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Hydroxylamine Promoted Fe(III)/Fe(II) Cycle on Ilmenite Surface to Enhance Persulfate Catalytic Activation and Aqueous Pharmaceutical Ibuprofen Degradation

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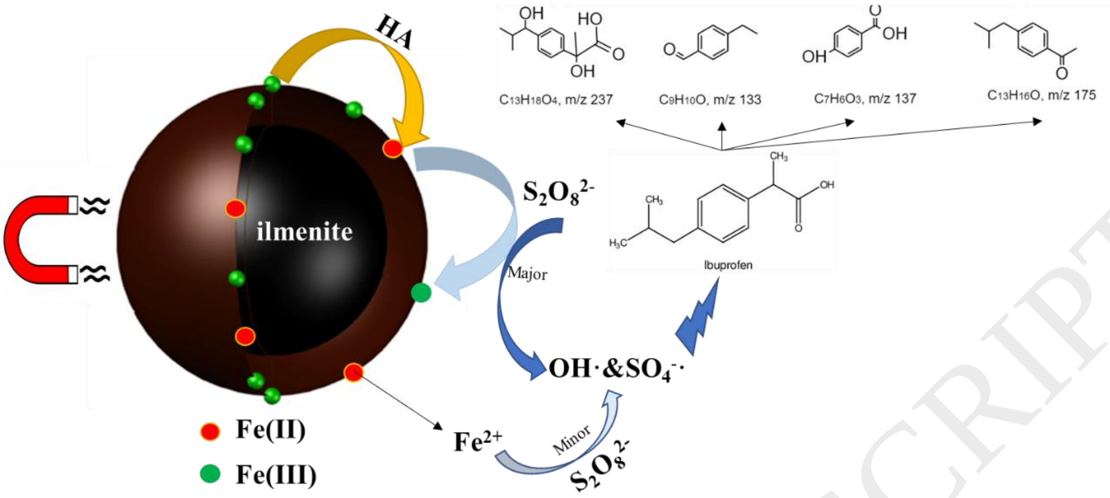
Graphical Abstract



Highlights

- Ilmenite coupled with hydroxylamine showed high reactivity in persulfate activation.
- Hydroxylamine enhanced radical generation by promoting surface Fe(III)/Fe(II) cycle.
- $SO_4^{-}\cdot$ and HO· were generated and contributed comparably to ibuprofen degradation.
- The performance under various conditions and in real wastewater was evaluated.
- An ibuprofen degradation pathway induced by $SO_4^{-}\cdot$ and HO· was proposed.

Abstract:

This study demonstrates a new system for the degradation of emerging pharmaceutical contaminants (e.g., ibuprofen) in water by coupling the naturally occurring ilmenite with hydroxylamine (HA) and persulfate (PS). Ilmenite was able to activate persulfate to generate sulfate radicals ($SO_4^{-}\cdot$) and hydroxyl radicals (HO·). The radical generation was greatly improved by adding small amount of hydroxylamine into the solution, due to the efficient Fe(III)/Fe(II) cycle on the ilmenite surface promoted by HA, which was confirmed by X-ray photoelectron spectroscopy and electron paramagnetic resonance (EPR) spectroscopy analysis. $SO_4^{-}\cdot$ and HO· contributed comparably to ibuprofen degradation, which was verified by the radical scavenging tests. The degradation was enhanced with increasing ilmenite, PS and HA dosages, but the HA exhibited strong scavenging effect at its high concentrations. The ilmenite/PS/HA process worked well in the real treated wastewater, because the surface-controlled radical generation was less affected by the water matrix. However, the formation of bromate in the bromide-containing water by this process should be concerned. Ibuprofen was partially mineralized, and the degradation products were identified by ESI-tqMS. A radical-induced degradation pathway was proposed based on the product identification. This work provides the mechanistic insights on persulfate activation based on the surface-controlled catalytic processes. It also offers a new strategy to degrade emerging contaminants in water and sheds light on the environmental functions of natural minerals.

Keywords: Emerging contaminant; Hydroxylamine; Natural ilmenite; Persulfate

1. Introduction

Contaminants of emerging concern (CECs), including pharmaceuticals and personal care products (PPCPs), are increasingly being detected at low levels in surface water, and there is concern that these compounds may have negative impacts on aquatic organisms and human beings [1–3]. They pose potential chronic toxicities, cause endocrine disruptions and induce antibiotic resistance to aquatic life and human beings [4,5]. These chemicals require additional considerations when applying existing ambient water quality criteria for the protection of aquatic organisms and human beings [6,7].

Advanced remediation technologies are required to deal with these chemicals, due to the relatively poor removal efficiency of the conventional water and wastewater treatment methods [3]. Advanced oxidation processes (AOPs), relying on the activation of oxidant precursors (e.g., hydrogen peroxide, persulfate, peroxymonosulfate, chlorine) and generation of reactive radical species, have emerged as good alternatives to treating the CECs [8–11]. Among them, oxysulfur radical-based AOPs (e.g., $SO_3^{\cdot-}$, $SO_4^{\cdot-}$, $SO_5^{\cdot-}$) are promising because the oxidant precursors (e.g., sulfite and persulfate) are easier to handle and has relatively lower cost [12–15]. These oxysulfur radicals can oxidize hydroxide/water to hydroxyl radicals, which complement with each other for the destruction of organic pollutants [13,16,17]. A number of methods have been reported to activate persulfate, including by UV light, electrolysis, ultrasonic radiation, and numerous metallic/non-metallic catalysts/materials [12,13,18–22]. Many of the current activation methods require high energy input (e.g., by UV, sonication and electrolysis) and/or noble materials, which limit their engineering applications in real-world practice. Instead, some naturally occurring materials have become increasingly popular to be used as the persulfate activators and/or catalysts [12,13]. Natural minerals, which contain transition metals, and are ubiquitous, easy-to-be obtained and relatively cheap, pose great potential to serve as persulfate activators and/or catalysts. The literature on the use of natural minerals for persulfate activation purposes are very limited in the current literature [23–29]. More experimental and pilot investigations are required to evaluate the feasibility of different minerals for persulfate activation, the process optimization under different environmental and operational conditions, the mechanisms for radical generation and the potential niche applications on environmental remediation.

Fundamentally, the radical generation mechanisms in the heterogeneous persulfate-activation systems are less understood [13,24]. Whether the radicals are generated in bulk solution or catalyst surfaces needs to be elucidated, and in fact some of the surface-bound catalysts are reported to be more reactive than those in the bulk solution [25–27]. Both sulfate radicals and hydroxyl radicals are generated theoretically, but whether both of them and how much do they respectively contribute to the degradation of certain organic compounds remain unknown and depends on the target compounds. This is critical to be figured out because it affects the degradation pathways as well as the intermediates/products, considering the rather complicated degradation mechanisms in such persulfate-based systems [13]. The organic pollutants are usually transformed to other compounds instead of fully mineralized [24,28]. Therefore, the identification of the degradation products and mechanistic pathways are also crucial to guarantee the used AOP does help detoxify the contaminated water, instead of producing more hazardous products. Moreover, whether the co-existing water matrices (e.g., dissolved organic matter and common anions) affect the process performance and will they be transformed to some undesired products in real water/wastewater scenarios need to be explored as well.

Persulfate has been reported to be effectively activated by the Fe^{2+}/surface-bound Fe(II), because these species are easy to donate one electron to persulfate for radical generation [29,30]. The reduction of Fe(III) by persulfate and generate radicals via subsequent chain reactions have also been reported, but the initial step (e.g., Fe(III) reduction) has a much lower reaction rate constant [17]. Most of the naturally occurring materials are under the aerobic conditions and the transition metals (e.g., Fe, Cu and Mn) inside/on the surface are at relatively higher valence state (e.g., Fe(III) and Mn(IV)) [17,31]. To accelerate the catalytic reactions, some reducing agents are used as the electron donor, to promote the reduction of metals from higher valence state to lower ones. Hydroxylamine (HA) is a common reducing chemical and has been used to enhance the Fe(III)/Fe(II) cycle of Fenton and Fenton-like reactions for the degradation of some model compounds (e.g., benzoic acid) [26,32,33]. Moreover, HA was reported to work better than other reductive agents (e.g., ascorbic acid, oxalate, and humic acid) in some heterogeneous Fenton systems, because it is a relatively weaker radical scavenger [25,26]. Despite these advantages, the chemical interactions between HA and natural minerals is less understood, which limits the application of mineral-dominant processes. Moreover, in the persulfate-based advanced oxidation processes, the role of HA on the persulfate activation and radical generation is anticipated to be interesting and deserve further investigation.

Therefore, this study was designed to fill the knowledge gaps as aforementioned. Natural ilmenite and ibuprofen were selected as the catalyst and target emerging contaminant respectively in this study. The role of hydroxylamine on the persulfate activation and radical generation in the ilmenite/persulfate system was specifically investigated and discussed. The radical generation mechanisms in this heterogenous system was elucidated. The performance of the process under different operational and environmental conditions was evaluated and the mechanistic pathway on ibuprofen degradation was explored.

2. Materials and methods

2.1 Chemicals and materials

Ibuprofen, sodium persulfate, sodium hydroxide, ethanol, hypochlorous acid, hydroxylamine, tert-butanol alcohol (TBA), and 5,5-dimethyl-1-pyrrolidine-n-oxide (DMPO) of reagent-grade were obtained from Sigma-Aldrich, USA. Pristine ilmenite was collected from a mining site in China. The raw mineral was mechanically crushed, and then selected by an electromagnetic and a gravity separator. Before the experiments, the ilmenite was sieved at 300-mesh and the final size of the ilmenite powder was smaller than 30 μm. The real wastewater samples were taken from a local wastewater treatment plant (Shatin WWTP) after the biologically treatment process. The water quality of the wastewater samples after 4.5-μm membrane filtration was provided in Table S1.

2.2 Experimental procedures

In batch tests, the ilmenite particles (0.05–1.0 g L^{-1}) were added to 100-mL flask containing ibuprofen at an initial concentration of 10 μmol L^{-1}. Sodium persulfate solution (0.5–4.0 mmol L^{-1}) and/or hydroxylamine solution (0.1–5.0 mmol L^{-1}) were then spiked to the solution to initiate the reaction. The pH of the reacting solution was unbuffered and measured as 6.5±0.5 throughout the reaction. Samples (1 mL) were collected by syringes at pre-determined time intervals, filtered with 0.45-μm membrane filters (Darmstadt, Germany), and then subjected to the measurement of residual oxidant and ibuprofen concentrations. Scavenging tests were conducted in the similar manner except that additional ethanol or tert-butanol at 50 mmol L^{-1} were added into the solution [34,35]. Tests in real wastewater were conducted in the similar manner except that the deionized water was replaced by the real treated wastewater after filter by 0.45-μm membrane filters.

To identify the degradation intermediates/products of ibuprofen, 50-mL liquid samples were collected, filtered with 0.45-μm membrane filters, enriched by liquid-liquid extraction and rotary evaporation, and analyzed by the electrospray ionization-triple quadruple mass spectrometry (ESI-tqMS) [36]. In addition, tests were performed to investigate the repeatedly use of ilmenite for ibuprofen catalytic degradation. In each reuse cycle, after 60-min reaction, the reacted ilmenite was magnetically separated and then gently rinsed by deionized water for three times. And it was reused for ibuprofen degradation in the same manner as described above. Parallel tests were conducted in the same manner except that the pristine and used ilmenites were magnetically separated, vacuum-freeze dried and subjected to characterization of several surface properties.

2.3 Analytical methods

The ibuprofen concentration was determined using an ultra-performance liquid chromatograph (HPLC, Shimadzu 6A) equipped with a C18 column (4.6 mm × 150 mm, 5 μm particle size) and a UV detector at 270 nm. The eluents for ibuprofen determination were methanol (70%) and pH-3 water (30%, prepared by diluting 687-μL phosphoric acid in 1-L deionized water) and was set at a flow rate of 1.0 mL/min. The intermediates and products of ibuprofen degradation were identified with a Waters HPLC/ESI-tqMS system equipped with an HSS T3 column (50 mm × 2.1 mm, 1.8 μm particle size). The eluents were methanol and water at a flow rate of 0.5 mL/min and the column temperature was set at 40 °C [29]. The concentrations of dissolved Fe(II) and Fe(III) were measured by the phenanthroline method [37]. An Electron Paramagnetic Resonance (EPR) Spectrometer (Bruker A300) was used to identify the radicals. Dissolved organic carbon was determined with a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu). Inorganic anions including bromate were measured using an ion chromatograph (Dionex, ICS 3000).

The elemental composition of ilmenite was determined by an X-ray photoelectron spectroscopy (XPS) analysis performed using an X-ray photo- electron spectroscope (PHI 5600, Physical Electronics Inc., USA) with Al Ka radiation (1486.6 eV). The crystal structure of ilmenite was characterized by a powder X-ray diffraction (XRD) spectrometer (PW-1830, Philips) with Cu Ka radiation (l1⁄41.5406 A) over a 2q range of 5–70°. The specific surface area and pore volume of ilmenite were measured using a BET surface area analyzer (SA 3100, Beckman Coulter Inc., USA). The magnetism of ilmenite was determined using a superconducting quantum interference magnetometer (MPMS-5S, Quantum Design Inc., USA).

3. Results and discussions

3.1 Characterization of ilmenite

XPS spectroscopy was firstly applied to identify the elemental composition and the valence states of the surface-bound metals of ilmenite. As shown in Fig. 1a, the XPS full spectrum suggests that O, Ti and Fe are the major components of virgin ilmenite, and the Fe, Ti and O account for 36, 32.2 and 29.6 wt.% respectively. Apart from Fe, Ti and O, other elements (e.g., Si, Al, K, Ca, Mg, Zn) are identified at trace amounts. In the Fe2p spectrum (Fig. 1b), the two peaks at the binding energy of 711.5 and 725.4 eV are identified, representing Fe(II) (40%) and Fe (III) (60%) respectively on virgin ilmenite surface [38]. Accounting for Ti2p and O2p orbitals, the major component in virgin ilmenite is anticipated to be $FeTiO_x$. The crystal form of virgin ilmenite was further confirmed by the XRD spectrum, as shown in Fig. 1c. The major peaks are identified at 2-theta of 32.65°, 35.3°, 43°, 56° and 63° in the XRD spectrum, and by comparing with the JCPDS card no. 21-1276, the main form of the crystal is $FeTiO_3$ [39]. More interestingly, the ilmenite has a saturation magnetization of approximately 0.6 emu/g (Fig. 1d). The magnetic feature suggests that the ilmenite can be easily magnetically separated from the treated water by an external magnet. The BET specific surface area and total pore volume are determined to be 1.2466 m^2 g^{-1} and 29.5 nm respectively, indicating the ilmenite has a relatively less porous structure, and is likely not to be a good adsorbent when applied in water treatment (Fig. S1) [24]. Table 1 summarizes the basic properties of virgin ilmenite as characterized and discussed here.

3.2 Degradation of ibuprofen in different systems

The degradation of ibuprofen (IBP) by different processes, including persulfate (PS) alone, ilmenite alone, PS + ilmenite and PS + ilmenite + HA system, was shown in Fig. 2a. Persulfate itself was not able to oxidize IBP under the tested conditions, which was consistent with reported literature [24]. Ilmenite alone hardly oxidized nor adsorb IBP, which was consistent with the fact that it has small specific surface area and poor porous structure, as discussed in Section 3.1. The coupling of HA and PS was not able to degrade IBP, indicating the HA itself could not activate PS. The coupling of PS with ilmenite could degrade IBP by 30% under the experimental conditions., which was hypothesized to be attributed to the radicals generated from the PS and ilmenite interaction [13]. The IBP degradation was largely improved by adding 0.5-mM HA in the PS + ilmenite system, with more than 95% of removal under the same tested conditions. The degradation of IBP followed the pseudo first-order kinetics and the degradation rate constants were determined to be 0.0048 and 0.0499 min^{-1} in the absence and presence of HA respectively. The 10-times higher reaction rate constant was anticipated to be attributed to the enhanced radical generation from PS and ilmenite interactions in the presence of HA. To verify this, tests were firstly conducted to identify the radical species and their contributions to IBP degradation in the PS + ilmenite + HA system. Ethanol (EtOH) and tert-butanol (TBA) were used as the radical scavengers. EtOH is highly reactive towards HO· (1.9 × 10^{9} M^{-1}s^{-1}) and $SO_4^{-}\cdot$ (5.6 × 10^{7} M^{-1}s^{-1}), and it was used to scavenge both two radicals [40]. TBA has a much higher reaction rate constant towards HO· (6.0 × 10^{8} M^{-1}s^{-1}) than that towards $SO_4^{-}\cdot$ (4.0 × 10^{5} M^{-1}s^{-1}), and it was used to scavenge HO· only [39]. As shown in Fig. 2b, the IBP degradation was completely hindered in the presence of 50-mM EtOH, verifying that the removal of IBP in the PS + ilmenite + HA system was attributed to the oxidation by radicals. On the other hand, the pseudo first-order rate constant decreased by 42.89% (from 0.0499 to 0.0285 min^{-1}) in the presence of 50-mM TBA, which demonstrated that both $SO_4^{-}\cdot$ and HO· were generated in the PS + ilmenite + HA system, and their relative contributions to the IBP degradation were 57% and 43%, respectively. Considering the second-order rate constants of IBP towards $SO_4^{-}\cdot$ and HO· have been reported to be 1.66 × 10^{9} and 3.43 × 10^{9} M^{-1} s^{-1}, respectively [41], the steady-state concentration (equal to the overall degradation rate divided by the second order rate constant) of $SO_4^{-}\cdot$ is calculated to be around 2.75 times higher than that of HO· in the PS + ilmenite + HA system.

3.3 Mechanisms of radical generation in the PS/ilmenite/HA system

The radical generation mechanisms in the heterogenous Fenton and Fenton-like processes remain less understood, and both the dissolved metal ions (e.g., Fe^{2+}) and the surface-bound metals have been reported to activate persulfate and generate radicals [13]. In this study, the concentrations of dissolved Fe^{2+} during ilmenite itself dissolution and/or ilmenite + PS interactions were monitored, and the maximum concentration of Fe^{2+} was 0.29 mg L^{-1} for the dosage of 0.2 g L^{-1} ilmenite and 1.0 mmol L^{-1} PS. Tests were firstly conducted to compare the capability of 0.2-g L^{-1} ilmenite and 0.29-mg L^{-1} Fe^{2+} in persulfate activation and radical generation under the same tested conditions. As shown in Fig. 3a, in the PS + Fe^{2+} + HA system, the IBP degradation rate constant was only 0.0118 min^{-1}, which was 4.22 times lower than the PS + ilmenite + HA system (0.0499 min^{-1}). The results indicated that dissolved Fe^{2+} was not the main activator of persulfate. With increasing ilmenite dosage from 0.05 to 1.0 g L^{-1}, the dissolved Fe^{2+} concentration increased from 0.12 to 2.96 mg L^{-1}. Fig. 3b correlates the IBP degradation rate constants with the dissolved Fe^{2+} concentrations, which was not in a linear, but a convex-type relationship. This result supported the anticipation that the dissolved Fe^{2+} was not the major catalyst in the PS + ilmenite + HA system. ESR spectra displays the signal strength of radical generation in the PS + Fe^{2+} + HA (purple line), PS + ilmenite (blue line) and PS + ilmenite + HA systems (red line). The signals had comparable strength in the PS + Fe^{2+} + HA (purple line) and PS + ilmenite (blue line) systems, but was much stronger in the PS + ilmenite + HA system, which further proved that instead of dissolved Fe^{2+}, other species was the dominant contributor to persulfate activation and radical generation.

In the heterogenous Fenton processes, the surface-bound Fe(II) has been reported to play an critical role in hydrogen peroxide activation [25,26]. And the HO· generation rate by the surface-bound Fe(II) was 10^2−10^4 times higher than the homogeneous Fenton processes [25]. The catalytical decomposition of hydrogen peroxide on the surface of minerals was also reported to be faster than that in the homogeneous systems [42]. Therefore, the surface-bound Fe(II) on the ilmenite was also anticipated to be the major catalytic activator to persulfate in the PS + ilmenite + HA system. The XPS Fe2p spectra (Fig. 3d) provides a strong proof that the surface-bound Fe(II) content was improved from 30% to 60% in the presence HA, which was consistent with the enhanced radical generation and IBP degradation as observed in previous sections. Detailed investigations are recommended to more accurately qualify and quantify the surface-bound Fe(II) species by using some advanced characterization methods (e.g., extended X-ray absorption spectroscopy), quantum chemical calculation (e.g., density functional theory) and mathematical modelling approaches.

3.4 Process performance under various conditions and in real wastewater matrix

Fig. 4 shows the effects of PS, ilmenite and HA dosages on the degradation of IBP in the PS + ilmenite + HA system. The degradation rate constants increased from

0.0135 to 0.1902 min^{-1} with increasing $FeTiO_3$ dosage from 005 to 1.0 g L^{-1} (Fig. 4a). The rate constants increased linearly with $FeTiO_3$ dosages (Fig. 4b). With increasing PS dosage from 0.5 to 4.0 mmol L^{-1}, the degradation rate constants increased from 0.0101 to 0.3682 min^{-1} (Fig. 4b). However, the rate constants did not show a linear relationship with the PS dosages (Fig. 4d), but in a concave-type relationship, and it was mainly due to the decreased solution pH (i.e., from 7.0 to 6.5, 5.3 and 4.0) in the presence higher concentration of PS, which favored the radical generation and IBP degradation [12]. The degradation rate constants increased with increasing HA dosages (Fig. 4e), because higher concentration of HA promoted the reduction of Fe(III) to Fe(II) on the ilmenite surface and enhanced the radical generation. However, the radical scavenging by HA was enhanced at higher HA concentrations as well, which explained the convex-type relationship between degradation rate constants and HA dosages (Fig. 4f). Results also indicated that the optimal dosages of PS, ilmenite and HA should be found, with due consideration of process efficiency and cost-effectiveness [13].

The process performance on IBP degradation was also tested in the real treated wastewater and compared with that in the synthetic water, as shown in Fig. 5a. The IBP degradation rate constant was 0.0499 and 0.0342 min^{-1}, respectively, in the synthetic water and real treated wastewater samples. The only 30% decrease in rate constant was unexpected, with due consideration of such high contents of TOC (7.65 mg C L^{-1} of TOC) and salts (2.5 g L^{-1} of salinity) in the treated wastewater (Table S1), which are considered as typical radical scavengers [13]. On the other hand, the results were reasonable, considering the surface-bound Fe(II) dominant catalytic activation of persulfate may less be affected by water matrix components [25], and the fact that the salts (e.g., chloride and bicarbonate) are also potentially transformed to other radicals (e.g., Cl·, Cl_2^-·, and CO_3^-·) by HO·/SO_4^-· and contribute to IBP degradation [15][43]. Considering the treated wastewater also contains relatively high level of bromide at 4.09 mg L^{-1} (because sweater is used for toilet flushing in Hong Kong), the potential generation of bromate from bromide oxidation in the PS + ilmenite + HA system was also examined. Around 200 μg/L of bromate was detected under the tested conditions, which suggested that the bromate formation should be concerned, when adopting the persulfate-based advanced oxidation process to treat bromide-containing water. The catalytic performance of ilmenite in the presence of HA was evaluated and shown in Fig. 5b. Under the experimental conditions, the ilmenite exhibited stable catalytic performance within the four cycles of tests, with less than 5% decrease in radical generation and IBP degradation in each cycle. Considering the magnetic feature, the ilmenite exhibits promising potentials as repeated-use catalyst in real-world applications.

3.5 Products and proposed pathways of ibuprofen degradation

Although was completely degraded, only 50% of the IBP was mineralized by the PS + ilmenite + HA process under the experimental conditions. The results indicated that the IBP was transformed to some intermediate/products. ESI-tqMS technique was thus applied to identify degradation products. Six major products were identified according to the full scan spectra, at mass to charge ratios (m/z) of 221, 237, 205, 175, 137 and 133, respectively (Fig. S2a). Product ion scan spectra was further adopted to analyze the possible structures of these products (Fig. S2b–d). The initial step of the reaction was anticipated to be the hydroxylation of IBP by OH· [44], which produced mono- and di-hydroxylated IBP, with a m/z of 221 and 237 respectively. The compound with a m/z of 133 was identified as 4-ethylbenzaldehyde, which was derived from mono-hydroxylated IBP via decarboxylation, hydroxylation and loss of 2-propanol [24]. 4-Hydroxybenzoic acid was proposed to represent the compound with a m/z of 137. For the compound with a m/z of 175, it was probably 4-isobutylacetophenone that was derived from the decarboxylation and sequential oxidation of IBP by both HO· and $SO_4^{-}\cdot$ [45]. It should be noted that this compound was reported to be even more toxic than the original ibuprofen, which raised another concern about the persulfate-based advanced oxidation process [46]. Fig. 6 illustrates a scheme for radical-induced IBP degradation in the PS + ilmenite + HA process, based on the products identified above. More studies are suggested on the control of degradation products/by-products of the persulfate-based advanced oxidation processes, to further pave the ways for real-world applications.

4 Conclusions

Persulfate-based catalytic processes have emerged as promising advanced oxidation processes for environmental remediation purposes. The development of high-efficiency, high-stability and low-cost persulfate catalyst/activator, the better understanding of the working mechanisms, and the subsequent process optimization are thus necessary to promote the real-world applications of persulfate-based AOPs. This study highlights a newly-identified, highly-efficient and stable, and low-cost catalyst for persulfate activation and degradation of aqueous emerging contaminant, by coupling the naturally occurring mineral (e.g., ilmenite) with hydroxylamine. Both $SO_4^{-}\cdot$ and $HO\cdot$ were generated from the catalytic persulfate activation, and they contributed comparably to ibuprofen degradation in water. The major catalytic species was the surface-bound Fe(II), instead of the dissolved Fe^{2+}, which was proved by several comparison tests and EPR and XPS analysis. The degradation was enhanced with increasing ilmenite, PS and HA dosages, but the optimized dose should be considered to avoid the excessive scavenging and wasting. The process worked relatively well in the real treated wastewater, but the formation of by-products should be concerned. A radical-induced degradation pathway was proposed to provide more mechanistic insights on the system.

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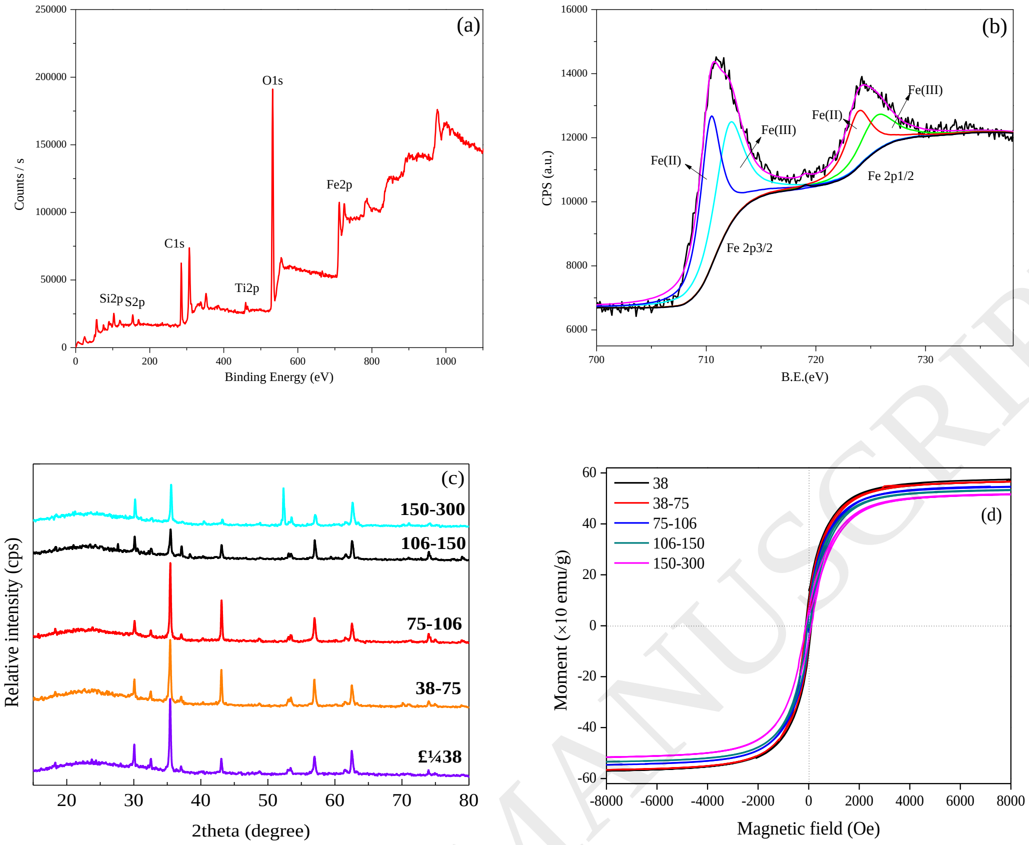

Fig. 1. (a). XPS full spectrum of virgin ilmenite; (b). Fe2p spectrum of virgin ilmenite; (c). XRD spectra of virgin ilmenite at different sieving sizes; (d). Magnetic hysteresis loop at 300 K of virgin ilmenite at different sieving sizes.

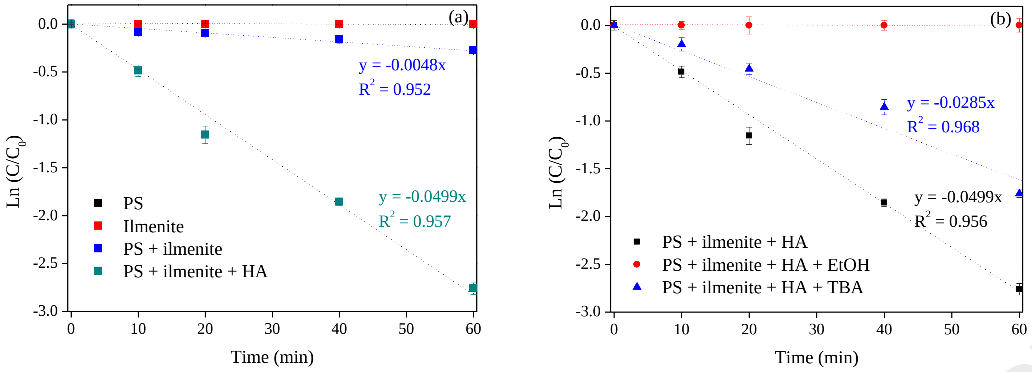

Fig. 2. (a). Time-dependent IBP degradation in the PS alone, ilmenite alone, PS + ilmenite and PS + ilmenite + HA systems; (b). Effects of ethanol and tert-butanol on the IBP degradation in the PS + ilmenite + HA system. Conditions: [IBP] = 10 µM, [PS] = 1.0 mM, [ilmenite] = 0.2 g/L, [HA] = 0.5 mM, initial pH = 7.0 and temperature = 25 ºC.

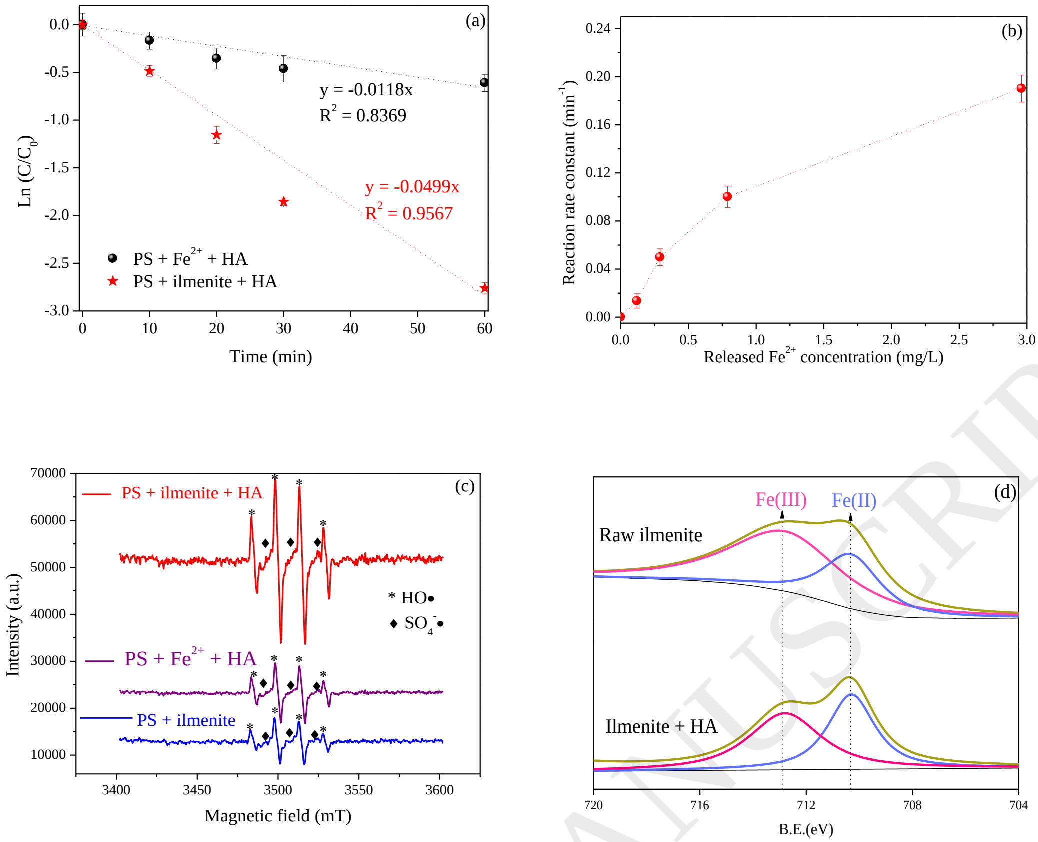

Fig. 3. (a). Comparison of ilmenite and dissolved Fe^{2+} on persulfate activation and IBP degradation; (b). Correlation between released Fe^{2+} concentration and the reaction rate constants; (c). EPR spectra of hydroxyl and sulfate radicals of different processes; (d). XPS Fe2p spectra of pristine ilmenite and reacted ilmenite with HA. Conditions: [IBP] = 10 µM, [PS] = 1.0 mM, [ilmenite] = 0.2 g/L, [HA] = 0.5 mM, [ilmenite] = 0.2 g/L, [EtOH] = [TBA] = 50 mM, initial pH = 7.0 and temperature = 25 ºC.

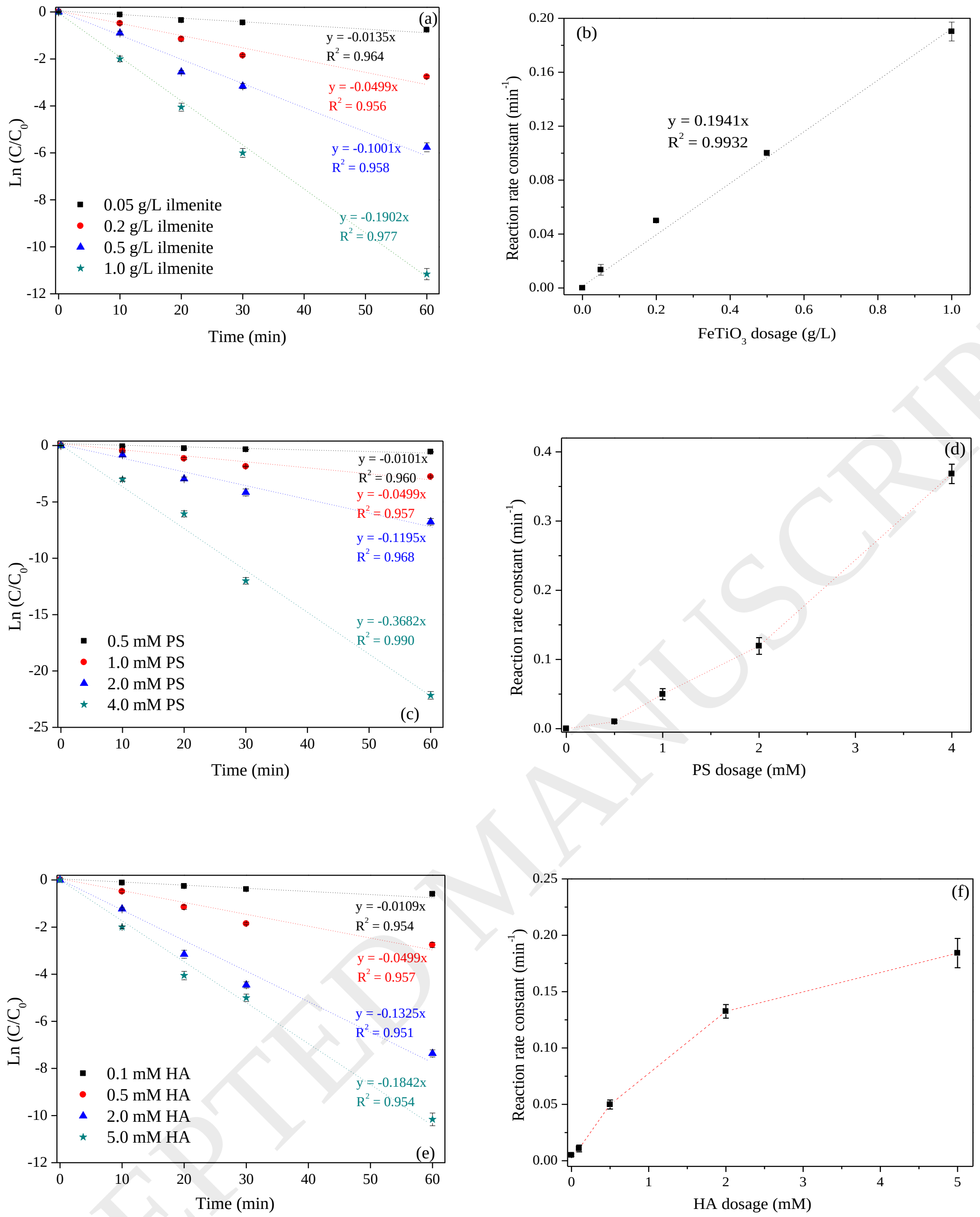

Fig. 4. (a,b). Effect of FeTiO$_3$ dosage on the IBP degradation; (c,d). Effect of persulfate dosage on the IBP degradation; (e,f). Effect of HA dosage on the CBZ degradation. Conditions: [IBP] = 10 μM, initial pH = 7.0 and temperature = 25 ºC.

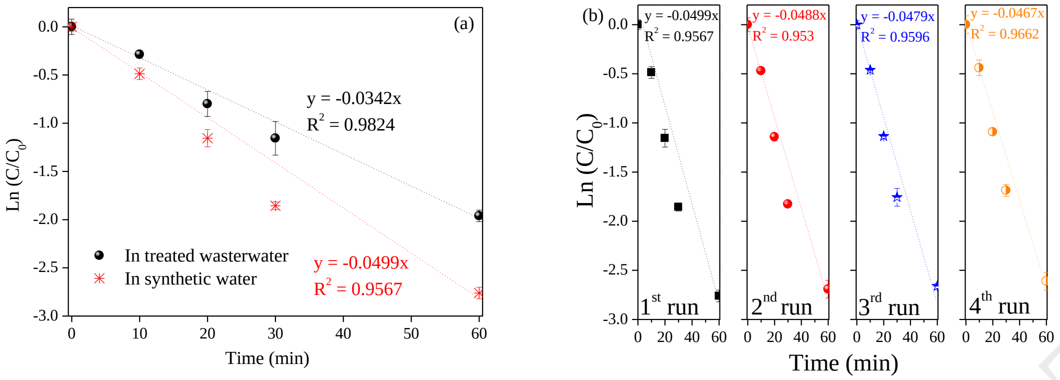

Fig. 5. (a). Comparison of IBP degradation by the ilmenite + PS + HA process in synthetic water and real treated wastewater; (b). Performance of ilmenite + PS + HA process for repeated use. Conditions: [IBP] = 10 µM, [PS] = 1.0 mM, [ilmenite] = 0.2 g/L, [HA] = 0.5 mM, initial pH = 7.0 and temperature = 25 ºC.

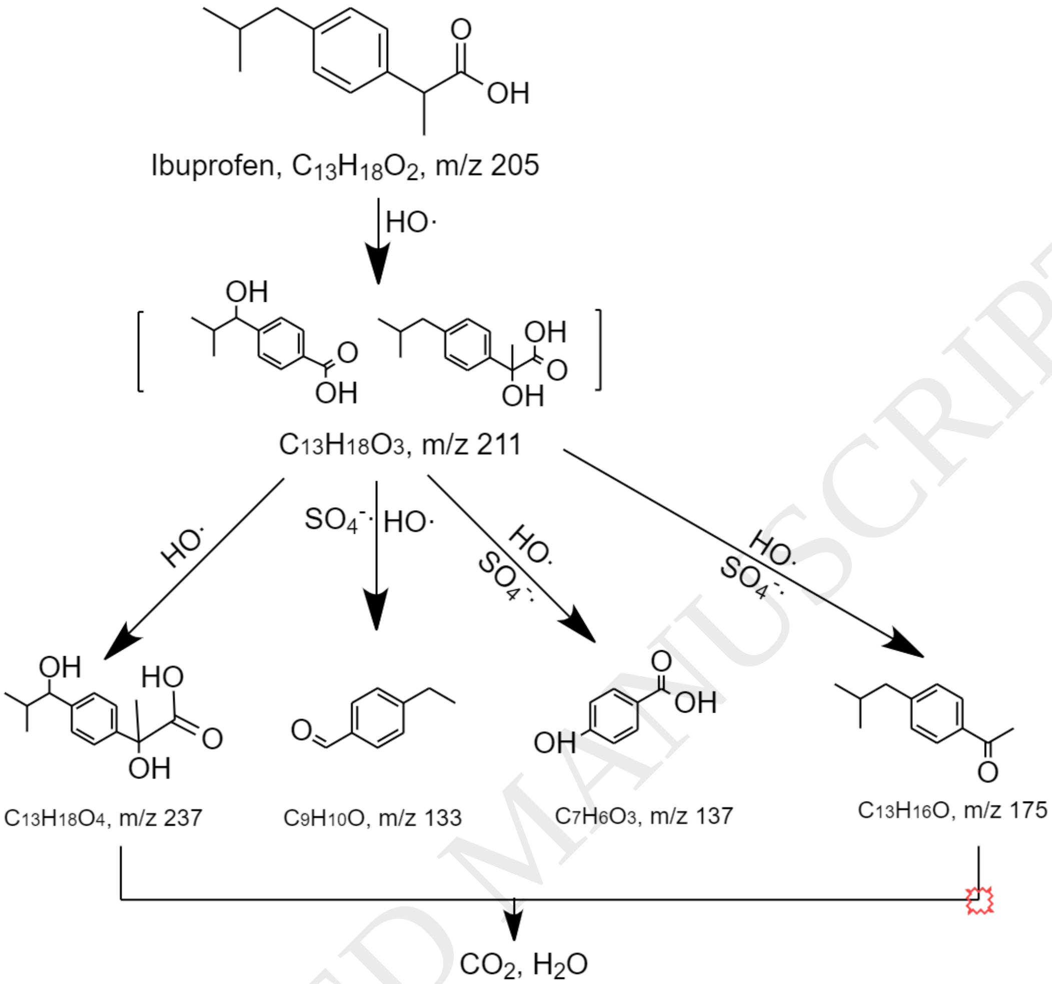

Fig. 6. A degradation pathway of IBP in the ilmenite + PS + HA process.

Conditions: [IBP] = 1 μM, [PS] = 1.0 mM, [ilmenite] = 0.2 g/L, [HA] = 0.5 mM, initial pH = 7.0 and temperature = 25 ºC.

Table 1. Characterization of pristine ilmenite mineral.

	Fe content (wt. %)	Ti content (wt. %)	S_{BET} (m^2/g)	TP_{size} (nm)	M_s (emu/g)
Ilmenite	39.0	35.2	1.2466	29.5	0.6