Characterization and application of surface-molecular-imprinted-polymer modified TiO₂ nanotubes for removal of perfluorinated chemicals
Lei Hu, Yi Li and Wenlong Zhang

ABSTRACT
The removal of perfluorinated chemicals (PFCs) during wastewater reclamation is a great concern. However, the existing advanced treatment processes are inefficient for the removal of PFCs from secondary effluents of municipal wastewater treatment plants (WWTPs) because other coexistent pollutants with less environmental significance are removed simultaneously. Therefore, research on high-selectivity, low-cost removal methods is needed. The S-MIP-TiO₂ nanotube (NT) photocatalysts were fabricated, characterized and tested for removal of PFCs from wastewater for the first time. Scanning electron microscopy and Fourier transform infrared spectroscopy show that the TiO₂ NTs (average diameter 60 nm) were successfully imprinted with functional groups (i.e. carboxyl). The adsorption selectivity and photocatalytic activity of the S-MIP-TiO₂ NTs over perfluorooctanoic acid (PFOA) were improved compared with neat TiO₂ NTs and interestingly, were higher at low PFOA concentrations (10 to 100 ng/L, as normal PFC concentrations in secondary effluents) than at high concentrations (10 to 1,000 mg/L). With S-MIP-TiO₂ NTs used as photocatalysts, some representative PFCs were selectively and rapidly removed from secondary effluents of a municipal WWTP. S-MIP-TiO₂ NTs exhibited excellent regeneration performance. Thus, photocatalytic treatment using is promising for effective removal of PFCs from secondary effluents of municipal WWTPs.

Key words | perfluorinated chemicals, removal, surface-molecular-imprinting, TiO₂ nanotubes

INTRODUCTION
In recent years, wastewater reclamation from municipal wastewater treatment plants (WWTPs) has been employed worldwide for various purposes, including landscape irrigation, impoundment, crop irrigation, and groundwater recharge to overdrawn aquifers (Zhang et al. 2011). However, many types of pollutants still exist in the effluents of municipal WWTPs after traditional treatment (Gupta et al. 2011b, 2012a). Among them, perfluorinated chemicals (PFCs) are at mean concentrations from ng/L to μg/L. Some PFCs, such as perfluorinated acid, are included in the European Union list of priority pollutants. These chemicals even at trace levels can induce extensive reproductive and sexual abnormalities in wildlife (Radjenovic et al. 2007). Thus, the removal of these PFCs during wastewater reclamation is a great concern.

Many methods, such as activated carbon adsorption, ozonation, UV radiation, UV/H₂O₂ degradation, and photo-degradation, have been developed to remove PFCs from wastewater (Zhang et al. 2012). Among them, activated carbon has been widely applied to remove organic matters from wastewater owing to its strong affinity to adsorb even low-concentration organic substances (Ali & Gupta 2006; Gupta et al. 2006, 2007; Gupta & Ali 2008; Gupta et al. 2011a). Photo-degradation is an environmentally friendly technique since it does not require chemical input or output (Gupta et al. 2007, 2011b, 2012b). TiO₂ is the most common photocatalyst due to its capability in removal of a wide range of pollutants, and shows other advantages including high photochemical stability, low toxicity and low-cost (Gupta et al. 2011a, 2012a).

However, the presence of low-level PFCs is accompanied by high levels of other low-toxicity biodegradable pollutants in secondary effluents of municipal WWTPs (Saadi et al. 2006). Current advanced treatment processes...
are inefficient for PFCs removal because other pollutants with less environmental significance were also removed simultaneously, which decreases the removal efficiency of PFCs and increases treatment costs (Czili & Horvath 2008). For these reasons, the research for highly selective and low-cost removal methods is still warranted.

Molecular imprinting is a useful technique for the preparation of polymeric materials as specific molecular recognition receptors (Piletsky et al. 2001; Haupt 2005). Molecularly imprinted polymers (MIPs) are prepared by copolymerization of a cross-linking agent with the complex formed from a template and polymerizable monomers that have functional groups specifically interacting with the template through covalent or non-covalent bonds. After the template is removed from the resulting polymer matrixes, binding sites having the size and shape complementary to the template are generated. These MIPs are synthesized with ‘tailor-made’ binding sites for a template (Haupt 2005). Recently, MIPs have been utilized for the selective removal of perfluorinated compounds from water (Meng et al. 2005; Le Noir et al. 2007; Zhang et al. 2011). Meng et al. (2005) suggested that MIPs with perfluorinated acid as template might be used to remove perfluorinated compounds from water. Le Noir et al. (2007) employed MIPs, based on bulk polymerization approach, to remove trace perfluorinated acid from aqueous solution using MIPs adsorbent column. Tran et al. (2014) used molecularly imprinted polymeric microspheres to remove phenolic estrogen pollutants from different sources of water. The results of the above studies show that MIPs adsorption is an effective method for the selective removal of trace targeted perfluorinated compounds from water.

However, adsorption is a non-destructive removal technology and MIPs need to be regenerated and reused for a lower treatment cost (Sansotera et al. 2014). The related research concerning simultaneous adsorption of perfluorinated compounds and polymer regeneration are very limited. Only recently, UV irradiation was used as a method to regenerate MIPs and destroy pollutants during solvent extraction (Jing et al. 2014). It has been reported in our previous research that TiO2 photocatalysis is more effective for the removal of perfluorinated compounds and perfluorinated activity from secondary effluents than UV irradiation (Zhang et al. 2012). However, to the best of our knowledge, there is no existing report regarding the selective removal of perfluorinated compounds using the technology combining of MIPs adsorption and TiO2 photocatalysis.

The main objective of this work was, therefore, to develop new surface-MIP-modified TiO2 (S-MIP-TiO2) nanotube (NT) photocatalysts to achieve selective removal of perfluorinated compounds from secondary effluents and simultaneous regeneration of polymers. The material characteristics, adsorption properties, and photocatalytic activity of the photocatalysts were investigated in details. The photocatalytic removal of PFCs and perfluorinated activity from practical secondary effluent using S-MIP-TiO2 NTs were also evaluated.

**MATERIAL AND METHODS**

**Reagents**

The titanium sheets (99.60%, 0.06 mm thick) were purchased from Haji Ltd for Titanium & Nickel, China. The five perfluorinated compounds [heptafluorobutyrlic acid (PFBA), perfluorovaleric acid (PFPeA), undecfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), and pentadecafluorooctanoic acid (PFOA)], methacrylic acid (MAA), trimethylolpropane trimethacrylate (TRIM), and 4,4’-azobis(4-cyanovaleric acid) (AIBN) were all purchased from Sigma-Aldrich (USA) and used without further purification. TRIM was of technical grade and all other reagents used were of high-performance liquid chromatography (HPLC) grade. Analytical standards for chromatography analyses were purchased from Sigma-Aldrich (USA).

**Preparation of TiO2 NTs and S-MIP-TiO2 NTs**

TiO2 NTs were prepared according to previous work (Su et al. 2009). Prior to anodization, titanium sheets were ultrasonically cleaned in acetone and deionized water. The cleaned titanium sheet was anodized at 20 V in an electrolyte containing 0.5 wt% NH4F and 1/12 M C2H2O4·2H2O at room temperature for 10 min in a two-electrode system with a nickel cathode. To induce crystallinity, the initially amorphous as-anodized sample was annealed at 500 °C for 120 min with heating and cooling rates of 2 °C·min⁻¹.

The MIP was prepared by precipitation polymerization method. The template (PFOA, 0.18 mmol) was first added into a bottle containing a mixture of solvent (anhydrous acetonitrile, 10 mL) and functional monomer (MAA, 0.87 mmol), and sonicated for 5 min at ambient temperature. The cross-linker (TRIM, 1.90 mmol) and initiator (AIBN, 0.0071 mmol) were then added into the solution. The solution was mixed uniformly by sonication for 5 min, and then was slowly dropped on two sides of TiO2 NTs to get a uniform coating. Afterwards, the coated-TiO2 NTs were fixed in the columniform quartz tube. The tube was
then sealed and purged with nitrogen for a further 20 min. Polymerization was carried out under UV light irradiation for 12 h. Then the coated-TiO2 NTs were washed with a mixture of methanol and acetic acid (volume ratio of 9:1) for four times, and each at a duration of 1.5 h. Then, the nanotube array was washed with methanol for 24 h. This was followed by extractions with methanol until no PFOA was detected in the eluates. The non-imprinted polymer (NIP) modified TiO2 nanotubes were synthesized and treated in the same way except that no template was added.

Characterization

The morphological characters of the samples were investigated using field emission scanning electron microscope (Hitachi, Model S-4800). The completion of the reaction in the preparation of the MIPs modified NTs was demonstrated by FD-5DX Fourier transform infrared spectroscopy (FT-IR). The crystal phases were determined by X-ray diffractometer (XRD, M21X, MAC Science Ltd, Japan) with Cu-Kα radiation.

Apparatus and methods for adsorption and photocatalytic degradation

The adsorption of PFOA on MIP-TiO2 NTs, NIP-TiO2 NTs and TiO2 NTs were performed by placing these samples in the solutions (300 mL) at different concentrations of PFOA (varied from 10 to 10⁹ ng/L). The whole process went on with continuous magnetic stirring for 2 h in the dark at room temperature. The amount of adsorbed PFOA was determined by measuring the difference between total PFOA amount and residual amount in solution.

The photocatalytic experiments were conducted in a water-jacketed cylindrical quartz photocatalytic reactor (60 cm height, 18 cm outer diameter, and 15 cm inner diameter) in the presence of the photocatalysts with the active area 400 cm²/L. The double-walled glass reservoir was equipped with a thermostatically controlled water flow between the outer walls. The aeration system at the bottom of the reactor was installed to improve mixing and mass transfer to the catalyst. An 8 W, low-pressure mercury UV lamp (Beijing Lighting Research Institute, ZW8S15W) with irradiating wavelength 254 nm as the light source was immersed in the photocatalytic reactor. Under the same conditions as in the photocatalytic experiments, the total useful radiation arriving to the reactor was determined to be 7.58 × 10⁻⁸ Einstein·s⁻¹ by chemical actinometry using potassium ferrioxalate (Sun & Bolton 1996). After the solution was stirred for 40 min to favor the organic adsorption onto the catalyst surface, the concentration of the pollutant was determined as the initial concentration, and then the irradiation started. The solution was sampled for analysis from the reactor cell using a glass syringe at specified time intervals during degradation.

Analytical methods

The concentrations of PFOA in ultrapure water were determined using liquid chromatography–mass spectrometry (LC-MS) equipped with electrospray interface (HP 1100 LC-MS, Trap SL System, Agilent, USA) in negative ionization mode for isolation of m/z 271 ([M-H]⁻ ion). During the process, the mobile-phase composition was methanol/water 75/25 (v/v) at a flow rate of 0.18 mL·min⁻¹. Stop time was set to be 6 min.

To determine the PFCs in secondary effluents, solid phase extraction (SPE) method was applied to concentrate the compounds from the wastewater sample using Oasis HLB resin cartridges (Waters Corporation, USA) previously washed with 10 mL of ethyl acetate, 10 mL methanol, and 15 mL ultrapure water. The dried eluate post SPE were derived with 100 μL pyridine and 50 μL N,O-bis(trimethylsilyl) trifluoroacetamide solution containing 1% trimethylchlorosilane (Sigma) at 70°C for 60 min, followed by cooling down to room temperature.

RESULTS AND DISCUSSION

Characterization of as-prepared photocatalyst

The surface morphologies of TiO2 NTs and S-MIP-TiO2 NTs are shown in Figure 1. Neat TiO2 NTs (Figure 1(a)) were composed of well-ordered and uniform TiO2 nanotubes, with pore sizes ranging from 55 to 75 nm, and the average pore size of approximately 60 nm, and a wall thickness of approximately 14 nm. Most S-MIP-TiO2 NTs (Figure 1(b)) were still open at the top end, similar with the TiO2 NTs. In the process of MIP modification, the mixture was supposed to diffuse down the length of the hollow core of the NTs. Hence, the inside surface of the NTs was modified with a thin MIP layer, decreasing the average diameter from approximately 60 to 50 nm.

Compared with TiO2 NTs (Figure 2(a)), the IR spectrum of the TiO2 NTs with a PFOA-imprinted layer (Figure 2(b)) had the characteristic peaks of PFOA at 3,446, 3,240, 2,930, 2,864, 1,590, and 1,250 cm⁻¹ (Cakmak et al. 2006), and the characteristic peaks of MAA at 1,650 and 1,820 cm⁻¹.
After removing PFOA using methanol and acetic acid, the characteristic peaks assigned to PFOA disappeared. In contrast, the characteristic peaks assigned to MAA were still clearly observed (Figure 2(c)). This result indicated that the functional monomer of the target molecule PFOA was successfully imprinted on the surface of TiO$_2$ NT.

Both the XRD spectra of the neat TiO$_2$ NTs (Figure 3(a)) and S-MIP-TiO$_2$ NTs (Figure 3(b)) exhibited clear characteristic diffraction peaks at 25.34°, 37.84°, 48.02°, 53.00°, 55.02°, 62.86°, 70.58°, and 76.24°, which were assigned to the anatase phase. The XRD patterns revealed the crystallization of TiO$_2$ NTs was not affected by the surface molecular imprinted process.

Adsorption of the template molecules

The adsorption of the template compounds PFOA on S-MIP-TiO$_2$ NTs, NIP-TiO$_2$ NTs, and TiO$_2$ NTs are shown in Figure 4. The adsorption isotherms were described by the Freundlich isotherm model ($Q_e = K_f C_e^{1/n}$). In this model, $Q_e$ is the amount of PFOA adsorbed per unit active surface area of the photocatalysts (mg·cm$^{-2}$), $C_e$ is the concentration of PFOA in solution (ng·L$^{-1}$), $K_f$ is the adsorption equilibrium constant representative of the adsorption capacity, and $1/n$ is a constant indicative of the adsorption intensity. The values of the parameters are listed in Table 1. In the investigated concentration range, $1/n$ of the S-MIP-TiO$_2$ NTs (0.2711) was higher than that of the NIP-TiO$_2$ NTs (0.1754) and TiO$_2$ NTs (0.1187). $K_f$ of the S-MIP-TiO$_2$ NTs was 3.89, higher than those for NIP-TiO$_2$ NTs and TiO$_2$ NTs (2.04 and 1.65, respectively). These results indicated that the adsorption capacity and intensity of both S-MIP-TiO$_2$ NTs and NIP-TiO$_2$ NTs were enhanced during the precipitation polymerization process. The S-MIP-TiO$_2$ NTs had the highest adsorption capacity and intensity among the three photocatalysts.
According to the adsorption isotherms, an adsorption hypothesis involving three types of potential binding sites on the surface of the modified photocatalyst was proposed as shown in Figure 5. For binding site type 1, only the template molecules could be bound theoretically because the binding sites require not only specific functional groups, but also matching target molecule sizes. Binding site type 2 could occur both specific by specific functional group recognition and non-specific adsorption via hydrogen bonding. Binding site type 3 could occur non-specific adsorption via hydrogen bonding. After polymerization, some functional monomers that do not form complexes could remain on the surface of the polymer. These monomers provide the possibility of non-specific adsorption via hydrogen bonding. Three types of potential binding sites could be formed on the surface of S-MIP-TiO₂ NTs, and one type (type 3) on the surface of NIP-TiO₂ NTs.

In general, the Freundlich model is suitable for assessing the adsorption isotherm of S-MIP-TiO₂ NTs. However, in the current study, the Freundlich model yielded a worse fit for the adsorption isotherm of PFOA on S-MIP-TiO₂ NTs (R² = 0.9361) than in previous studies (R² ≥ 0.99) (Zhang et al. 2008). This discrepancy can be explained by the fact that the investigated adsorption concentration range (from 10 ng/L to 1,000 mg/L) was much wider than those in previous studies (from 1 to 1,000 mg/L) (Zhang & Hu 2008). The adsorption isotherms of PFOA on S-MIP-TiO₂ NTs are shown in Figure 4. It could be found that the Freundlich model constant 1/n at low concentrations of PFOA (from 10 to 10⁵ ng/L) was higher than that at high concentrations (from 10⁶ to 10⁹ ng/L). It indicated that the adsorption intensity of PFOA on S-MIP-TiO₂ NTs at low concentrations (from 10 to 10⁵ ng/L) was higher than that at high concentrations (from 10⁶ to 10⁹ ng/L). According to the adsorption hypothesis proposed in this study, the adsorption of template compounds on the S-MIP-TiO₂ NTs had two different adsorption mechanisms, i.e. functional group recognition and interaction between π electrons. The attractive force of functional group recognition between carboxyl and phenolic hydroxyl is stronger than the interaction force between π electrons in the phenol aromatic ring and in the cross-linker (Wang et al. 2006; An et al. 2008; Alizadeh & Akhoundian 2010). Therefore, the adsorption of low concentration PFOA on S-MIP-TiO₂ NTs most resulted from functional group recognition (potential binding sites 1 and 2). In contrast, the weak interaction forces (potential binding site 3) were the major adsorption mechanism at high concentrations of PFOA. It can be deduced that the functional group recognition exhibited higher adsorption intensity towards the template molecules than weak interaction.

**Photocatalytic removal of the template molecules**

The photocatalytic degradation activities of the S-MIP-TiO₂ NTs, NIP-TiO₂ NTs, and TiO₂ NTs were evaluated in an aqueous PFOA solution. The photocatalytic reaction kinetics followed the Langmuir–Hinshelwood model (Zhang et al. 2011).

\[
r = \frac{dC}{dt} = \frac{hKC}{1 + KC}
\]  

Table 1 | Freundlich isotherm parameters for adsorption PFOA

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Initial concentration (ng/L)</th>
<th>(1/n)</th>
<th>(R^2)</th>
<th>(1/n)</th>
<th>(R^2)</th>
<th>(1/n)</th>
<th>(R^2)</th>
<th>(K_f)</th>
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<tr>
<td></td>
<td>[10, 10²]</td>
<td></td>
<td></td>
<td>[10⁴, 10⁷]</td>
<td></td>
<td>[10, 10⁹]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-MIP-TiO₂ NTs</td>
<td>0.3381</td>
<td>0.9969</td>
<td></td>
<td>0.1253</td>
<td>0.9958</td>
<td>0.2711</td>
<td>0.9316</td>
<td>3.89</td>
</tr>
<tr>
<td>NIP-TiO₂ NTs</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.1754</td>
<td>0.9969</td>
<td>2.04</td>
</tr>
<tr>
<td>TiO₂ NTs</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.1187</td>
<td>0.9985</td>
<td>1.65</td>
</tr>
</tbody>
</table>
where \( C \) is the PFOA concentration, \( k \) is the degradation rate constant, and \( K \) is the adsorption equilibrium constant. In the current study, the PFOA concentration \( C \) was less than \( 1 \times 10^{-3} \text{ mol·L}^{-1} \), which made \( KC < 1 \). Hence, Equation (1) can be transformed into:

\[
\frac{dC}{dt} = kKC = k_{\text{app}}C
\]  

(2)

The integration of Equation (2) would lead to the expected relationship:

\[
\ln\left(\frac{C_0}{C}\right) = k_{\text{app}}t
\]  

(3)

\[
k_{\text{app}} = kK
\]  

(4)

where \( C_0 \) and \( C \) are the concentrations of PFOA at the beginning and at time \( t \), respectively, and \( k_{\text{app}} \) is the apparent degradation rate constant. PFOA degradation in the UV irradiation experiments also followed a pseudo-first-order kinetics (Sansotera et al. 2014). As shown in Figure 6, the apparent first-order rate constant \( k_{\text{app}} \) in a different process can be easily calculated: 0.0040 min\(^{-1}\) in the photolysis process, 0.0225 min\(^{-1}\) for the TiO\(_2\) NTs, 0.0316 min\(^{-1}\) for the NIP-TiO\(_2\) NTs, and 0.0732 for the S-MIP-TiO\(_2\) NTs in the photocatalytic process, respectively. These results indicated that TiO\(_2\) photocatalysis was more efficient than direct photolysis for PFOA removal, and the photocatalytic degradation process was enhanced with the presence of the MIP layer.

In this process, the photocatalytic reaction started with the adsorption of the template compound molecules PFOA on the MIPs layers located on the surface TiO\(_2\) NTs. Then the adsorbed PFOA molecules were oxidized by the generated \( \cdot \text{OH} \) radicals during photocatalysis.

Therefore, the photocatalytic degradation rate strongly depended on the amount of PFOA adsorbed on the photocatalyst surface, and on the amount of \( \cdot \text{OH} \) generated during photocatalysis, as shown in Equation (4). It has been confirmed that the adsorption capacity and intensity of PFOA on S-MIP-TiO\(_2\) NTs was higher than TiO\(_2\) NTs, although the incident light would be hindered by MIPs layer on the surface of TiO\(_2\) NTs, and thus hinder the \( \cdot \text{OH} \) generation during S-MIP-TiO\(_2\) photocatalysis (Liu et al. 2010). Therefore, the enhanced photocatalytic degradation should result from the enhanced adsorption capacity and intensity despite the negative effects of MIPs layer.

The effect of concentration on the photocatalytic degradation rate of PFOA was also investigated. As shown in Figure 7, when the initial PFOA concentration increased from 10\(^2\) ng/L to 10\(^9\) ng/L, \( k_{\text{app}} \) of PFOA degradation decreased from 0.784 to 0.071 min\(^{-1}\) using the S-MIP-TiO\(_2\) NTs, and from 0.109 to 0.029 min\(^{-1}\) using the TiO\(_2\) NTs. The ratio of the \( k \) values using S-MIP-TiO\(_2\) NTs to TiO\(_2\) NTs was decreased from 7.19 to 2.45. The result indicated

\[\text{Figure 5} \quad \text{Three potential binding sites on the surface of the modified photocatalyst.}\]

\[\text{Figure 6} \quad \text{Kinetic data for direct photolysis and photocatalytic degradation of PFOA over S-MIP-TiO}_2\text{NTs, NIP-TiO}_2\text{NTs, and TiO}_2\text{NTs. The initial concentration of PFOA was 10 \mu g/L.}\]

\[\text{Figure 7} \quad \text{Initial concentration dependence of the degradation rate constant of PFOA over the corresponding S-MIP-TiO}_2\text{NTs and TiO}_2\text{NTs.}\]
that the degradation selectivity of S-MIP-TiO$_2$ NTs towards the template compounds (PFOA) was increased as the initial concentration of PFOA was decreased, which would be helpful for the selective removal of the low-level template compounds in wastewater.

Based on the above analysis, the S-MIP-TiO$_2$ NTs not only exhibited outstanding adsorption capacity and photocatalytic activity toward the template compounds, but also had higher adsorption intensity and photocatalytic selectivity at low concentrations than that at high concentrations. Therefore, photocatalytic treatment using S-MIP-TiO$_2$ NT as photocatalysts may be a promising approach for the removal of trace perfluorinated compounds from secondary effluents.

**Photocatalytic removal of PFCs**

The feasibility of applying S-MIP-TiO$_2$ NTs for the selective removal of perfluorinated compounds from wastewater was evaluated by investigating the photocatalytic removal efficiency of five perfluorinated compounds (PFBA, PFPeA, PFOA, PFHxA, and PFHpA) from the secondary effluents of a municipal WWTP as shown in Figure 8. The initial concentration of five PFCs was 10 $\mu$g/L. These compounds were chosen as the representative chemicals to be detected in the secondary effluents because of their wide occurrence and high potential toxicity.

It is known that the photocatalytic degradation process can be divided into two stages, i.e. adsorption and photocatalytic degradation phases. In adsorption phase (0-40 min), the functional group recognition was the major adsorption mechanism because the concentrations of PFCs in secondary effluent range from ng/L to $\mu$g/L. As shown in previous work, the functional group recognition is the chemical interaction between the functional groups ($\sim$OH) in target molecules and the footprints groups (carboxyl) in polymer. Therefore, the compounds comprising the functional groups in their molecules (such as PFBA, PFPeA, PFHxA, and PFHpA) were chemically adsorbed on the surface of S-MIP-TiO$_2$ NTs, resulting in an enhanced photocatalytic degradation and a rapid removal of PFCs. In comparison, the compounds without these functional groups were not enhanced adsorbed and degraded during the same process.

The pH value of the solution is an important parameter, which affects the adsorption behavior of the ion in many cases. The adsorbent surface was charged through the protonation of functional groups and the electrostatic attraction between adsorbents and adsorbates usually plays a major role. It can be found that the adsorption is pH dependent, and the adsorption amount of PFOA decreased with increasing solution pH value. Therefore, the electrostatic interaction played an important role in the sorption process at acidic pH values. With increasing solution pH, the adsorption amount of the MIPs and NIPs adsorbents for PFOA decreased. It indicated that the adsorption of PFOA onto the MIPs and NIPs adsorbents was mainly attributed to the electrostatic attraction Other forces including hydrophobic interaction and hydrogen binding may be involved in the adsorption in the whole pH range, but their contributions are limited in this study. It also can be found that the MIPs adsorbents had higher sorption capacity than that of the NIPs adsorbents at pH values from 4 to 6, showing the good selective adsorption. The initial pH value of the solution is 5 in this work.

The S-MIP-TiO$_2$ NTs were also reused to test its stability for the removal of perfluorinated activity from the secondary effluents. It was found that the removal efficiency was slightly reduced after each use and finally stable at about 82% after five cycles. The result indicates that photocatalytic treatment using S-MIP-TiO$_2$ NTs could be a promising approach for effectively eliminating PFCs from secondary effluents of municipal WWTPs.

**CONCLUSIONS**

Surface-molecular-imprinted polymer-modified TiO$_2$ nanotube (S-MIP-TiO$_2$ NT) photocatalysts were prepared. The MIP layer provided the neat TiO$_2$ NTs with selective molecular adsorption ability, leading to outstanding adsorption capacity and intensity and enhanced photocatalytic selectivity and activity over PFOA. Moreover, the modified photocatalysts exhibit higher adsorption intensity and
photocatalytic selectivity at low concentrations than at high concentrations.

The photocatalytic removal of PFCs and perfluorinated activity from secondary effluents of a municipal WWTP was considerably enhanced using S-MIP-TiO₂ NTs than using TiO₂ NTs. The S-MIP-TiO₂ NTs developed here also exhibit excellent regeneration performance. Therefore, photocatalytic treatment with S-MIP-TiO₂ NTs could be a promising approach for effective elimination of PFCs from secondary effluents of municipal WWTPs. This method would help to reduce ecological risk during wastewater reclamation.

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