Selective photocatalytic degradation of nitrobenzene facilitated by molecular imprinting with a transition state analog

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A B S T R A C T

Photocatalysis with the aid of molecular imprinted photocatalysts provide a highly selective method to remove highly toxic organic pollutants (HTOPs). However, some HTOPs (e.g., nitrobenzene (NB)) cannot be used directly as template due to their low solubility or high toxicity. For removing such HTOPs, the present work designed novel molecularly imprinted polymers (MIP) coated photocatalysts (TSA-MIP-TiO_2) by using transition state analog (TSA) as template. For the target pollutant NB, both 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) were respectively selected as the TSA template to prepare TSA-MIP-TiO_2 (2NP-P25 and 4NP-P25). In comparison with neat Degussa P25 TiO_2, the obtained TSA-MIP-TiO_2 not only increased the photocatalytic degradation of NB, but also inhibited the accumulation of unwanted intermediates. In the presence of bisphenol A (BPA, 225 μmol L^{-1}) as a non-target pollutant, the photocatalytic degradation rate constants of NB (15 μmol L^{-1}) over 2NP-P25 and 4NP-P25 were about 4.4 and 3.6 times that over neat P25 TiO_2, respectively, whereas the BPA degradation over TSA-MIP-TiO_2 was slower than that over neat P25. The much enhanced photocatalytic activity and selectivity can be explained by that TSA-MIP-TiO_2 possesses specific molecular recognition to the reaction transition state, which decreases the reaction apparent activation energy.

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1. Introduction

Nowadays, some organic pollutants in contaminated water are high toxic, persistent, and bio-accumulated to aquatic organisms, and their disposal has become a major environmental concern [1,2]. This serious problem indicates that selective removal of highly toxic organic pollutants (HTOPs) from waste water is necessary and important [3]. To achieve this purpose, high molecular selectivity should be provided by the treatment approach. In the literature [4], several methods have been proposed to enhance the selectivity of TiO_2 photocatalysts. Ghosh-Mukerji et al. prepared a photocatalyst with a molecular recognition sites located in the vicinity of TiO_2 micro-domains, where β-cyclodextrin was used as the host and benzene and 2-methyl-1,4-naphthoquinone as guests [5]. A more interesting method is the selective photocatalysis of TiO_2 with the aid of molecular imprinting technology [6,7]. Recently, our group developed another strategy to obtain highly selective photocatalysis by coating various types of molecularly imprinted polymers (MIPs) onto the surface of TiO_2 [8–12]. In these researches, the target pollutants were directly used as

real templates during the preparation of the photocatalysts. Thus, these types of catalysts might be named as real substrate molecularly imprinted polymers coated photocatalysts (RS-MIP-TiO_2) [8,9]. Our reported MIP photocatalysts not only showed high selectivity to the degradation of the target pollutants, but also had a good lifetime [8]. This is attributed to the used functional monomer o-phenylenediamine (OPDA) for the preparation of MIP coating. The use of OPDA produces a polymeric skeleton with a polyaniline-like structure, and the good chemical and photochemical stability of the polyaniline layer coated TiO_2 under UV irradiation have been well reported [13–15]. Therefore, this method has now been a common way to prepare photocatalysts for selectively removing HTOPs [16–20]. For example, Lu et al. prepared MIP coated TiO_2 nanotube arrays as electrodes to photoelectrocatalytically decompose tetracycline hydrochloride under a simulated solar light irradiation [19].

As the toxicity and potential environmental impacts of substances are well understood, more and more compounds are grouped as HTOPs. However, the RS-MIP-TiO_2 methodology is not always available in the removal of a wide variety of HTOPs, because many HTOPs cannot be used directly as template. There are at least two serious problems in the synthesis of MIPs for these target HTOPs: (i) weak interactions between the target HTOP and the monomers, and (ii) low solubility of the target HTOP in the polymerization solution. To overcome these problems, we

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introduced the analogs complementary to substructures of the target to prepare the enzyme-like photocatalytic MIP composites [11]. In this method, appropriate templates were selected as alternatives to the target substrates, named as structural analogs (SA). More recently, imprinted films consisting of TiO$_2$ particles were prepared via the low-temperature titanyl sulfate method by Sharabi and Paz [20]. They also found that the substrates being imprinted with diethyl hydroxymethyl phosphonate were very effective in the degradation of diisopropyl methylphosphonate.

However, some HTOPs cannot be selectively removed by either RS-MIP-TiO$_2$ or SA-MIP-TiO$_2$ (e.g., nitrobenzene (NB), halogenated benzene and alkyl benzene). To achieve the selective removal of such HTOPs by photocatalysis, other types of MIP-TiO$_2$ catalysts should be proposed. It is worthy of noting that MIPs imprinted with transition state analog (TSA) templates generally showed higher binding affinities for their TSA than reaction substrates, implying that they were functioned by stabilizing the reaction transition state [21]. In this work, we prepared a new type of photocatalysts by using TSA as template. Here, NB was chosen as a model pollutant, because it is toxic in environment, only slightly soluble in water and non-degradable by conventional chemical oxidation [22]. When a proper TSA is selected as the template, MIP-coated photocatalysts (TSA-MIP-TiO$_2$) are synthesized by in situ polymerization of a functional monomer in the presence of dispersed TiO$_2$ nanoparticles. The photocatalytic experiments confirmed that specific recognition and selective degradation of the target pollutants over TSA-MIP-TiO$_2$ photocatalysts. To the best of our knowledge, this is the first of use molecular imprinting with a TSA based methodology for the selective removal of HTOPs by photocatalysis.

2. Materials and methods

2.1. Chemical and solutions

P25 TiO$_2$ nanoparticles (ca. 80% anatase, 20% rutile; BET area, ca. 50 m^2 g^{-1}) were provided by Degussa (Germany). NB, 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) were supplied from Shanghai Chemical Reagent Company. NaOH and HCl were provided from Tianjin Chemical Reagent Co., Ltd. All the chemicals were of analytical reagent grade and used as received without further purification. HPLC-grade methanol was obtained from Tedia and water was prepared by a Milli-Q-Plus ultra-pure water system.

2.2. Preparation of TSA-MIP-TiO$_2$ photocatalyst

The preparation procedures for TSA-MIP-TiO$_2$ photocatalysts were similar to that in our previous work [9]. Typically, 0.24 g of OPDA and 0.13 g of TSA template (2-NP or 4-NP) were added into 40 mL of water. The pH value of the solution was adjusted to pH 2 and the solution was stirred for 20 min to form a complex between OPDA and 2-NP (or 4-NP). After adding 0.4 g of P25 TiO$_2$ nanoparticles, the mixture was sonicated for 3 min. Polymerization was initiated with UV irradiation (250-W Hg lamp) for 60 min. After a polymerization reaction for 24 h, the templates were removed by Na$_2$CO$_3$ solution (0.13 g L^{-1}) for 5 times. The photocatalysts were further washed with distilled water and dried at 60 °C. When 2-NP (or 4-NP) was used as TSA templates, the as-prepared photocatalysts were correspondingly named as 2NP-P25 (or 4NP-P25). When the polymerization was conducted in the absence of templates, the synthesized control photocatalyst was named as NIP-P25.

2.3. Apparatus and methods for photocatalysis

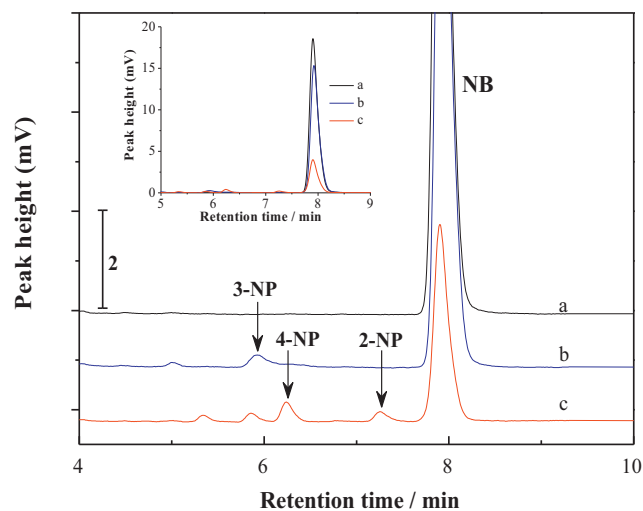The photocatalytic degradation experiment was carried out in a cylindrical glass reactor, where a Philips 9-W UV lamp (λ_{max}

Fig. 1. HPLC diagrams of NB solutions ($c_0 = 50 \,\mu$mol L^{-1}): (a) before degradation (black line), (b) after UV irradiation alone for 30 min (blue line), and (c) after UV irradiation for 30 min in the presence of neat P25 TiO$_2$ (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

253.7 nm) was located in the axial position. In this work, the loading of the photocatalysts was 0.1 g L^{-1} through all experiments. Before the illumination, a 20 min stirring of the suspension was conducted to achieve the adsorption equilibrium of the organic compounds, and then the concentration of the pollutant(s) was determined as the initial concentration c_0. Subsequently, samples were taken for analysis at different UV time intervals. After the samples were centrifuged at 14,000 rpm for 15 min to separate TiO$_2$ particles, the supernatants were filtered through 0.45 μm membranes and then analyzed. The remained concentrations of the pollutants and intermediates were measured on a PU-2089 HPLC (JASCO), equipped with a C18 ODS column and an ultraviolet detector. The mobile phase was a methanol–water mixture in a volume ratio of 60:40 (v/v) at 1 mL min^{-1}. The detection wavelengths were selected at 267 nm for NB, 318 nm for 4-NP, and 275 nm for both 2-NP and 3-NP, respectively. To check reproducibility, the experiment was carried out in duplicate.

3. Results and discussion

3.1. Selection of transition state analogs

In recent years, MIPs have been used for creating transition-state imprinted enzymes as artificial "catalytic antibodies" [23]. During the catalysis, MIPs provide the possibility to mimic the active sites of natural enzymes, and the enhancement of the catalytic activity on MIPs was generated against a stable analog of the transition state [24]. Thus, the first challenge in this work was to find a proper template as a stable transition state analog for the preparation of TSA-MIP-TiO$_2$ photocatalysts.

In the literature, the degradation pathway of NB by advanced oxidation processes has been studied [25–28], in which NB was oxidized primarily by hydroxyl radical to form a hydroxynitrocyclohexadienyl radical. This means that hydroxynitrocyclohexadienyl radical can be as the transition state during the photocatalytic degradation of NB. However, it is known that this radical was unstable. To find a stable transition state analog, the main intermediates during the degradation of NB under the direct photolysis and over the neat P25 TiO$_2$ were investigated by using HPLC technology. Fig. 1 illustrated the HPLC chromatograms of the NB degradation solution after a 30 min UV illumination in the presence of