

Photocatalytic Degradation of Norfloxacin By Magnetic Molecularly Imprinted Polymers: Influencing Factors And Mechanisms

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Abstract

Novel magnetic molecularly imprinted polymers (MMIP) were prepared for selective removal of norfloxacin from ambient water by effectively utilizing photocatalytic degradation and magnetic separation techniques. The imprinted materials with titanium layer and multihole surface showed excellent photocatalytic property. In this paper, the kinetics of photocatalytic degradation of norfloxacin by MMIP was explored, and the influences of environmental factors, including solution pH, humic acid, common ions and water media on photocatalytic performance of the materials were elucidated. The results showed that MMIP had good adaptability and could degrade norfloxacin within 60 min, but the degradation rate constant decreased by 40.3% and 66.4% in tap water and surface water, respectively. According to the intermediates, the possible degradation pathways of norfloxacin were analyzed, speculating that norfloxacin might be degraded into small molecules after de-piperazine ring, de-carboxyl group and de-fluorine. Moreover, the mineralization ratio of norfloxacin could reach 84.2% after ultraviolet irradiation for 150 min. In the study of photocatalytic in-situ regeneration and recovery performance of MMIP, the total removal efficiency of norfloxacin was still 99.0% after seven cycles of adsorption-degradation tests. And the low cobalt release of MMIP by molecular imprinting technology enhanced the security of the materials.

Introduction

In recent years, the production and consumption of antibiotics have been increased all over the world, while their potential adverse effects on ecology and human health have attracted more attention. A literature research showed that 110 antibiotics have been detected in China's environment, most of these were in aquatic environments (Huang et al. 2020). Through cluster analysis, seven dominant antibiotics, including norfloxacin, can be discovered in almost all environmental compartments with concentrations up to several micrograms per liter. In some bodies of water in European countries, such as wastewater, surface water, groundwater and drinking water, quinolones were the most frequently detected antibiotics (Carvalho and Santos 2016). These phenomena indicated that quinolone antibiotics were more likely to accumulate in the environment and had strong persistence (Xi et al. 2019). Norfloxacin is a kind of fluoroquinolones drug with stable chemical structure and poor biodegradability. However, traditional sewage treatment technologies are not enough to remove norfloxacin effectively because of its special properties such as low concentration and high bio-toxicity (de Souza Santos et al. 2014). The main migration pathways of norfloxacin are the discharge of livestock wastewater, effluent and sludge into surface water, groundwater and soil, respectively (Huang et al. 2020). Therefore, it is urgent to develop the effective technology for norfloxacin removal from drinking water and wastewater.

Although antibiotics such as norfloxacin are ubiquitous in the environment, their concentration is lower than that of other conventional organics. Molecularly imprinted polymers (MIP) can selectively adsorb trace pollutants in water environment (BelBruno 2019), which is extremely beneficial for the removal of norfloxacin with low concentration and high toxicity. Tan et al. (2013) synthesized ofloxacin imprinted polymers on the surface of mesoporous carbon nanoparticles to prove the feasibility of MIP to remove

fluoroquinolone antibiotics from seawater. MIP had high selectivity and affinity for template molecules, for they contained a large number of “tailor-made” binding sites (Shen et al. 2012). Similarly, fluoroquinolone imprinted polymers had also been developed for the extraction and detection of relevant antibiotics in actual water samples (Barahona et al. 2019). However, such imprinted materials cannot degrade the adsorbed pollutants, resulting in poor regeneration performance of the polymers, while elution may well cause environmental pollution.

Photocatalysis reaction can effectively degrade organic pollutants (Dong et al. 2015). The use of photocatalysis to remove pollutants adsorbed on MIP is a new technology (Sajini et al. 2019). The degradation of the target adsorbent on the MIP surface allows the materials to be reused. Due to the selective adsorption of MIP, they exhibit better photocatalytic activity to the target material. Some representative estrogenic chemicals could be selectively and rapidly removed from secondary effluents of municipal wastewater treatment plants using photocatalyst prepared by surface molecularly imprinted TiO_2 nanotubes (Zhang et al. 2013). Compared with organic imprinting, the synthetic method of inorganic imprinting nano TiO_2 layer on microspheres was demonstrated higher catalytic efficiency for the degradation of bisphenol A under ultraviolet light (Ye et al. 2019). A TiO_2 -based imprinted material showed outstanding photocatalytic in-situ regeneration performance, after eleven regeneration cycles, the adsorption and degradation removal efficiency of MIP to norfloxacin did not decrease significantly (Wei et al. 2018). In addition, some imprinted polymers that can degrade template molecules in visible light had also been prepared (Du et al. 2020), but their degradation efficiency was not as outstanding as that under ultraviolet light. However, the imprinted photocatalytic materials listed above are difficult to separate from the solution. The material must be centrifuged from the decontaminated water to achieve reuse, whereas the recovery ratio is low.

Nowadays, there have been many researches to fix powdered materials on various substrates (Shan et al. 2010). For photocatalytic materials, the most common is the glass substrate (Pestana et al. 2015). However, material immobilization would reduce the exposure area of the catalyst, and the loaded materials might be lost due to the continuous scouring and friction of the water flow (Jiang et al. 2019). Magnetic separation technology is different from immobilization technology, which has the characteristics of environmental protection and high efficiency. The synthesized material has its own magnetism, which can separate from the solution by applying an external magnetic field (Wang et al. 2015). The magnetic molecularly imprinted composite material prepared by cross-linking chitosan and $\gamma\text{-Fe}_2\text{O}_3$ particles showed effective norfloxacin adsorption performance when mixing with other organic matter in the effluent of the actual sewage treatment plant (Wu et al. 2016). Heterojunction of magnetic core CuFe_2O_4 and photocatalyst $\text{g-C}_3\text{N}_4$ improved the separation efficiency of photoinduced electron-hole pairs (Yao et al. 2015). More experiments showed the degradation mechanism of magnetic nano-photocatalyst was similar to that of single photocatalyst (Kumar et al. 2019). It can be seen that magnetic separation technology combined with molecular imprinting and photocatalysis technology has good development prospects.

In this paper, we synthesized magnetic molecularly imprinted polymers with specific recognition ability for norfloxacin and photocatalytic in-situ regeneration. Magnetic cores, TiO_2 coating and surface molecular imprinting modification were adopted to realize the photocatalytic regeneration and magnetic separation recovery. Based on previous research about the adsorption performance, we have reported the characterization and selective adsorption properties of the materials towards norfloxacin (Fang et al. 2021). However, the degradation efficiency of target pollutants and the regeneration of MMIP still need to be investigated. Here, the kinetics of photocatalytic degradation was studied, and the influences of different environmental media factors on the photocatalytic degradation performance of the material were systematically explored. Besides, the products, pathways and mineralization of photocatalytic reactions were further analyzed to evaluate the security and sustainability of the materials.

Materials And Methods

2.1 Chemicals and materials

Norfloxacin ($\text{C}_{16}\text{H}_{18}\text{FN}_3\text{O}_3$, 98.0%), ferric chloride (FeCl_3 , 99.0%), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, AR) and tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, 99.0%) were obtained from Aladdin Industrial Corporation (Shanghai, China). Methanol, acetonitrile and phosphoric acid were all of HPLC grade, purchased from Sigma-Aldrich (USA). Ethylene glycol, polyethylene glycol, sodium acetate, ammonium hexafluorotitanate, boric acid, hydrochloric acid, sodium hydrate, sodium chloride, sodium sulfate, sodium nitrate and other analytical reagents were uniformly purchased from Sinopharm Chemical Reagent Company (Shanghai, China). A 10 W ultraviolet lamp used was from Heraeus Holding (Hanau, Germany). All reagents were used directly without further purification.

2.2 Preparation and characterization of MMIP

The synthesis of MMIP consisted of three steps. Firstly, 50 mmol FeCl_3 and 25 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 400 ml ethylene glycol. Then 36 g sodium acetate and 10 g polyethylene glycol were added into the mixture. The suspension was transferred into Teflon-lined reaction kettle, and heated at 200°C for 8 h to get CoFe_2O_4 . Secondly, 2 g CoFe_2O_4 was added into a mixture solution containing anhydrous ethanol and tetrabutyl titanate. The suspension was heated at 150°C for 10 h in autoclave to obtain $\text{CoFe}_2\text{O}_4@\text{TiO}_2$. At last, 200 mg $\text{CoFe}_2\text{O}_4@\text{TiO}_2$ nanoparticles, 20 mg norfloxacin, 3.96 g ammonium hexafluorotitanate and 2.60 g boric acid were dissolved in deionized water, stirred for 2 h and then natural deposited. The molecularly imprinted particles were calcined under 350°C to remove templates.

The morphological characterization and surface elements of the materials were carried out using scanning electron microscope with an X-ray energy spectrometer (GeminiSEM 300, Zeiss, Germany).

2.3 Photocatalytic degradation experiments

After the reaction reached the adsorption equilibrium, the magnetic photocatalytic material was regenerated in-situ by ultraviolet photocatalytic degradation. 40 mg material was put into 100 mL

norfloxacin solution with a concentration of 2 mg L^{-1} . After stirring 60 min at 25°C , the reaction vessel was illuminated by a 254 nm ultraviolet lamp with power of 10 W. The light source was turned on in advance and preheated for 10 min which intensity can be stabilized at about $927 \mu\text{W cm}^{-2}$. Samples were then taken out at regular intervals and filtered by a $0.45 \mu\text{m}$ filter. Photocatalytic kinetics of MMIP was investigated over various initial concentrations ranging from 1 mg L^{-1} to 25 mg L^{-1} . The environmental factors including pH values, concentrations of humic acid, different ions and water media were selected to research the photocatalytic performance of the material. The degradation efficiency was defined as:

$$\text{Efficiency}(\%) = \frac{c_0 - c_1}{c_0} \quad (1)$$

Where c_0 (mg L^{-1}) and c_1 (mg L^{-1}) were the concentration of adsorption equilibrium and after photodegradation, respectively.

2.4 Analytical methods

The concentrations of norfloxacin were measured by high performance liquid chromatography (1200 Series, Agilent, USA) equipped with a XDB C18 column ($4.6 \text{ mm} \times 150 \text{ mm}$, $5 \mu\text{m}$) and a fluorescence detector which excitation and emission wavelength were 280 nm and 450 nm, respectively. The mobile phase was consisted of acetonitrile and 0.1 wt% phosphoric acid water solution at the volume ratio of 30:70 and flow rate of 1.0 mL min^{-1} . The intermediate degradation products were detected by liquid chromatography-mass spectrometry (6460 Triple Quad, Agilent, USA). The samples were extracted on solid phase extraction column ($3 \text{ mL}/60 \text{ mg}$, Oasis HLB, Waters) and concentrated by nitrogen blowing. The liquid chromatography separation was carried out on Agilent Zorbax SB C18 column ($2.1 \text{ mm} \times 150 \text{ mm}$, $3.5 \mu\text{m}$) and gradient elution was performed with acetonitrile and 0.25 wt% formic acid at a flow rate of 0.20 mL min^{-1} . Mass spectrometry analysis was adopted using an electrospray ionization source in positive mode and scanning range of m/z was $100 \sim 1000 \text{ amu}$. The removal efficiency of total organic carbon (TOC) was adopted to characterize the mineralization of norfloxacin. Samples for the detection of TOC were measured through combustion catalytic oxidation at 680°C by using total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan). In addition, the accurate concentration of cobalt was determined by inductively coupled plasma mass spectrometer (NexION 300Q, PerkinElmer, the United States).

Results And Discussion

3.1 Characterization of MMIP

The morphology of MMIP was confirmed by SEM image showing in Fig. 1a. It can be noted that there were a lot of nanoparticles on the surface of MMIP, which were presumed to be the generated imprinted layer and partially exposed TiO_2 particles. These features were corresponding to the XRD results of MMIP we obtained previously (Fang et al. 2021). Such a surface characteristic was conducive to enhancing the

photocatalytic degradation of the target at the interface. At the same time, numerous Bubble-like nanoholes can be observed on the surface, which may be formed by the imprinted cavity left by MMIP after removing the template molecules at high temperature. The porous structure of MMIP made it more specific and better to capture target pollutants. The chemical element composition of molecularly imprinted materials was analyzed by EDS, as shown in Fig. 1b, indicated the presence of Co, Fe, Ti, C and O in MMIP, where the atomic ratios of Ti/O and Fe/O were 21.2% and 23.2%, respectively. The sufficient Ti content provided a material basis for the photodegradation of norfloxacin.

3.2 Photocatalytic degradation reaction kinetics

The magnetic imprinted material had an anatase crystal structure after CoFe_2O_4 coated by the TiO_2 layer and the surface modification of the molecular imprinting layer, which was conducive to photocatalysis of organic pollutants. Generally, the photocatalytic degradation reaction was a rate-limiting reaction that depended on the concentration of norfloxacin on the surface of the imprinted photocatalytic material and the concentration of hydroxyl radicals (Behnajady et al. 2007). It was assumed that the light intensity and the oxygen concentration in the solution remain unchanged during the process. Using the Langmuir model and considering the direct photodegradation of norfloxacin under ultraviolet light, the catalytic degradation rate equation of norfloxacin can be obtained as (Kumar and Porkodi 2008):

$$r_{\text{NOR}} = \frac{k_c K_{\text{NOR}}}{1 + K_{\text{NOR}} C_{\text{NOR}0}} + K' \quad (2)$$

Where r_{NOR} was the comprehensive degradation rate of norfloxacin, K_{NOR} was the adsorption equilibrium constant of norfloxacin, k_c was the photocatalytic degradation rate constant of norfloxacin on material surface, K' was the direct photodegradation rate constant of norfloxacin under ultraviolet light and $C_{\text{NOR}0}$ was the initial concentration of norfloxacin.

Five different initial concentrations were selected to explore the catalytic degradation rate of the material. Figure 2a showed that the photocatalytic degradation rate of norfloxacin decreased by 77.3% when the initial concentration increased from 1 mg L^{-1} to 25 mg L^{-1} . Figure 2b displayed the fitting result of the photocatalytic degradation rate equation of norfloxacin. The main parameters are as follows: $k_c = 1.058 \text{ mg L}^{-1} \text{ min}^{-1}$, $K_{\text{NOR}} = 0.196 \text{ L min}^{-1}$ and $K' = 0.008 \text{ min}^{-1}$. So the final kinetic fitting equation for the photocatalytic degradation of norfloxacin by the imprinted photocatalytic material can be expressed as the following formula:

$$r_{\text{NOR}} = \frac{0.207}{1 + 0.196 C_{\text{NOR}0}} + 0.008 \quad (3)$$

According to the fitting results, the rate constant of direct photodegradation of norfloxacin under ultraviolet light was relatively small. Most of norfloxacin molecules were adsorbed on the surface of MMIP, and could only degrade on its surface, so that the amount of norfloxacin available for photolysis in

the solution was less. For the model fitting results without K' , the k_c was 18.5% larger and the K_{NOR} was 14.3% smaller. Therefore, although the direct photodegradation rate constant of norfloxacin was small, this term in the equation cannot be ignored.

3.3 Effect of environmental factors on photocatalytic degradation

Similar to the adsorption performance, some environmental factors also affect the degradation behavior of norfloxacin by magnetic molecularly imprinting materials. We explored the effects of solution pH, humic acid, common ions and water media on the photocatalytic degradation performance of MMIP.

3.3.1 Solution pH

In the study of the adsorption performance of magnetic imprinting materials, it was found that pH had an evident impact on the adsorption and removal of norfloxacin (Fang et al. 2021). In this experiment, the pH of the solution was adjusted to 3–11 to further explore the effect of it on the photocatalytic degradation performance of MMIP. Due to the low discrimination of pH on the degradation process at a high dosage, the dosage was selected as 0.1 g L^{-1} to amplify the difference. The experimental results are shown in Fig. 3. When the pH was neutral, the photodegradation rate was the fastest, and the photocatalytic reaction rate constant was 0.075 min^{-1} . Under acidic and alkaline conditions, especially at pH = 11, the photocatalytic degradation rate decreased significantly. This is mainly because the activity of the catalyst is closely related to the charged properties of its surface (Gumy et al. 2006). The electrostatic interaction of solvent molecules, target substances and hydroxyl radicals on the photocatalyst surface is greatly affected by pH, which in turn affects the photocatalytic reaction rate. And low pH solution inhibited the hydrolysis of fluorine, while high pH solution enhanced the stability of piperazine rings in the structure (Paul et al. 2010). In addition, MMIP had the best adsorption effect on norfloxacin under neutral conditions, so more norfloxacin was adsorbed on the surface of the catalyst that also promoted the photocatalytic reaction process.

3.3.2 Humic acid

Humic acid is a common free radical trapping agent due to the presence of unsaturated functional groups, which reduces the efficiency of free radicals in the reaction system. In the degradation reaction of TiO_2 as catalyst, humic acid served as a scavenger of hydroxyl radical, hindering the activity of TiO_2 (Tang et al. 2018). Here, solutions with different humic acid concentrations were used as the reaction media, and their concentrations were characterized by TOC as $\text{TOC}_1 = 0.154 \text{ mg L}^{-1}$, $\text{TOC}_2 = 1.823 \text{ mg L}^{-1}$, $\text{TOC}_3 = 2.523 \text{ mg L}^{-1}$, and $\text{TOC}_4 = 4.427 \text{ mg L}^{-1}$, respectively. The effect of humic acid on ultraviolet photocatalytic degradation of norfloxacin is shown in Fig. 4. Obviously, with the increase of humic acid concentration, the photocatalytic degradation rate decreased, and when the TOC concentration was 1.823 mg L^{-1} , the degradation rate decreased by 41.8%, but the rate almost did not decrease in the low concentration of humic acid solution. Humic acid can occupy the specific adsorption site of imprinted material, thus reducing the adsorption and removal efficiency of norfloxacin. It should be noted the results of this experiment showed that the imprinted material still had a strong competitiveness in

photocatalytic degradation of the target in the low concentration of humic acid environment, and norfloxacin could be completely degraded within 60 min in a highly concentrated humic acid solution. In the experiment of using TiO_2 to degrade tetracycline under UVA-LED light, the photocatalytic degradation efficiency was reduced by 75.5% in the presence of 1 mg L^{-1} humic acid, but the efficiency was almost unchanged with the increase of humic acid concentration (Li and Hu 2016).

3.3.3 Common ions

The actual water body composition is more complex and contains a lot of ions. In order to explore the influence of different ions on the photocatalytic degradation of norfloxacin by MMIP, Na^+ , Fe^{3+} , SO_4^{2-} , NO_3^- with a concentration of 0.1 mM were selected as experimental ions. As shown in Fig. 5, Fe^{3+} and NO_3^- had conspicuous impact on degradation rate, and the other two ions had no obvious influence. Various ions had different effects on the adsorption of norfloxacin by MMIP in the initial adsorption process, and the photocatalytic performance of the material was the best when the pH was neutral. However, the cations and anions would affect the pH value of the solution, thereby changing the charging properties of reducing substances and photocatalytic materials. In addition, the ions could react with the surface adsorption sites of the photocatalytic material to affect the photocatalytic reaction (Gumy et al. 2006). Take Fe^{3+} for example, the presence of Fe^{3+} will significantly reduce the photochemical reaction rate, mainly due to the negative effect of Fe^{3+} on the adsorption stage (Fang et al. 2021). Secondly, the hydrolysis of Fe^{3+} will reduce the pH value of the solution, altering the electrostatic interaction between the photocatalyst surface and solvent molecules, target substances and hydroxyl radicals, respectively. Chen et al. (2017) found that Fe^{3+} could reduce the number of oxygen-containing free radicals in the photocatalytic chain reaction by trapping photoelectrons. In addition, the presence of NO_3^- in a photocatalytic system will affect the binding of the target substance to hydroxyl radicals (Tang et al. 2016).

3.3.4 Water media

The practical application of the material was tested and ultrapure water, tap water and surface water samples were selected as the reaction media. The common water quality indexes of each water body sample are shown in Table 1. Figure 6 revealed that surface water had the greatest weakening effect on the photocatalytic degradation of norfloxacin, and the degradation rate constant was reduced to 0.050 min^{-1} . The main reasons that weaken the degradation rate may come down to three aspects. The first is the influence of water turbidity. For surface water, because of its high turbidity and poor transmission of ultraviolet light, the intensity of illumination would decrease when it reached the surface of MMIP. Colloid particles and suspended solids in the water can absorb and scatter some of the light so that the production efficiency of hydroxyl radical would be reduced accordingly. The effect of dissolved compounds on the degradation of norfloxacin by MMIP was also obvious. Especially, the presence of anions and cations such as Fe^{3+} and NO_3^- in natural waters will reduce the generation rate of hydroxyl radicals. Humic acid and other substances could compete with the target substances for hydroxyl radicals and photons, resulting in the decrease of the photocatalytic degradation rate of the target substances. The third aspect is that the selective adsorption ability of imprinted materials to norfloxacin

is different in water media. In surface water, the adsorption removal efficiency of norfloxacin was relatively low, reducing the possibility of hydroxyl radical colliding with norfloxacin. Nevertheless, the photocatalytic degradation process could still be degraded in a short time, implying the photocatalytic degradation performance of magnetic imprinted materials has satisfied adaptability in different water media.

Table 1
Conventional water quality indexes for surface water and tap water samples

Water quality indexes	Surface water	Tap water
pH	7.94	6.78
UV ₂₅₄	0.033	0.010
TOC (mg L ⁻¹)	13.590	3.242
Na ⁺ (mg L ⁻¹)	14.690	12.840
K ⁺ (mg L ⁻¹)	3.623	2.577
Fe ³⁺ (mg L ⁻¹)	0.383	0.271
SO (mg L ⁻¹)	98.400	41.700
NO (mg L ⁻¹)	15.610	9.870

3.4 Photocatalytic degradation reaction mechanism

3.4.1 Identification of photocatalytic degradation products

In order to in-depth research the process and mechanism of photocatalytic degradation of norfloxacin by MMIP, the degradation products of norfloxacin were qualitatively analyzed by liquid chromatography-mass spectrometry. As the illumination time increases, the number of peaks in the mass spectrum continues to increase, which means that new substances are constantly being produced. Figure 7 lists the mass spectrogram corresponding to some chromatographic peaks.

The modification of molecularly imprinted layer on the surface of TiO₂ can improve the adsorption performance of the material, thereby increasing the degradation efficiency of target pollutants (de Escobar et al. 2018). However, the photocatalytic mechanism still belongs to advanced oxidation reaction. According to the analysis of the molecular weight of the product, a total of nine intermediates were detected and the possible molecular structures were proposed. Products 1 to 4 indicated the gradual degradation process of piperazine ring on the benzene ring. The hydrogen on the methyl was replaced by hydroxyl, which was then oxidized to ketone, and the ring was further disconnected until only an amino group was left in the original position of piperazine ring. Product 5 with a protonated form of m/z 276 was in all probability formed due to the removal of the carboxyl. The formation of product 6 might be

derived from two degradation pathways. It is the basic molecular structure of fluoroquinolone antibiotics and lacks the piperazine ring and carboxyl group compared with norfloxacin. In a complex system of photocatalysis, the sequence in which the piperazine ring and carboxyl groups were degraded and removed was not clear, but the resulting product may have the same structure. The other two products 7 and 8 with the m/z of 318 and 249 respectively, reflecting that fluorine on the benzene ring was likely to be replaced by hydroxyl in the degradation process. Another product 9 also demonstrated the likelihood of direct removal of fluorine by photocatalytic degradation. The possible reaction pathway is deduced and summarized as shown in Fig. 8. On the whole, the photocatalytic degradation rate of norfloxacin by ultraviolet is fast, and the formative specific adsorption sites might re-adsorb the target, realizing the completely removal of pollutants.

3.4.2 Mineralization ratio

The mineralization ratio in the photocatalytic system is represented by the removal efficiency of TOC. The trend of the mineralization ratio during the photocatalytic degradation of norfloxacin by MMIP material is shown in Fig. 9. After 150 min of irradiation under ultraviolet light, the mineralization of norfloxacin was basically stable, reaching a maximum of 84.2%. Compared with other methods, the mineralization ratio of ultraviolet photocatalytic degradation is higher (Estrada-Flórez et al. 2020), and some comparison results are displayed in Table 2. The degree of mineralization of organic pollutants was relatively high in the reaction process, which indicated norfloxacin was finally degraded into inorganic small molecules after photocatalytic degradation, showing a well ecological friendliness and application value.

Table 2

Comparison of mineralization ratios of norfloxacin photocatalytic degradation by different materials

Photocatalyst	Reaction conditions	Light source	Time (min)	Mineralization ratio	Reference
BiOBr UiO-66-NH ₂	NOR = 10.0 mg L ⁻¹ , dosage = 0.3 g L ⁻¹	Simulated solar light	270	60.58%	(Yang et al. 2019)
Bi/Fe-ZnO	NOR = 20.0 mg L ⁻¹ , HSO = 0.6 mM dosage = 2.0 g L ⁻¹	Simulated solar light	400	65.0%	(Shah et al. 2018)
Ag/AgCl-CeO ₂	NOR = 10.0 mg L ⁻¹ , dosage = 0.6 g L ⁻¹	Visible light	150	59.61%	(Wen et al. 2017)
Graphene/TiO ₂	NOR = 20.0 mg L ⁻¹ , dosage = 1.0 g L ⁻¹	Simulated solar light	600	86.2%	(Li et al. 2013)
MMIP	NOR = 2.0 mg L ⁻¹ , dosage = 0.4 g L ⁻¹	Ultraviolet light	150	84.2%	This work

3.5 Material stability and safety

3.5.1 Assessment of regeneration capacity

The performance of photocatalytic regeneration and recycling of magnetic imprinted materials was also studied. Adsorption was performed for two hours to reach saturation, and then photocatalytic in-situ regeneration was performed for two hours. After that, the concentration of norfloxacin in the solution was reset to the initial concentration, and the next round of adsorption experiment was replicated. The recycling performance of the magnetic imprinted material is shown in Fig. 10. After seven cycles, the total removal efficiency of norfloxacin could still reach 99.0%, and the adsorption performance did not decrease significantly, indicating the excellent recycling ability of MMIP. Norfloxacin can be desorbed automatically and release the active sites after degrading into small molecule structure, so as to achieve in-situ regeneration. Compared with other regeneration methods, such as acid-base elution, organic solvent elution and calcination, using advanced oxidation technology is more effective, and ultraviolet photocatalytic regeneration method has the advantages of convenience and environmental protection.

3.5.2 Cobalt release

A release experiment of cobalt from the material was conducted as a safety evaluation. Excessive discharge of cobalt-containing wastewater has an impact on the environment, and its toxicity to aquatic animals and crops is greater (Chen et al. 2020). The amount of cobalt in environmental waters is stipulated not to exceed 0.05 mg L^{-1} (Saad et al. 2020). Take the basic carrier as a comparison, CoFe_2O_4 and MMIP materials of 0.4 g L^{-1} were added to the deionized water, respectively. The solutions were kept stirring, and samples were taken every day to determine the concentration of cobalt released. The results are shown in Fig. 11. During the testing period of 10 days, the cobalt release concentration of CoFe_2O_4 increased gradually and reached $124.30 \text{ } \mu\text{g L}^{-1}$ on the 10th day. Correspondingly, the release concentration of cobalt in MMIP material was significantly lower than that of CoFe_2O_4 , and the cobalt concentration in the solution was relatively stable, which the average cobalt concentration measured in 10 days was $4.22 \text{ } \mu\text{g L}^{-1}$. It can be seen that after the modification of molecularly imprinted layer, the metal precipitation behavior of the material is controlled, and the enhancement of safety performance improves the application potential of the material.

Conclusion

In summary, the novel magnetic molecularly imprinted polymers can effectively degrade norfloxacin under ultraviolet light and has the ability of in-site regeneration and sustainable utilization. The successful synthesis of the imprinted titanium layer and the porous surface enhance the photocatalytic degradation of the target template molecules at the interface. The fitting kinetic equation showed that the degradation rate of norfloxacin with low concentration was higher by imprinted photocatalyst. Humic acid and common ions can influence the degradation rate of norfloxacin, among which Fe^{3+} had the most significant effect. The main pathways of the photocatalytic degradation of norfloxacin were proposed, including transformation and removal of piperazine rings, decarboxylation and replacement or direct removal of fluorine. After 150 min of ultraviolet light irradiation, norfloxacin was eventually

degraded with a high mineralization ratio of 84.2%, accompanied by the release of specific adsorption sites, thus achieving in-situ regeneration of the material. The content of cobalt released by MMIP was far below than that of cobalt ferrite nanoparticles, indicating that molecular imprinting technology was conducive to reduce the release of cobalt. This study showed that MMIP was an attractive and potential material to treat trace amounts of antibiotics in water.

Declarations

Ethics approval Not applicable

Consent to participate Not applicable

Consent for publication Not applicable

Availability of data and materials

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

LF: Supervision, methodology, interpretation of data, writing–review and editing. KT and DW: Experimental operation, formal analysis, writing–original draft preparation. YZ and YZ: Interpretation of data, writing–review and editing. All authors read and approved the final manuscript.

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Figures

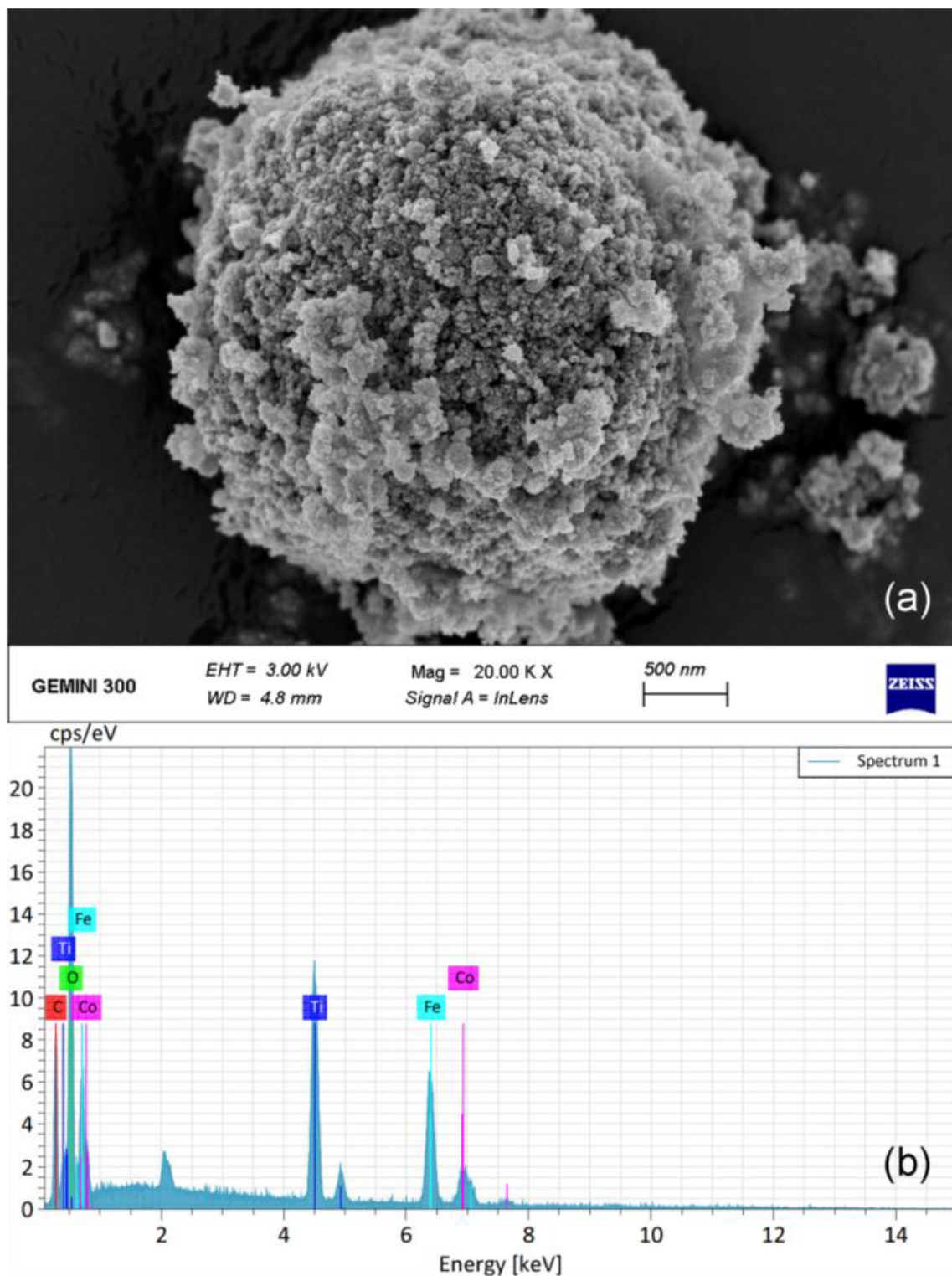


Figure 1

SEM image (a) and EDS (b) of the synthesized MMIP

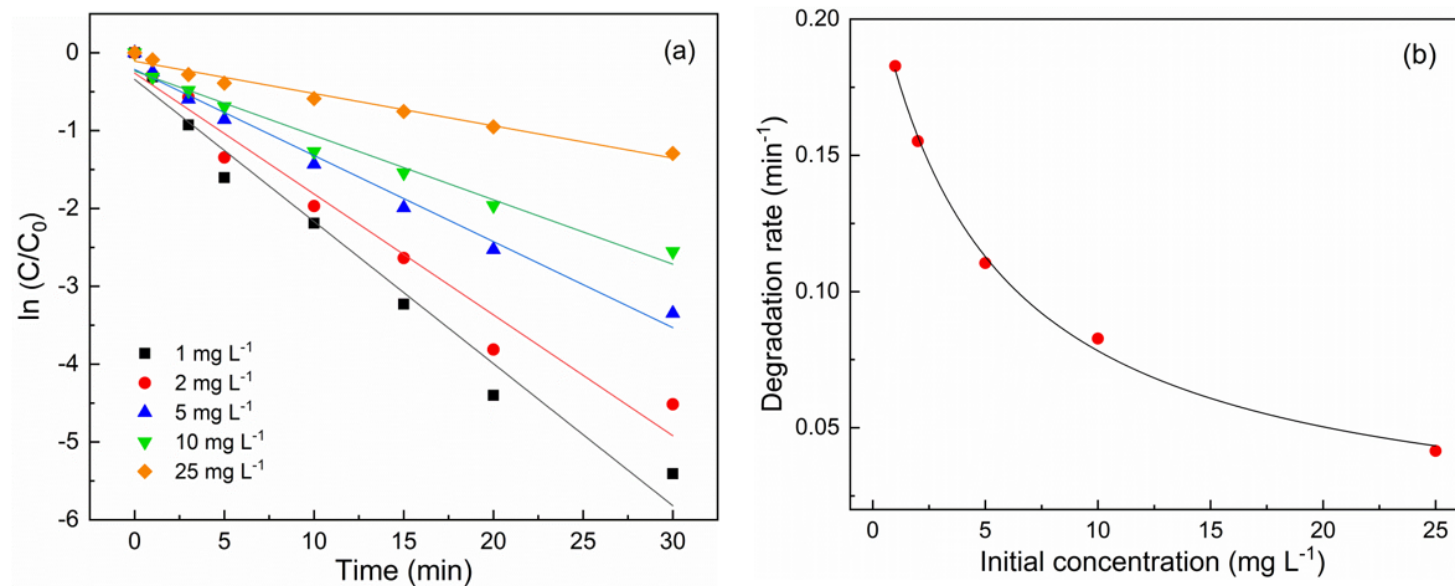


Figure 2

Kinetics (a) and fitting (b) of photocatalytic degradation of norfloxacin by MMIP

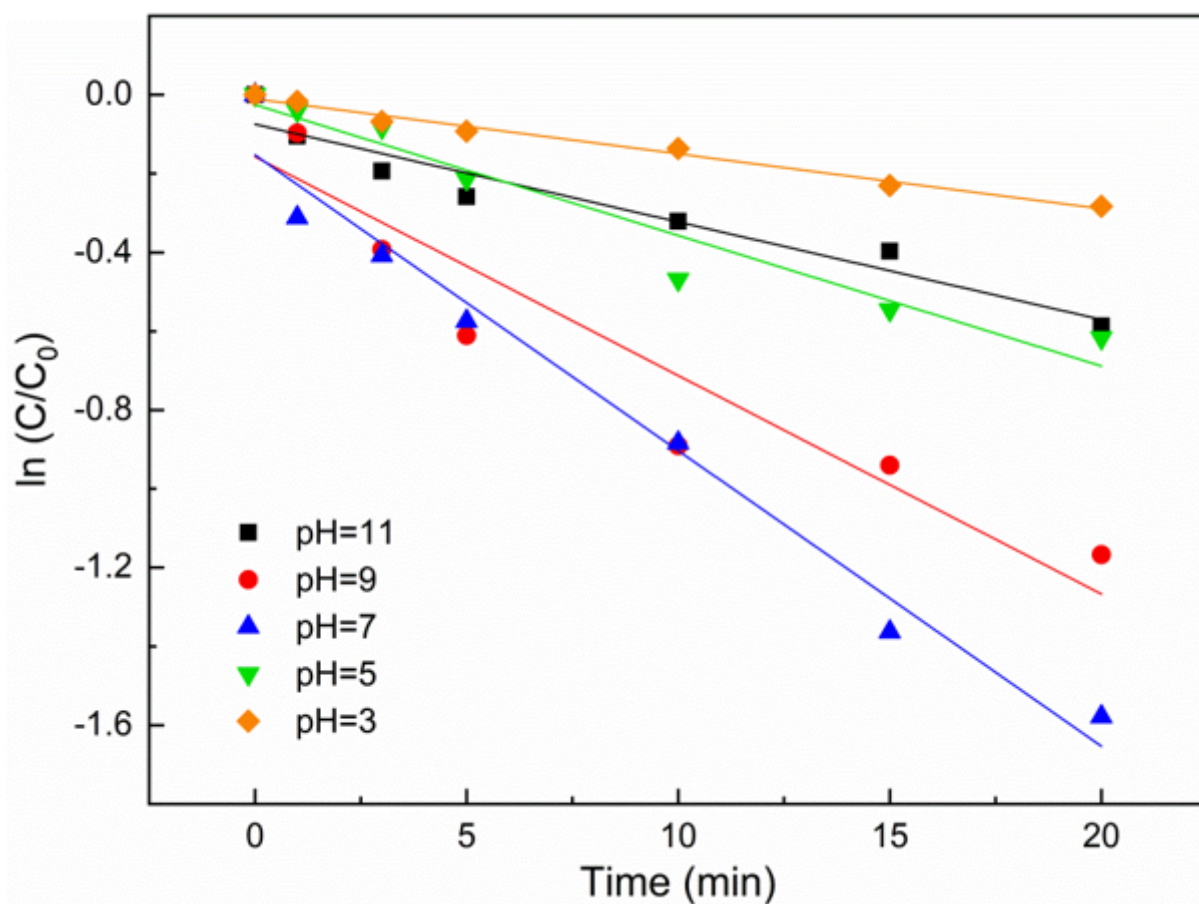


Figure 3

Influence of solution pH on photocatalytic degradation of norfloxacin by MMIP

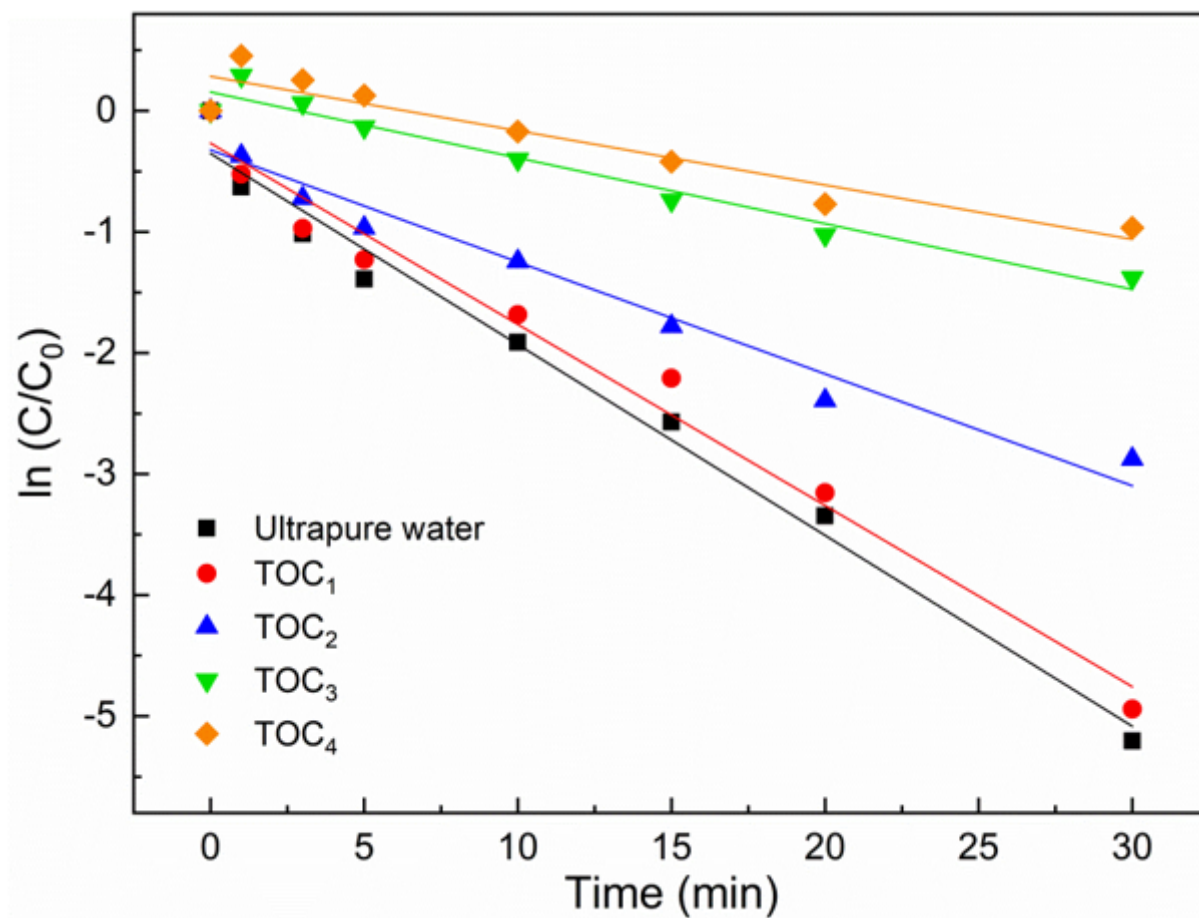


Figure 4

Influence of humic acid on photocatalytic degradation of norfloxacin by MMIP

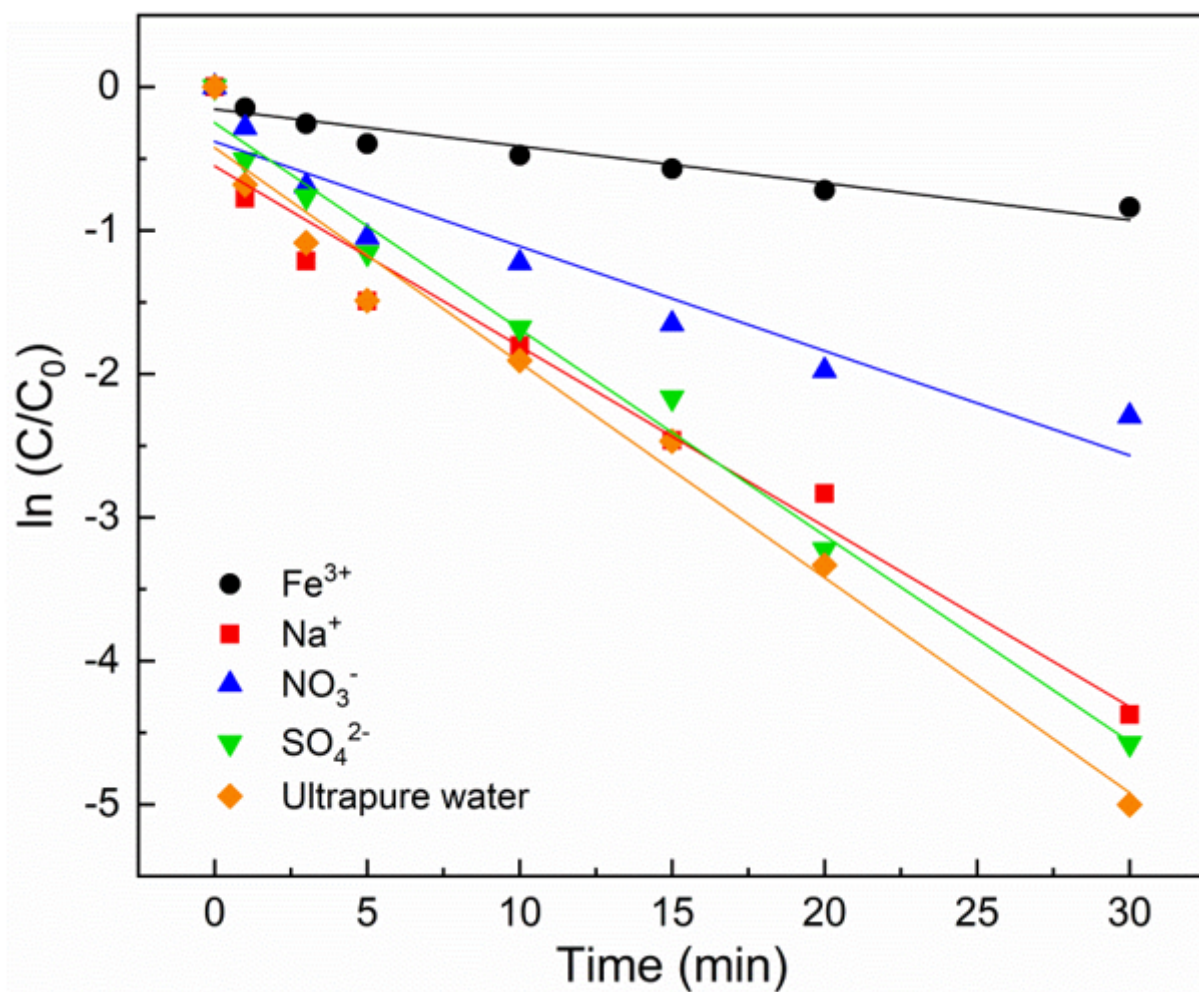


Figure 5

Influence of common ions on photocatalytic degradation of norfloxacin by MMIP

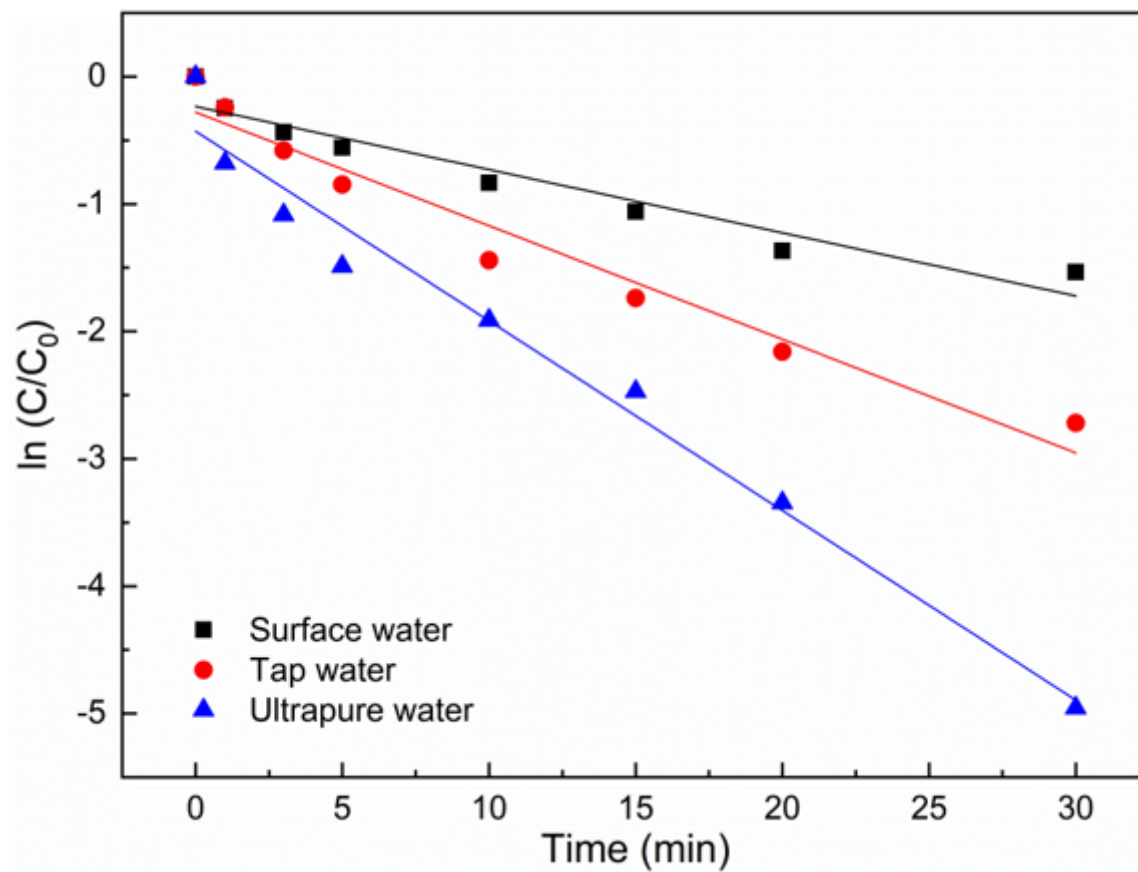


Figure 6

Influence of water mediums on photocatalytic degradation of norfloxacin by MMIP

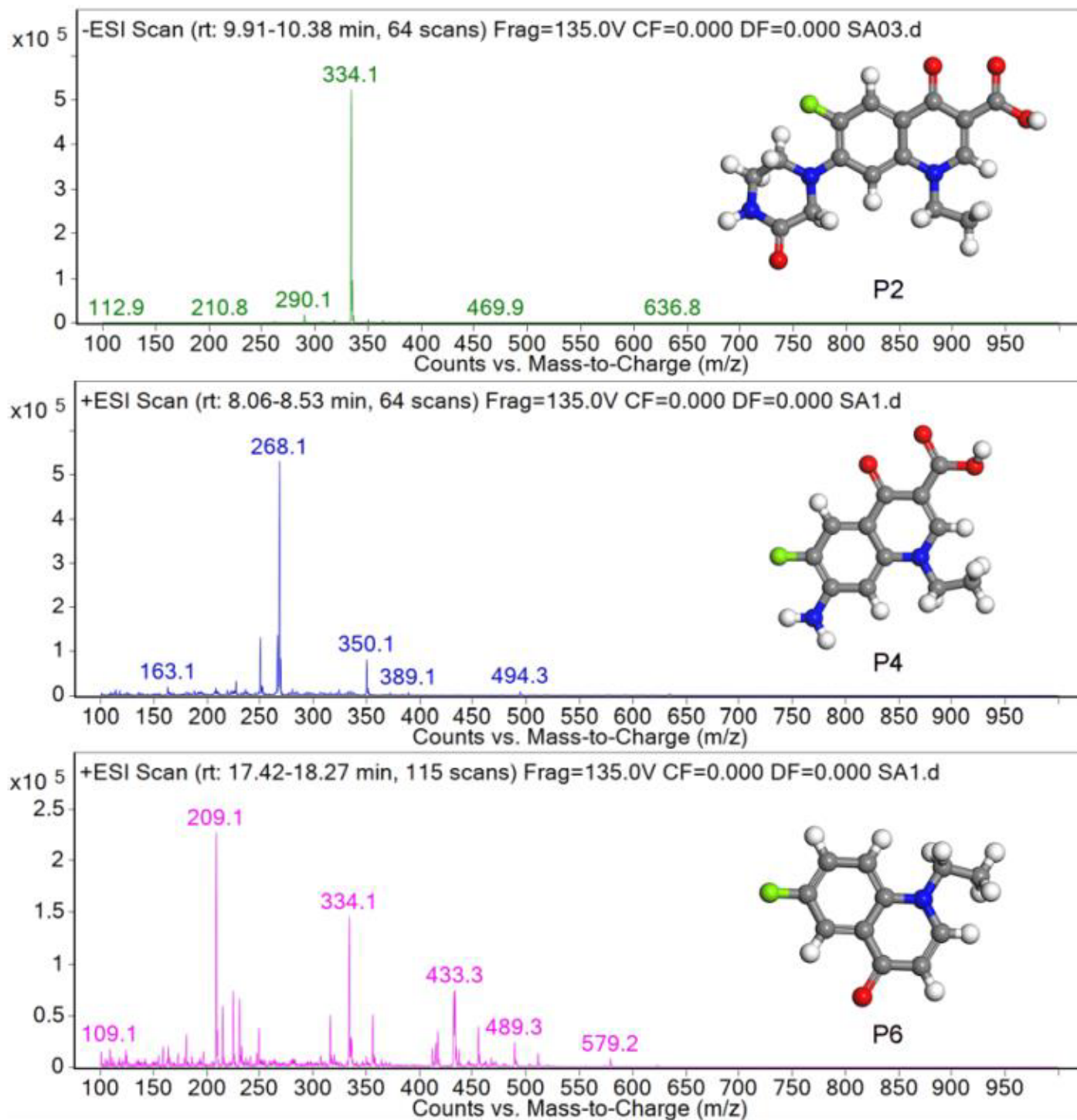


Figure 7

Part of the mass spectrogram corresponding to the chromatographic peaks

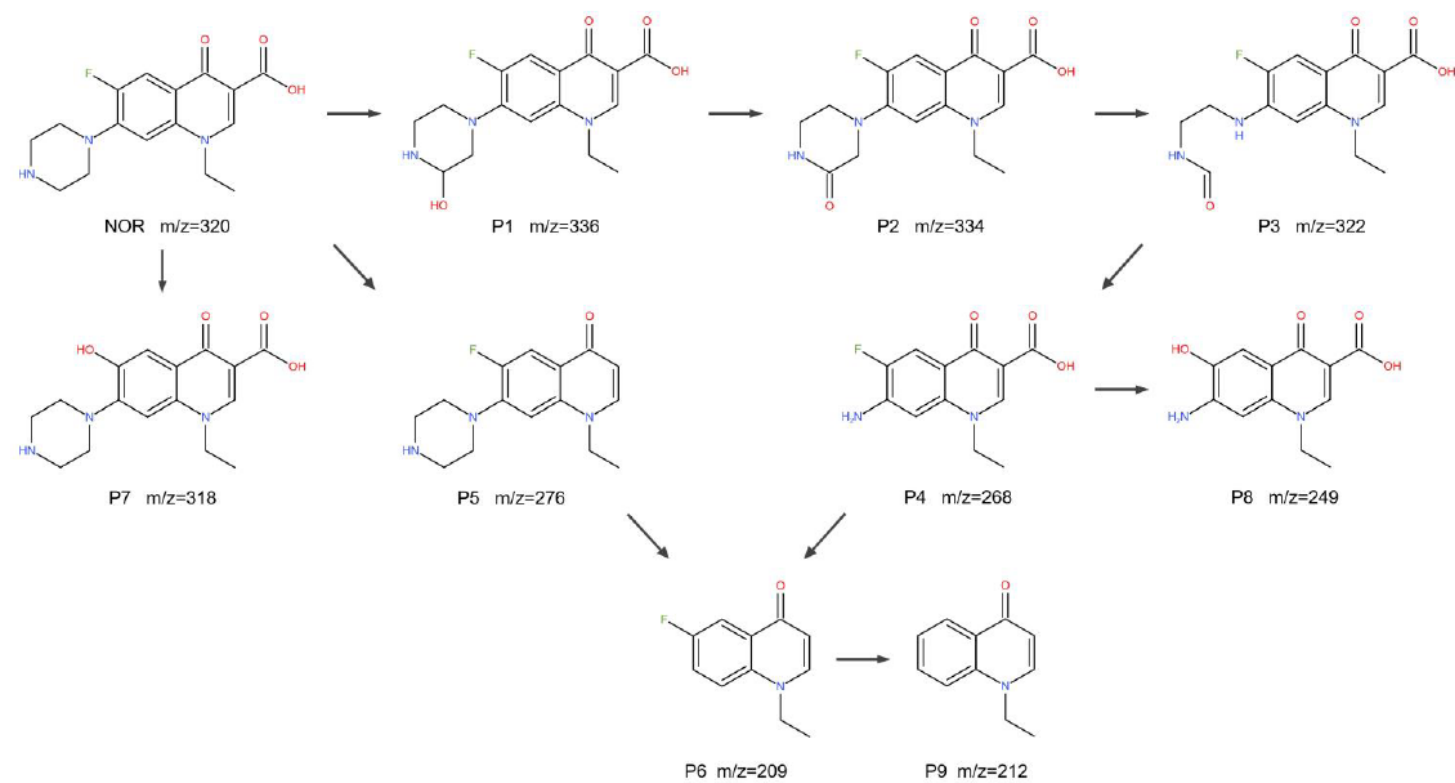


Figure 8

Possible pathways of photocatalytic degradation of norfloxacin by MMIP

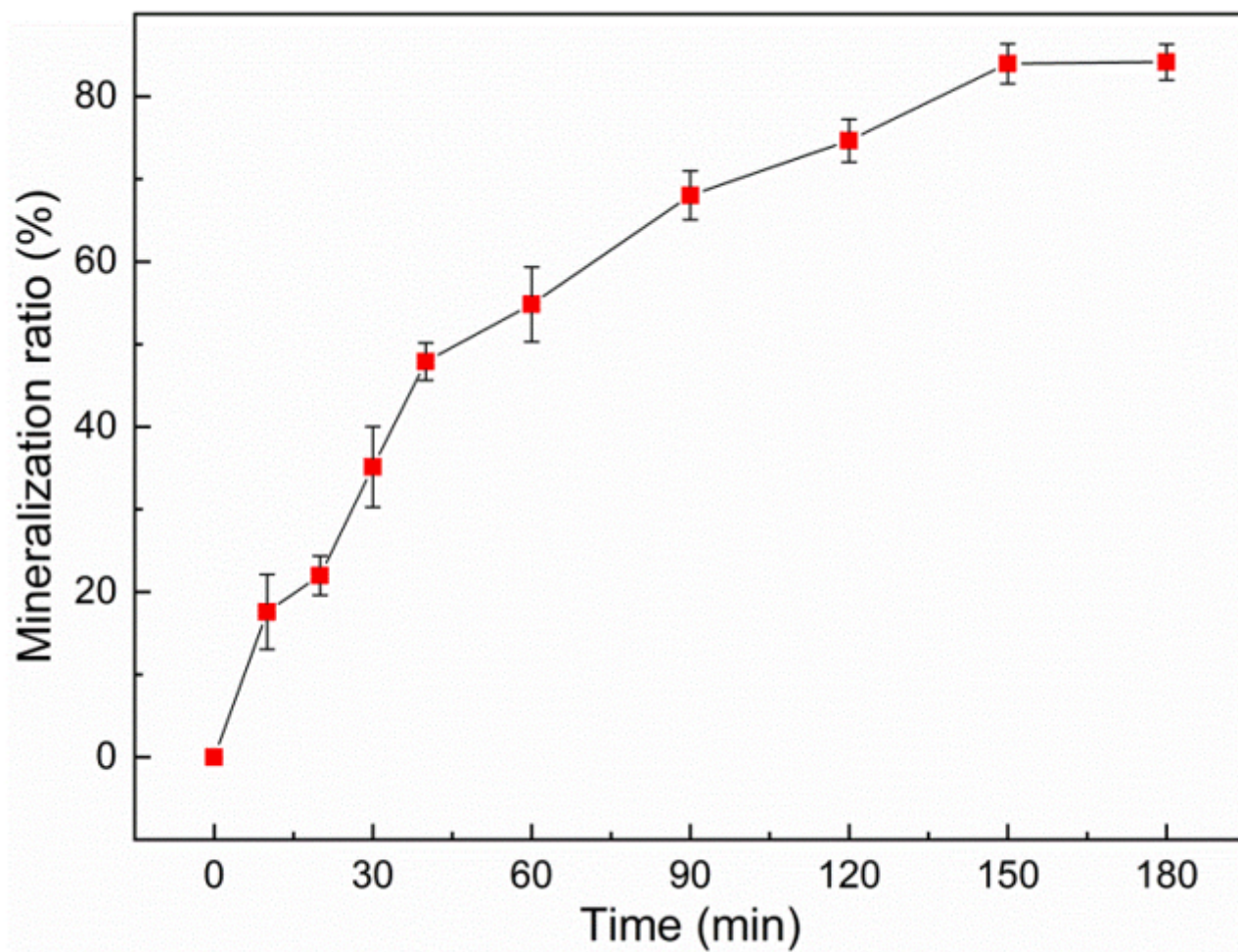


Figure 9

Mineralization ratio of photocatalytic degradation of norfloxacin by MMIP

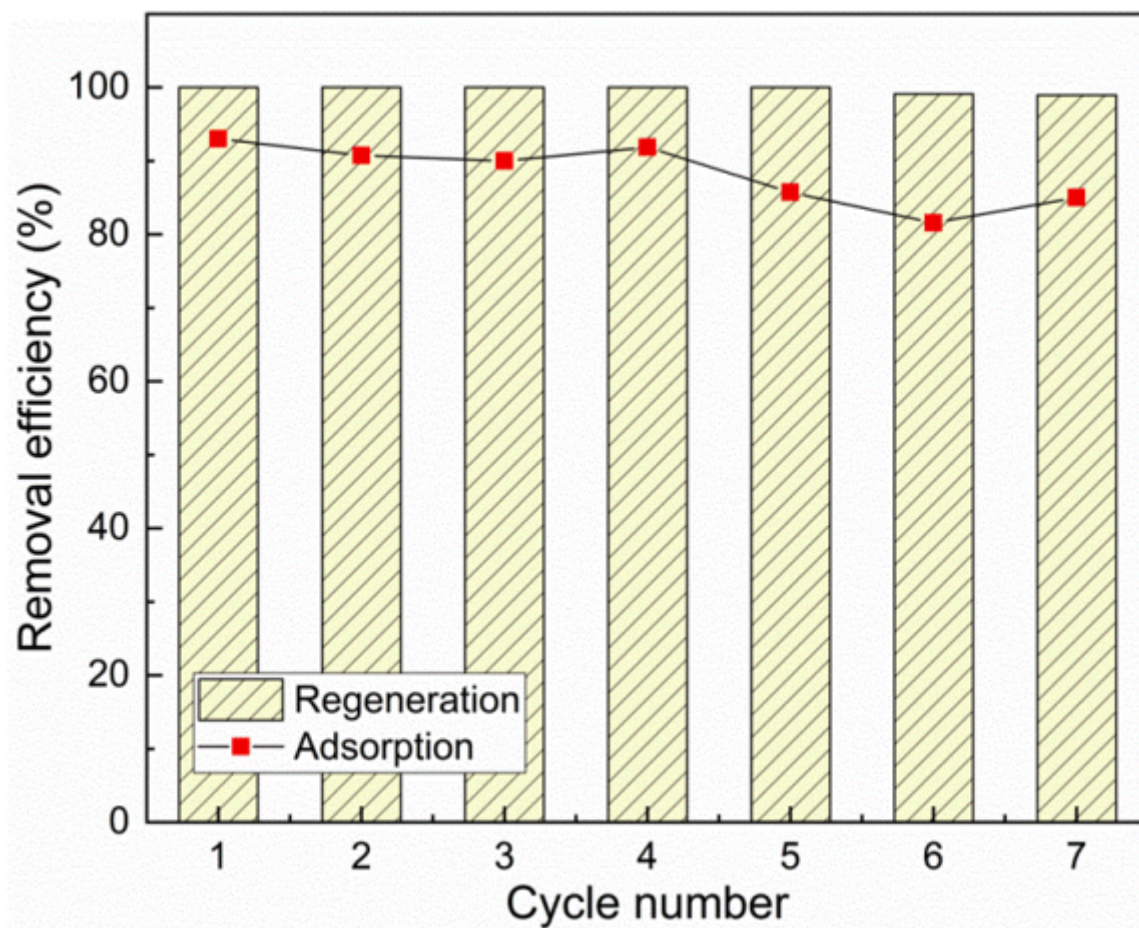


Figure 10

In-situ regeneration and recycling performance of MMIP

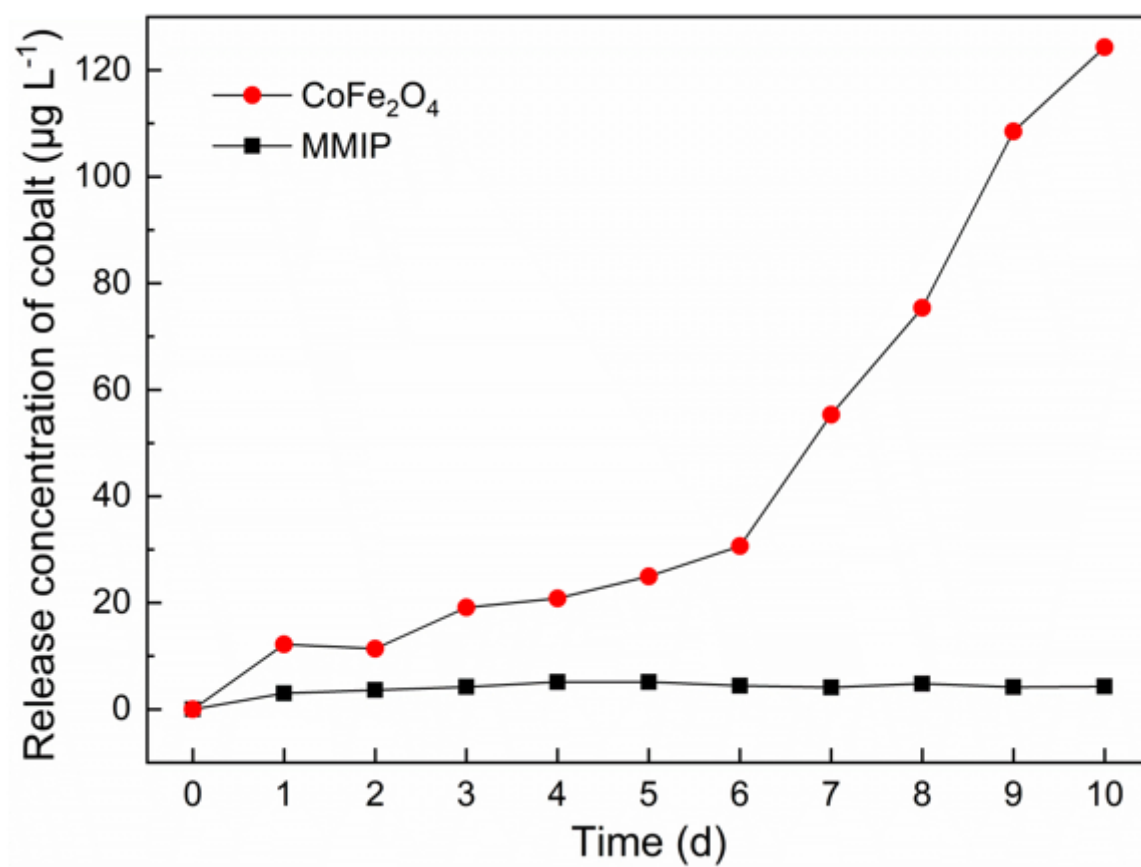


Figure 11

Concentration of cobalt released by CoFe_2O_4 and MMIP in aqueous solution