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Photocatalytic degradation of chlorophenols using star block copolymers: Removal efficiency, by-products and toxicity of catalyst

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HIGHLIGHTS

- ▶ Photocatalytic degradation of chlorophenols using block copolymer was performed.
- ▶ Removal efficiency for catalysts as an existence of hydrophobicity was compared.
- ▶ Pathways during the photocatalytic degradation were elucidated identified.
- ▶ The newly synthesized two types of star block copolymers are non-toxic to organism.

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ABSTRACT

This study investigated the photocatalytic degradation of chlorophenols using two different types of porphyrin core star block copolymers (P-PSD and P-PD) with irradiation using visible light. Both P-PSD and P-PD catalysts show similar tendencies in the degradation of chlorophenols. Pentachlorophenol degraded faster than other chlorinated phenols (pentachlorophenol > 2,4,6-trichlorophenol > 2,4-dichlorophenol). The removal rate of chlorophenols using P-PSD was higher than the removal rate using P-PD, a difference which could be attributed to the hydrophobicity of P-PSD. The degradation intermediates and by-products of the chlorophenols were also identified. The analysis results revealed that the degradation of highly-chlorinated phenols was more rapid than the degradation of the less-chlorinated phenols, as confirmed by residual chlorinated compound and chloride ions that were released. The newly synthesized P-PSD catalyst is non-toxic to bacteria. For these reasons, the process of photocatalytic degradation using porphyrin core star block copolymers has potential advantages for the degradation of dissolved chlorophenol pollutants in water.

1. Introduction

Chlorophenols have been used extensively in many industrial products such as petrochemicals, pharmaceuticals, dyes, pulp industries, pesticides, and paint [1–6]. Therefore, chlorophenols have become common chloroaromatic pollutants [7]. Because of the high toxicity of these compounds and their resistance to biodegradation, chlorophenols persist in the environment and constitute an important category of soil, and water (surface and ground) pollutants [8,9]. Many chlorophenols have been categorized as mutagenic and carcinogenic agents [10]. Under certain conditions, chlorophenols serve as precursors for highly toxic chlorinated diaryl ether compounds such as dioxins [11]. Because of their adverse effects, chlorophenols have been listed as priority pollutants by the US Environmental Protection Agency (EPA) [12] and European regulatory authorities [13]. 2,4,6-trichlorophenol (2,4,6-TCP) and 2,4-dichlorophenol (2,4-DCP) are listed on the Drinking Water Contaminant Candidate List (CCL) [14]. In recent years, extensive attention has been given to the treatment of wastewater and groundwater contaminated with chlorinated organic compounds [15,16]. The development of effective and rapid methods for complete degradation of chlorophenol is of great interest.

Over the last few years, several remediation methods including thermal, chemical or biological treatment have been studied [13]. Because of the high toxicity of chlorophenols and the resistance

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of chlorophenols to biodegradation, biological methods are often not effective [17,18]. Biological techniques are often associated with problems in the degradation of chlorophenols, such as the production of more toxic intermediates and by-products [19]. More efficient advanced oxidation processes such as photocatalysis have been considered potential methods for the degradation of chlorophenols [20,21]. Several efficient photocatalysts and modified photocatalysts have been reported in the literature [22]. Among the photocatalysts, porphyrins are of particular interest because of their high molar absorption coefficients in the visible region, high quantum yields of photo-excited triplet states, and ability to generate singlet molecular oxygen [23]. A wide variety of porphyrins (including metal containing, metal free, and composite porphyrins) have been used in chlorophenol degradation [24]. The use of porphyrins as photocatalysts is difficult because of the low solubility of these compounds in water [25].

Poor water solubility of porphyrins limits their use as efficient photocatalysts [25]. To use a porphyrin as an effective photocatalyst for the degradation of chlorophenolic compounds, we have recently synthesized amphiphilic porphyrin with polystyrene (P-PSD) star block copolymer, which consists of a core (styrene as a hydrophobic material and/or photocatalyst) – shell (2-dimethylamino ethyl acrylate as a hydrophilic material) structure [26]. P-PSD was found to be a more effective than other known photocatalysts such as α-Fe_2O_3 and TiO_2, for removing chlorophenols [26]. In the present study, we investigate the photocatalytic degradation efficiency and kinetics of two different types (presence/absence of polystyrene) of star block copolymer for three different chlorophenols. All the possible mechanisms and pathways (including by-products and intermediates) observed during the photocatalytic degradation were identified. The toxicity of untreated and photocatalytically treated chlorophenols was assessed.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals, solvents and reagents were obtained from Sigma–Aldrich, Korea and were used without further purification. All aqueous solutions were prepared by the Barnstead Nanopure system and showed a minimum resistivity of 18.0 MΩ cm.

2.2. Synthesis of polydimethylamino ethyl acrylate with a porphyrin core star block copolymer (P-PD)

A 50 mL round bottom flask was heated under vacuum. Upon reaching room temperature, the flask was purged using Ar gas. Porphyrin-chain transfer agent (P-CTA; 178 mg, 0.02 M), azobisisobutyronitrile (AIBN; 1.5 mg, 0.0092 mM) and 2-dimethylamino ethyl acrylate (DMAEA; 2.6 mg, 8 M) were dried under vacuum for an hour. Dimethyl formamide (DMF; 2.3 mL) was injected into the flask under the Ar atmosphere, and the solution was stirred until a clear wine color was observed. The reacting solution was degassed three times in three steps: freezing, pumping, and thawing. The reaction was then carried out after the reactor had been immersed in an 80 °C oil bath. After the reaction was completed, the reaction mixture was quenched using liquid nitrogen. The DMF in the reacted solution was evaporated, and the solution was then diluted by adding 5 mL of tetrahydrofuran (THF). The porphyrin-(*b*-DMAEA) star polymer (P-PD) was precipitated by dropping into 500 mL of *n*-hexane. P-PD was obtained by decantation. The P-PD product was dried under vacuum at room temperature for 48 h and used for characterization and degradation studies.

2.3. Synthesis of polystyrene-block-polydimethylamino ethyl acrylate with a porphyrin core amphiphilic star block copolymer (P-PSD)

The overall processes and conditions, except the type and quantity of initial substrates, were the same as those described for the synthesis of P-PD. Briefly, porphyrin–polystyrene (P-PS; 1 g, 20 mM), AIBN (1 mg, 6.1 mM) and DMAEA (4.4 g, 30.9 M) were dried under vacuum for 1 h. DMF (1 mL) was injected into the flask under the Ar atmosphere, and the solution was stirred until a clear yellow color was observed. P-PSD was ultimately collected, dried and used for degradation studies.

2.4. Star block copolymer (P-PSD and P-PD) analysis

P-PSD and P-PD were characterized via size exclusion chromatography (SEC), comprised of a Shodex GPC LF-804 column, CTS 30 column oven, Youngrin refractive index (RI) detector and HITACHI L-6000 pump, with tetrahydrofuran (THF) used as the eluent, at a flow rate of 1.0 mL/min, to analyze for the number average molecular weight (M_n) and polydispersity index (PDI; weight average molecular weight (M_w)/number average molecular weight (M_n)). ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Unity INOVA (^{1}H: 300 MHz). Dynamic light scattering (DLS) analysis were performed for measure the size of star block copolymers by using zetasizer nano ZS from Malvern at 25 °C. The concentration of the polymer in aqueous solution was 0.2 mg/mL.

2.5. Photocatalytic degradation of chlorophenol compounds

To determine the photolysis rate kinetics of the two types of star block copolymers (porphyrin-(*b*-DMAEA) (P-PD) and porphyrin-(polystyrene-*b*-DMAEA) (P-PSD)) and to compare their efficiency in degrading chlorophenols with the presence of polystyrene (hydrophobic block), kinetic batch experiments were conducted with three chlorophenols (2,4-DCP, 2,4,6-TCP and PCP). Photoreactor vessels containing 40 mL of individual aqueous solution of the chlorophenols (30 μM) were placed in a photoreactor chamber (Fig. S1), with a cooling fan for adjusting the air temperature (25 °C), a stirrer and a darkroom (W 20 cm, D 25 cm, H 25 cm). Photocatalytic degradation was performed using six visible light lamps (Philips PL-L; 4 W; emission wavelength: 350–650 nm). The light intensity was measured with a pyranometer (Apogee, PYR-P) and determined to be 1.105 mW/cm^2. Tests for investigation of visible-light activation were carried out with a UV cut-off filter which blocks irradiation of UV fractions below 400 nm spectrum. P-PD or P-PSD (1 μM) was injected into the chlorophenol solution and stirred at 300 rpm. At predetermined intervals, 1 mL samples were withdrawn from the reactors and filtered through a syringe filter (Puradisc Nylon 25 mm; 0.45 μm) to measure the residual chlorophenol concentration by HPLC. An HPLC instrument (Perkin Elmer, Massachusetts, USA), equipped with a C18 column (Zorbax Eclipse XDB-C18; 4.6 mm × 150 mm; 3.5 μm) and a fluorescence detector at an excitation wavelength of 230 nm, was used to perform the analysis. Elution was carried out using 20:80 v/v of 1% phosphoric acid:acetonitrile at a flow rate of 1 mL/min. The column temperature was kept at 40 °C.

2.6. Analysis of photocatalytic degradation by-products of chlorophenols

For the analysis of the chlorophenol photocatalytic degradation by-products using liquid chromatography–electron spray ionization–mass spectrometry (LC–ESI–MS), the control and treated samples were acidified with formic acid to pH 2.4 and extracted using a Sep-Pak vac C_{18} solid phase extraction (SPE) kit (Waters, Ireland). The SPE column was conditioned using 6 mL of hexane,