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ORIGINAL PAPER

Photobiodegradation of phenol with ultraviolet irradiation of new ceramic biofilm carriers

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Abstract Activated sludge acclimated to biodegrade phenol was allowed to attach on and in light porous ceramic carriers and to function as a biofilm in a photolytic circulating-bed bioreactor (PCBBR). Phenol degradation in the PCBBR was investigated following three protocols: photolysis with ultraviolet light alone (P), biodegradation alone (B), and the two mechanisms operating simultaneously (P/B). Phenol was degraded at approximately equal rates by B and P/B, each of which was much faster than the rate by P. Furthermore, phenol was mineralized to a significantly greater extent with P/B than with either P or B. SEM showed that the biofilm survived well inside macropores that presumably shaded the microorganisms from UV irradiation, even though the UV light greatly reduced biofilm on outer surface of the carriers in the P/B experiments. Rapid biodegradation of phenol, enhanced mineralization, and survival of bacteria inside macropores demonstrated that being in a biofilm inside the porous carriers protected the bacteria from UV-light toxicity, allowing intimate coupling of photolysis and biodegradation.

Keywords Biofilm · Circulating-bed bioreactor · Phenol · Photobiodegradation · Photolysis

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Introduction

The development of the chemical industry and the resultant widespread use of compounds potentially harmful to the environment (anticorrosive agents, herbicides, insecticides, etc.) have been essential to the development of modern agricultural and industrial practices, but also have resulted in the pollution of the environment (e.g., through seepage into groundwater and wastewater discharges). Some of these compounds are biologically recalcitrant and inhibitory organics, which greatly reduces microorganisms' ability to biodegrade the compounds during treatment or in nature.

Recently, advanced oxidation processes (AOPs), e.g., Fenton's reagent, ozone, photocatalysis, and ultraviolet irradiation (Scott and Ollis 1995) have been accepted for the treatment of wastewater. These methods allow compounds with complex structures to be transformed into simpler and/or less harmful compounds that can be biodegraded more readily by microorganisms. (Manilal et al. 1992; Sakthivel et al.

2001; Wang et al. 2003; Enriquez et al.; 2004; Reddy et al. 2004; Mohanty et al. 2005, Marsolek et al. 2008). In particular, photocatalytic or photolytic oxidation (together denoted photo(cata)lysis) has been shown to be a good pre-treatment before biodegradation (Balcioglu and Arslan 1998; Li and Zhao 1999; Hu and Wang 1999; Li et al. 2005; Suryaman et al. 2006; Alinsafi et al. 2007).

A challenge with using photo(cata)lysis as a pre-treatment to biodegradation is choosing the proper level of photo(cata)lysis, since it is too expensive to rely on it for full mineralization. Instead, the idea is to use only enough photo(cata)lysis to make the target contaminants rapidly biodegradable (Marsolek et al. 2008). One problem is preventing photo(cata)lysis from doing too much transformation before biodegradation. Besides wasting energy, too much photo (cata)lysis can generate products that are themselves inhibitory or recalcitrant. Thus, it is desirable to have a means to transfer the readily biodegradable products to biodegradation as soon as they are formed.

One way to achieve this goal is to have photo (cata)lysis combined with biodegradation in a single photobiodegradation process; this is called *intimate coupling* of photo(cata)lysis and biodegradation, and it was demonstrated by Marsolek et al. (2008) in the photocatalytic circulating-bed biofilm reactor (PCBBR) that contained TiO_2 photocatalyst. In their PCBBR, the bacteria accumulated in the macropores of a porous biofilm carrier, where they were protected from UV light and free radicals inherent to photocatalysis. Without protection, the processes could not be combined, because the UV light and free radicals generated during photodegradation killed the microorganisms.

The original macroporous carriers (Marsolek et al. 2008) were made of treated cellulose. While the carriers had an ideal pore structure for accumulating and protecting the bacteria, they were gradually oxidized and charred when exposed to hydroxyl free radicals. Thus, the cellulosic carriers are not suitable for sustained PCBBR operation. To overcome these difficulties, we produced a light, porous ceramic carrier. We evaluate the suitability of the new ceramic carriers for intimately coupled photobiolysis by studying the simultaneous UV photolysis and biodegradation of phenol, including the relative activity of the two processes in a bench-scale PCBBR.

Materials and methods

Light-weight porous ceramic carrier

Carborundum powder as foaming agent was put into light silicate including kaoline and feldspar powders at a weight ratio of 95–98:5–2 and mixed fully. Then, the mixed powders were pressed to form a brick that was calcined at about 1200°C after drying at 100°C to get a light, porous ceramic brick. During calcining, carborundum expanded at the melting point of the mixture powder as the physical and chemical reactions of kaoline and feldspar produced gas and formed many pores. The pores were closed inside the ceramic carrier when the temperature was decreased, and this resulted in a porous ceramic with a specific gravity of 0.95. The porous ceramic brick was broken into particles with diameters of 2–3 mm. The small ceramic particles were glazed and re-calcined at 600°C in order to get ceramic particles with specific gravity of 1.03–1.05, which is ideal for use in a circulating-bed reactor.

Photolytic circulating-bed bioreactor (PCBBR)

The PCBBR was made of quartz glass with a working volume of 150 ml, as shown in Fig. 1. Water and carriers circulated due to air-lift pumping created by aeration during the experiments. During batch experiments, the water inlet was closed. During continuous-flow experiments, influent was supplied by a

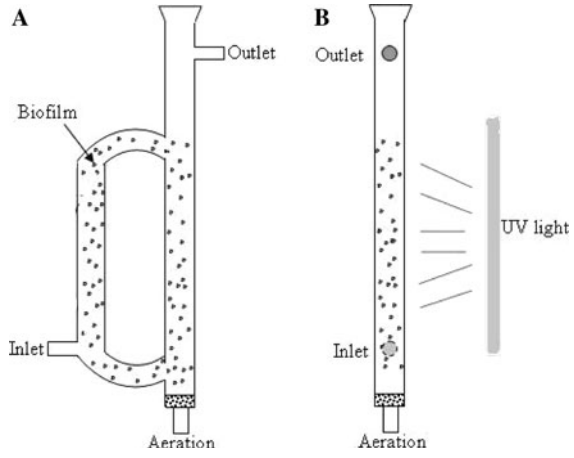

Fig. 1 Photolytic Circulating-Bed Bioreactor (PCBBR) and UV light source. **a** Schematic of the PCBBR; **b** positioning between the PCBBR and the UV light source

peristaltic pump through the inlet, and effluent was discharged by overflow through the outlet. The ultraviolet wavelength was 254 nm, and the power was 24 W. The distance between reactor and light source was approximately 50 mm. No TiO_2 photocatalyst was used in our experiments; thus, the reactions were photolytic, not photocatalytic.

Synthetic wastewater containing phenol

Synthetic wastewater was created by adding phenol and inorganic salts to tap water. The concentration of phenol was 50–200 mg l^{-1}, depending on the experiment. The inorganic salts included $(NH_4)_2SO_4$ 0.1 g/l, KH_2PO_4 0.5 g/l, Na_2HPO_4 0.5 g/l, $MgSO_4 \cdot 7H_2O$ 0.5 g/l, and yeast extract 0.02 g/l.

Acclimation and incubation of phenol-degrading bacteria

Activated sludge from a secondary clarifier at the Longhua municipal wastewater treatment plant in Shanghai was acclimated by using phenol and inorganic salts medium at 23–25°C for 2 weeks, with the solution changed every day during acclimation. The inorganic salts were: ammonium sulfate, 0.1 g l^{-1}; potassium dihydrogenphosphate, 0.5 g l^{-1}; disodium hydrogenphosphate, 0.5 g l^{-1}; magnesium sulfate, 0.5 g l^{-1}; and yeast extract, 0.02 g l^{-1}. The concentration of phenol was increased gradually from 50 to 200 mg l^{-1} during acclimation. Then, the carriers were immersed in a medium containing 3000 mg l^{-1} of mixed liquor suspended solids (MLSS) concentration for 24 h. The medium was aerated and the carriers were mixed. The microorganisms were adsorbed on and in the porous ceramic carriers.

Analytical methods

4-Amino antipyrine spectrophotometry was used for the analysis of phenol (Wei 2002). A TOC analyzer (Elementar Liqui TOC, Germany) was used for the analysis of TOC. The samples were taken from PCBBR and filtered through a 0.45-μm cellulose acetate membrane filter before analysis.

Carriers with biofilm were removed from the PCBBR operating without UV light and with UV light. These carriers with biofilm and bare carriers were viewed with scanning electron microscope (Model: JEOL 6380LV, Japan) at 20 kV (Zhang et al. 2002).

UV light intensity was measured with an illuminometer (model: BG-2254, China).

Degradation of phenol

Three protocols, i.e., UV photodegradation alone (P), biodegradation alone (B), and coupled UV photobiodegradation (P/B), were used to evaluate phenol degradation in batch and continuous-flow experiments. All experiments were carried out at 23–25°C. The UV light intensity was 0.46 mW/cm^2, corresponding to 24 W of UV light for P and P/B experiments. The hydraulic resident time (HRT) was 7 h for the continuous-flow experiments.

UV photodegradation (P)

A solution including phenol with a concentration of 50 mg l^{-1} was fed into the reactor. The solution and the ceramic carrier without biofilm were circulated by aeration with constant UV exposure. During the batch experiment, samples were taken at regular intervals and analyzed to determine phenol concentration. After the batch experiment, the process was switched to continuous flow, and the influent concentration was increased gradually to about 180 mg l^{-1}.

Biodegradation (B)

The ceramic carrier was immersed into acclimated activated sludge for 24 h and put into the reactor along with the synthetic wastewater including phenol at a concentration of 50 mg l^{-1}. The ceramic carriers were circulated by aeration, and the UV light was off. Samples were taken at regular intervals and used to determine the concentration of phenol. As described above, phenol was degraded in a continuous flow experiment after the batch experiment, and its concentration in influent was increased gradually to about 130 mg l^{-1} during this continuous flow experiment.

Coupled UV photo biodegradation (P/B)

Wastewater including phenol was degraded by coupled UV photobiodegradation under batch conditions

at first and then under continuous-flow conditions. The UV light was on for the entire experiment. The concentration of phenol was 50 mg l^{-1} during the batch experiment, and it was increased from 50 to 200 mg l^{-1} during the continuous-flow experiment.

Results and discussion

Comparison of the different methods of degrading phenol

Figure 2 shows the results of experiments conducted under batch conditions. During these experiments, phenol was degraded with each of the three protocols. Under batch conditions, the rate of biodegradation of phenol alone (B) was approximately the same as the rate of coupled UV photobiodegradation of phenol (P/B), each of which was approximately 22 times the rate of UV photolysis of phenol alone (P). These results show that the microorganisms in the pores of the ceramic carrier were protected from UV light, presumably because the ceramic carrier served as a shading shelter for the microorganisms (Marsolek et al. 2008).

Figure 3 shows the results of the experiments conducted under continuous-flow conditions using the three protocols. Phenol removal was only 50 percent with UV photolysis alone (P), but nearly 100 percent with biodegradation alone (B); during most of the operation with coupled UV photobiodegradation (P/B), phenol removal also was nearly 100 percent. When the influent phenol concentration was increased from 148 to 188 mg l^{-1}, the effluent concentration increased slightly, but the effluent phenol concentration decreased to close to zero after 48 h. Similar to the results from the batch experiments, the results in Fig. 3 indicate that the carriers protected the microorganisms from UV light.

Relationship between the degradation protocol and phenol mineralization

It is undesirable that partially oxidized product (e.g., phenolics, organic acids, and aldehydes, Miao et al. 1995; Zhou et al. 2003) remain it the reactor effluent, since they have residual oxygen demand and may be harmful to the environment or humans. Therefore, full mineralization is usually the main goal of the treatment of wastewater containing biologically recalcitrant and inhibitory organics. The TOC (total organic carbon) removal ratio was an important index used to measure the degree of phenol mineralization in our experiments.

Average TOC removal efficiencies for all protocols are shown in Fig. 4 for continuous-flow conditions at an HRT of 7 h. The average TOC removal efficiency with UV photobiodegradation (P/B) was the highest (42–66%), although phenol removal was nearly 100% for P/B. Biodegradation alone (B) had a significantly lower removal efficiency (25–40%), despite also having 100% phenol removal. Thus, photolysis intimately coupled to biodegradation increased the degree of phenol mineralization, even though both treatments achieved essentially 100% phenol removal. Since phenol was absent in both experiments, the improved TOC removal in the P/B experiments had to have been through photolytic action making other organic materials in the solution more readily biodegradable. The likely candidates are intermediate products of phenol photolysis, soluble

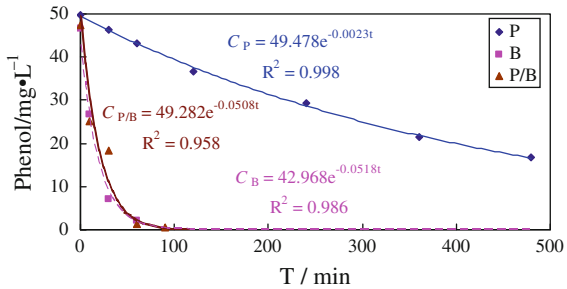

Fig. 2 UV photodegradation alone (P), biodegradation alone (B), and coupled UV photobiodegradation (P/B) of phenol under batch conditions

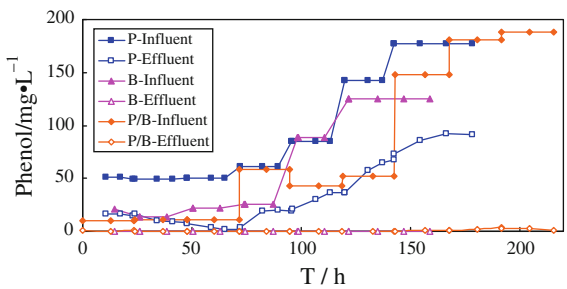

Fig. 3 Phenol degradation with UV photodegradation alone (P), biodegradation alone (B), and coupled UV photobiodegradation (P/B) under continuous flow conditions

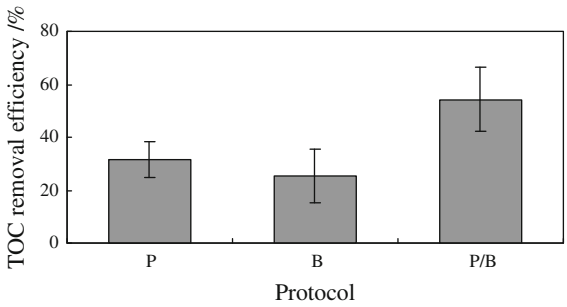

Fig. 4 Average TOC-removal efficiency with UV photodegradation (P), biodegradation (B), and coupled UV photobiodegradation (P/B) in the continuous-flow experiments at an HRT of 7 h

microbial products (SMP), and organic components in the yeast extract. The results support the underlying hypothesis of intimate coupling: readily biodegradable products are biodegraded as soon as they are formed by photolysis (Marsolek et al. 2008).

The TOC-removal efficiency with photodegradation alone was 30–40%. This value was more than that with B, but a direct comparison is not appropriate, because the P experiment contained no yeast extract, which contributed to TOC in the B and P/B experiments. Besides phenol and yeast extract, residual TOC in the B and P/B experiments could have included partially oxidized phenol, biomass, or

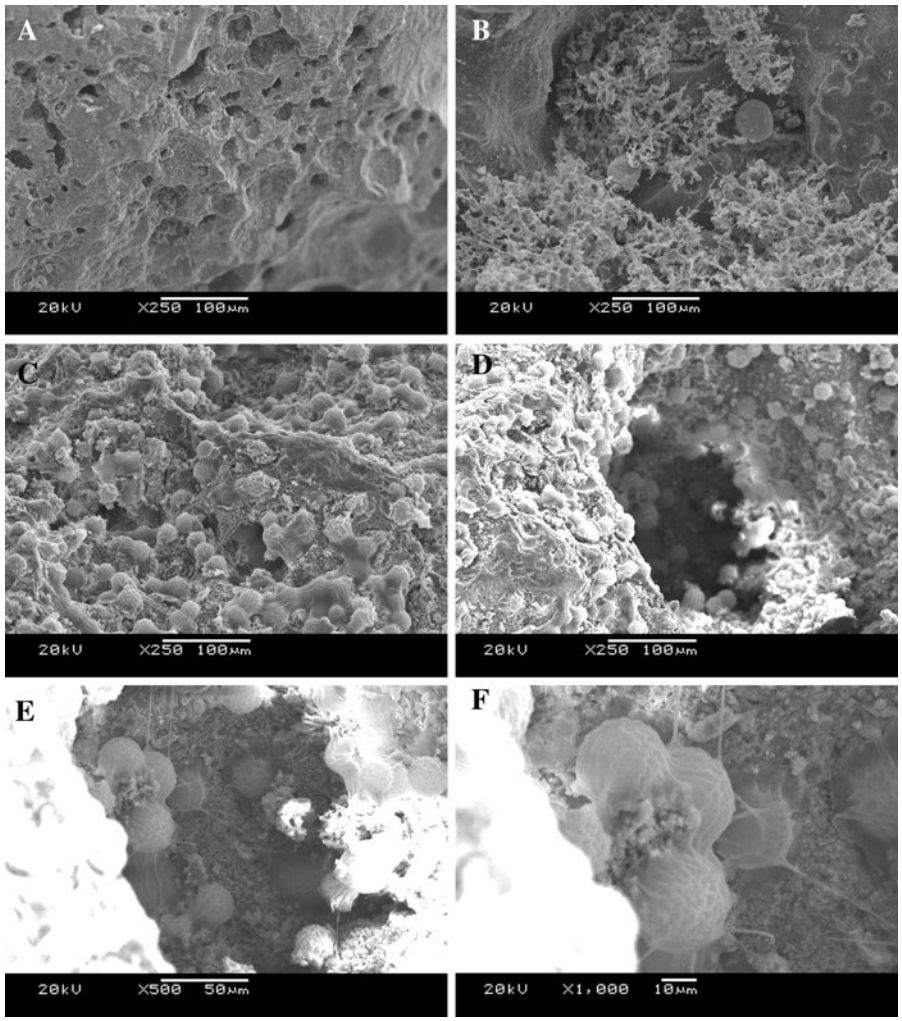

Fig. 5 SEMs of the macroporous ceramic carriers: (**a**) bare carrier; (**b**) biofilm adsorbed on the ceramic carrier after inoculation in activated sludge; (**c**) biofilm grown on the ceramic carrier taken from the PCBBR after the B experiments; (**d**) biofilm grown inside and outside the macropores of ceramic carrier taken from the PCBBR after P/B experiments; and (**e**) and (**f**) the magnified SEMs corresponding to the macropores of (**d**)

soluble microbial products (Laspidou and Rittmann 2002), all of which would contribute to TOC.

The relation between porous ceramic carrier and its biofilm

Figure 5 shows SEMs of the carriers. Figure 5a is the bare ceramic carrier at 250× magnification; many macropores remained after the foaming agent volatilized under high temperature. When the ceramic carrier was immersed into acclimated activated sludge, a variety of microorganisms adsorbed either in the macrospores and surface, as shown in Fig. 5b. Carriers removed from the PCBBR after phenol biodegradation (B experiments, Fig. 5c) harbored a much higher density of bacteria that were dominated by coccoids. After the PCBBR was operated under UV light irradiation (P/B experiments, Fig. 5d), the density of bacteria on the exterior surface was visibly lower, but healthy-looking bacteria remained in the macropores (Fig. 5e and f). Presumably, the biofilm inside the macropores were active in degrading phenol, because they were shaded from UV irradiation (Marsolek et al. 2008).

Conclusions

(1) Acclimated phenol-degrading microorganisms accumulated on macroporous ceramic carriers and could biodegrade phenol equally rapidly with or without UV irradiation. The batch rates were about 22 times faster than for UV photodegradation alone, and phenol was driven to an undetectable concentration in continuous flow.
(2) Ceramic carriers sampled after photobiodegradation experiments had a lower density of bacteria on their exterior surface, compared to biodegradation experiments, but the density remained high in the macropores.
(3) The extent of phenol mineralization under intimately coupled UV photobiodegradation was greater than the extent under with biodegradation alone, supporting the second objective of photobiodgradation: that readily biodegradable products were biodegraded as soon as they were formed by photolysis.

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