the Formation and Effect of High Valent Fe(IV)

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Abstract

The role of high-valent Fe has rarely been explored in persulfate-based heterogeneous reaction. Herein, the existence of Fe(IV) is verified in a visible light-assisted FeTiO₃/persulfate system using methyl phenyl sulfoxide as the probe. The FeTiO₃/persulfate/light system is capable of selectively degrading aromatic compounds with a higher ionization potential including tetracycline and bisphenol A by photo-generated high-valent Fe(IV). The contributions from SO₄^{•-}, [•]OH and ¹O₂ are excluded. The comparable efficiency in the dark requires higher dosages and suffers from a rapid deactivation. Based on XPS, Raman and EPR analyses, the poor dark activity is caused by the formation of a complex between *in situ* formed Fe(III) and SO₄²⁻ on the FeTiO₃ surface; this complex is, however, the key intermediate for Fe(IV) production under the light irradiation. This study reveals the long-ignored role of SO₄²⁻ as an abundant species in iron-based persulfate systems. We also call for re-evaluating the real oxidation mechanism in other persulfate-based reactions considering the different oxidation mechanisms of radicals and high-valent iron.

Keywords

FeTiO₃; persulfate; high valent Fe(IV); irradiation; selective degradation

This manuscript is dedicated to, and in memory of, the late Prof. Maria Flytzani

1. Introduction

Fenton and Fenton-like reactions in advanced oxidation processes (AOPs) have received intense attention for the elimination of recalcitrant pollutant through the generation of aggressive species such as the hydroxyl ($\cdot\text{OH}$), superoxide (O_2^-) and sulfate (SO_4^-) radicals.[1] Iron-based species (simplified as Fes) are the most commonly used catalysts in both homogeneous and heterogeneous systems.[2-7] For the Fes/ H_2O_2 system, there was a long-standing argument about the role of the high-valent Fe(IV) and $\cdot\text{OH}$ as the active species. The contribution from Fe(IV) in acidic environment was finally excluded by Bakac et al using dimethyl sulfoxide (DMSO) as the probe.[8] Later, it was confirmed that Fe(IV) is the active species at neutral pH.[9] Similar to $\cdot\text{OH}$ generation from Fes/ H_2O_2 , [10-13] the activation of persulfate ($\text{S}_2\text{O}_8^{2-}$, PS) by Fes is one of the most popular approaches for producing SO_4^- radical that has a higher oxidizing power ($E^0 = 2.5\text{--}3.1$ V vs NHE) comparable to that of $\cdot\text{OH}$ ($E^0 = 2.8$ V vs NHE) and a longer lifetime (300 μs) than $\cdot\text{OH}$ (40 μs). [14-18] It is commonly observed that SO_4^- can be further evolved into $\cdot\text{OH}$, particularly in basic conditions and both of these radicals can be the active species for organic degradation. [19-23] The contribution of SO_4^- rather than that of $\cdot\text{OH}$ to organic degradation is usually identified through the alcohol scavenging strategy since $\cdot\text{OH}$ shows similar reactivity toward EtOH and tert-butyl alcohol (TBA) while SO_4^- shows higher reactivity toward EtOH. [24] In contrast, Jiang et al. recently verified the existence of Fe(IV) in a homogeneous Fe^{2+} /PS system using methyl phenyl sulfoxide (PMSO) as the probe. [25] They doubted that the different alcohol scavenging effect could be attributed to the higher reactivity of Fe(IV) for EtOH instead of TBA and claimed that Fe(IV) rather than SO_4^- should be the real active species toward organic degradation.

The oxidation process by Fe(IV) is achieved mainly by oxygen/hydrogen atom transfer, [26-28] which could result in a better selectivity towards organic degradation compared with the more aggressive SO_4^- or $\cdot\text{OH}$. The verification of Fe(IV) in the homogeneous PS-based system may lift the curtain on study about the possible role of Fe(IV) for organic degradation in

versatile Fe-containing systems. The heterogeneous reaction benefits from good separability, wide availability of Fe ore in nature and flexible utilization of light or electricity.[29] The reaction on the catalyst surface may lead to a different redox path compared with that in homogeneous reaction.[30] It is thus highly urgent to explore the relation between PS decomposition and the formation of Fe(IV) in the heterogeneous reaction considering the different redox characteristics of Fe(IV) and $\text{SO}_4^{\cdot-}$.

Iron and titanium oxides are abundant in nature and show low biotoxicity. Herein, FeTiO_3 as the main component of ilmenite with a band gap of 2.4-2.9 eV is used for the activation of PS under dark conditions ($\text{FeTiO}_3/\text{PS}/\text{dark}$) and the visible light irradiation ($\text{FeTiO}_3/\text{PS}/\text{light}$). Selective and stable degradation to phenolic compounds with higher ionization potential was achieved in the $\text{FeTiO}_3/\text{PS}/\text{light}$ system, while nonselective degradation and rapid deactivation were observed in the $\text{FeTiO}_3/\text{PS}/\text{dark}$ system. The contribution from Fe(III)- SO_4 complex on the FeTiO_3 surface to the formation of Fe(IV) and the role of Fe(IV) as the active species in the selective organic degradation were verified through the combination of EPR, XPS and ^1H NMR analyses.

2. Experimental Section

2.1 Chemicals and Materials

Titanium isopropoxide (TTIP), tetrabutylammonium hydroxide (TBAH, 10%), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), potassium hydroxide (KOH), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), potassium iodide (KI), sodium acetate (NaAc), acetic acid (HAc), 2, 4-dichlorophenol (2, 4-DCP) and hydrogen peroxide (H_2O_2 , 30%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Tetracycline hydrochloride (TC), terephthalic acid (TPA), bisphenol A (BPA) and dimethyl sulfoxide (DMSO) were obtained from Aladdin Co. Methyl phenyl sulfone (PMSO_2) and methyl phenyl sulfoxide (PMSO) were purchased from Macklin. All of the reagents used in this work were at least analytical grade and ultrapure water was used for all experiments.

2.2 Preparation of Catalyst

The FeTiO_3 catalyst was fabricated using a simple solvothermal method reported previously.[31] Briefly, TTIP (0.6 mL) was added to a mixture of TBAH (5 mL) and ultrapure water (10 mL) under vigorously stirring until it became clear. Then, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.556 g) was dissolved in ultrapure water (5 mL) to form a light green solution in another beaker. The above solutions were mixed and then, the pH was adjusted to 14 using KOH. The resulting suspension was transferred to a Teflon-lined stainless steel autoclaves and placed in an oven at 220°C for 12 h. The obtained products were washed with water and ethanol and dried prior to use.

2.3 Characterization

The crystal phases of the as-prepared samples were analyzed by XRD conducted in order to identify the samples' microstructure characteristics. The XRD data were collected in the range of $5\text{--}80^\circ$ (2θ) and recorded on a Rigaku D/MAX-2550 diffractometer using $\text{Cu K}\alpha$ radiation with the wavelength of $1.5406\text{ \AA}$, typically operating at a voltage of 40 kV and current of 100 mA. Transmission electron microscopy (TEM) was conducted with a JEOL JEM-2100EX electron microscope, using an accelerating voltage of 200 kV. Raman measurements were performed at room temperature using a Via + Reflex Raman spectrometer with the excitation wavelength of 532 nm. The BET surface area of the sample was determined by nitrogen adsorption at 77 K (Micromeritics ASAP2010). The sample was degassed at 373 K prior to the measurement. TC values were monitored using a SHIMADZU SPD-M20A reverse-phase high-performance liquid chromatography (HPLC) system at a flow rate of $1\text{ mL}\cdot\text{min}^{-1}$ with a RX-C18 column ($4.6 \times 250\text{ mm}$, $5\text{ }\mu\text{m}$) and a diode array UV-vis detector (356 nm). The mobile phase A was composed of 0.01 M oxalic acid, while mobile phase B was pure acetonitrile, and the ration of A to B is 4:1. The leaching concentration of Fe was calculated using an inductively coupled plasma-atomic emissions spectrometer (ICP-AES, Vanan 710).

The detection of radicals and EPR spectrum are recorded on 100G-18KG/EMX-8/2.7 Electro-Spin Resonance Spectrometer.

2.4 Organic Degradation

Organic stock solutions with high concentration were prepared. Aliquots of the stock solutions were combined to achieve the initial experimental conditions. All of the reactions were carried out at room temperature under exposure to air. The light source was a 300 W Xe lamp equipped with wavelength cut off filters ($\lambda \geq 420$ nm) and the reactor vessel was placed 12 cm away from the lamp. The optical power is 570 mW and the optical density is 697 mW/cm². A certain amount of the catalyst was firstly mixed with organics solution and stirred in the dark for 30 min to achieve the adsorption/desorption equilibrium. The experiments commenced by injecting PS into the solution. During the degradation process, an appropriate amount of the turbid solution was immediately withdrawn from the above solution with syringes at fixed time intervals and filtered with 0.22 μ m polytetrafluoroethylene syringe filters and it was observed that the filtration had no obvious impact on the organic concentration. The clear liquid was immediately analyzed by HPLC. Organic degradation in the dark was carried out in a similar manner except for the absence of light irradiation. All of the experiments were performed at least 3 times; with the error bars in figures representing the standard deviation. For the TC degradation carried out in buffer solution, the pH was maintained at 4 by adding 5 mL buffer solution, which consists of 75 mM sodium acetate and 125 mM acetic acid. The buffer of 8 and 10 were composed of 10 mM Borate/25 mM phosphate and 12.5 mM Borate/40 mM sodium hydroxide, respectively. After the reaction, the pH difference was no more than 0.2, which show that pH buffers have excellent stability.

2.5 Stability and Reusability

To test the stability and reusability of FeTiO₃/PS/light and FeTiO₃/PS/dark systems, the catalyst was washed with methanol and ultrapure water several times after each cycle and

then was immediately applied for the next cycle. Mixed cycle performance was conducted by applying the catalyst used 5 times in the dark for the light irradiation system.

3. Results and Discussion

3.1. Structure of FeTiO₃

Figures 1a and 1b are the TEM and SEM images of the prepared FeTiO₃ particles, which have a hexagonal plate-like structure with a side length of ca. 800 nm and a thickness of ca. 50 nm. The XRD patterns of the as-prepared FeTiO₃ are shown in Figure 1c. The peaks at 2θ of 23.8°, 32.5°, 35.3°, 40.3°, 48.7°, 53.0°, 61.5° and 63.3° agree well with the ilmenite FeTiO₃ structure (JCPDS Card No. 29-0733). The sharp peaks demonstrate the high crystallinity of FeTiO₃.

3.2. Fe(IV) and Radical Species

Currently, it remains unclear whether Fe(IV) is generated through activating PS in the heterogeneous iron-containing system, where SO₄^{•-} or [•]OH hydrolyzed from SO₄^{•-} has long been recognized as the dominant reactive species for organic degradation. Here, the formation of Fe(IV) in the FeTiO₃/PS/light system is explored using PMSO as the probe, which as a sulfoxide can be oxidized to the corresponding sulfones by Fe(IV) through an oxygen atom transfer step. According to the HPLC analysis (**Figures 2a**, S1, Table S1), PMSO₂ can be detected under the visible light irradiation, but is absent in the dark. The reacted PMSO molecules are almost completely transformed to PMSO₂ according to the formation efficiency of η (PMSO₂) (Figure S1), demonstrating the formation of Fe(IV) species. Mossbauer spectroscopy was further adopted to confirm the existence of the Fe(IV) species. According to the Mossbauer spectrum of the FeTiO₃ after the light irradiation in the presence of PS (Figure 2b), ca. 42% of Fe(II) is oxidized, among which 4.5% is attributed to Fe(IV). Besides, EPR tests were further performed using DMPO as a radical spin trapping agent to understand the formation and evolution of possible radical species in different FeTiO₃/PS systems. As

observed from Figure 2c, the FeTiO₃/PS/dark system shows negligible signal attributed to DMPO-SO₄⁻, indicating the poor ability of FeTiO₃ to activate PS under dark conditions. By contrast, the FeTiO₃/PS/light system presents distinct signals attributed to DMPO-[•]OH.[32] The [•]OH radical is possibly formed from the hydrolysis of SO₄⁻ or the oxidation of OH⁻/H₂O by photo-generated hole according to the previous reports.[33-36] Moreover, the existence of singlet oxygen (¹O₂) is also verified using TEMP as the probe (Figure 2d).

3.3. Organic Degradation

The organic degradation performance of the FeTiO₃/PS/light system was evaluated using tetracycline hydrochloride (TC), bisphenol A (BPA), terephthalic acid (TPA) and 2, 4-dichlorophenol (2, 4-DCP) as the pollutant models. As shown in **Figure 3a**, only ca. 20% of TPA is degraded within 1 h in the presence of 0.10 g/L of FeTiO₃. 2, 4-DCP is removed with a moderate efficiency of ca. 50%. It is noted over 80% of BPA is degraded and the complete elimination of TC is achieved within 1 h. In comparison, no selective oxidation was observed in the UV/PS system (Figure S2). Moreover, all the organics are recalcitrant to degradation under dark conditions (Figure 3b). The photocatalysis by FeTiO₃ can be excluded according to the low efficiency of ca. 19% toward TC elimination under the visible light irradiation in the absence of PS (Figure S3a). Meanwhile, the substitution of H₂O₂ to PS leads to a negligible removal of TC regardless of whether the light irradiation is used (Figure S3b), demonstrating the essential role of PS for the degradation. It seems the degradation performance of the FeTiO₃/PS/light system is strongly correlated with the ionization potential (IP) of the organics. Specifically, TC and BPA with electron-donating groups such as hydroxyl and amido usually have lower IP values, which are more readily to be degraded, whereas TPA and 2,4-DCP with electron-withdrawing carboxyl and halogen atom are less prone to degradation.[37, 38]

The influences of the PS concentration and catalyst dosage in the FeTiO₃/PS/light system were further investigated over TC, where ca. 80% of TC can still be degraded when the PS

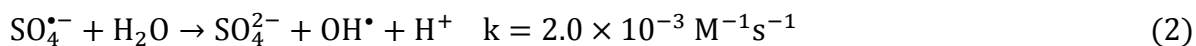
concentration decreases from 2 mM to 1 mM (Figure S4a). The apparent rate constant for the degradation of TC with 1 mM of PS is calculated as 9.60 (**Equation 1**, Figure S4). Moreover, the interference from pH variation during the degradation is excluded according to the preserved activity in the pH buffering solution (pH = 4, Figure 3c); The effect of homogenous reaction by leached iron ($0.028 \text{ mg} \cdot \text{L}^{-1}$ after 1h) is also denied based on the control experiments in the homogeneous Fe^{2+} or Fe^{3+} system (Figure S3c).[39, 40]

$$V = dc/dt = 9.60[\text{K}_2\text{S}_2\text{O}_8]^{0.9667} [\text{FeTiO}_3]^{1.6667} \quad (1)$$

3.4. Identifying the Active Species

As demonstrated above, there are radicals including $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ and $^1\text{O}_2$ besides Fe (IV) in the $\text{FeTiO}_3/\text{PS}/\text{light}$ system, which are all possible reactive species for the organic degradation. Taking TC degradation as the model, radical quenching experiments were carried out to identify the real reactive species in the $\text{FeTiO}_3/\text{PS}/\text{light}$ system. EtOH and TBA are the most commonly used alcohol scavengers due to their different reactivity with the $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ radicals (EtOH for both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, TBA for $\cdot\text{OH}$, Table S2).[25] The concentrations of scavengers are 100 times higher than that of PS in order to ensure the full quenching effect. **Figure 4** shows that the presences of EtOH and TBA decrease the removal efficiency to ca. 25% and 52%, respectively. This result is generally used to demonstrate that $\text{SO}_4^{\cdot-}$ radicals are the main species for the organic degradation; however, this is inconsistent with the EPR analyses considering the strong $\text{DMPO} \cdot \text{OH}$ and negligible $\text{DMPO} \cdot \text{SO}_4^{\cdot-}$ signals. Moreover, it is doubtful that the hydrolysis of $\text{SO}_4^{\cdot-}$ could lead to the complete disappearance of the $\text{DMPO} \cdot \text{SO}_4^{\cdot-}$ signal in EPR spectrum considering the low reaction kinetics in acidic conditions (**Equation 2**),[41, 42] which suggests that $\text{DMPO} \cdot \text{OH}$ adduct may be not formed from $\cdot\text{OH}$ radical. It was recently reported by Jiang et al that the more severe activity-inhibition by EtOH could be ascribed to the higher reaction kinetics of Fe(IV) toward EtOH ($2.51 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) than TBA ($6.0 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$, Table S2).[25] Therefore, it is highly possible the

strong EPR signal of the DMPO-OH[•] adduct under the acidic conditions may be due to the direct oxidation of DMPO by Fe(IV) in the similar manner revealed from Mn(VII) (Scheme 1).[41, 43, 44]



DMSO was further used to exclude the possible contribution from OH[•]. [45] Similar to the situation for PMSO, Fe(IV) is capable of oxidizing DMSO to DMSO₂ through oxygen transfer, while OH[•] generates methyl sulfinic acid (DMSO₃H) through a completely different path. [46] The presence of DMSO in FeTiO₃/PS/light system causes an adverse effect on TC degradation (Figure 4a). According to the ¹H NMR spectrum, only the peak of DMSO₂ can be clearly observed besides the strongest peak of DMSO. [47] The absence of signal attributed to methyl sulfinic acid confirms the adverse effect for TC degradation by DMSO should be related to the consumption of Fe(IV) instead of OH[•] radical (Figure 4b, inset).

Regarding the possible contribution from ¹O₂, FeTiO₃/H₂O₂/light was adopted as a control system which presents distinct EPR signals attributed to the ring-opening product oxidized from ¹O₂, similar to that observed from the FeTiO₃/PS/light system (Figure S5). [32] However, the low activity of the H₂O₂ system suggests that ¹O₂ is not the active species for TC degradation. It is also found that the system with tryptophan, which is a commonly used capture agent for ¹O₂, had little effect on the degradation performance (Figure 4a), thus further excluding the role of ¹O₂ as the reactive species. The above results well suggest the selective degradation of aromatic compound with higher IP should be achieved via the formation of high-valent Fe (IV) species on the FeTiO₃ surface.

3.5. Degradation Stability

Using the FeTiO₃/PS/dark system with 1 mM PS as the illustration, FeTiO₃/PS/light system well maintains the degradation activity toward TC for 5 cycles (Figure 5a). Considering the inevitable mass loss during the recycling operation, the FeTiO₃/PS/light system is very efficient and stable in each cycle. The simultaneous increases of the PS (5 mM) and FeTiO₃

(0.2 g/L) concentrations under dark conditions can achieve reaction kinetics (**Equation 3**) comparable to that in the FeTiO₃/PS/light system with less agent dosage (1 mM PS + 0.1 g/L FeTiO₃, Figure S6). However, the degradation performance of the FeTiO₃/PS/dark system deteriorates rapidly during the recycling experiment, which is even reduced to 15.3% in the fifth cycle (Figure 5b), implying the vital role of the light irradiation in maintaining the degradation stability of the FeTiO₃/PS/light system. Moreover, it is interesting to note the deactivated sample recycled from the 5-run dark reaction shows an improved apparent rate constant ($K = 16.70$, **Equation 4**) compared with the fresh sample ($K = 9.60$, Figure 5c, Table S6). The corresponding discussion about the enhanced visible light activity of the deactivated sample will be stated in the subsequent mechanism section.

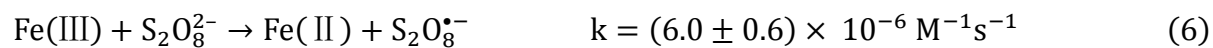
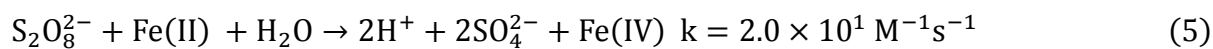
$$V = dc/dt = 10.87[K_2S_2O_8]^{1.619} [FeTiO_3]^{3.0333} \quad (3)$$

$$V = dc/dt = 16.70[K_2S_2O_8]^{0.9667} [FeTiO_3]^{1.6667} \quad (4)$$

3.6. Relation between Fe(IV) formation and PS decomposition

To understand the effect of the light irradiation on the evolution of PS and the formation of Fe(IV) species, the decomposition of PS by FeTiO₃ was investigated in the buffer solution (pH = 4) with and without the light irradiation. As seen from Figure S7, the decomposition efficiency is only slightly increased from the light irradiation, which re-confirms the formation of SO₄^{•-} from PS is not the determinative factor for the organics degradation (Equation 3). XPS analyses were used to understand the variation of Fe valence after the reaction. It is found that the percentage of Fe(III) after the light reaction is higher than that after the dark reaction (**Figure 6a**). Similar to the H₂O₂-based Fenton reaction, it is generally accepted that the oxidation of Fe(II) to Fe(III) in PS-based system is kinetically faster than the reduction of Fe(III) to Fe(II) (**Equations 5, 6**), and the light irradiation helps reduce Fe(III) to Fe(II), thus promoting the formation of SO₄^{•-}. However, the higher Fe(III) content from the light reaction together with the insignificant EPR signal of DMPO-SO₄^{•-} excludes the

possibility that the enhanced activity in the FeTiO₃/PS/light system is attributed to the accelerated recycling of Fe(II) from Fe(III).



Raman spectroscopy was adopted to explore the surface chemistry of FeTiO₃ before and after the reactions. It is observed that a new peak at approximately 980 cm⁻¹ appears after the reaction (Figure 6b); this peak should be ascribed to the surface sulfate according to previous reports,[48-51] which is accordant with the S 2p XPS spectrum with a distinct peak at ~169 eV (Figure 6c). [30, 52, 53] The low concentration of Fe(IV) should be the reason for failing to obtain Raman signal since Raman spectroscopy is an inelastic scattering spectroscopy with low sensitivity. The theoretic calculation was further carried out to understand the sulfate adsorption on the surface of FeTiO₃. The (1 1 1) facet was adopted for sulfate adsorption (Figure S8). The geometry with sulfate on Fe atoms shows a more thermodynamically favorable adsorption (-226.2 kcal/mol) compared with that adsorbed on Ti atoms (-219.7 kcal/mol). Based on these results, it is conferred Fe(III) is oxidized to high-valent Fe(IV) by the photo-generated hole (**Equation 8**),[54, 55] and the remained electron is consumed by in situ formed SO₄^{•-} around the surface (**Equation 9**), leading to the formation of SO₄²⁻. In this case, an efficient hole-electron charge separation can be achieved, which is accordant with the decreased photoluminescence intensity of FeTiO₃ in the presence of PS (Figure S9). Therefore, it is assumed that SO₄²⁻ helps stabilize the surface Fe(III) through forming ≡Fe(III)-SO₄ complex, thus increasing the Fe(III) content observed from XPS.



3.7. Influence of pH on the Fe(IV) formation

The influence of pH on the Fe(IV) formation was further explored to understand the working pH range of the FeTiO₃/PS/light system. Substrate adsorption experiments proved that pH values had little effect on it (Figure S10). Figure 7 indicates the degradation activity for TC exhibits a clear dependence on pH. Over 50% of TC can be degraded in a wide pH range of 4-10 within 1 h, except for pH of 6 where the degradation is almost completely suppressed. Since the isoelectric point of FeTiO₃ is approximately pH = 6, it is inferred the inhibition of the reaction is attributed to the less effective formation of the surface complex between S₂O₈²⁻ and the catalyst. Under the more acidic conditions (pH = 4), S₂O₈²⁻ can be electrostatically adsorbed on the FeTiO₃ surface and complex with Fe(II), promoting the decomposition of S₂O₈²⁻. In neutral to basic conditions, (OH)_m-Fe(III) complex could be first formed, which also favors the transformation to Fe(IV) in the initial stage under the light irradiation. With the continuous formation of SO₄²⁻, (SO₄²⁻)_n(OH)_{m-n}-Fe(III) is could be formed due to the greater complexing ability of SO₄²⁻ than OH⁻ in the presence of abundant SO₄²⁻, further promoting the formation of surface Fe(IV) species.

3.8. Fe(IV)-induced Degradation Pathway and Mechanism

The intermediate products of TC degradation were further detected by UPLC-MS/MS to explore the Fe(IV)-induced degradation pathway. Possible reactive intermediates were listed (Table S7 and Figure S11) and the transformation pathway was proposed accordingly (Figure S12). Fe(IV) species firstly attack electron-donating groups such as amino, hydroxyl and methyl groups, leading to the formation of dihydroxylated, demethylated and deamidated intermediates, which then undergo the ring-opening for further degradation. This transformation pathway is accordant with previous reports that the oxidation process by Fe(IV) is mainly achieved by oxygen/hydrogen atom transfer.[26-28] The degradation process by Fe(IV) species is similar to the electrophilic attack by sulfate radical. The degradation

intermediates including dihydroxylated, demethylated and deamidated intermediates may also be present in reaction systems with hydroxyl or sulfate radicals.[56-60] However, since the contribution of sulfate radical and its derivative of hydroxyl radical has been excluded in FeTiO₃/PS/light system, the degradation of TC should be caused by Fe(IV) through oxygen/hydrogen atom transfer attack.

The TOC removal rate of the FeTiO₃/PS/light system for the treatment of 5 mg/L of TC is ca. 45% after 3 h light irradiation (Figure S13), demonstrating a comparatively mild mineralization ability of Fe(IV) species. The complete mineralization of TC can be achieved in the FeTiO₃/PS/dark system with a significantly improved PS concentration (40 mM), which should be attributed to the more aggressive sulfate and hydroxyl radicals. It seems that the degradation induced by Fe(IV) is much milder compared with that induced by sulfate and hydroxyl radicals. The selective mild degradation on the catalyst surface is expected to help alleviate the dilemma caused by the severe consumption of aggressive radicals by natural organic matters in real aqueous environment.

For the FeS/PS system, it is generally believed that SO₄^{•-} and [•]OH are the dominant radicals that commonly coexist in the homogeneous or heterogeneous reaction. The latter is considered as the hydrolytic derivative of SO₄^{•-}, particularly in highly alkaline conditions (pH > 10), where the base-activation of S₂O₈²⁻ will also be involved.[42] Here, the pH for all of the reaction systems is controlled in the range of 4-10, and thus the evolution of [•]OH can be neglected considering its low reaction rate compared with other evolution processes of SO₄^{•-}. The reason for the negligible SO₄^{•-} and the formation of Fe(IV) in the FeTiO₃/PS/light system is inferred as follows. The decomposition of PS leads to the formation of SO₄^{•-} and Fe(III). SO₄^{•-} tends to be adsorbed by FeTiO₃ through complexing with the surficial iron species. The local concentration of Fe(II) around surficial SO₄^{•-} is thus increased. The adsorbed SO₄^{•-} is further consumed by Fe(II) and reduced to SO₄²⁻, which accelerates the formation of Fe(III)-SO₄

complex on the FeTiO₃ surface. Under dark conditions, Fe(II) sites are shielded by the surficial Fe(III)-SO₄ complex. This gives rise to the rapid deactivation of FeTiO₃ in the dark, but is the key step for the formation of surface ≡Fe(IV) under visible light irradiation, which can be further oxidized to Fe(IV) by the photo-generated hole.

4. Conclusion

In this work, the formation of Fe(IV) from a visible light-irradiated FeTiO₃/PS system is clearly verified using PMSO as the probe. SO₄²⁻ decomposed *in situ* from PS plays a vital role in the formation of surface Fe(IV) because its formation promotes the hole-electron separation and it can form surface complex with Fe(III), which as an abundant species in PS-based systems has long been neglected. The novel oxidative system with Fe(IV) as the active species can be utilized for the selective removal of organic contaminants in complicated wastewater matrices because of its unique reaction selectivity. The insignificant iron leaching under acidic conditions benefitting from the stabilization effect of SO₄²⁻ makes the FeTiO₃/PS/light system a strong candidate for acidic waste water treatment without the second pollution. The effective activity in neutral to basic conditions further widens the range of possible application conditions. FeTiO₃ is a stable mineral compound that is widely present in rich ilmenite ores, a fact which is helpful for promoting the use of natural ores for environment remediation. Moreover, sulfate ions are widely found in nature. The visible light activity of the corresponding ≡Fe(SO₄)_m complex further makes this system a robust candidate for the *in situ* oxidation processes.

Appendix A. Supplementary data

The other supplementary details data to this article.

Acknowledgements

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Conflict of Interest

The authors declare no competing financial interest.

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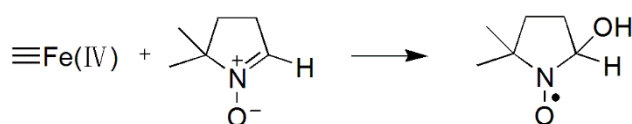
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Scheme 1. DMPO-•OH derived from the oxidation of DMPO by Fe(IV) through direct oxidation.

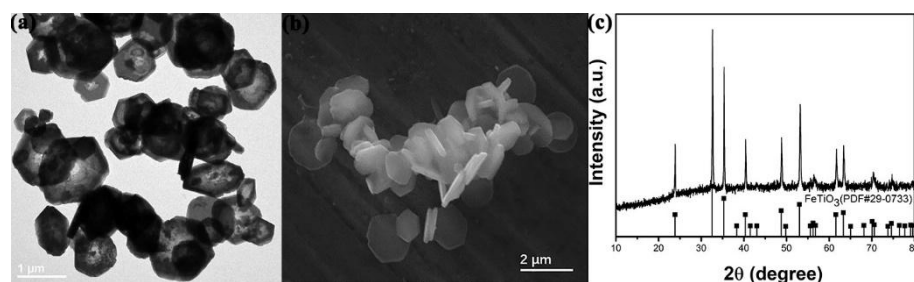


Figure 1. (a) TEM image, (b) SEM image and (c) XRD patterns of FeTiO₃.

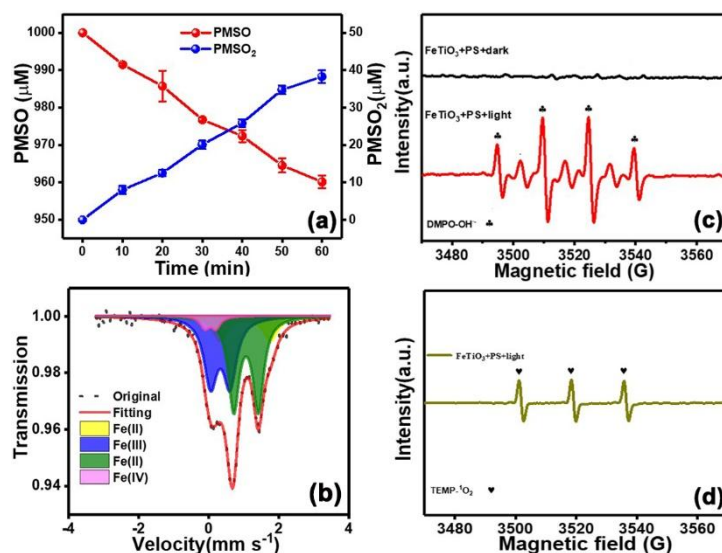


Figure 2. (a) Oxidation of PMSO and production of PMSO₂ in FeTiO₃/PS/light system (pH=4); (b) Mossbauer spectrum of recycled FeTiO₃ from the FeTiO₃/PS/Light system; (c) EPR spectra of the DMPO adduct formed from the FeTiO₃/PS/light and FeTiO₃/PS/dark

systems; (d) EPR spectrum of TEMP-¹O₂ formed from the FeTiO₃/PS/light system. (Cat.: 0.1 g·L⁻¹, PS: 1 mM, DMPO: 0.1 mM, TEMP: 0.1 mM, reaction time: 20 min).

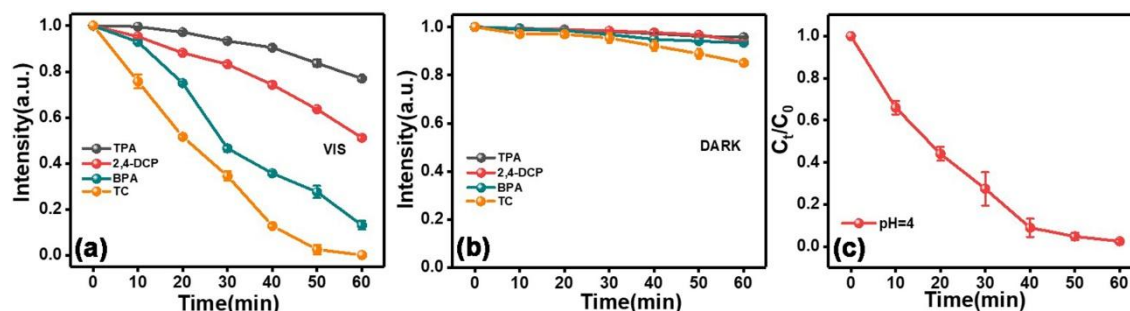


Figure 3. Degradation of aromatics in the FeTiO₃/PS system ($C_{\text{FeTiO}_3} = 0.1 \text{ g}\cdot\text{L}^{-1}$): (a) under the visible light irradiation; (b) in the dark. The TC concentration is 20 mg/L and the corresponding PS concentration is 2 mM. For other reactions, the aromatics concentration is fixed at 10 mg/L and the PS concentration is 5 mM; (c) Influence of pH buffer solution on TC degradation (Cat.: $0.1 \text{ g}\cdot\text{L}^{-1}$, TC: $20 \text{ mg}\cdot\text{L}^{-1}$, PS: 2 mM).

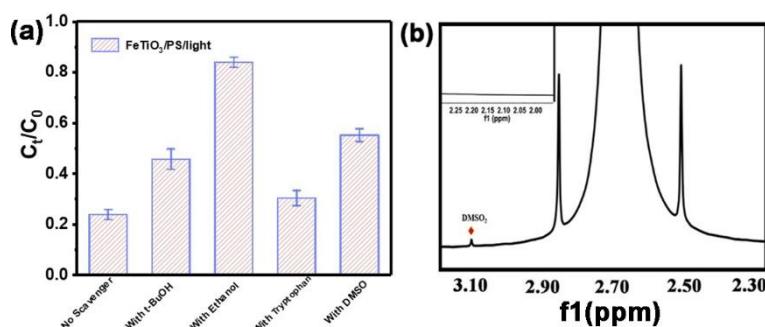


Figure 4. (a) Performances of the FeTiO₃/PS/light system with different scavengers (Cat.: $0.1 \text{ g}\cdot\text{L}^{-1}$, TC: $20 \text{ mg}\cdot\text{L}^{-1}$, PS: 1 mM, TBA: 100 mM, ethanol: 100 mM, tryptophan: 10 mg and DMSO: 100 mM, initial pH = 4); (b) ¹H NMR spectrum of the product obtained in D₂O (0.2 g/L of FeTiO₃, 2 mM of PS, 10 mL of DMSO, light). The DMSO₂ peak is denoted by a diamond.

. DMPO-[•]OH derived from the oxidation of DMPO by Fe(IV) through direct oxidation.

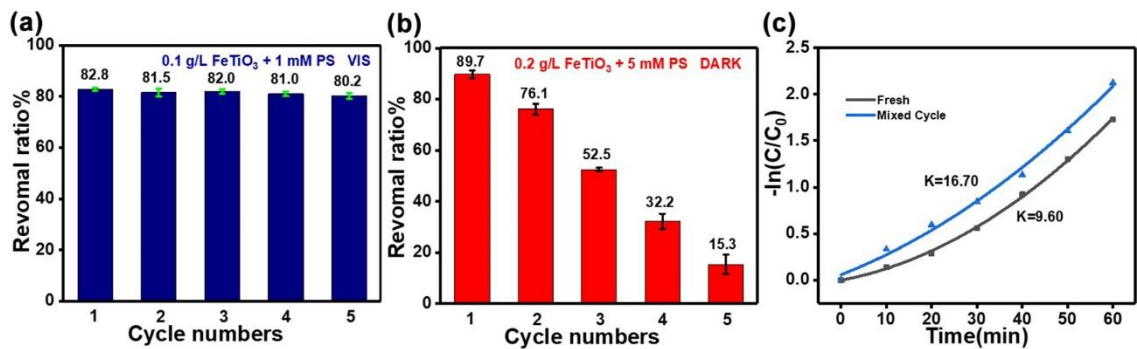


Figure 5. (a) Cyclic performance of the FeTiO₃/PS/light system (Cat.: 0.1 g·L⁻¹, TC: 20 mg·L⁻¹, PS: 1 mM); (b) Cyclic performance of the FeTiO₃/PS/dark system (Cat.: 0.2 g·L⁻¹, TC: 20 mg·L⁻¹, PS: 5 mM); (c) The simulated reaction kinetics of the fresh sample and the deactivated sample recycled from 5-run dark reaction.

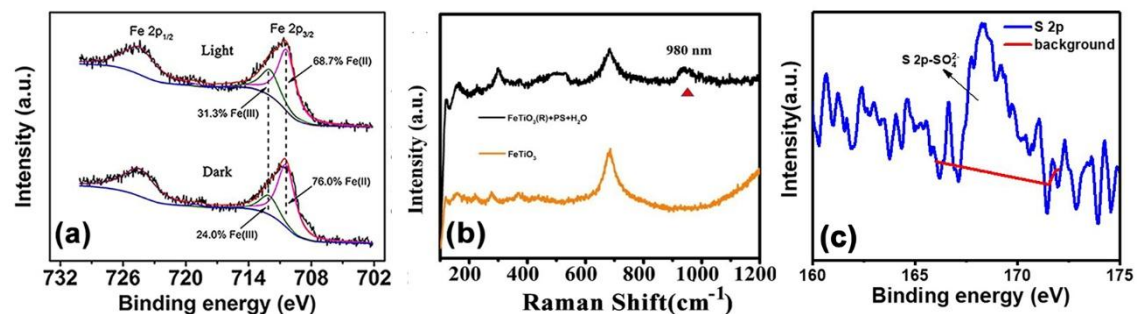


Figure 6. (a) XPS spectra for Fe 2p regions of FeTiO₃ in light and dark systems; XPS spectra of FeTiO₃ after dark reaction (b) S 2p; (c) Raman spectra of the FeTiO₃ before and after reaction.

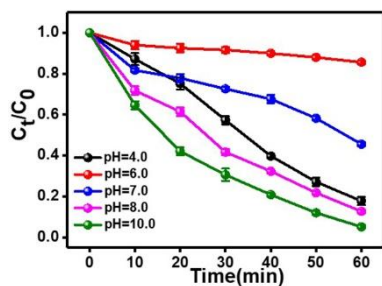
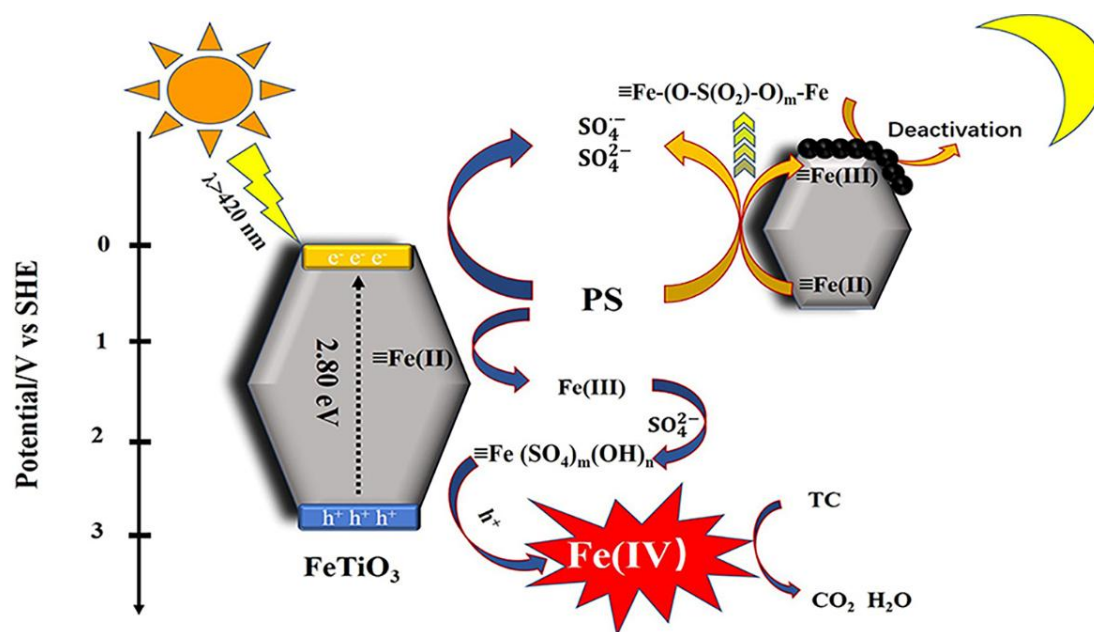


Figure 7. Influence of pH on the TC degradation efficiency of the FeTiO₃/PS/light system (Cat.: 0.1 g·L⁻¹, TC: 20 mg·L⁻¹, PS: 1 mM).

1

Graphical abstract



2

3 The in situ formed surficial Fe(III)-SO₄ complex causes the deactivation of
 4 FeTiO₃/PS system under the dark conditions, which however is the key intermediate
 5 for the further evolution to Fe(IV) species by photo-induced hole under the visible
 6 light irradiation. Selective and recyclable degradation of aromatics with higher
 7 ionization potential can be achieved over Fe(IV) formed from the FeTiO₃/PS/light
 8 system.

9

Highlights

- The FeTiO₃/PS system shows selectively photocatalytic performance towards phenolics
- A complex is in situ formed from Fe(III) and SO₄²⁻ on the FeTiO₃ surface
- The complex is the key intermediate for Fe(IV) production
- The photo-generated high-valent Fe(IV) is responsible for the selective degradation

Supplementary Material

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