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ScienceDirect
Chemosphere 66 (2007) 2201–2209
CHEMOSPHERE
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Sequential photochemical–biological degradation of chlorophenols

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Received 2 May 2006; received in revised form 16 August 2006; accepted 18 August 2006
Available online 9 November 2006

Abstract

$UV/TiO_2/H_2O_2$, UV/TiO_2 and UV/H_2O_2 were compared as pre-treatment processes for the detoxification of mixtures of 4-chlorophenol (4CP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) prior to their biological treatment. When each chlorophenol was initially supplied at 50 mg l^{-1}, $UV/TiO_2/H_2O_2$ treatment supported the highest pollutant removal, COD removal, and dechlorination efficiencies followed by UV/TiO_2 and UV/H_2O_2. The remaining toxicity to *Lipedium sativum* was similar after all pre-treatments. Chlorophenol photodegradation was always well described by a first order model kinetic ($r^2 > 0.94$) and the shortest 4CP, DCP, TCP and PCP half-lives of 8.7, 7.1, 4.5 and 3.3 h, respectively, were achieved during $UV/TiO_2/H_2O_2$ treatment. No pollutant removal was observed in the controls conducted with H_2O_2 or TiO_2 only. Inoculation of all the photochemically pre-treated mixtures with activated sludge microflora was followed by complete removal of the remaining pollutants. Combined $UV/TiO_2/H_2O_2$-biological supported the highest detoxification, dechlorination (99%) and COD removal (88%) efficiencies. Similar results were achieved when each chlorophenol was supplied at 100 mg l^{-1}. COD and Cl mass balances indicated UV, UV/H_2O_2, and UV/TiO_2 treatments lead to the formation of recalcitrant photoproducts, some of which were chlorinated.

Keywords: Advanced oxidation processes; Biodegradation; Hazardous pollutants; Industrial wastewater; Photodegradation

1. Introduction

Chlorohenols are extensively used in many industrial applications and enter the environment through accidental spillage and/or as degradation products of other compounds (Czaplicka, 2004). They are therefore commonly found in soil, sediments, surface water, and wastewater (Annachhatre and Gheewala, 1996; Czaplicka, 2004) and are listed as priority environmental pollutants by the US EPA because of their high toxicity, carcinogenicity, and persistence (ATSDR, 2005).

Although many chlorophenols are biodegradable under aerobic or anaerobic conditions (Chaudhry and Chapalamadugu, 1991), they are rather toxic to microorganisms as for instance, 4-chlorophenol (4CP) ad 2,4-dichlorophenol (DCP) can strongly inhibit activated sludge bacteria at 20–30 mg l^{-1} (Ren and Frymier, 2002). It might therefore be very difficult to biologically treat highly loaded groundwaters or wastewaters which might contain up to 190 mg chlorophenol l^{-1} (Langwaldt et al., 1998; Vidal and Diez, 2003). In cases where microbial inhibition might occur, it is thus preferable to pretreat the contaminated stream prior to its biological treatment in order to reduce its toxicity. These hybrid physicochemical–biological processes combine the high versatility of physicochemical treatment with the cost-efficiency of biological processes by consuming less energy than what is needed for the full physicochemical mineralization of the pollutants. Thus, various photochemical treatments have been successively used to break down toxic and/or poorly biodegradable pollutants into less toxic and/or more biodegradable molecules that can then be easily biodegraded (Amat et al., 2003; Sarria et al., 2003; Tabrizi and Mehrvar, 2004).

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doi:10.1016/j.chemosphere.2006.08.036

Unfortunately, photochemical pre-treatments can also produce more toxic and/or non-biodegradable photoproducts (Svenson and Hynning, 1997; Bláha et al., 2004) which can even inhibit the subsequent biological stage (Essam et al., 2006). These processes should therefore be carefully investigated and optimized to minimize the duration of the physicochemical step while ensuring proper conditions for subsequent biological treatment.

With this regards, the sequential physicochemical–biological treatment of mixtures of 4CP, DCP, 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) was evaluated using UV light in combination with TiO_2 and H_2O_2. Theses advanced photochemical oxidation processes are based on the photochemical generation of hydroxyl radicals (OH) via H_2O_2 photolysis (UV/H_2O_2), H_2O photocatalysis (UV/TiO_2) or H_2O_2 photocatalysis ($UV/H_2O_2/TiO_2$) (Herrmann, 1999; Pera-Titus et al., 2004). These highly reactive species are then capable to oxidize a large range of organic pollutants (Pera-Titus et al., 2004).

2. Materials and methods

All chemicals were reagent grade. 4CP, DCP, TCP and PCP were obtained from Sigma-Aldrich, TiO_2 from Merck and H_2O_2 (60%) from Acros organics. Stock solutions of DCP (5 g l^{-1}), TCP (1 g l^{-1}), PCP (0.5 g l^{-1}) and 4CP (5 g l^{-1}) were prepared in 0.2% NaOH. All experiments were conducted at 23 ± 2 °C.

2.1. Photodegradation

Unless otherwise specified, all tests were conducted in mineral salt medium (MSM) composed of (mg l^{-1} in deionized water): K_2HPO_4 4000, Na_2HPO_4 5200, KNO_3 3000, $CaCl_2 \cdot 7H_2O$ 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. This medium has been used in similar studies (Guieysse et al., 2004; Guieysse and Viklund, 2005) and simulates the potential matrix effects from compounds present in wastewater. Nitrate was used as nitrogen source to avoid microbial nitrification. The pH remained to approximately 7 during all treatments.

Photochemical tests were conducted in 12 × 10 ml-quartz tubes each filled with 6 ml of MSM containing 4CP, DCP, TCP and PCP at initial individual concentrations of 50 or 100 mg l^{-1}. When needed, 1 TiO_2 g l^{-1} and/or 50 mM H_2O_2 were also added to the medium. The tubes were then irradiated for 40 h (initial concentrations of 50 mg l^{-1}) or 56 h (initial concentrations of 100 mg l^{-1}) at 300 μW cm^{-2} (Lutron UV-340, Sagitta, Sweden) with two 18 W UV blue-lamps (Sylvania Reptistar, Sylvania, USA, approximately 30% UVA – 5% UVB) placed 15 cm away from the tubes. Light intensity (15 cm) measured by potassium ferrioxalate actinometry (Hatchard and Parker, 1956) was 1.15×10^{-5} Einstein s^{-1}. The tubes were mechanically agitated using a rocking shaker. Control tests supplied with TiO_2 or H_2O_2 and not irradiated were incubated under the same conditions (initial chlorophenol concentration of 50 mg l^{-1}). Control tests irradiated with UV (photolytic treatment) but not supplied with TiO_2 or H_2O_2 were only conducted for the mixture of chlorophenol at initial concentrations of 100 mg l^{-1}. Data from Essam et al. (2006) served as control at 50 mg l^{-1} as these experiments were carried out under the exact same conditions.

In the mixture supplied with 50 mg l^{-1} of each chlorophenol, samples of 100 μl and 0.5 ml were periodically withdrawn from three tubes randomly selected to record the chlorophenols and chloride concentrations, respectively, and saved at 4 °C prior to analysis. In the mixture

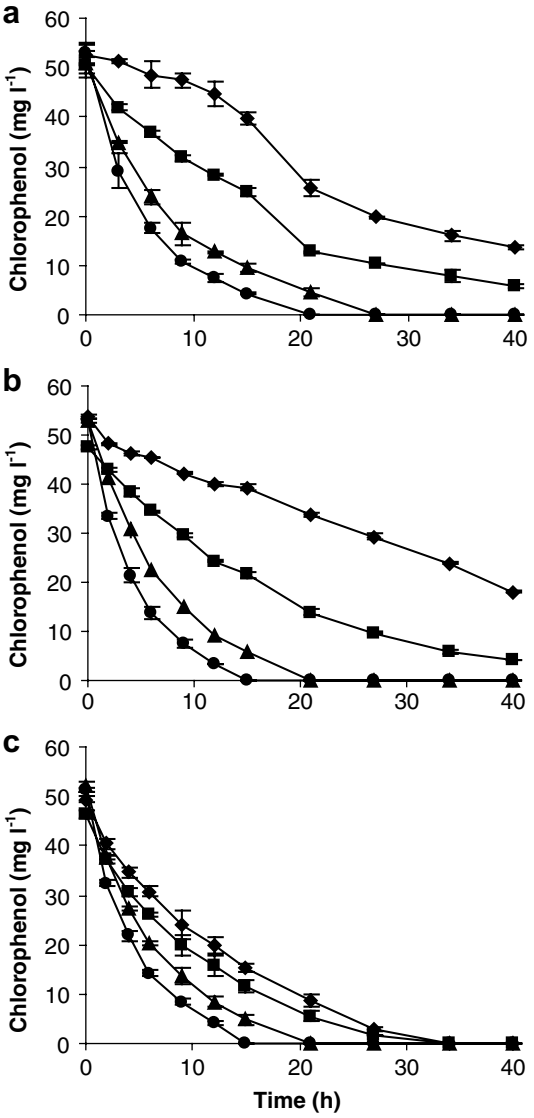

Fig. 1. Changes in the concentration of 4CP (diamonds), 2.4-DCP (squares), TCP (triangles) and PCP (circles) initially supplied at 50 mg l^{-1} in MSM and treated during 40 h with (a) UV/TiO_2, (b) UV/H_2O_2, and (c) $UV/TiO_2/H_2O_2$. The data shown represents the average on triplicates ± standard deviations.

supplied with 100 mg l^{-1}, these samples were only at the start and at the end (56 h) of the experiment. After pretreatment, the liquid fractions from the 12 replicates were combined to allow sufficient volume for sampling and for the subsequent biological tests. When needed, TiO_2 was first removed by centrifuging the tubes at 1400 g for 15 min (Mistral 1000, UK) and any remaining H_2O_2 was destructed by heating the tubes in a water bath at 45 °C for at least 2 h (according to instructions from US Peroxide, USA). Samples of 10 ml and 8 ml were then withdrawn for COD and toxicity measurements, respectively, and immediately analyzed.

2.2. Biodegradation tests

For each test (including the controls), 3 × 10 ml of pretreated samples were transferred into 3 × 25 ml cultivation flasks and each flask was inoculated with 0.8 ml of activated sludge sample (Lund wastewater treatment plant, Lund, Sweden). This inoculum is representative of wastewater treatment processes and provides a high microbial diversity that should favor the mineralization of the chlorophenols photoproducts. All flasks were closed with rubber septa and aluminum caps and incubated in the dark on a rotary shaker at 150 rpm for 28 d in order to allow microbial acclimation (OECD, 1993). Two additional sets of controls were prepared using flasks supplied with non-pretreated solutions and incubated for 28 d under the same conditions. One set was inoculated to estimate the background effects from microbial activity whereas the other set was not to estimate potential abiotic losses. Microbial activity was controlled by analyzing the flasks gas phase composition after 1 and 3 d of incubation according to Essam et al. (2006). Samples were periodically withdrawn for chloride (0.5 ml) and chlorophenol (100 μl) analysis. COD (10 ml samples) and toxicity (8 ml samples) were only measured at the end of incubation. All samples were centrifuged for 10 min at 11300*g* (Biofuge 13, Heraeus, Germany) and the supernatants were used for analysis.

2.3. Analysis

Samples for chlorophenol analysis were injected on a Waters 2690 HPLC system (USA) equipped with an autosampler and a diode-array detector from the same manufacturer. 4CP, DCP and TCP were eluted through a Supelcosil LC-8 column using a mobile phase composed of methanol, water, and acetic acid (60:39:1 v/v) and UV detection was performed at 280 nm. PCP was eluted through a Supelcosil LC-18 column using a mobile phase composed of acetonitrile and water (80:20 v/v) and UV detection was conducted at 302 nm. External standards were used to enable quantitative determination and the limit of detection was 1 mg l^{-1} for all compounds.

The COD was measured using LCK 414 test tubes (Dr Lange, Germany) and a Lasa 100 photometer equipped

Table 1
Efficiency of photochemical–biological treatment of a mixture of 4CP, DCP, TCP and PCP each supplied at 50 mg l^{-1}

Treatment		UV[a]	UV/TiO_2	UV/H_2O_2	UV/H_2O_2/TiO_2
Initial					
Phytotoxicity (%)	Undiluted	100	100	100	100
	10-fold diluted	35 ± 17	40 ± 3	41 ± 3	40 ± 4
COD (mg l^{-1})		220 ± 8	221 ± 8	244 ± 13	237 ± 9
Photochemical treatment (40 h)					
Phytotoxicity (%)	Undiluted	89 ± 11	73 ± 3	77 ± 2	66 ± 3
	10-fold diluted	0	0	0	0
COD removal (%)		20 ± 1	33 ± 5	38 ± 6	62 ± 11
Cl (mg l^{-1})		52 ± 1	72 ± 1	74 ± 0	86 ± 0
Pollutant	4-CP	15 ± 0	74 ± 1	66 ± 0	100
	DCP	78 ± 0	88 ± 1	91 ± 0	100
	TCP	100	100	100	100
	PCP	100	100	100	100
Pollutant $t_{1/2}$ (h)	4-CP	Not calculable	21.3	28	8.7
	DCP	21.5	12.4	11.6	7.1
	TCP	5.9	6	4.8	4.5
	PCP	3.5	4	3.1	3.3
Photochemical + biological					
Phytotoxicity (%)	Undiluted	75 ± 4	49 ± 4	54 ± 3	48 ± 3
	10-fold diluted	0	0	0	0
COD removal (%)		44 ± 3	64 ± 7	66 ± 6	87 ± 13
Cl (mg l^{-1})		67 ± 0	84 ± 0	90 ± 1	95 ± 0
Pollutant			100% for all CPs in all tests		

[a] Data from Essam et al. (2006).

with a LT 100 heater from the same manufacturer. For chloride analysis, samples were diluted 25 times (mixture of CPs at 50 mg l^{-1}) or 50 times (Mixture of CPs at 100 mg l^{-1}) in deionized water and injected onto a FIAStar 5000 analyzer (Foss Tecator, Sweden) according to the manufacturer instructions.

To assess toxicity, five seeds of *Lipedium sativum* were placed on a 5.5 cm (Ø) filter paper in a glass dish filled with 2 ml of undiluted or 10-folds diluted samples. The dishes were then covered and incubated in complete darkness for 5 d. Blanks were done with tap water without pollutants. Three Petri dishes were prepared for each test and the toxicity effect was calculated as the ratio (%) of the average stem length of the 15 test seeds by the average stem length of the 15 control seeds. Outliers were rejected using the Grubb's test at the 5% significant level.

All results represent the average from 15 (toxicity) or 3 (other tests) replicates ± the standard deviation on these replicates. When necessary, results were analyzed with one-way analysis of variance at the 5% significant level.

3. Results

3.1. Photochemical treatment at 50 mg l^{-1}

All photochemical treatments were followed by pollutant removal according to a first order kinetics ($r^2 > 0.94$, Fig. 1) in the following order of decreasing rate: PCP > TCP > DCP > 4CP. UV/TiO_2/H_2O_2 treatment supported the highest pollutant removal, detoxification, and COD removal efficiencies (Table 1). All pre-treatments were followed by Cl release (Fig. 2a) and complete removal of TCP and PCP. All treatments significantly reduced the toxicity of both the undiluted and the diluted mixtures (Table 1) although none allowed for complete detoxification or complete COD removal (Table 1). No significant pollutant removal, detoxification, or COD removal was detected in the non irradiated samples supplied with H_2O_2 or TiO_2.

Inoculation of all pre-treated samples was followed by O_2 consumption CO_2 release (data not shown), and chloride release (Fig. 2b). It also led to the complete removal of the remaining, pollutants detoxification, and COD removal (Table 1). The best COD removal (87%) was achieved in the samples pre-treated with UV/TiO_2/H_2O_2. Neither pollutant removal nor biological activity was observed in the non-irradiated samples.

3.2. Photochemical treatment at 100 mg l^{-1}

All pre-treatments detoxified the 10-fold diluted mixture but only UV/TiO_2/H_2O_2 significantly detoxified the undiluted mixture (Table 2). All treatments were followed by chloride release and pollutant removal (Table 2) although complete pollutant removal was only observed in the tubes treated by UV/TiO_2/H_2O_2. This treatment also supported the highest COD removal rate and there was no significant difference in the COD removal after treatment with UV/TiO_2 and UV/H_2O_2. UV irradiation supported the lowest pollutant removal, COD removal and detoxification efficiencies.

No pollutant removal, chloride release, COD removal or signs of biological activity were observed after inoculation of the samples pre-treated by UV-photolysis. Inoculation of samples pre-treated by UV/TiO_2 and UV/H_2O_2 was followed by the complete removal of the remaining pollutants and chloride release (Fig. 3) with subsequent detoxification and COD removal (Table 2). Inoculation of samples pre-treated with UV/TiO_2/H_2O_2 supported complete dechlorination and the highest COD removal efficiency reported in the present study (Table 2).

3.3. COD and Cl mass balances

As the direct characterization (by GC-MS or LC-MS) of the products released during pre-treatment failed, an attempt was made to follow their fate by using COD and Cl mass balances. The amounts of theoretical oxygen demand (ThOD) and organic-chloride (ThCl) contributed by the chlorophenols were first calculated from the pollutant concentrations experimentally measured. The ThOD/

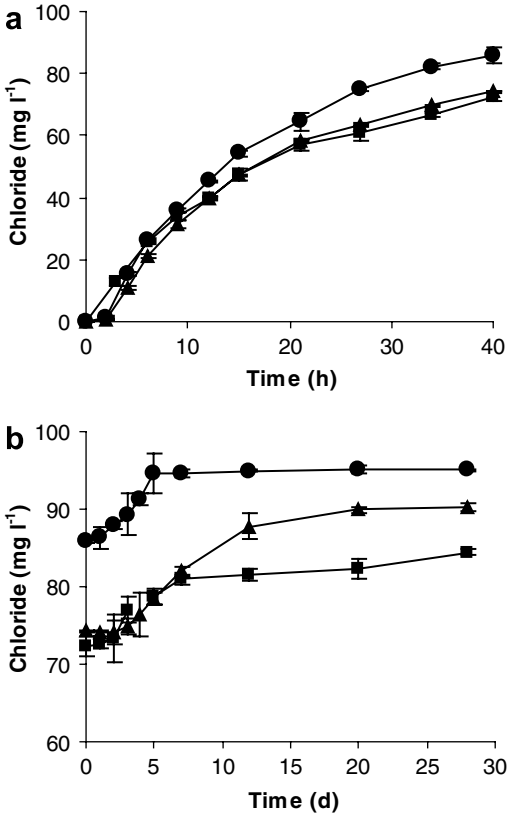

Fig. 2. Change in chloride concentration in tubes supplied with a mixture of 4CP, DCP, TCP, and PCP initially supplied at 50 mg l^{-1} in MSM during (a) pre-treatment by UV/TiO_2 (squares), UV/H_2O_2 (triangles) and UV/H_2O_2/TiO_2 (circles); and (b) biological treatment of the same pre-treated mixture. The data shown represents the average on triplicates ± standard deviations.

Table 2
Efficiency of photochemical–biological treatment of a mixture of 4CP, DCP, TCP and PCP each supplied at 100 mg l^{-1}

Treatment		UV	UV/TiO_2	UV/H_2O_2	UV/H_2O_2/TiO_2
Initial					
Phytotoxicity (%)	Undiluted	100	100	100	100
	10-fold diluted	91 ± 9	92 ± 5	94 ± 5	94 ± 5
COD (mg l^{-1})		422 ± 13	431 ± 10	469 ± 11	478 ± 11
Photochemical treatment (56 h)					
Phytotoxicity (%)	Undiluted	100	96 ± 4	93 ± 4	76 ± 4
	10-fold diluted	18 ± 10	0	0	0
COD removal (%)		17 ± 6	25 ± 3	32 ± 5	65 ± 4
Cl (mg l^{-1})		107 ± 9	125 ± 2	136 ± 5	166 ± 2
Pollutant removal (%)	4-CP	14 ± 1	36 ± 2	34 ± 2	100
	DCP	58 ± 7	81 ± 2	76 ± 1	100
	TCP	91 ± 4	100	100	100
	PCP	100	100	100	100
Photochemical–biological treatment (28 d)					
Phytotoxicity (%)	Undiluted	100	70 ± 3	66 ± 3	49 ± 4
	10-fold diluted	18 ± 10	0	0	0
COD removal (%)		17 ± 6	63 ± 5	64 ± 4	88 ± 7
Cl (mg l^{-1})		110 ± 4	166 ± 1	169 ± 1	189 ± 3
Pollutant removal (%)	4-CP	14 ± 1	100	100	100
	DCP	58 ± 7	100	100	100
	TCP	91 ± 4	100	100	100
	PCP	100	100	100	100

COD ratio of untreated mixtures ranged from 0.9–1.1, showing these parameters could be compared. The COD mass balance was thus based on the assumption that the COD measured in the samples was only due to the chlorophenols and their products. COD contributions from the medium (20 mg l^{-1} in fresh MSM), the inoculum, or from biological products released during microbial growth were therefore neglected. The COD hypothetically due to degradation products was then calculated as CODpro (mg l^{-1}) = COD − ThOD. The fraction of the ThOD removed found as products was the calculated as CODpro (%) = CODpro/($ThOD_0$ − ThOD) where $ThOD_0$ was the ThOD initially introduced from the chlorophenols. The amount of chloride hypothetically found in organic products was calculated as: Clpro (mg l^{-1}) = $ThCl_0$ − ThCl–Cl; $ThCl_0$ being the amount of chloride initially found in the chlorophenols and Cl the chloride concentration experimentally measured. The rates of dechlorination (%) were then calculated as Cl/($ThCl_0$ − ThCl). Cl analyses were not biased by other sources of chloride as the initial Cl values were always below the detection limit.

At 50 mg l^{-1} initial chlorophenol concentration, UV/H_2O_2 and UV/TiO_2 treatments (Fig. 4a) yielded the largest amounts of photoproducts. However, since different COD removal efficiencies were reported (Table 1), the fraction of ThOD removed converted into photoproducts was the highest for UV and lowest for UV/TiO_2/H_2O_2 (Fig. 4b). Biological treatment of pre-treated mixture was unable to reduce the CODpro from UV photolysis as the COD removal observed was only due to the biodegradation of the remaining 4CP and DCP. The observed increase in CODpro was most likely due to COD added from the inoculum or released during biological treatment. Taking this into account, biological treatment was able to remove nearly all the photoproducts formed during UV/TiO_2/H_2O_2 treatment but only a fraction of the products formed during UV/TiO_2 and UV/H_2O_2 treatments. Similar results were achieved when the chlorophenols were introduced at 100 mg l^{-1} each (Fig. 5).

At both 50 and 100 mg l^{-1} initial concentrations, the amount of chloride found in products levels after photochemical treatment followed the same order: UV > UV/TiO_2 > UV/H_2O_2 > UV/TiO_2/H_2O_2 (Figs. 4 and 5). Biological treatment of samples submitted to UV irradiation did not lead to a significant reduction of Clpro, showing the Cl release observed (50 mg l^{-1}) was only due to the biodegradation of the remaining 4CP and DCP. Nearly complete dechlorination (>98%) was only achieved with combined UV/TiO_2/H_2O_2 – biological treatment. Mass balances analysis therefore suggests photoproducts were formed during all photochemical treatment, with at least some of them being chlorinated. The reduction of CODpro and Clpro after inoculation shows at least a fraction of these photoproducts (including the chlorinated species) were biodegraded.

4. Discussion

In a recent study using mixtures of PCP, TCP, DCP and 4CP, Essam et al. (2006) showed UV photolysis generated

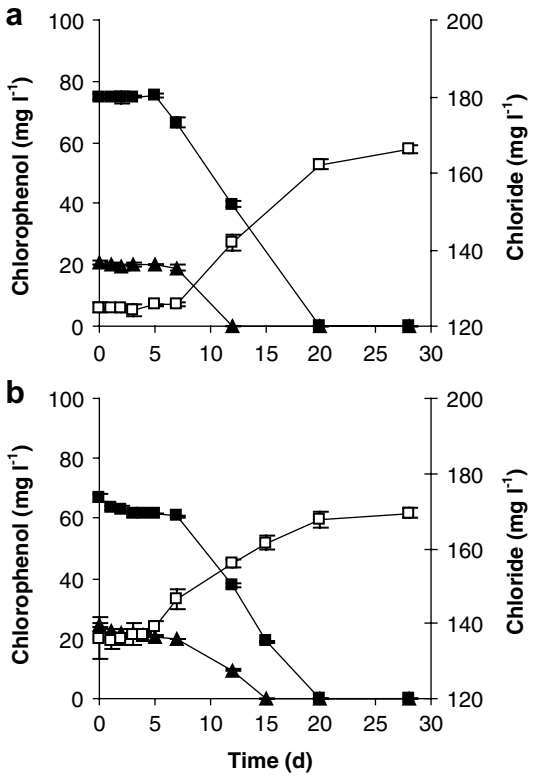

Fig. 3. Change in remaining 4-CP (closed squares), 2.4-DCP (closed triangles) and chloride (open squares) concentrations in cultivation tubes supplied with a mixture of 4CP, DCP, TCP, and PCP each initially supplied at 100 mg l^{-1} in MSM, pre-treated 56 h by (a) UV/TiO_2; or (b) UV/H_2O_2 before being inoculated with activated sludge samples and incubated for 28 d. The data shown represents the average on triplicates ± standard deviations.

recalcitrant photoproducts that were not further biodegraded and even inhibited the subsequent biological treatment when each chlorophenol was supplied at 100 mg l^{-1}. This was confirmed in this study since although PCP and TCP (the two most toxic compounds) were nearly completely removed after UV irradiation, the remaining 4CP, DCP and TCP were not biodegraded. An additional biodegradation control conducted with a non-irradiated mixture of 4CP, DCP and TCP at 84, 42, and 12 mg l^{-1}, respectively (their respective final concentrations after UV photolysis, Table 2) showed all contaminants were removed within 2 weeks of incubation. This demonstrated toxicity of the irradiated mixture was also caused by photoproducts and not only the remaining chlorophenols. Essam et al. (2006) also reported the formation of toxic photoproducts only occurred when the contaminants were irradiated simultaneously, which is a serious problem because pollutants are always founds in mixtures in contaminated streams. Several advanced photochemical treatments were therefore compared for their efficiency to detoxify mixtures of chlorophenols. The biodegradability of the treated samples was evaluated in terms of COD removal, dechlorination and detoxification efficiencies.

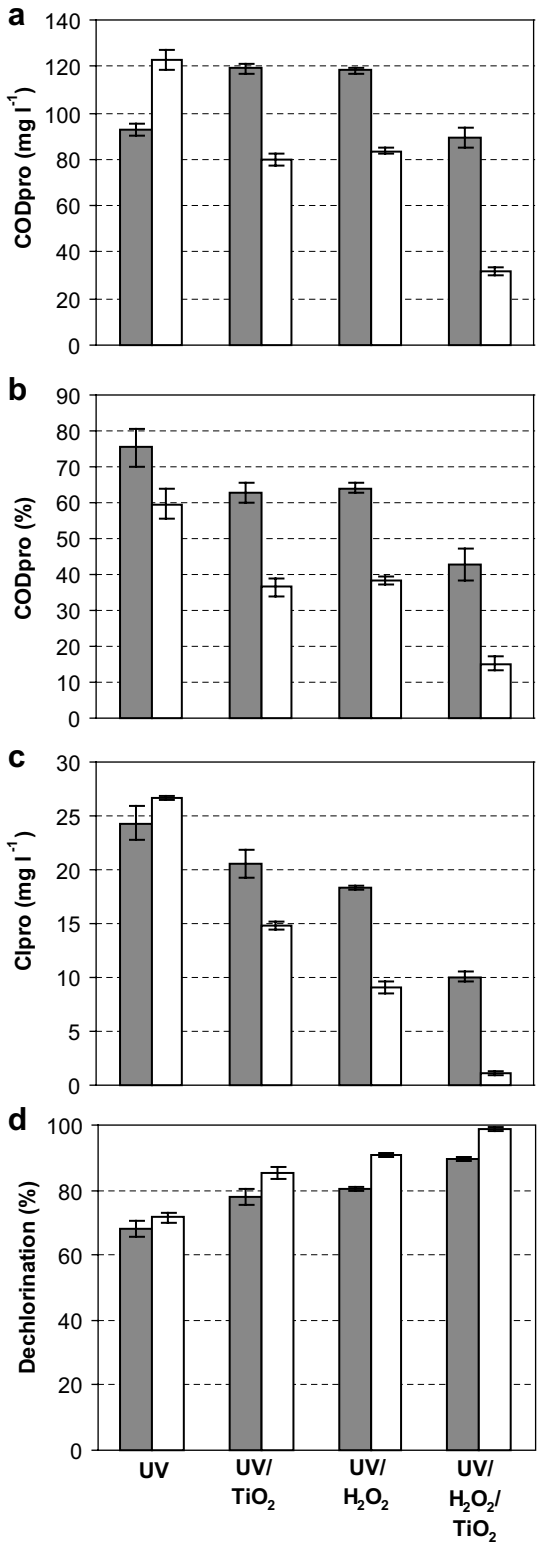

Fig. 4. (a) Amount of COD hypothetically found as products; (b) fraction of the ThOD removed converted into products; (c) amount of chloride hypothetically found in degradation products; and (d) dechlorination efficiency in MSM supplied with 50 mg l^{-1} of 4CP, DCP, TCP, and PCP after photochemical treatment (gray bars) and combined photochemical–biological treatment (white bars). The data shown represents the average on triplicates ± standard deviations. Data for UV photolysis was calculated from the data of Essam et al. (2006).

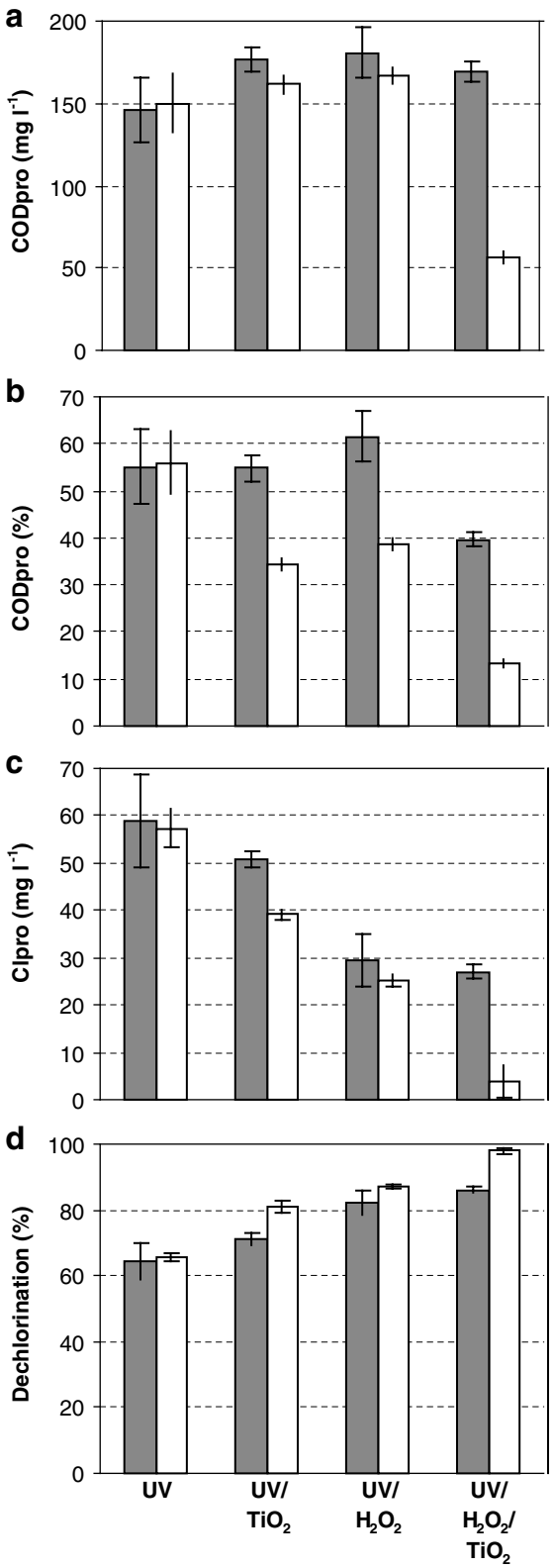

Fig. 5. (a) Amount of COD hypothetically found as products; (b) fraction of the ThOD removed converted into products; (c) amount of chloride hypothetically found in degradation products; and (d) dechlorination efficiency in MSM supplied with 100 mg l^{-1} of 4CP, DCP, TCP, and PCP after photochemical treatment (gray bars) and combined photochemical–biological treatment (white bars). The data shown represents the average on triplicates ± standard deviations.

Regardless the initial pollutant concentration tested, the advanced photochemical treatments were more efficient than UV photolysis in degrading and dechlorinating the pollutants as well as detoxifying the mixture. However, only UV/TiO_2/H_2O_2 treatment was efficient in releasing biodegradable photoproducts. Consequently, the sequential UV/TiO_2/H_2O_2-biological treatment supported the highest dechlorination, COD removal and detoxification efficiency achieved in this study. The remaining toxicity of 50% was comparable to the inhibition cause by the activated sludge sample used as inoculum. The remaining COD was in the range of the value measured in the control test inoculated and not provided with any chlorophenols. It was therefore likely due to dissolved compounds present in the inoculum and/or biological products released during microbial growth. Both UV/TiO_2 and UV/H_2O_2 were efficient to detoxify the pollutant mixtures and allow the subsequent biodegradation of the remaining DCP and CP. However, mass balance analysis evidenced that a fraction of the photoproducts formed were not biodegraded. Indeed, the photochemical treatment of chlorophenols can generate the formation of biodegradable compounds such as chlorinated catechols, chlorinated benzoquinones, hydroxlated benzoquinones and hydroquinones (Mills and Hoffmann, 1993; Theurich et al., 1996; Jardim et al., 1997; Bhatkhande et al., 2002) as well as non-biodegradable chlorinated photoproducts such as chlorinated hydroxybiphenyls, hydroxylated and chlorinated dimers (Theurich et al., 1996; Hirvonen et al., 2000).

UV/H_2O_2 treatment yielded less chlorinated photoproducts than UV/TiO_2 treatment, yet, their performances were very similar with regards to the pollutant removal, COD removal, and detoxification efficiencies achieved after biological treatment. UV/TiO_2 treatment can be more economical than UV/H_2O_2 when using solar radiation (Yawalkar et al., 2001). However, the use of TiO_2 is still limited by the difficulty of immobilizing or recycling the catalyst (Yatmaz et al., 2001; Rao et al., 2003).

Chlorophenol photodegradation by UV/TiO_2 and UV/H_2O_2 is generally described by pseudo-first order kinetics with half-lives ranging from a few min to a few h (Pera-Titus et al., 2004). The relatively long half-lives achieved in our study can be explained by the use of the mild oxidation conditions (simulated solar irradiation, neutral pH) and mineral medium in order to lower costs and ease the subsequent biological treatment (no need for pH neutralization). The fastest pollutant removal rates achieved during UV/TiO_2/H_2O_2 treatment can be explained by the fact $OH^{\cdot}$ generation by H_2O_2 photocatalysis (UV/TiO_2/H_2O_2) is more efficient than by H_2O photocatalysis (UV/TiO_2) or H_2O_2 photolysis (UV/H_2O_2). This is in agreement with Lee et al. (2003) who reported fastest degradation of oxalic and citric acids during UV/H_2O_2/TiO_2 treatment (4 UV lamps, 254 nm) than during UV/H_2O_2 and UV treatments. UV/H_2O_2 treatment of the 50 mg l^{-1} mixture of chlorophenol in Fe-free MSM yield similar removal rates than when iron was present but UV/H_2O_2 was more efficient when the

pollutants were supplied in ultrapure water, showing ionic species in the MSM (i.e., SO_4^{2-}) acted as radical scavengers (data not shown).

The rates of pollutant removal (PCP > TCP > DCP > 4CP) were in the same order of the excitation coefficients of these compounds (Essam et al., 2006), which could indicate that activation by UV-irradiation and attack by hydroxyl radicals were both involved in the chlorophenol photodegradation. Miller et al. (1988) also reported faster TCP photodegradation than DCP during UV photolysis or UV/H_2O_2 treatment (4.63 pE m^{-2} s^{-1}). However, Doong et al. (2000) reported that DCP was removed faster than 4CP at pH 12.5 during UV/TiO_2 treatment whereas the reverse order was observed at pH 2.5, showing the individual rates of degradation within mixtures also depend on the experimental conditions used. The advanced photochemical treatments were less specific than UV photolysis in targeting the most toxic and recalcitrant pollutants (TCP, PCP) which photodegradation rates only slightly increased during UV/H_2O_2 and UV/TiO_2/H_2O_2 treatments and even decreased during UV/TiO_2 treatment (Table 1). Hence, because hydroxyl radicals attack organics rather unspecifically, advanced photochemical processes are intrinsically less energy efficient than UV photolysis.

5. Conclusions

UV/TiO_2/H_2O_2, UV/H_2O_2, and UV/TiO_2 treatments were efficient in removing 4CP, DCP, TCP and PCP from mixtures at initial concentrations of 50 or 100 mg l^{-1}. UV/TiO_2/H_2O_2 treatment supported the highest pollutant photodegradation rates and highest dechlorination efficiency. Consequently, the biodegradation of the photoproducts was feasible and the combined UV/TiO_2/H_2O_2 – biological treatment allowed for complete pollutant removal, complete detoxification, >98% dechlorination rate and nearly complete COD removal. UV/TiO_2 and UV/H_2O_2 were efficient in removing the pollutants, detoxifying the mixture, and allowing the subsequent biodegradation of the remaining 4CP and DCP. However, evidence was found that recalcitrant photoproducts (some of which were chlorinated) were formed. UV/TiO_2/H_2O_2 treatment should therefore be recommended when treating mixture of chlorophenols. These results also show photochemical–biological processes cannot be only evaluated in regards to their pollutant removal efficiency and that special care must be taken in following the fate of photoproducts.

Acknowledgements

This project was supported by funds from the Swedish International Development and Cooperation Agency (SIDA, Project 2002-6971) under the Swedish-MENA research link program. This work falls within the framework of the Egyptian Academy of Scientific Research and Technology's National Strategy for Biotechnology and Genetic Engineering Program whose support of the Microbial Biotechnology Center is acknowledged.

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