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Rapid degradation of bisphenol A using air as the oxidant catalyzed by polynuclear phthalocyanine complexes under visible light irradiation

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Abstract

The photocatalytic dechlorination and destruction of bisphenol A (BPA) using air as the oxidant catalyzed by polynuclear phthalocyanine complexes under visible light irradiation have been studied. Among the four complexes studied (FePPc, CuPPc, ZnPPc, AlPPc), ZnPPc and AlPPc show high catalytic activities. Under ambient conditions of temperature and pressure, an initial BPA concentration of 1 mM in water was completely converted to CO_2 and carboxylic acid in 20 min with a catalyst/substrate molar ratio of 2:100 using a 100 W tungsten lamp as the light source. Six HPLC peaks indicating intermediate products appeared in chromatograms monitored at 254 nm. Oxalic acid and maleic acid were detected as their methyl esters in the resulting solution by GC–MS after treated with trimethylsulfonium hydroxide. TOC measurements indicated that 21.3% of the carbon was mineralized after an hour of reaction. When sunlight was used as the light source, BPA could also be degraded efficiently. Full conversion of BPA and its intermediate products were observed in 40 min without stirring and blowing air. The results of ESR measurements suggested that the reaction possibly proceeded via the pathway with singlet oxygen. A possible reaction sequence of the degradation of BPA was proposed. The influences of catalyst/substrate molar ratio, flow rate of the air, and pH were investigated.

Keywords: Bisphenol A; Photocatalysis; Degradation; Visible light; Singlet oxygen; Sunlight

1. Introduction

Recently, several types of environmental pollutants referred to as endocrine disruptors (EDs) have been suggested to be associated with abnormal sexual development and abnormal feminizing responses of animals in a number of reports [1]. Bisphenol A [2,2-bis(4-hydroxyphenyl) propane or BPA], which is a compound widely used as the monomer for the production of polycarbonate plastics and as a major component of epoxy resin, is widely suspected to act as an ED [2,3]. The BPA originating from the plastic products and various wastewaters has been found in rivers, lakes and ocean [4–6]. The adverse influence of BPA on aquatic animal has been of great concern [7,8].

Various methods have been suggested to remove BPA from water, such as biological method [9–12], chemical oxidation [13–14], electrochemical oxidation [15] and photocatalytic method [16,17]. Among them, photocatalysis has been the focus of numerous investigations in recent years for the potential use sunlight as the energy source to degrade pollutions [18,19]. As the most widely studied material in the field of photocatalysis, TiO_2 has been used to degrade BPA successfully [16,17]. However, TiO_2 can only be excited by high energy UV radiation with a wavelength of no longer than 387.5 nm for its high band gap ($E_g \approx 3.2$ eV). This practically rules out the use of sunlight as the energy source [20].

Since metallophthalocyanine complexes have intense absorption bands in the longer wavelength region of the vis-

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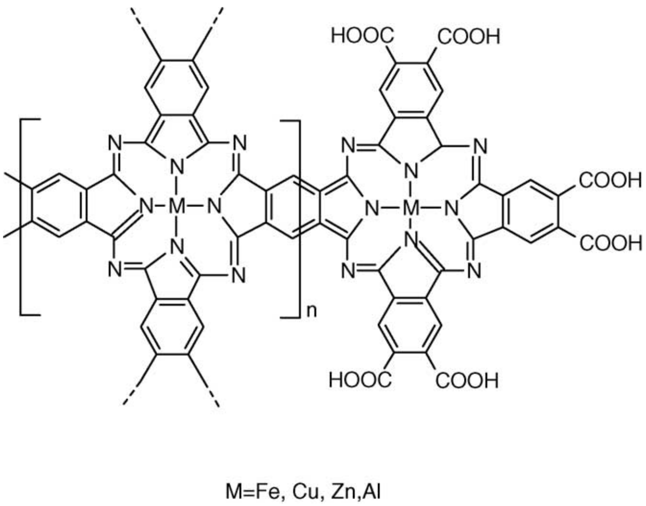

Fig. 1. Structure of the polynuclear zinc polyphthalocyanine.

ible light in a solar spectrum and high quantum yield for photoexcited triplet state ($\Phi > 0.40$) with a long lifetime, they are attractive sensitizers for photoreduction of water and carbon dioxide, as well as a photodynamic therapy [21]. The photooxidation of substrates by oxygen in the presence of visible light activation of photosensitizers is of increasing interest. Various photosensitizers, such as dyes, porphyrines and phthalocyanines, have been used to be photosensitizers to oxidize thiols, sulfide, thioethers, phenol and monochlorophenols [22–26] Recently, polynuclear metal phthalocyanine complexes have attracted attentions because of their increased catalytic properties compared to mononuclear one [27,28]. Some polynuclear cobalt phthalocyanine complexes exhibit a much higher specific activity to activate the oxygen than the mononuclear compound in the oxidation of sulfide [29]. As the photocatalyst in the photooxidation of sulfide, thiosulfate, and phenol, the catalytic activity per mole of the polynuclear zinc and aluminium complexes is two to five times higher than that of the respective mononuclear phthalocyanine complexes [30,31].

Here we report rapid destruction of BPA and its intermediate products using air as the oxidant catalyzed by polynuclear phthalocyanine complexes under visible light irradiation. The major goals of this study were to examine the catalytic activity of different complexes of PPc (Fig. 1) under visible light irradiation for the degradation of BPA; and to optimize the operating conditions by investigating the effect of catalyst/substrate molar ratio, flow rate of the air and pH.

2. Materials and methods

2.1. Materials

BPA (99%) was purchased from Acros and used without further purification. Triethylsulfonium hydroxide was obtained from Tokyo Kasi. Polynuclear phthalocyanine complexes were synthesized according to the published method [32,33]. The water used in all experiments was purified with a Milli-Q water ion-exchange system.

2.2. Preparation and characterization of the catalysts

9.17 mmol 1,2,4,5-benzeneeracarboxylic dianhydride, 5 mmol metal chloride, 24.5 mmol urea, 0.73 mmol ammonium molybdate were mixed and heated for 3 h at 250 °C in a flask. The powdered reaction mixture was extracted for 20 h with dimethylsulfoxide in a Soxhlet apparatus and washed with acetone. Then the product was stirred with 300 ml of 3 mol l^{-1} hydrochloric acid for 16 h at room temperature and washed with water and acetone. The end imide groups in the polynuclear complexes were transformed into carboxylic groups upon heating the mixture for 5 h using 15 ml solution contain 1.2 g sodium hydroxide and 6 g sodium chloride. After filtration, the product was acidified with 2 mol l^{-1} hydrochloric acid and isolated and dried. Dark green products were prepared with a yield of 30–40%. FT-IR spectra were recorded on a PE2000 spectrophotometer, using KBr pellets. Elemental analyses were carried on Flash EA1112 elemental analyzer. The metal content was determined by flame atomic adsorption spectrophotometric method after treatment by conc. sulfuric and conc. nitric acid [32]. The UV–vis absorption spectra of polynuclear phthalocyanine complexes were shown in Fig. 2. Their UV–vis spectras show a maximum adsorption at 680–690 nm and a shoulder at 615–630 nm. The complexes synthesized different times gave the same results, suggesting the synthetic reproduction is very good. From the results of UV–vis spectra of the complexes, it can be seen that the aggregation of polynuclear phthalocyanine complexes in solution is a smaller extent than that of mononuclear complexes to receive a higher catalytic activity than mononuclear ones [34].

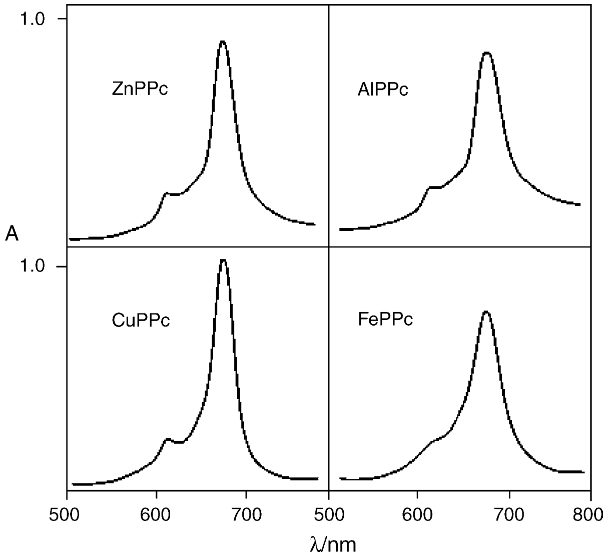

Fig. 2. The UV–vis spectra of ZnPPc, AlPPc, CuPPc and FePPc in water at 0.015 mmol l^{-1}, pH = 11.