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 by effectively utilizing photocatalytic degradation and magnetic separation techniques. The imprinted material with titanium layer and multi-hole surface showed an 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 MMIP were elucidated. The results showed that MMIP had good adaptability and could degrade norfloxacin within 60 min, but the degradation rate constant decreased in surface water. Based on the identification of intermediate products, the possible degradation pathways of norfloxacin were analysed, speculating that it might be degraded into small molecules in the form of 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, and the low cobalt release of MMIP enhanced the security of the material. The results of adsorption and degradation cycle tests showed that MMIP obtained by molecular imprinting technology had excellent performance in sustainable use for micro organic pollutants removal.

1. Introduction

In recent years, the production and consumption of antibiotics have been increasing all over the world, while their potential adverse effects on the environment and human health have attracted more attention. A literature research showed that 110 antibiotics have been detected in China’s environment, most of these in aquatic environments [1]. Through cluster analysis, seven dominant antibiotics, including norfloxacin, could be discovered in almost all environmental compartments with concentrations up to several micrograms per litre. In some kinds of waters in European countries, such as wastewater, surface water, groundwater and drinking water, quinolones were the most frequently detected antibiotics [2]. Those findings indicated that
quinolone antibiotics were more likely to accumulate in the environment and had strong persistence [3]. Norfloxacin is a kind of fluoroquinolones drug with stable chemical structure and poor biodegradability. Traditional sewage treatment technologies are not enough to remove norfloxacin effectively because of its special properties such as low concentration and high bio-toxicity [4]. The main entry routes of norfloxacin into the environment are the discharge of livestock wastewater, effluent and sludge into surface water, groundwater and soil, respectively [1]. Therefore, it is urgent to develop an 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 organic chemicals. Molecularly imprinted polymers (MIP) can selectively adsorb trace pollutants in water environments [5], what is extremely beneficial for the removal of norfloxacin. Tan et al. [6] 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 [7,8]. Similarly, fluoroquinolone imprinted polymers were also developed for the extraction and detection of relevant antibiotics in actual water samples [9]. However, such imprinted materials cannot degrade the adsorbed pollutants, resulting in poor regeneration performance of the polymers, while the elution method may well cause environmental pollution.

Photocatalysis reaction can effectively degrade organic pollutants in wastewater. The use of photocatalysis to remove pollutants adsorbed on MIP is a new technology [10]. The degradation of the target adsorbent on MIP surface allows the materials to be reused. Due to the selective adsorption, they exhibit better photocatalytic activity to the target material. 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 [11]. TiO$_2$-based photocatalytic materials were generally considered as the preferred materials for the degradation of organic matter [12,13]. In addition, some imprinted polymers that can degrade template molecules under visible light irradiation had also been prepared [14], but their efficiencies were not as outstanding as that of ultraviolet light. Even so, the imprinted photocatalytic materials listed above are difficult to separate from the solution. The material must be centrifuged from the decontaminated water to be reused, whereas the recovery ratio is low.

Over the years, there have been many researchers to fix powdered materials on various substrates [15,16]. For photocatalytic materials, glass substrate was frequently used [17]. 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 [18]. Magnetic separation technology is different from immobilization technology, which has the characteristics of environmental protection and high efficiency. The resulting material can separate from the solution by applying an external magnetic field [19]. A magnetic molecularly imprinted composite material showed an effective norfloxacin adsorption performance when mixing with other organic matter in the effluent of the actual sewage treatment plant, which was prepared by cross-linking chitosan and γ-Fe$_2$O$_3$ particles [20]. In addition, a study has found that heterojunction of magnetic core CuFe$_2$O$_4$ and photocatalyst g-C$_3$N$_4$ improved the separation efficiency of the photoinduced electron–hole pairs [21]. More experiments demonstrated that the degradation mechanism of magnetic nano-photocatalyst was similar to that of single photocatalyst [22]. It can be seen that magnetic separation technology combined with molecular imprinting and photocatalysis 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 function of the material. In addition to the selective adsorption performance of MMIP towards norfloxacin, the degradation efficiency of the target pollutants and its regeneration property are also significant and worth investigating. Here, the photocatalytic degradation kinetics of MMIP was studied, and the influences of different environmental media factors on the photocatalytic degradation performance were systematically explored. Besides, the products, pathways and mineralization of photocatalytic reactions were further analysed to evaluate the security and sustainability of the material.

2. Material and methods

2.1. Chemicals and materials

Norfloxacin (C$_{16}$H$_{19}$FN$_3$O$_3$, 98.0%), ferric chloride (FeCl$_3$, 99.0%), cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O, 99.0%) and tetrabutyl titanate (Ti (OC$_4$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 hexafluorotitanicate, 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 FeCl₃ and 25 mmol CoCl₂·6H₂O 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 CoFe₂O₄. Secondly, 2 g CoFe₂O₄ was added into a mixture solution containing 300 mL anhydrous ethanol and 5 mL tetrabutyl titanate. The suspension was heated at 150°C for 10 h in autoclave to obtain CoFe₂O₄@TiO₂. At last, 200 mg CoFe₂O₄@TiO₂ nanoparticles, 20 mg norfloxacin, 3.96 g ammonium hexafluorotitanate and 2.60 g boric acid were dissolved in 100 mL deionized water, stirred for 2 h and then natural deposited. The molecularly imprinted particles were calcined under 350°C for 2 h to remove templates.

The morphological characteristic and surface elements of the materials were carried out using scanning electron microscope (SEM, GeminiSEM 300, Zeiss, Germany) with an X-ray energy dispersive spectrometer (EDS, Quantax 70, Bruker, Germany).

2.3. Photocatalytic degradation experiments

After the adsorption reaction reached 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. After stirring 60 min at 25°C, the reaction vessel was illuminated by a 254 nm ultraviolet lamp with a 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 μW/cm². Samples were then taken out at regular intervals and filtered by a 0.45 μm filter. Photocatalytic kinetics of MMIP was investigated over various initial concentrations ranging from 1 mg/L to 25 mg/L. 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:

\[
\text{Efficiency} = \frac{C_0 - C_1}{C_0} \times 100% \tag{1}
\]

where \(C_0\) (mg/L) and \(C_1\) (mg/L) 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 the XDB C18 column (4.6 mm×150 mm, 5 μm). A fluorescence detector with the excitation wavelength of 280 nm and the emission wavelength of 450 nm was used. The mobile phase 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. The intermediate degradation products were detected by liquid chromatography-mass spectrometry (6460 Triple Quad, Agilent, USA). The samples were extracted on solid phase extraction columns (3 mL/60 mg, Oasis HLB, Waters) and concentrated by nitrogen blowing. The liquid chromatography separation was carried out on the Agilent Zorbax SB C18 column (2.1 mm×150 mm, 3.5 μm) and gradient elution was performed with acetonitrile and 0.25 wt% formic acid at a flow rate of 0.20 mL/min. The mass spectrometry analysis was adopted using an electrospray ionization source in positive mode and scanning range of m/z was 100~1000 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).

3. Results and discussion

3.1. Characterization of MMIP

The morphology of MMIP was confirmed by SEM image shown in Figure 1(a). 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 TiO₂ particles. This feature was
corresponding to the X-ray diffraction result for MMIP we obtained previously [23]. Such a surface characteristic was conducive to enhancing the photocatalytic degradation of the target at the interface. In addition, 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 a high temperature. The porous structure made the material more specific and better to capture target pollutants. As shown in Figure 1(b), chemical elements such as Co, Fe, Ti, C and O were present in MMIP, among which 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$_2$O$_4$ coated by the TiO$_2$ layer and the surface modification with molecular imprinting, which was conducive to photocatalysis of organic pollutants. Generally, the photocatalytic degradation reaction was a rate-limiting reaction that depended on the
concentration of pollutants and hydroxyl radicals on the surface of the imprinted photocatalytic material. The Langmuir–Hinshelwood model can often be used to describe this process [24]. It was assumed that the light intensity and the oxygen concentration in the solution remain unchanged during the process. However, some fluoroquinolones, such as norfloxacin would degrade slightly when exposed to ultraviolet light [25]. So using the Langmuir-Hinshelwood model and considering the direct photodegradation of norfloxacin under ultraviolet light, the actual photocatalytic degradation rate equation applied to norfloxacin can be obtained as:

$$r_{\text{NOR}} = \frac{k_c K_{\text{NOR}}}{1 + K_{\text{NOR}} C_{\text{NOR}_0}} + K'$$  \hspace{1cm} (2)

where $r_{\text{NOR}} \text{ (min}^{-1})$ was the comprehensive degradation rate of norfloxacin, $K_{\text{NOR}} \text{ (L/min)}$ was the adsorption equilibrium constant of norfloxacin, $k_c \text{ (mg/(L·min))}$ was the photocatalytic degradation rate constant of norfloxacin on material surface, $K' \text{ (min}^{-1})$ was the direct photodegradation rate constant of norfloxacin under ultraviolet light and $C_{\text{NOR}_0} \text{ (mg/L)}$ was the initial concentration of norfloxacin.

Five different initial concentrations of the target were selected in the experiments. Figure 2(a) showed that the photocatalytic degradation rate of norfloxacin decreased significantly when the initial concentration increased from 1 to 25 mg/L. Figure 2(b) displayed the fitting result of the rate equation to norfloxacin. The main parameters are as follows: $k_c = 1.058 \text{ mg/(L·min)}$, $K_{\text{NOR}} = 0.196 \text{ L/min}$, $K' = 0.008 \text{ min}^{-1}$ and correlation coefficient $R^2 = 0.99$. So the final kinetic fitting equation for norfloxacin photocatalytic degraded by MMIP can be expressed as the following formula:

$$r_{\text{NOR}} = \frac{0.207}{1 + 0.196C_{\text{NOR}_0}} + 0.008$$  \hspace{1cm} (3)

According to the fitting result, the direct photodegradation rate constant of norfloxacin was relatively small. Under the same irradiation conditions, the measured rate constant in a pure system without MMIP was 0.022 min$^{-1}$, which was higher than the fitting result. It may be that the presence of MMIP increased the turbidity of the solution and weakened the ultraviolet intensity in the photocatalytic experiment. Most of the norfloxacin molecules were adsorbed to the surface of MMIP, so that there was less norfloxacin available for direct photolysis in the solution. In the absence of $K'$, the result of model fitting was that $k_c$ increased by 18.5% and $K_{\text{NOR}}$ decreased by 14.3%. 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 behaviour 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, it was found that pH had an evident impact on norfloxacin adsorption removal by MMIP [23]. 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. Due to the low discrimination of pH on the degradation process at a high dosage, the dosage was selected as 0.1 g/L to amplify the difference in this section. The experimental results are shown in Figure 3.
When the pH was neutral, the photocatalytic degradation rate was the fastest, and the rate constant was 0.075 min$^{-1}$. Under acidic and alkaline conditions, especially at pH=11, the reaction rate decreased significantly. This is mainly because the activity of the catalyst is closely related to the charged properties of its surface. 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 [26]. In addition, MMIP had the best adsorption performance to norfloroxacin under neutral condition, which promoted the catalytic reaction process on its surface.

### 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 a catalyst, humic acid served as a scavenger of hydroxyl radical, hindering the activity of TiO$_2$ [27]. Here, solutions with different humic acid concentrations were used as the reaction media, and their concentrations were characterized by TOC as TOC$_1$=0.154 mg/L, TOC$_2$=1.823 mg/L, TOC$_3$=2.523 mg/L, and TOC$_4$=4.427 mg/L, respectively. The effect of humic acid on ultraviolet photocatalytic degradation of norfloroxacin is shown in Figure 3(b). Obviously, with the increase of humic acid concentration, the photocatalytic degradation rate decreased, and when the TOC concentration was 1.823 mg/L, the rate decreased by about 40%, but there was almost no reduction at low concentration. Humic acid can occupy the specific adsorption site of the material, thus reducing the adsorption and removal efficiency of norfloroxacin. It should be noted the results of this experiment showed that MMIP still had a strong competitiveness in photocatalytic degradation of the target in the low concentration of humic acid environment, and norfloroxacin 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 efficiency reduced by 75.5\% in the presence of 1 mg/L humic acid, but it hardly changed with the increase of humic acid concentration [28].

### 3.3.3. Common ions

The actual water body composition is quite 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$_2$$^-$$^-$ and NO$_3^-$ at a concentration of 0.1 mmol/L were selected as the experimental ions. As shown in Figure 3(c), Fe$^{3+}$ and NO$_3^-$ had conspicuous impact on degradation rate, whereas 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 was the best when the pH was neutral. However, some cations and anions would change the pH value of the solution, thereby disturbing the charging properties of reducing substances and photocatalytic materials. In addition, inorganic ions could affect the photocatalytic degradation activity of environmental pollutants [29]. 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 [23]. 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. [30] found that Fe$^{3+}$ could reduce the number of oxygen-containing free radicals in the photocatalytic chain reaction by trapping photoelectrons, and the presence of NO$_3^-$ in this system will affect the binding of the target substances to hydroxyl radicals [31].

### 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. Some water quality parameters of samples are shown in Table 1. Figure 3(d) revealed that surface water weakened the photocatalytic degradation of norfloxacin the most, 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 was also obvious. Especially, the presence of anions and cations such as Fe$^{3+}$ and NO$_3^-$ in natural waters will decrease 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. The third aspect is that the selective adsorption ability of MMIP 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 the magnetic imprinted material has satisfied adaptability in different water media.

### 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 were qualitatively analysed by liquid chromatography-mass spectrometry. As the illumination time lasts, the number of peaks in the mass spectrum continues to increase, which means the new substances are constantly being produced. Figure 4 lists the mass spectrogram corresponding to some chromatographic peaks.

The modification of molecularly imprinted layer on the surface of TiO$_2$ can improve the adsorption performance of the material, thereby increasing the degradation efficiency of target pollutants [32]. 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...

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**Table 1.** Some water quality parameters for surface water and tap water samples.

| Water quality parameters | Surface water | Tap water |
|--------------------------|--------------|-----------|
| pH                       | 7.94         | 6.78      |
| UV$_{254}$               | 0.073        | 0.010     |
| Turbidity (NTU)          | 4.3          | 0.2       |
| TOC (mg/L)               | 13.590       | 3.242     |
| Na$^+$ (mg/L)            | 14.690       | 12.840    |
| K$^+$ (mg/L)             | 3.623        | 2.577     |
| Fe$^{3+}$ (mg/L)         | 0.383        | 0.271     |
| SO$_2$$^-$$^-$ (mg/L)    | 98.400       | 41.700    |
| NO$_3^-$ (mg/L)          | 15.610       | 9.870     |
Figure 4. Part of the mass spectrogram corresponding to the chromatographic peaks.

Figure 5. Possible pathways of photocatalytic degradation of norfloxacin by MMIP.
were detected and the possible molecular structures were proposed. Products 1–4 indicated the gradual degradation process of a 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 reflected that fluorine on the benzene ring was likely to be replaced by hydroxyl, and another product 9 also demonstrated the likelihood of direct removal of fluorine in the degradation process. The possible reaction pathway is deduced and summarized as shown in Figure 5. Generally, 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, and the trend during the photocatalytic degradation of norfloxacin by MMIP is shown in Figure 6. 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 [33], and some comparison results are displayed in Table 2. The mineralization efficiency of the target substance is not outstanding in visible light catalysis, for the degradation is insufficient, and the use of simulated sunlight generally takes a longer irradiation time in the experiment. According to the above analysis, many intermediates would be generated during the degradation of norfloxacin. The experiment showed that these organic intermediates were easier to decompose under ultraviolet irradiation. The higher degree of mineralization indicated that norfloxacin was finally degraded into inorganic small molecules after photocatalytic degradation, showing a well ecological friendliness.

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 2 h to reach saturation, and then photocatalytic in-situ regeneration was performed for 2 h. 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 MMIP is shown in Figure 7. 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 structures, 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 [38]. The amount of cobalt in environmental waters is stipulated not to exceed 0.05 mg/L [39]. Take the basic carrier as a comparison, CoFe₂O₄ and MMIP of 0.4 g/L were added to the deionized water, respectively. The solutions were kept stirring,
and the samples were taken every day to determine the concentration of cobalt released. The results are shown in Figure 8. During the testing period of 10 d, the cobalt release concentration of CoFe$_2$O$_4$ increased gradually and reached 124.30 μg/L on the 10th day. Correspondingly, the release concentration of cobalt by MMIP was significantly lower than that of CoFe$_2$O$_4$, and remained relatively stable in the solution, which the average cobalt concentration measured in 10 d was 4.22 μg/L. It can be seen that after the modification of molecularly imprinted layer, the metal precipitation behaviour of the material is controlled. The enhancement of safety performance improves the application potential of the material.

4. Conclusion

In summary, the novel magnetic molecularly imprinted polymers can effectively degrade norflaxacin 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 norflaxacin with low concentration was higher by MMIP. Humic acid and common ions can influence the degradation rate of norflaxacin, among which Fe$^{3+}$ had the most significant effect. The main pathways of the photocatalytic degradation of norflaxacin were proposed, including transformation and removal of piperazine rings, decarboxylation and replacement or direct removal of fluorine. After 150 min of ultraviolet light irradiation, norflaxacin 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.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Data availability statement

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

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