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Degradation of the ciprofloxacin antibiotic by photo-Fenton reaction using a Nafion/iron membrane: role of hydroxyl radicals

Fei Wang^{1,2} · Yichen Zhang³ · Hao Ming^{3,4} · Li Wang³ · Zhongyuan Zhao³ · Yuehong Wang⁵ · Jiyan Liang³ · Yan Qin⁶

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Abstract

Antibiotic pollution in waters is a major health issue that induces antimicrobial resistance and, in turn, the inefficacy of actual antibiotics to cure diseases. There is therefore a need for antibiotic removal from water and wastewater, yet actual remediation techniques are limited. Here, we studied the degradation of ciprofloxacin by the photo-Fenton reaction using a Nafion/ Fe^{3+} membrane as catalyst, with focus on the effect of hydroxyl (·OH) on membrane stability and recycling. Concentration of ciprofloxacin and ·OH were measured by high-performance liquid chromatography (HPLC). The Nafion membrane was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), attenuated total reflection (ATR) and X-ray photoelectron spectroscopy (XPS). Results show that the Nafion/Fe³⁺ membrane degrades ciprofloxacin completely within 4 h. After membrane recycling, degradation efficiency is reduced due to the loss of Fe³⁺ ions during membrane regeneration. Moreover, ·OH alters the carbon backbone of the membrane.

Keywords Heterogeneous-fenton catalyst \cdot Nafion \cdot Fe³⁺ immobilization \cdot Ciprofloxacin degradation

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☐ Jiyan Liang liangjiyan2017@126.com

- ⊠ Yan Qin qinyan1912@163.com
- ¹ School of Environment, Harbin Institute of Technology, Harbin 150090, China
- ² National Key Laboratory of Human Factors Engineering, China Astronaut Research and Training Center, Beijing 100094, China
- ³ School of Science, Shenyang University of Technology, Shenyang 110870, China
- ⁴ Shenyang Institute of Science and Technology, Shenyang 110167, China
- ⁵ Key Laboratory of Song Liao Aquatic Environment, Jilin Jianzhu University, Changchun 130118, China
- ⁶ Shenyang Medical College, Shenyang 110034, China

Introduction

During the last 30 years, environmental issues about the chemical and biological contaminations of water have become a major concern for society and the industry (Crini and Lichtfouse 2018). There are more and more difficult-todegrade organic substances in domestic sewage and industrial wastewater. Antibiotic pollutants have the characteristics of being difficult to degrade, highly toxic and stable. The use of antibiotics has considerably increased since the last century (Shi et al. 2019). More than 50,000 tons of antibiotics are directly discarded into the environment such as water and soils. Gao et al. (2012) used high-performance liquid chromatography tandem mass spectrometry to detect 25 antibiotics of five classes in the coastal areas of the South Yellow Sea. They found that the concentrations of fluoroquinolones and sulfonamides were relatively high, of 46.5%. Ahmed et al. prepared ciprofloxacin with activated carbon using microwave, which showed that the activated carbon could degrade norfloxacin and ciprofloxacin to 98% and 96%, respectively (Ahmed and Theydan 2014). Dewitte et al. used ozone method to treat ciprofloxacin antibiotics in water. Although ciprofloxacin can be degraded, the byproducts produced by the degradation of ciprofloxacin have certain toxicity. Although this treatment method can degrade ciprofloxacin, its cost is high, ciprofloxacin cannot be completely mineralized, and it may produce strong toxic intermediate products (Dewitte et al. 2008).

The abatement of contaminants in aqueous solution activated by Fenton reagent has gained interest. In order to overcome the disadvantages of Fenton process, researchers have focused more on the heterogeneous Fenton process (Nidheesh 2015). Heterogeneous Fenton systems have been reported to set out with a slower kinetics when compared with the homogeneous systems during the degradation of the organic pollutants. Their usefulness follows from high reactivity and non-selectivity of the generated hydroxyl radicals (·OH), which can resolve numerous organic compounds. Introducing ultraviolet light into Fenton reaction can improve the efficiency of Fenton reaction. In the Photo-Fenton process, the ultraviolet (UV) light can assist the reduction of Fe^{3+} to Fe^{2+} to react with H_2O_2 to generate ·OH through the reaction (Jain et al. 2018). Photochemicalassisted Fenton reaction was effective for contaminant's oxidation from aqueous solution at optimal pH of around 3. At this pH, the predominant ferric iron species is $Fe(OH)^{2+}$ which absorbs strongly UV light (Tarkwa et al. 2018).

Inbasekaran Muthuvel et al. prepared Fe (III) immobilized fire clay catalyst, Fe (III–Al₂O₃ catalyst and heterogeneous bentonite Fenton catalyst and used them in natural sunlight degradation of acid dyes. The fire clay catalyst and Fe-bentonite catalyst were found to be stable, reusable and efficient over a wide pH range of 2–7. Higher efficiency of the Fe (III)–Al₂O₃ catalyst in solar light than in UV light (Muthuvel et al. 2008, 2012, 2014).

Recently, Fe ions have been immobilized on Nafion membranes, as a heterogeneous Fenton catalyst, which can effectively reduce the dissolution of Fe ions (Fernandez et al. 1999). When 2, 4-dichlorophenol (1 mM) is degraded, it can be used continuously for four times and still maintain high degradation efficiency (Sabhi and Kiwi 2001). When degrading orange II (0.05 mM), it was used five times in succession, and orange II was degraded, and the Nafion membrane maintained high catalytic performance (Fernandez et al. 1998).

Nafion membrane has an aliphatic perfluorinated backbone with ether-linked side chains ending in sulfonate cation exchange sites (Laconti et al. 2003). It is a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether with a semicrystalline structure (Patil et al. 2005). This structure gives Nafion membrane long-term stability under oxidizing or reducing conditions (Panchenko et al. 2004). However, when the Nafion/Fe³⁺ membrane is used as a heterogeneous Fenton catalyst to degrade organic matter, Fe ions are eluted and the Nafion membrane structure is attacked, resulting in a limited life of Nafion membrane.

Nafion membrane failure is mainly due to its mechanical degradation. Fluorine loss causes the membrane to be degraded, which is a direct measure of the degradation rate of the Nafion membrane (Pozio et al. 2003). In order to prevent membrane failure, research and development of Nafion membranes have been carried out (Mališ et al. 2016; Tang et al. 2007). Reports on Nafion oxidation suggest that the reactive oxygen attacks the carboxyl groups at the chain ends and the sulfoxide groups on the side chains (Zhang et al. 2009; Kinumoto et al. 2006; Sugawara et al. 2011). Oxidative degradation of the carboxyl group produces a new carboxyl group upon decomposition of the group (Shah et al. 2009). The polymer chain becomes shorter as a result of this cycle of unzipping reactions, the membrane eventually becomes thinner, and pinholes appear (Fernandes and Ticianelli 2009; Kundu et al. 2008). Sulfoxide is a proton transfer group and sulfoxide cleavage from the polymer reduces proton diffusion in the polymer. Collier et al. (2006) has conducted extensive research on membrane degradation and discussed some detailed mechanisms of degradation and some possible mitigation strategies.

Here, we studied the performance of Nafion membranes and cycle stability. The Nafion membrane was pretreated and loaded with Fe^{3+} to prepare a heterogeneous Fenton catalyst. The production rate of \cdot OH under different conditions and the degradation amount of ciprofloxacin were determined in the presence of ultraviolet light.

Experimental section

Materials

Nafion perfluorinated membranes were obtained from Dupont. FeCl₃· $6H_2O$, H_2O_2 , HCl, ciprofloxacin, H_2SO_4 and NaOH were analytical reagent. Glacial acetic acid, methanol, acetonitrile, citric acid, 2,5-dihydroxybenzoic acid, triethylamine and salicylic acid were guaranteed reagent, and experimental water is ultrapure water.

Methods

The detection of \cdot OH in solution was carried out via Agilent Technologies 1200 Seris High Performance Liquid Chromatography (HPLC) provided with a HPLC in column (C-18, 4.6 mm*250 mm). The mobile phase was water (pH is adjusted to 3.5 with acetic acid)–methanol (60:40), and the column temperature is 30 °C. The detection wavelength is 254 nm, peak at 10 min. The flow rate was 1 mL/min and the injection volume was 10 µL.

Ciprofloxacin was detected in solution HPLC in column (C-18, 4.6 mm*150 mm). The mobile phase was 0.05 mol/L citric acid solution (pH is adjusted to 3.5 with triethyl-amine)–acetonitrile (82:18), the detection wavelength was 277 nm, and the column temperature was 30 °C, peak at

5.4 min. The flow rate was 1 mL/min, and the injection volume was 10 μ L.

Phenanthroline spectrophotometry was used to determine the total iron concentration, and an ultraviolet-visible spectrophotometer was used to measure the absorbance at 510 nm. And get the standard curve of iron. Absorbance = $0.0036 \times C_{Fe} + 0.0016$.

Attenuated total reflection (ATR) spectroscopy of Nafon/ Fe³⁺ membranes was performed using Nicolet iS5, DLaTGS detector, KBr beam splitter and 633 nm He–Ne laser.

X-ray photoelectron spectroscopy (XPS) analysis of Nafon/Fe³⁺ membranes was performed using Escalab 250xi. Al X-ray source (hv = 1486.6 eV, tube voltage is 15 kV, tube current is 12 mA. Calculated power is 180 W, and diameter beam spot is 500 microns). The evaluation of the binding energy of Nafion/Fe³⁺ membrane was carried out following the standard procedures, according to Shirley applying background correction, by subtracting X-ray satellites to evaluate XPS data.

X-ray diffraction (XRD) analysis was carried out by X-ray diffractometer (SHIMADZU, XRD-700), CuK α , λ =0.1540 nm, the filter was Ni, the tube flow was 30.0 mA, the tube pressure was 40 kV, and the scanning speed was 5°/min.

Scanning electron microscopy (SEM) and energy-dispersive spectrometer (EDS) were carried out using a Hitachi SU8010N field emission scanning electron microscope, zooming in to $5-200 \mu m$.

Nafion/Fe³⁺ membrane preparation

Experiments were conducted with Nafion perfluorinated membrane (Dupont 117, 0.007 in thick). The Nafion membrane was washed successively for 1 h in 80°C ultrapure water, 5% H_2O_2 , ultrapure water and 1 M H_2SO_4 , in order to remove organic compounds on the surface of the membrane.

The Fe³⁺ was loaded on the Nafion by dipping this membrane in FeCl₃· $6H_2O$ (0.036 mol/L) for 2 h and subsequently washing the Nafion until thorough removal of all Cl ions. Finally, the washed membrane was dipped in NaOH (0.01 M) and washed by ultrapure water at room temperature. The amount of Fe loading on the prepared Nafion/Fe³⁺ membrane was about 2.50% (w/w) determined by Spectrophotometry.

Photoreactor and Irradiation Procedures

The experimental setup was a photocatalytic reactor equipped with a quartz trap, and the source was a 300-W high pressure mercury lamp. The photocatalytic activity of the Nafion/Fe ion membranes was evaluated in 200-mL glass reaction vessels. 1 g Nafion membrane was added each time. A magnetic stirrer was used during the experiment to make the solution homogeneous. In the ciprofloxacin degradation experiment, the concentration of ciprofloxacin and H_2O_2 was 50 mg/L and 100 mg/L, respectively. The concentration of ciprofloxacin was determined by HPLC and sampled every 30 min. The ·OH generated in the Fenton reaction is captured by SA to form a stable product 2, 5-dihydroxybenzoic acid, and the concentration of ·OH is calculated by measuring the concentration of 2, 5-dihydroxybenzoic acid by HPLC.

Results and discussion

Characterization of the Nafion/Fe³⁺ membrane

The pretreated Nafion membrane showed a yellow color after soaking in $\text{FeCl}_3 \cdot \text{GH}_2\text{O}$, and the color changed from yellow to brownish yellow after soaking into NaOH solution. Microanalysis of Nafion membrane was performed by SEM and EDS. Figure 1 shows the SEM and EDS plots of the Nafion membrane after treatment in different conditions. Observation of the SEM image of the Nafion membrane (Fig. 1a, b) shows that the pretreated Nafion membrane and the ion exchanged Nafion membrane have similar appearance. Elemental analysis revealed the presence of iron on the ion exchanged Nafion membrane. After alkaline rinsing (Fig. 1c), deposit formation was observed, revealing clusters distributed on the polymer surface, and EDS analysis confirmed the presence of Fe and Na in the membrane.

Photocatalytic degradation of ciprofloxacin mediated by Nafion/Fe³⁺-membranes

The degradation of ciprofloxacin under light irradiation in the presence of H_2O_2 and Nafion/Fe³⁺ membrane in 4 h is shown in Figure S1. Ciprofloxacin was almost degraded completely within 4 h, while the degradation rate is faster in the first two hours, and slower in the last two hours. The efficiency of 96.7% can be achieved in 3 h. In order to investigate the amount of ion elution during the degradation process, the amount of iron ions in the solution was determined by spectrophotometry to be 0.52 mg/L. The SO₄²⁻ content is below the detection limit and cannot be detected.

Figure 2a shows the effect of different concentrations of hydrogen peroxide on the degradation of ciprofloxacin. It can be seen from the figure that when the concentration of hydrogen peroxide is 100 mg/L and 150 mg/L, and the degradation rate of ciprofloxacin is the highest. Ciprofloxacin degradation effect is not much different at four concentrations. Therefore, we determined the amount of •OH radicals produced.

Figure 2b shows the amount of hydroxyl radicals formed by hydrogen peroxide at different concentrations. Salicylic



Fig. 1 Scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) analysis for **a** the Nafion membrane. **b** membrane exchanged with a 0.036 mol/L solution of FeCl₃· $6H_2O$, **c** mem-

brane exchanged with a 0.036 mol/L solution of $\rm FeCl_3{\cdot}6H_2O$ and rinsed with NaOH 0.01 M

acid acted as a capture agent to produce 2,5-dihydroxybenzoic acid to calculate the amount of hydroxyl radicals. As the H_2O_2 concentration increased, the amount of $\cdot OH$ produced increased. However, a high concentration of H_2O_2 in the solution produces a large amount of $\cdot OH$, part of which was consumed by the undesirable reaction to form HO_2 . H_2O and O_2 . Therefore, high H_2O_2 concentration will cause waste and is not preferred to the formation of \cdot OH radicals. 50 mg/L H₂O₂ is enough to achieve better degradation, but in order to investigate the stability of the membrane, 100 mg/L H₂O₂ was used during the experiment.

Nafion/Fe³⁺ membrane, as a heterogeneous Fenton catalyst, can catalyze ciprofloxacin degrading in the presence of ultraviolet light. The degradation rate reached 97.78% within



Fig.2 a Effect of different concentrations of H_2O_2 on the degradation of ciprofloxacin **b** Effect of different concentrations of H_2O_2 on the generation rate of 2,5-dihydroxybenzoic acid. Filled black circle:

4 h and reached 86.55% after 2 h. Therefore, the Nafion/Fe³⁺ can membrane used five cycles to catalyze the degradation of tion

ciprofloxacin, and the degradation rate was observed. Figure 3a shows the five cycles degradation of ciprofloxacin in the presence of H_2O_2 and Nafion/Fe³⁺ membrane under light irradiation. It can be seen that the degradation rate 80% or more can be maintained during the first two cycles, while after five cycles of continuous use of the Nafion/Fe³⁺ membrane, the rate decreased to about 20%.

Meanwhile, the elution amounts of iron ions in the fivecycle were 0.969 mg/L, 1.42 mg/L, 0.67 mg/L, 0.87 mg/L and 1.47 mg/L, respectively. The dissolution of iron ions





50 mg/L H₂O₂, filled red circle: 100 mg/L H₂O₂, filled pointed up blue triangle: 150 mg/L H₂O₂, filled pointed down magenta triangle: 200 mg/L H₂O₂

can be used as evidence for a homogeneous catalytic reaction, and the dissolution of iron could lead the decrease in catalytic activity. As cycle number increased, the residual amount of Fe on the membrane decreased, resulting in a decrease in catalytic activity. Therefore, Fe is immobilized on the membrane through electrostatic action.

The XRD for the Nafion membrane after degrading ciprofloxacin is shown in Fig. 3b. The diffraction peaks at 2θ of about 18° and 40° can be attributed to the diffraction peaks produced by the semicrystalline structure of the Nafion membrane. The diffraction peaks attributable to Fe₃O₄, compared by PDF card at 2θ about 30°, revealed more





Fig.3 a Mineralization of ciprofloxacin in the presence of H_2O_2 (100 mg/L) mediated by Nafion/Fe³⁺ membrane five times, pH=3 and 20°C. (filled black circle: once, filled red circle: twice, filled pointed up blue triangle: three times, filled pointed down magenta tri-

angle: four times, filled olive diamond: five times). **b** X-ray diffraction of degradation ciprofloxacin once and degradation ciprofloxacin five times. a, Degradation ciprofloxacin once; b, Degradation ciprofloxacin five times

crystallization after five times degradation of ciprofloxacin (Wang et al. 2016; Taufiq et al. 2015; Prabhu et al. 2015). The more the Nafion/Fe³⁺ membrane is used, the greater the degree of crystallization.

When irradiation with ultraviolet light, part of Fe^{3+} were reduced to Fe^{2+} , which play the main role of catalysis. In the catalytic process, Fe^{3+} and Fe^{2+} coprecipitate, thus generating a peak of Fe_3O_4 . The Fe^{3+} and Fe^{2+} ions are electrostatically adsorbed on the membrane, so the decrease in the reaction rate may be due to the heterogeneous Fenton reaction caused by the formation of Fe_3O_4 . Hence, the decrease in efficiency in multiple degradations may be due to (a) Fe^{3+} dissolution leading to a decrease in Fe content on the membrane. (b) Conversion of Fe^{3+} to Fe_3O_4 is known by XRD.

Study of the stability of the Nafion/Fe³⁺ membrane

During the use of the Nafion/Fe³⁺ membrane, its life expectancy is reduced, possibly due to the attack of OH. Therefore, the Nafion/Fe³⁺ membrane stability test was carried out. In the absence of contaminants, \cdot OH would attack Nafion/Fe³⁺ membrane which may lead failure of membrane. The concentrations of \cdot OH influenced the extent of damage to the Nafion membrane. So, four concentrations of H₂O₂ were used to study the stability of Nafion membrane under attack of \cdot OH, which was breakdown test. However, none of F⁻ or SO₄²⁻ was detected, which means a satisfactory stability.

Figure 4a presents the results of XPS observations of the Fe species showing the XPS Fe $(2p_{3/2})$, 711.38 eV, and Fe $(2p_{1/2})$, 725.18 eV, of the Dupont 117 Nafion/ Fe³⁺ membrane before and after breakdown test. Among the two peaks in the XPS diagram of a, the Fe $(2p_{3/2})$ peak is stronger and narrower than Fe $(2p_{1/2})$, and the area of Fe $(2p_{3/2})$ peak area

is larger than Fe $(2p_{1/2})$. That is because in the spin–orbit (j-j) coupling, Fe $(2p_{3/2})$ has the degeneracy of the four states, Fe $(2p_{1/2})$ has only two states (Yamashita and Hayes 2008; Parra et al. 2004). Only Fe₂O₃ has associated satellite peaks. The satellite peak of Fe $(2p_{3/2})$ for Fe₂O₃ is located approximately 8 eV higher than the main Fe $(2p_{3/2})$ peak (Yamashita and Hayes 2008).

Figure 4a and b shows a pronounced peak after the attacked of \cdot OH at 711.85 eV for Fe³⁺ species, possibly a more stable phase of Fe³⁺ oxide Fe₃O₄. It can be seen that the Nafion/Fe³⁺ membrane is composed of Fe₃O₄ materials containing Fe²⁺ and Fe³⁺. Under UV light and H₂O₂ catalysis, part of Fe³⁺ is converted to Fe²⁺, and Fe³⁺ and Fe²⁺ are contained in the Nafion membrane. Figure 4a–c shows that it does not contain satellite, so stably contains Fe³⁺ and Fe²⁺ oxide Fe₃O₄. This is the same as the XRD characterization. The relative content of Fe in the Nafion membrane increased after five times breakdown test, indicating that the catalyst inner layer may act as an iron reservoir during the reaction (Mahdi et al. 1992). In the present case, it may be suggested that the iron oxide cluster reacts with the Nafion layer during the reaction (Kiwi et al. 2002).

Figure 4b presents the results of XPS observations for the F, showing the XPS F (1 s) line around 688.6 eV in the Nafion/Fe³⁺ membrane. The Nafion/Fe³⁺ membrane before use presents $-CF_3$ groups and high amounts of $-CF_2$ and -CF groups. In the Nafion/Fe³⁺ membrane breakdown test, \cdot OH will cause a certain degree of damage to Nafion membrane, mainly to destroy the carbon-side backbone structure. After five cycles of breakdown test, the Nafion/Fe³⁺ membrane structure was damaged, and the relative content of F increased. The C content decreased after the reaction, indicating the breakdown of carbon backbone during use (show in Table S1), so the increase in the F content after



Fig. 4 a X-ray photoelectron spectroscopy (XPS) of Fe (2p) on the Nafion/Fe³⁺ membrane before and after breakdown test. **b** XPS of F (1 s) on the Nafion/Fe³⁺ membrane before and after breakdown test: a, after pretreatment (before test); b, once; and c, five times

the reaction is a side effect of a decrease in the C content on Nafion/Fe³⁺ membrane. \cdot OH attacks Nafion/Fe³⁺ membrane many times, the side chains fall off, and the Nafion/ Fe³⁺ membrane also has a certain service life.

The attenuated total reflection (ATR) spectra Nafion/ Fe³⁺ membrane before and after breakdown test are shown in Figure S2 A. The peak at 1057.8 cm⁻¹ represents the stretching vibration of the C-C bond of the long-chain skeleton. The peak at 980.6 cm^{-1} is attributed to the $-SO_3H$ symmetric stretching vibration. 1206.3 cm⁻¹ and 1146.4 cm⁻¹ are antisymmetric and symmetric telescopic vibrations of $-CF_2$. The peak at 625.8 cm⁻¹ is the vibration of the C-F bond (Buzzoni et al. 1995). The broad peak is attributed to -CF₂ asymmetric stretching vibration, and the peak at 1637 cm^{-1} is attributed to the O–H bending vibration of the hydrophilic region. The broad peak at 3103 to 3603 cm^{-1} is O–H stretching vibration. As can be seen from the Figure S2 A, there is no significant change between a, b and c which means the perfluorosulfonic acid membrane skeleton is not attacked by oxidation, after catalyzing the heterogeneous Fenton reaction.

Figure S2 B shows SEM of the Nafion/Fe³⁺ membrane after the breakdown test. The concentration of H_2O_2 is 100 mg/L. It can be seen from the SEM image that there is no significant change in the Nafion/Fe³⁺ membrane.

Conclusions

In this experiment, Fe³⁺ was loaded on a Nafion membrane to prepare a heterogeneous Fenton catalyst. In the presence of ultraviolet light, the cycle performance and stability of the Nafion membrane were investigated. Ciprofloxacin was almost degraded completely within 4 h, while the efficiency 96.7% can be achieved in 3 h. However, during the cyclic test, the degradation rate 80% or more can be maintained at the first two cycles, while after five cycles of continuous use of the Nafion/Fe³⁺ membrane, the rate decreased to about 20%. It can be seen from the XRD characterization that a new crystallization peak appears, whose crystallization increased meanwhile five cycles of the reaction. Considering the ion dissolution results, it can be inferred that the decrease in efficiency may be due to Fe^{3+} dissolution and conversion from Fe^{3+} to Fe_3O_4 . •OH attacks Nafion/Fe³⁺ membrane, mainly to destroy the carbon side backbone structure. The side chains fall off, Nafion/Fe³⁺ membrane has a loss of F and C during use, and the Nafion/Fe³⁺ membrane also has a limited service life.

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