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Solar-based detoxification of phenol and *p*-nitrophenol by sequential TiO_2 photocatalysis and photosynthetically aerated biological treatment

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ABSTRACT

Simulated solar UV/TiO_2 photocatalysis was efficient to detoxify a mixture of 100 mg phenol l^{-1} and 50 mg *p*-nitrophenol (PNP) l^{-1} and allow the subsequent biodegradation of the remaining pollutants and their photocatalytic products under photosynthetic aeration with *Chlorella vulgaris*. Photocatalytic degradation of phenol and PNP was well described by pseudo-first order kinetics ($r^2 > 0.98$) with removal rate constants of 1.9×10^{-4} and 2.8×10^{-4} min^{-1}, respectively, when the pollutants were provided together and 5.7×10^{-4} and 9.7×10^{-4} min^{-1}, respectively, when they were provided individually. Photocatalytic pre-treatment of the mixture during 60 h removed 50 ± 1% and 62 ± 2% of the phenol and PNP initially present but only 11 ± 3% of the initial COD. Hydroquinone, nitrate and catechol were identified as PNP photocatalytic products and catechol and hydroquinone as phenol photocatalytic products. Subsequent biological treatment of the pre-treated samples removed the remaining contaminants and their photocatalytic products as well as 81–83% of the initial COD, allowing complete detoxification of the mixture to *C. vulgaris*. Similar detoxification efficiencies were recorded after biological treatment of the irradiated mixture with activated sludge microflora or with an acclimated consortia composed of a phenol-degrading *Alcaligenes* sp. and a PNP-degrading *Arthrobacter* sp., although the acclimated strains biodegraded the remaining pollutants faster. Biological treatment of the non-irradiated mixture was inefficient due to *C. vulgaris* inhibition.

1. Introduction

Because mechanical aeration can represent up to 55% of all the energy used during wastewater treatment (Tchobanoglous et al., 2003), algal photosynthesis can be advantageously used to provide O_2 during the aerobic removal of dissolved organic matter (Mara and Pearson, 1986). This also prevents the hazardous spraying of microorganisms and organic pollutants (Bell et al., 1993) and assists the elimination of pathogens by increasing the temperature and the pH (due to CO_2 fixation) of the treated effluent (Oswald, 2003). Finally, microalgae growth enhances the removal of nutrients (Muñoz et al., 2005) and heavy metals (Muñoz et al., 2006) and produces a rich biomass that can be further used as fertilizers

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Abbreviations: AC, acclimated culture; AS, activated sludge; COD, chemical oxygen demand; xh-EC50, effective concentration inhibiting 50% of the target population after *x* h of exposure; OECD, Organization for Economic Cooperation and Development; ThOD, Theoretical chemical Oxygen Demand; PNP, *p*-nitrophenol

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or digested to produce biogas (Muñoz and Guieysse, 2006). Unfortunately, and despite all their advantages, algal–bacterial processes have hitherto been limited to municipal wastewater treatment, probably because of the high sensitivity of the algae towards toxic pollutants that might be found in industrial wastes (Muñoz and Guieysse, 2006). In such cases, sunlight can support wastewater pre-treatment by direct irradiation or photocatalysis in order to convert recalcitrant and/or toxic pollutants into biodegradable and biocompatible products that can then be biologically treated (Sarria et al., 2002, 2003). Significant energy saving could therefore be achieved by combining solar-based pre-treatment with solar-based biological treatment. However, sequential solar-based photocatalysis and photosynthetically aerated biological treatment has, to the best of our knowledge, never been reported.

This study was therefore conducted to compare the potential of simulated solar irradiation (UV) and photocatalysis (UV/TiO_2) to detoxify a mixture of phenol (100 mg l^{-1}) and *p*-nitrophenol (PNP, 50 mg l^{-1}) prior to its biological treatment under photosynthetic aeration. Direct irradiation is easy to perform but can generate toxic photocatalytic products during the treatment of chlorophenols and nitroaromatics (Dzengel et al., 1999; Essam et al., 2006). In comparison, photocatalysis is fast and efficient because it is based on the photoproduction of hydroxyl radicals with high oxidation potential (1.9–2.7 V) (Pandiyan et al., 2002). Unfortunately, recovering the catalyst can be difficult and increases treatment costs. Phenol and PNP were selected for being priority widespread toxic pollutants (ATSDR—Agency for Toxic Substances and Disease Registry, 2005).

2. Materials and methods

All chemicals were reagent grade. Phenol, PNP and anatase TiO_2 (particle size $\leqslant 44\,\mu m$) were purchased from Sigma-Aldrich. All experiments were conducted in triplicate at $23 \pm 2\,^{\circ}C$. When sterile conditions were needed the glassware and the medium were autoclaved and the stock solutions were sterilized by filtration through 0.2 μm sterile membranes.

2.1. Microorganisms

Activated sludge microflora (AS) was obtained from Lund wastewater treatment plant (Sweden). A phenol-degrading *Alcaligenes* sp. (Genbank accession number DQ120520) and a PNP-degrading *Arthrobacter* sp. (Genbank accession number DQ412707) were isolated from the aeration tank of the wastewater treatment plant of a coke company (Cairo, Egypt). Microbial acclimation, selection and enrichment were performed by successive transfer of suspended-batch cultures at increasing phenol or PNP concentration supplied as sole carbon and energy sources (Essam, 2006). Pure isolates were obtained by cultivating pure colonies withdrawn from agar plates and characterized by partial 16S rRNA sequencing (Essam, 2006). These strains were always used together in a culture referred to as acclimated consortia in the following. A microalgal strain morphologically characterized as *Chlorella vulgaris* was also isolated from the stabilization pond of the same treatment plant.

Screening, isolation and maintenance of all microbial cultures were conducted using a mineral salt medium (MSM) composed of (in mg l^{-1} of deionized water): K_2HPO_4, 4000; Na_2HPO_4, 5200; $(NH_4)_2SO_4$, 1950; $CaCl_2 \cdot 7H_2O$, 10; $MgSO_4 \cdot 7H_2O$, 500; $FeSO_4 \cdot 7H_2O$, 10; $MnCl_2 \cdot 4H_2O$, 5.5; $ZnCl_2$, 0.68; $CoCl_2 \cdot 6H_2O$, 1.2; $NiCl_2 \cdot 6H_2O$, 1.2; $CuCl_2 \cdot 2H_2O$, 0.85; H_3BO_3, 0.0031; $NaMoO_4 \cdot 2H_2O$, 0.012; $NaSeO_3 \cdot 5H_2O$, 0.013; $NaWO_4 \cdot 2H_2O$, 0.0165 (Essam et al., 2006, 2007). The pH was adjusted to 7 with 2 N NaOH. This medium was enriched with 500 mg phenol l^{-1}, 50 mg PNP l^{-1} or 4000 mg $NaHCO_3$ l^{-1} for cultivation of *Alcaligenes*, *Arthrobacter* or *Chlorella*, respectively.

2.2. Phenol and PNP toxicity to the selected microalgae

Test tubes of 12 ml were filled with 9 ml MSM containing phenol (10, 25, 50 or 100 mg l^{-1}) or PNP (10, 20, 25 or 50 mg l^{-1}) and 2 g $NaHCO_3$ l^{-1}, inoculated with 0.54 ml of *C. vulgaris* culture, flushed with N_2 gas (to remove any atmospheric O_2), sealed with plastic screw caps and incubated under continuous agitation (150 rpm) and illumination (4000 lx = 18 μW cm^{-2}, Philips TLD 36 W/840 lamp). After 72 h, 2 ml samples were withdrawn and analyzed to measure the chlorophyll content according to Porra and Grimme (1974). Blanks were conducted without adding any pollutants and algal inhibition (%) was calculated as the reduction of the average chlorophyll content in the test samples compared to that in the blanks. These tests were performed under sterile conditions.

2.3. UV-irradiation treatments

UV-irradiation tests were conducted in MSM to allow for subsequent biodegradation studies (Essam et al., 2006, 2007) and buffer the pH (which always remained approx. 7). To allow enough volume for sampling and biodegradation tests, 25 aliquots of 6 ml of MSM supplied with 50 mg PNP l^{-1} and/or 100 mg phenol l^{-1} were transferred into 25 × 10 ml glass tubes (10 cm length) placed beside each other on a rocking shaker. For photocatalysis tests, 1 g TiO_2 l^{-1} was added to each tube (Essam et al., 2007; Ksibi et al., 2003) and the mixtures were sonicated for 5 min to obtain a homogenous suspension. The tubes were then gently shaken and irradiated at 300 μW cm^{-2} (at 15 cm) with two 18 W UV blue lamps (Sylvania Reptistar, Sylvania, USA, approx. 30% UVA–5% UVB). Light intensity within 250–500 nm measured by potassium ferrioxalate actinometry (Hatchard and Parker, 1956) was 1.15×10^{-5} Einstein s^{-1}. A set of controls pre-treated with TiO_2 alone but not irradiated was performed under the same conditions. Samples were periodically withdrawn from three test tubes randomly selected to monitor the concentration of remaining pollutants (1 ml) and nitrate (0.5 ml) and saved at 4 °C prior to analysis. The liquid fractions from each set of experiment were collected and mixed after 60 h of irradiation and samples were withdrawn for COD (10 ml), phytotoxicity (8 ml) and algal-toxicity (20 ml) analysis and immediately treated. TiO_2 was removed by centrifuging the tubes at 1400 g for 15 min (Mistral 1000) before the supernatants were mixed. This experiment was repeated 3 times to provide triplicates for the biodegradation tests.