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Biological and photocatalytic treatment integrated with separation and reuse of titanium dioxide on the removal of chlorophenols in tap water

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ABSTRACT

We investigated biological, photocatalytic, and combination of biological and photocatalytic treatments in order to remove a mixture of 2-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, and pentachlorophenol in tap water (total: 100 mg L^{-1}, each: 25 mg L^{-1}). The removal of chlorinated phenols was conducted with a flow biological treatment and a circulative flow photocatalytic treatment under black light and sunlight irradiations integrated with titanium dioxide separation and reuse. The combined biological–photocatalytic treatment significantly shortened the degradation and mineralization time of both the biological treatment and the photocatalytic treatment. The removed chlorophenols per hour by the combined biological–photocatalytic treatment was 25.8 mg h^{-1}, whereas by the combined photocatalytic–biological treatment was 10.5 mg h^{-1}. After a large portion of biodegradable 2-chlorophenol and 2,4-dichlorophenol, and around half amount of slightly biodegradable 2,4,5-trichlorophenol were removed by the biological treatment, the remained three chlorophenols, biorecalcitrant pentachlorophenol, and biodegradation products were completely removed by the subsequent photocatalytic treatment. Since titanium dioxide particles in tap water spontaneously sedimented on standing after the photocatalytic treatment, the combined treatment can be operated by integrating with the titanium dioxide separation and reuse. The TiO_2 particles were recovered and reused at least three times without significantly decreasing the removal efficiency.

1. Introduction

The industrial activity and domestic use generate high amounts of residual wastewater, whose direct disposal to natural channels causes a considerable effect in the environment. Because of an increasing social and political concern on the environment, the research field of water purification has been extensively growing in the last decades, comprising both polluted wastewaters and groundwaters from seas, rivers and lakes, as water quality control and regulations against hazardous pollutants have become stricter in many countries. On this way, chlorophenols (CPs) constitute a particular group of priority toxic pollutants, because most of them are toxic and hardly biodegradable, and are difficult to remove from the environment [1]. Chlorophenols have been widely used as bactericides, insecticides, herbicides, fungicides and wood preservative as well as intermediates of dyes. Because of their numerous origins, they are commonly found in industrial wastewaters, soil, sediment, and surface and ground waters, and cause severe environmental problems [2]. Hence, suitable and effective methods must be developed to remove them either to less harmful intermediates or to complete mineralization.

Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of wastewaters containing biorecalcitrant compounds, like chlorophenols. Some AOPs: UV photolysis [3], H_2O_2/UV [4], ozone [5], ozone/UV, fenton/UV [6], fenton [7] and TiO_2/UV [8–10] have been studied for decomposing of chlorophenols. The UV light required may come from an artificial source or sunlight [11–13]. Unfortunately, the AOPs can also produce more toxic and/or biorecalcitrant intermediate/products [14,15]. On the other hand, biological remediation methods under aerobic or anaerobic conditions for decomposing chlorophenols have been also studied [16–18]. They are also less versatile as microbial activity is more easily affected by the toxicity. Therefore, alternative methods of combined AOPs and biological treatment have been proposed [19,20]. The combined treatment can be a AOPs followed by biological treatment [21–24] or a biological treatment followed by AOPs [25–28]. In case of the combined photochemical–biological treatment of chlorophenols using small scale reactors [3], special cares should be taken in the following fate of photoproducts and a pre-conditioning (removal of H_2O_2,

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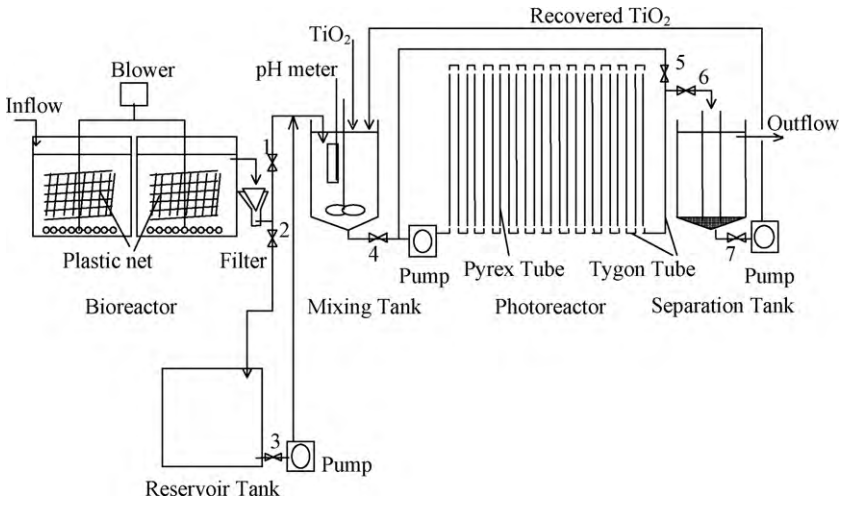

Fig. 1. Schematic system of the combination of biological and photocatalytic treatments.

O_3 or TiO_2) for subsequent biological treatment. Moreover, the required time for the mineralization of low loading chlorophenols (quantity or concentration) in the photochemical treatment itself seems to be shorter than in the photochemical–biological treatment.

It was reported that the electrolytes in water lower the degradation efficiency due to coagulation of TiO_2 particles [29]. The high flow rate prevented the coagulation of suspended TiO_2 by electrolytes in the tap water, while the electrolytes enabled easy separation of the fine TiO_2 particles by standing after the photocatalytic treatment [30]. The recovered TiO_2 was reused at some repeated treatments [29–33]. An easy separation of TiO_2 particles may promote the application of TiO_2 particles in the suspension photocatalytic treatment.

The combined biological–photocatalytic treatment was effective to decompose a mixture chlorophenols ($100\,mg\,L^{-1}$) and significantly shortened the degradation time of biological treatment only [34]. However, the comparative studies with combined photocatalytic–biological treatment of chlorophenols mixture and each chlorophenols have not been evaluated. In addition, the comprehensive evaluations of a single treatment and TiO_2 reuse have not been considered yet. In this study, the comparative studies between combined biological–photocatalytic treatment and combined photocatalytic–biological treatment, and also single treatment (biological or photocatalytic) of chlorophenols mixture and each 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP), and pentachlorophenol (PCP) in tap water were evaluated in flow biological, circulative-flow photocatalytic (TiO_2 suspension), and flow biological–photocatalytic reactors, integrated with the separation and reuse of TiO_2 and the application of sunlight. These operation modes should be carefully optimized to minimize the duration of the treatments.

2. Experimental

2.1. Materials

All chemicals were of reagent-grade quality and were used as received. Activated sludge was obtained from a domestic sewage treatment facility in Toyama city and used after separation from the large particles. TiO_2 particles (Degussa P-25, Nippon Aerosil Co.; 15–40 nm particle size; $50 \pm 15\,m^2\,g^{-1}$ BET surface area; 70% anatase-type) were used as a photocatalyst. The chlorophenols solutions were prepared with tap water of Toyama city. The electrolytes in tap water were as follows: $Na^+ = 1.9$, $K^+ = 0.5$, $Ca^{2+} = 7.8$, $Mg^{2+} = 1.0$, $Cl^- = 3.3$, $SO_4{}^{2-} = 9.0$, $HCO_3{}^- = 18.9\,mg\,L^{-1}$. The chlorophenols solution in deionized water was prepared and used for comparison. A growth medium of 2-CP ($10\,mg\,L^{-1}$) and the nutrient (KH_2PO_4 (420), K_2HPO_4 (375), $(NH_4)_2SO_4$ (244), NaCl (30), $CaCl_2$ (30), $MgSO_4{\cdot}7H_2O$ (61.4), and $FeCl_2{\cdot}4H_2O$ ($4.7\,mg\,L^{-1}$)) [25] was prepared with distilled water.

2.2. Apparatus

The apparatus used for the combined treatment is shown in Fig. 1, comprised of bioreactor, photoreactor and TiO_2 separator [30]. The two bioreactors are made of polypropylene (45 cm × 30 cm × 25 cm height, 2 tanks) with a total working volume of 40 L. Six plastic nets (30 cm × 10 cm, thickness: 5 cm, surface area: $100\,m^2\,m^{-3}$, polypropylene Hechimaron 350-500, Shinko Nairon Co.) were vertically installed in each bioreactor to immobilize any microorganisms on their surfaces. Aeration was performed with an air pump.

The photocatalytic treatment was carried out in the tubular photoreactor [33]. Pyrex tubes (24 pieces, 1 piece: 75 cm length and 0.6 cm i.d., total volume: 510 mL), of which each end was attached to tygon tubes, were installed onto a horizontal stainless steel plate (200 cm × 100 cm) at the same distance, and furthermore the head and tail parts of the combined pyrex tubes were combined with a black hose covered tygon tube. The total volume of the pyrex tubes and the tygon tubes was 800 mL. Irradiation was performed with black light lamps (20 × 20 W, λ_{max}: 352 nm) or sunlight. Black light irradiation was conducted inside a surrounding wall of which the inside is covered with reflecting stainless steel plates. A top panel covered with stainless steel sheet, under which the black lights were attached and hanged, was inserted inside the surrounding wall and held 20 cm above the tube with plugs set inside the wall. Sunlight irradiation was performed by removing the surrounding wall and the top panel.

The mixing tank (31 cm height and 21 cm i.d.) was equipped with a mechanical stirring and covered with black flannel. The flow of the TiO_2 slurry or suspension was adjusted by a rolled pump. The photocatalytically treated effluents were flowed into a separation tank (31 cm height and 21 cm i.d., inside column: 10 cm i.d., total volume: 10 L) and overflowed out.

Table 1
Biological and photocatalytic treatments of each CP (100 mg L^{-1}).

Treatment	2-CP	2,4-DCP	2,4,5-TCP	PCP
Control test[a]				
CP removal (%)	1 ± 0	1 ± 0	1 ± 0	1 ± 0
TOC removal (%)	0	0	0	0
Biological[b]				
CP removal (%)	99 ± 1	98 ± 1	82 ± 1	25 ± 0
Removed CP (mg h^{-1})	47.5	47.0	39.4	12.0
TOC removal (%)	91 ± 1	85 ± 0	62 ± 0	1 ± 1
Photocatalytic[c]				
CP removal (%)	40 ± 2	60 ± 1	80 ± 1	99 ± 1
Removed CP (mg h^{-1})	5.3	8.0	10.7	13.2
TOC removal (%)	25 ± 1	50 ± 0	75 ± 1	95 ± 0
Biological + photocatalytic[d]				
CP removal (%)			100 (60[e])	
Removed CP (mg h^{-1})			33.3	
TOC removal (%)			92 ± 1	
Photocatalytic + biological[f]				
CP removal (%)			100 (80[g])	
Removed CP (mg h^{-1})			8.6	
TOC removal (%)			84 ± 1	

[a] Control test: batch (vol: 5 L) with aeration only.
[b] Biological treatment (vol: 40 L) at flow rate of 8 mL min^{-1}.
[c] Photocatalytic treatment (vol: 0.8 L) at circulative flow 600 mL min^{-1} for 6 h.
[d] Biological treatment (40 L) at flow rate of 33 mL min^{-1} + photocatalytic treatment (0.8 L) for 2 h.
[e] First treatment: biological (40 L) at flow rate of 33 mL min^{-1}.
[f] Photocatalytic treatment (0.8 L) for 6 h + biological treatment (40 L) at flow rate of 4 mL min^{-1}.
[g] First treatment: photocatalytic (0.8 L) for 6 h.

2.3. Procedures

2.3.1. Biological and photocatalytic treatments

The activated sludge (10 L) was placed in each the two bioreactors which contained 10 L tap water and aerated with air (0.5 L min^{-1}) at room temperature for 1 week. The growth medium (5 L) was then added to the bioreactors after withdrawal of the same volume of the solution from the bioreactors for a week of acclimation and the cultivation was continued with chlorophenols as reported [34]. The flow biological treatments of each chlorophenol (100 mg L^{-1}) and the mixture of chlorophenols (each: 25 and total: 100 mg L^{-1}) were then conducted by varying the flow rate. In all experiments, the temperature was room temperature (24 ± 2 °C) and the pH of the chlorophenol solutions was not adjusted during the course of the experiment.

The TiO_2 particles were added to the biologically treated or non-treated chlorophenol solution in the mixing tank and mechanically stirred. The photocatalytic treatments were carried out in the photoreactor by varying the flow rate (circulative mode) or the irradiation time under the black light or sunlight. The sunlight photocatalytic treatment was conducted outside on top of the roof of the second floor building at sunny day. The TiO_2 particles were separated from the water by a spontaneous sedimentation method.

2.3.2. Combined biological–photocatalytic treatment

The chlorophenols solution (100 mg L^{-1}) flowed into the bioreactor at various flow rates and the effluent was passed through a filter to the TiO_2 mixing tank with valve 1 open. After the biologically treated solution (10 L) had been collected in the mixing tank, TiO_2 was added and the suspension was mechanically stirred. While 10 L of the biologically treated chlorophenols solution was treated by the circulative mode in the photocatalytic reactor, the effluent flowing from the bioreactor was collected into a reservoir tank with valve 2 open. The 800 mL TiO_2 suspension was input into the photoreactor and circulated by various flow rates with valve 5 open. After the circulation, the effluent flowed into the separation tank with valve 6 open. The next TiO_2 suspension (800 mL) was then input into the photoreactor. In case of the combined photocatalytic–biological treatment, the photocatalytic treatment

Table 2
Biological and photocatalytic treatments of mixture CPs (each 25, total 100 mg L^{-1}).

Treatment	No[a]	Bio[b]	Photo[c]	Total (Bio); Bio + Photo[d]	Total (Photo); Photo + Bio[e]
CP removal (%)					
2-CP	1 ± 0	91 ± 1	99 ± 1	100 (83)	100 (54)
2,4-DCP	1 ± 0	89 ± 1	100	100 (80)	100 (67)
2,4,5-TCP	1 ± 1	71 ± 1	100	100 (60)	100 (86)
PCP	1 ± 1	16 ± 1	100	100 (13)	100 (99)
Removed CPs (mg h^{-1})	0	31.6	5,7	25.8	10.5
TOC (mg L^{-1})	42	14 ± 1	15 ± 1	2 ± 1	10 ± 1
TOC removal (%)	0	66 ± 1	64 ± 1	95 ± 1	77 ± 1

[a] Control test: batch (vol: 5 L) with aeration only.
[b] Biological treatment (vol: 40 L) at flow rate of 8 mL min^{-1}.
[c] Photocatalytic treatment (vol: 0.8 L) at circulative flow for 14 h.
[d] Biological treatment (40 L) at flow rate of 12 mL min^{-1} + photocatalytic treatment (0.8 L) for 2 h.
[e] Photocatalytic treatment (0.8 L) for 6 h + biological treatment (40 L) at flow rate of 4 mL min^{-1}.

was conducted at first and then followed by the biological treatment.

2.3.3. Separation and reuse of TiO_2

After the photocatalytic treatment, the TiO_2 particles were separated from the water by a spontaneous sedimentation method in the separation tank. The treated transparent water in the separation tank was overflowed, and the sedimented TiO_2 (or slurry) was recycled (valve 7 open) after 10 L photocatalytic treatment finished, and reused for the next 10 L photocatalytic treatment. When the chlorophenols removal efficiency decreases, the used TiO_2 particles can be replaced with the fresh one.

2.4. Analysis

About 2 mL of the effluents that flowed from the bioreactor and the photoreactor were withdrawn at timed intervals and immediately filtered using a syringe equipped with a disposal filter having a pore size of 0.2 μm. The concentration of TOC in the water was measured by a Shimadzu TOC-500 analyzer. The concentration of chlorophenols was measured by a HPLC system equipped with a PU-980 pump, a 970 UV-Vis detector (Jasco), and a Mightysil RP-18 column (Kanto Chemicals). The measurement was made using the mobile phase of CH_3CN: NaH_2PO_4 (20 mM) = 50:50 at the wavelength of 215 nm. The transparency of the treated water was measured at 400 nm by a UV-1600 Shimadzu spectrophotometer. The light intensities of the black light and sunlight were measured by an illuminometer (ORC UV-MO2) at the wavelength of 320–390 nm and estimated to be 1.7 mW cm^{-2} and 2.6–3.5 mW cm^{-2}, respectively.

3. Results and discussion

3.1. Biological treatment

A batch control test of chlorophenols with only aeration confirmed no degradation results. Table 1 summarises the results of the biological, photocatalytic and combined treatments of each chlorophenol (100 mg L^{-1}). Each chlorophenol solution flowed into the bioreactor at various flow rates, and residence time was estimated by dividing the volume of the chlorophenol solution (40 L) in the two bioreactors by the flow rate. The chlorophenols exponentially decreased with increasing the residence time (or decreasing the flow rate). The removal was in the order of 2-CP > 2,4-DCP > 2,4,5-TCP > PCP (Fig. 2). In these results, 2-CP and 2,4-DCP were rapidly degraded, while 2,4,5-TCP was slowly, and PCP was very slowly degraded. It has been known that the biodegradation rates of chlorophenols decrease with the increasing number of chlorine atoms [2]. 2-CP, 4-CP, 2,4-DCP, 2,6-DCP, and 2,4,6-TCP were each rapidly degraded, while 3-CP, 3,4-DCP, 2,4,5-TCP, and PCP were each very slowly degraded aerobically by microorganisms [16]. A long time was required for the degradation of PCP, which is in accordance with the reports [2,16,35]. Therefore, the removal of chlorophenols was lower in the mixture (each: 25, total 100 mg L^{-1}) due to the inhibition effects of 2,4,5-TCP and PCP (Table 2). The removal order of 2-CP > 2,4-DCP > 2,4,5-TCP > PCP was also observed in the mixture of chlorophenols (Fig. 3) [34]. On the other hand, the removal order of 2-CP > 4-CP > 2,4-DCP ≅ 2,4,6-TCP was reported in the mixture containing no PCP [18].

The peaks of biodegradation products were confirmed by HPLC analysis. However, it was very difficult to determine the products. Therefore, the kind of biodegradation products and the degradation pathway were not identified. The aerobically degradation pathway of chlorophenols has been commonly known to form chlorocatechols and chlorinated hydroquinones, which subsequently undergo ring cleavage [2,36]. An attempt was conducted

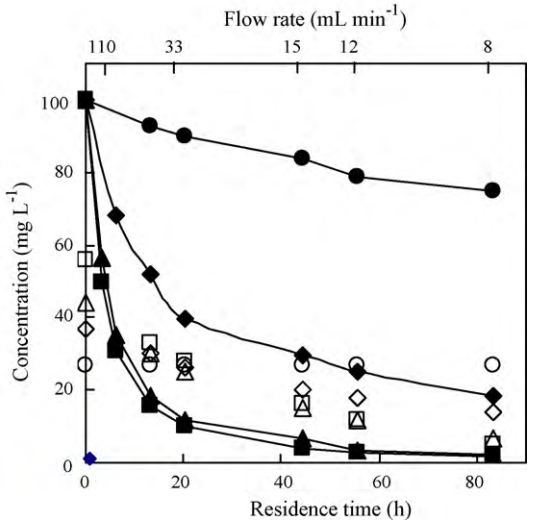

Fig. 2. Biological degradation of each 2-CP (■; TOC (□)), 2,4-DCP (▲; TOC (△)), 2,4,5-TCP (♦; TOC (◊)), and PCP (●; TOC (○)) at the initial concentrations of 100 mg L^{-1}.

to follow the fate of degradation products by using TOC analysis. The TOC mass balance was based on the assumption that the TOC measured in the samples was only due to the chlorophenols and their degradation products. The TOC measured in the bioreactor before the chlorophenol flowed into was around 0.1 mg L^{-1}. Therefore, other TOC contributions from the nutrient, microorganisms, or products released during microbial growth can be neglected. The decrease in TOC of each chlorophenol has not been reported previously [34]. The TOC of the remained chlorophenol in both mixture and each was a little greater than the theoretically calculated TOC (Figs. 2 and 3). The TOC measured in the degradation of 2,4,5-TCP at flow rate of 8 mL min^{-1} was 13.8 mg L^{-1} (Fig. 2), while the remained 2,4,5-TCP was 18 mg L^{-1} (equals to the theoretical TOC of 6.6 mg L^{-1}). Then, the TOC of the degradation products is 7.2 mg L^{-1}. A more time or lower flow rate is required to mineralize the remained 2,4,5-TCP and the biodegradation products.

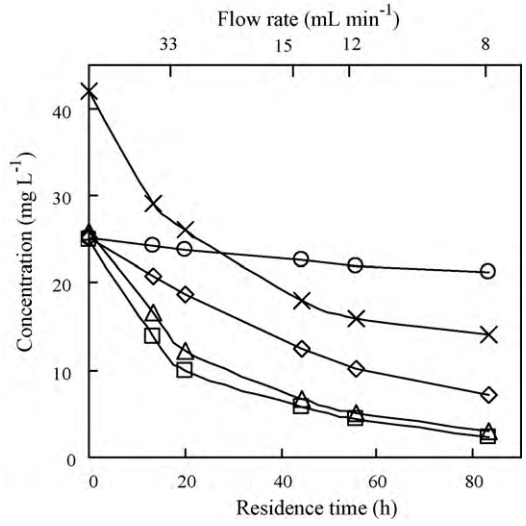

Fig. 3. Biological degradation of the mixture of 2-CP (□), 2,4-DCP (△), 2,4,5-TCP (◊), and PCP (○), and TOC (×) at concentration of 100 mg L^{-1} (each 25 mg L^{-1}).

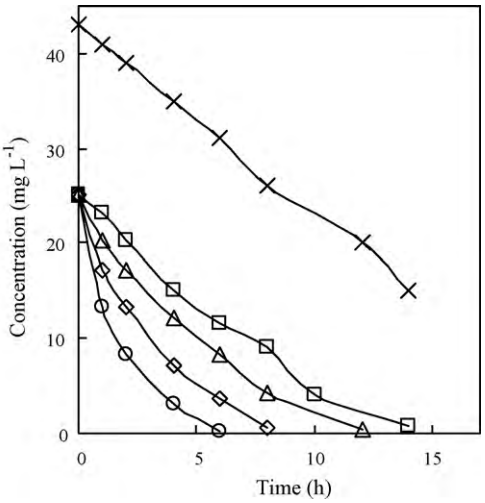

Fig. 4. Photocatalytic degradation of the mixture of 2-CP (□), 2,4-DCP (△), 2,4,5-TCP (◊), and PCP (○), and TOC (×) at concentration of 100 mg L^{-1} (800 mL, each 25 mg L^{-1}), circulative flow rate of 600 mL min^{-1} and TiO_2 of 0.50 g L^{-1} with black light irradiation.

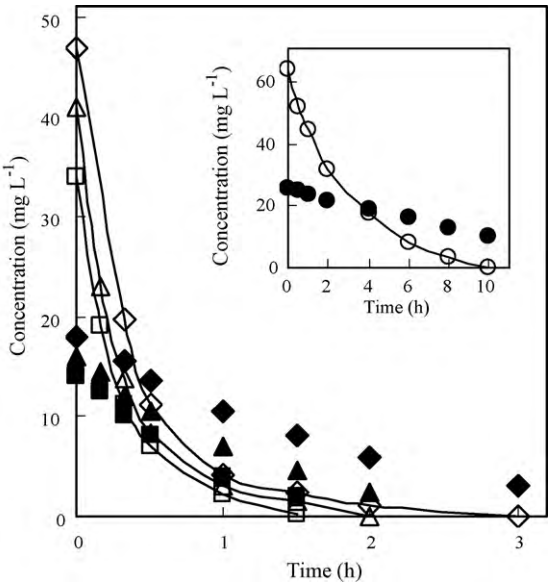

Fig. 5. Photocatalytic degradation of the biologically treated CPs mixture at flow rates of 33 (CPs (○); TOC (●)), 15 (CPs (◊); TOC (♦)), 12 (CPs (△); TOC (▲)) and 8 mL min^{-1} (CPs (□); TOC (■)).

3.2. Photocatalytic treatment

The results of the photocatalytic degradation of each chlorophenol (100 mg L^{-1}, 800 mL) under black light irradiation at the circulative flow rate of 600 mL min^{-1} were summarized in Table 1. The circulative flow rate of 600 mL min^{-1} was found to be the optimum when the tubular photoreactor was used [34]. The results indicated that the removals were in the order of PCP > 2,4,5-TCP > 2,4-DCP > 2-CP. The same order was also observed for the removals of the mixture chlorophenols (Fig. 4). The PCP was rapidly degraded, while 2-CP and 2,4-DCP were slowly degraded. Essam et al. [3] reported the removals of the chlorophenols mixture were in the order of PCP > 2,4,6-TCP > 2,4-DCP > 4-CP. Besides, each chlorophenol was removed in the same order of PCP > 2,4,6-TCP > 2,4-DCP > 4-CP ≅ 2-CP [37]. On the other hand, the photocatalytic degradation of chlorophenols can generate the formation of biodegradable compounds such as chlorinated catechols, chlorinated benzoquinones and chlorinated hydroquinones [8,14,37] as well as those of biorecalcitrant compounds such as chlorinated hydroxybiphenyls, hydroxylated and chlorinated dimmers [14,15]. In this study, TOC mass balance analysis indicated the formation of photocatalytic degradation products. The TOC measured in the photocatalytic degradation of 2,4,5-TCP was 9.1 mg L^{-1} (Table 1), while the remained 2,4,5-TCP was 20 mg L^{-1} (equals to the theoretical TOC of 7.3 mg L^{-1}). Hence, the TOC of the degradation products is 1.8 mg L^{-1}. In the photocatalytic degradation of the chlorophenols mixture (Fig. 4), all chlorophenols were removed after 14 h but the TOC was still remained (15 mg L^{-1}). A more time is required for the TOC removal.

The photocatalytic treatment was conducted in batch circulative treatment of 800 mL solution. If we compare with the biological treatment that worked at 40 L solution, the photocatalytic treatment of the chlorophenols mixture needs 50 times of 14 h irradiation time. That means both the photocatalytic treatment and the biological treatment require a long time for high loading chlorophenols mixture. The light intensity of black light is always same in all experiment. If the treated solution increases, a ratio of TiO_2 which are not irradiated is increased [25]. Therefore, a more long time is required for the photocatalytic treatment of 40 L solution in one time.

3.3. Combined treatment of each chlorophenols

The removal of PCP was easy in the photocatalytic treatment, whereas the removal was difficult in the biological treatment. The removals of 2-CP and 2,4-DCP were easy in the biological treatment, whereas they were more difficult than 2,4,5-TCP in the photocatalytic treatment. These results indicated that the combined treatment is not required for the removals of 2-CP, 2,4-DCP or PCP. However, the combined treatment may be required for the removal of 2,4,5-TCP. In the relatively same removal percentage (Table 1), removed TCP per hour in the biological treatment was 39.4 mg h^{-1}, whereas in the photocatalytic treatment was 10.7 mg h^{-1}. However, the TOC removal in the biological treatment was lower than in the photocatalytic treatment. The combined treatments increased the TOC removal of 2,4,5-TCP. The combined biological–photocatalytic treatment was better than the combined photocatalytic–biological treatment in the removal of 2,4,5-TCP. The photocatalytic treatment of biologically treated 2,4,5-TCP after the biological treatment at flow rate 33 mL min^{-1} was the best.

3.4. Combined biological–photocatalytic treatment of chlorophenols mixture

Both the photocatalytic and the biological treatments were time-consuming to mineralize the mixture of chlorophenols (Figs. 3 and 4). Hence, the combined treatment was necessary. The photocatalytic treatments of biologically treated chlorophenols mixture were conducted after the biological treatment at each flow rates of 33, 15, 12, and 8 mL min^{-1} (Fig. 5). After the 33 mL min^{-1} biological treatment, the remained chlorophenols mixture of 64 mg L^{-1} was completely removed in 10 h by the photocatalytic treatment. The remained chlorophenols mixture decreases with the decreasing flow rate or the increasing biological treatment time, then resulting in decreasing photocatalytic treatment time.

For completely chlorophenols removal, the removed chlorophenols amounts in the combined treatments (Figs. 3 and 5) at 33, 15, 12, and 8 mL min^{-1} biological treatment were 7.6, 20.6, 25.8, and 25.1 mg h^{-1}, respectively. The 12 mL min^{-1} biological treatment followed by photocatalytic treatment was the best combined

treatment, which required the shortest time for mineralization of chlorophenols mixture. Around 83% of 2-CP, 80% of 2,4-DCP, 60% of 2,4,5-TCP and 13% of PCP were removed by the biological treatment at the flow rate of 12 mL min^{-1} and the remained chlorophenols were completely removed by the subsequent photocatalytic treatment (Table 2). Meanwhile, 95% of TOC was removed in the combined biological–photocatalytic treatment.

3.5. Combined photocatalytic–biological treatment of chlorophenols mixture

The combined photocatalytic- biological treatment of mixture chlorophenols was also evaluated. The PCP should be removed completely in the photocatalytic treatment, due to the inhibition effect of PCP to the microorganism activity. As shown in Fig. 4, the combined photocatalytic–biological treatment was better conducted after 6 h photocatalytic treatment (when PCP was completely removed). However, the removed chlorophenols per hour (10.5 mg h^{-1}) was lower than those in the combined biological–photocatalytic treatment (Table 2). When the photocatalytic treatment was conducted in a short time, the subsequent biological treatment required a long time due to the inhibition effect of the biorecalcitrant PCP. Besides, the photocatalytic treatment of chlorophenols generates biorecalcitrant products [14,15], which is difficult to be decomposed in the subsequent biological treatment. It was reported that the biological treatment was able to remove only a fraction of the photocatalytic product [3]. Therefore, it will be necessary to prolong the time of photocatalytic treatment in the photocatalytic treatment combined with subsequent biological treatment.

Around 54% of 2-CP, 67% of 2,4-DCP, 86% of 2,4,5-TCP, and 99% of PCP were removed by the photocatalytic treatment and the remained chlorophenols were completely removed by the subsequent biological treatment. The TOC removal in the combined photocatalytic–biological treatment (77%) was lower than those in the combined biological–photocatalytic treatment (95%). Therefore, the combined biological–photocatalytic treatment was better than the combined photocatalytic–biological treatment in the mineralization of chlorophenols mixture.

3.6. Sunlight irradiation

To save electric energy of the black light, the sunlight was used as a light source for the photocatalytic treatment. The combined biological–photocatalytic treatment can be more economic when using sunlight irradiation in the photocatalytic treatment. Most sunlight irradiation impinging on the earth surface are in visible wavelengths (400–700 nm), but few are infrared (above 700 nm) and ultraviolet (under 400 nm) wavelengths. Only a relative small part (less than 5%) of the sunlight spectrum can be used by TiO_2 (in UV wavelength) for the photocatalytic treatment [11], but as the energy source is so cheap and abundant. On the other hand, the wavelength of the black light lamp is in the range of 315–400 nm. Fig. 6 shows TOC changes by sunlight and black light irradiations in the photocatalytic degradation of biologically treated chlorophenols mixture flowed at the rate of 15 mL min^{-1}. The removal of TOC under sunlight was slightly faster than those under black light irradiation due to a slightly higher intensity of sunlight than that of black light. Similar results were also achieved for the removal of the chlorophenols mixture. Therefore, we can use sunlight in sunny day and black light in cloudy and rainy days by turns for the photocatalytic treatment.

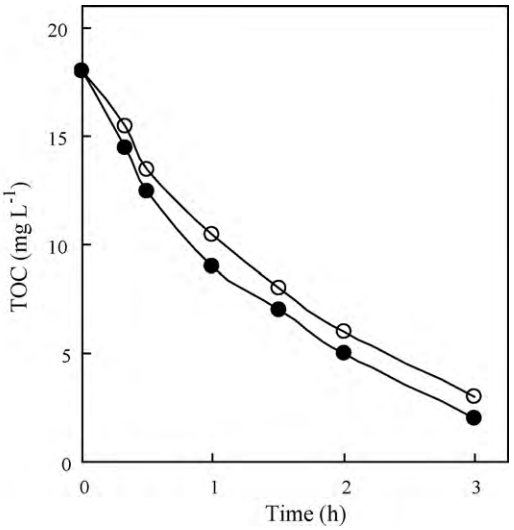

Fig. 6. TOC changes by sunlight (●) and black light (○) irradiations in the photocatalytic degradation of biologically treated CPs mixture at circulation flow rate of 600 mL min^{-1} and TiO_2 of 0.50 g L^{-1}.

3.7. Separation and reuse of TiO_2

It was required to separate TiO_2 particles after the photocatalytic treatment [29–33]. In this study, fortunately, the TiO_2 particles were rapidly sedimented by only standing the TiO_2 suspension. Fig. 7 shows the sedimentation of TiO_2 after photocatalytic treatment when tap and deionized waters were used as original water. After 6 h, the transmittance of the supernatant solution was 98%, which was clear enough to flow out. This is due to the coagulation caused by the electrolytes in the tap water of pH 7, which is near to the isoelectric point of TiO_2 (6.4–6.6) [38]. At pH 7, since the TiO_2 particle surface is occupied by dominant neutral groups (TiOH), and a little amount of charged species ($TiO^- > TiOH_2^+$), electrostatic repulsion among the TiO_2 particles decreases. Electrolytes in the tap water neutralize the charged species and decrease the thickness of the electrochemical double layer of the particles, resulting in the least repulsion among the particles and promote coagulation [39].

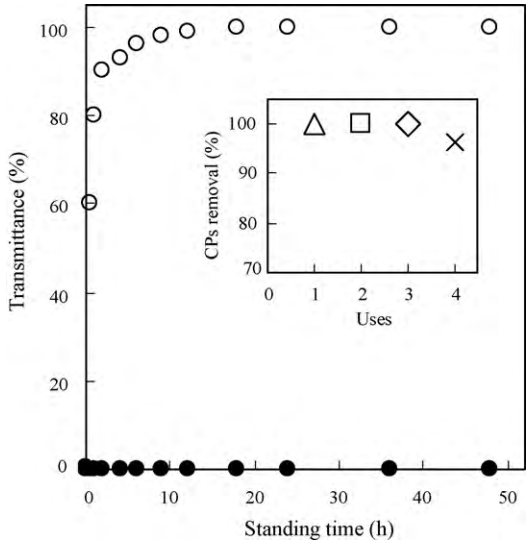

Fig. 7. Transmittance of water on 48 h standing the suspension of TiO_2 (0.50 g L^{-1}) after the photocatalytic degradation of CPs mixture in tap water (○) and deionized water (●), and CPs mixture removal at 1st (△), 2nd (□), 3rd (◊) and 4th (×) uses of TiO_2 particles.

The sedimented TiO_2 particles were recovered with valve 7 open, and reused at least three times without significantly decreasing the removal efficiency (Fig. 7). Furthermore, the used TiO_2 particles were replaced with the fresh one.

4. Conclusion

The combined biological–photocatalytic treatment integrated with reuse of TiO_2 seems to be suitable for the mineralization of high loading chlorophenols and the effective use of TiO_2 particles. The combined biological–photocatalytic treatment was better than the combined photocatalytic–biological treatment, and effective to decompose the mixture of biodegradable and biorecalcitrant chlorophenols. The combined biological–photocatalytic treatment significantly shortened the degradation and mineralization time of the mixture of chlorophenols. The removal of PCP was easy in the photocatalytic treatment. The removals of 2-CP and 2,4-DCP were easy in the biological treatment. The combined treatment was required for the removal of 2,4,5-TCP. Sunlight irradiation was successfully used and saving of electrical energy of black light was possible. After photocatalytic treatment, the TiO_2 particles were spontaneously sedimented in the separation tank. The combined system can be operated by integrating with the TiO_2 separation and reuse.

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