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Molecularly imprinted photocatalyst with a structural analogue of template and its application

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HIGHLIGHTS

- ▶ Molecularly imprinted photocatalyst was prepared by substrate analog template.
- ▶ A group of chlorophenols was rapidly mineralized on the imprinted photocatalysts.
- ▶ Detection of organochlorine on CPs was achieved based on the complete dechlorination.
- ▶ Total organochlorine might be used to estimate the toxicity and persistence of CPs.

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ABSTRACT

To realize selective mineralization of low-level chlorophenols (CPs) in the presence of high-level ordinary pollutants, molecularly imprinted polymers (MIPs) coated photocatalyst was prepared using substrate analog as template. The pseudo-template imprinted photocatalysts showed rapid decomposition ability toward a group of CPs. Based on the complete dechlorination and spectrophotometry, a new method was proposed to detect the total organochlorine on CPs in water samples. The method showed good linearity when the concentrations of the total organochlorine on CPs is in the range of 12.0–200.0 μmol L^{-1}. The detection limit is 1 μmol L^{-1} for this method. When this method was applied to measure the total organochlorine of the CPs in both tap water and river water samples, an average recovery ranged from 96.3% to 105.1% was obtained with RSD values less than 5%. In this green and simple method, the common inorganic ions in water showed no interference for the detection. The determination of the total organochlorine on the CPs might be used for estimation of the toxicity and the persistence of the water samples.

1. Introduction

Chlorophenols (CPs), which contain one or more covalently bonded chlorine atoms from mono- to penta-chlorine substituted, have been widely used in industry, household, and forest industries. When drinking water supplies (e.g. surface and ground water) are contaminated by CPs, a threat to humans will be presented because of the toxicity and persistence of CPs [1]. For example, CPs may cause a noticeable effect (e.g. disagreeable taste and odor) on drinking water at a concentration as low as 0.1 μg L^{-1} [2]. Therefore, both the United States Environmental Protection Agency [3] and the European Parliament and the Council of the European Union [4] listed the CPs as priority pollutants.

However, CPs degraded slowly in the environment because of their broad-spectrum antimicrobial properties [5] and could produce more complicated molecules such as phenoxyacetic acids, chlorobenzenes and dioxins [6]. Thus, it is necessary to develop a purification method that can be used to remove the bio-recalcitrant CPs. Recently, advanced oxidation processes (AOPs) had emerged as a promising way for the degradation of toxic pollutants or converting the toxic pollutants to biologically degradable substances [7,8]. In this field, radiolysis [9], ozone [10], ozone/UV [11], H_2O_2 [12] microwaves [13], Fenton reagent [14], and photocatalytic processes [15,16] had been investigated for the chemical degradation of CPs. Czaplicka had reviewed the photodegradation kinetics and mechanism of CPs by AOPs [17]. The experimental parameters e.g. pH, dissociation degree, presence of oxidants in solution and reaction rate constant of chlorophenols had been discussed. However, the degradation of CPs by AOPs was largely dependent upon the in situ generation of hydroxyl radicals, leading to no selective degradation. Unfortunately, in wastewater system, the highly hazardous

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and non-biodegradable CPs at low levels always coexist with lowly toxic pollutants at high levels, a prior degradation of the high-level biodegradable pollutants will be occurred by AOPs [18]. An economic method to treat such wastewater system is to selectively remove the highly hazardous CPs first using photodegradation and then handle it by biodegradation. The key of this method is changed to promote the selectivity of AOPs for the highly toxic CPs.

On the other hand, it has been reported that both the toxicity [19] and the degradation [20] of CPs were dependent upon the degree of chlorination, the position of the chlorine atoms, and the purity of the sample. Therefore, measurement of the total chlorine on CPs and their chloro derivatives can be used to approximately determine the toxicity and the persistence of CPs. Theoretically, we can detect all CPs by LC–MS or GC-MS [21], and then calculate the total chlorine on chlorophenols. However, this method is tedious and time-consuming. A promising approach is to mineralize CPs completely, and analyze the free chloride ions in the solution by ion liquid chromatography [22] or derivative spectrophotometry [23]. Until now, this method is not successful because of the incomplete dechlorination of CPs by the traditional AOPs (e.g. Fenton process [24,25], UV or UV/H_2O_2 [26] and photocatalysis by TiO_2 [27]).

In this paper, we described a new way to selectively and rapidly mineralize CPs based on molecularly imprinted polymers (MIPs) coated P25 TiO_2 photocatalysts (MIP-P25). MIPs are cross-linked synthetic materials that have specific binding capacity and selectivity against a target molecule (template) [28]. In our previous work, by using *o*-phenylenediamine (oPDA) as monomer and the target pollutant as the template, a core-shell structured MIP-P25 had been prepared. The MIP-P25 photocatalysts enhanced the photodegradation of the target organic compound and its intermediates [29,30]. Recently, using 2,4-dinitrophenol (2,4-DNP) as substrate analog (SA) template, another type of imprinted photocatalysts (SA-MIP-P25) was also prepared. The SA-MIP-P25 obtained showed much better degradation ability toward pentachlorophenol (PCP). Moreover, due to the enzyme-like effects of the photocatalysts, SA-MIP-P25 completely inhibited the generation of toxic aromatics during the degradation. The mechanism study indicated the interactions between PCP (the chlorines and hydroxyl group) and the amino groups on poly(oPDA) played important roles for the selective recognition, mineralization and dechlorination [31].

Because other CPs (mono- to tetra-chlorine substituted CPs) also contained chlorines and hydroxyl group on their structures, CPs might show high binding affinity and degradation activity on the SA-MIP-P25. In this paper, the selective degradation of the CPs on SA-MIP-P25 will be investigated first. The dechlorination ability of SA-MIP-P25 toward CPs will be also studied. A fast and complete dechlorination indicates that the free chloride ions in the degradation solution can be used to calculate the total chlorine on CPs. To the best of our knowledge, this is the first selective photodegradation of a group of CPs to be reported and also the first using complete dechlorination based methodology for the quantitation of organochlorine on CPs.

2. Experimental

2.1. Materials

P25 TiO_2 nanoparticles (a mixture of 80% anatase and 20% rutile; BET area, ca. 50 $m^2\,g^{-1}$) were purchased from Degussa. 2,4-DNP and oPDA were obtained from Shanghai Chemical Reagent Company. Phenol, 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and PCP were purchased from Sigma–Aldrich. Sodium chloride (NaCl), ferric nitrate and mercuric thiocyanate were also obtained from Sigma–Aldrich. All these analytical purity chemicals were used without further purification. Methanol (HPLC gradient grade) was purchased from Honeywell Specialty Chemicals (Seelze, Germany). The pH value of the solution was adjusted by H_2SO_4 (2 mol L^{-1}) and NaOH (2 mol L^{-1}) solutions.

2.2. Standard solutions and real samples

Stock standard solutions of phenol, 4-CP, 2,4-DCP and 2,4,6-TCP (100.0 mg L^{-1}) were prepared by dissolving them in pure water (pH 6.5). PCP solution (50.0 mg L^{-1}) was prepared by dissolving sodium pentachlorophenol in water, followed by adjusting the pH value to 6.5. These standard solutions were stored at 4 °C in the cold room. Photocatalytic solutions were prepared by diluting of the standard solutions at room temperature.

Standard solution of chloride ion was prepared as follows: NaCl was kept at 500 °C for 1 h. After cooling in a desiccator, 0.5844 g of NaCl was dissolved in water. The mixture was then transferred to a 1000-mL flask. A standard NaCl solution with a concentration of 10.0 mmol L^{-1} was obtained by the constant volume. These standard solutions of chloride ion were also stored at 4 °C in the cold room for further application.

Tap water samples were collected from our laboratory. Other water samples were collected from a local river (Höje å – Lunds reningsverksdammar, Sweden). These samples were filtered through 0.22 μm filters to remove solid particles. All these real samples were used freshly.

2.3. Preparation of catalyst

The MIP-coated photocatalysts were prepared according to our previous method [31]. Typically, 0.22 mmol of oPDA and 0.22 mmol of 2,4-DNP were dissolved into 40 mL of water (pH = 2). The solution was stirred for 20 min to form a complex between the template and the monomers. After addition of P25 TiO_2 nanoparticles (0.4 g), the mixture was ultrasonicated for 3 min. Polymerization was initiated with a 60-min irradiation of UV light (250-W Hg lamp). The reaction was conducted for 24 h at room temperature. After the polymerization, Na_2CO_3 solution (0.13 g L^{-1}) was used to remove the templates. When no template was detected in the extraction solution, the composites were further washed five times with distilled water. The composites were dried and ground. The photocatalysts obtained were named as DNP-P25. Similarly, NIP-P25 (to act as a control) was also synthesized when polymerization was carried out in the absence of templates.

2.4. Characterization

FTIR was used to determine the chemical composition of MIP-P25 photocatalysts. Attenuated total reflection (ATR) infrared spectra were recorded on a Perkin-Elmer FTIR instrument (Perkin-Elmer Instruments) in the 4000–375 cm^{-1} region with a resolution of 4 cm^{-1}, with 32 scans, and at 25 °C.

The morphology of DNP-P25 photocatalysts was observed via the high-resolution transmission electron microscopy (HRTEM) on a JEM-2010FEF TEM.

UV–vis solid-state reflection spectra were measured on a Shimadzu UV-2550 spectrophotometer ($BaSO_4$ was used as a reference).

Elemental analysis measurements were carried out on a CHN Elemental Analyzer, Series II (Perkin-Elmer Corp.).

The size distribution of photocatalysts with or without MIP layer was investigated using dynamic light scattering (DLS) on a Zetasizer Nano ZS instrument equipped with the DTS Ver. 5.03 (Malvern Instruments Ltd., Worcestershire, UK) software package. The laser source for the DLS apparatus was a 4 mW He–Ne laser with a wavelength at 632.8 nm. The catalyst particles were dispersed in ethanol with a concentration of $\sim$ 10 μg mL^{-1}. Before the DLS