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Comparison study of dyestuff wastewater treatment by the coupled photocatalytic oxidation and biofilm process

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Abstract

Degradation of Rhodamine B (RhB) and COD by means of the coupled photocatalytic oxidation (PCO) and biofilm systems has been studied. The coupled PCO-biofilm systems were divided into two operation systems. The one (R1) consisted of a pre-PCO and a post-biofilm reactor system and the other (R2) was a pre-biofilm and a post-PCO reactor system. In a batch experiment, the order of initial decolorization rate was photocatalytic oxidation > adsorption > photolysis. The color removal rate of RhB was decreased with an increase of the initial COD concentration. In a continuous experimental study, almost all color was removed in the PCO reactor. During 180 days, the color and COD removal efficiencies in the R2 (pre-biofilm + post-PCO) system were higher than those in the R1 (pre-PCO + post-biofilm) system. In our experimental ranges, the PCO process was superior to Fenton oxidation in the color and COD removal.

Keywords: Photocalytic reactor; Biofilm reactor; Dye; Color removal; COD removal

1. Introduction

Dyes are the colored organic compounds that represent an increasing environmental danger. During textile dyeing and finishing processes a large amount of effluent with high organic strength and colors can be introduced into aquatic systems.

Biological treatment of wastewater is often the most economical alternative when compared to other treatment options. In general, conventional aerobic biological treatment processes do not treat dye wastewater effectively because of the large degree of aromatics present in the molecules and the stability of modern dyes and results in problems of sludge bulking, rising sludge and pin point floc formation [1–3].

An advanced oxidation processes (AOP) have been used to enhance the biotreatability of wastewaters containing various and non-biodegradable organics such as dyestuffs by generating hydroxyl radicals (OH) as a powerful oxidizing species. Among the various AOPs, photocatalytic oxidation (PCO) has proven effective in degrading several dyestuffs.

PCO can be used to destroy dye compounds using semiconductors such as the anatase form titanium dioxide and UV light irradiation [4].

Although TiO_2 sensitized PCO has been intensively studied and proved to be capable of oxidizing most organics, the separation of TiO_2 after photo oxidation is the main problem [5]. TiO_2 can be immobilizing some media for ease separation from water after PCO; however, it was also found that the reaction rate in a suspension system was about three to five times faster than that in an immobilized system.

Also, one of the major drawbacks of AOPs is that their operational costs are relatively high compared to those of the biological treatment process and complete mineralization needs prolonged irradiation causing a great obstacle for the application of photocatalytic degradation in the wastewater treatment. Therefore, the photocatalysis process has been proposed as a useful pre- or post-treatment for biological treatment [6]. A promising alternative to complete oxidation of biorecalcitrant wastewaters is the use of an AOP as a pretreatment step to convert initially biorecalcitrant com-

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pounds to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biomass and water. More recently, very interesting coupled systems have been proposed to treat several kinds of industrial wastewaters: upflow anaerobic sludge blanket (UASB) pretreatment followed by H_2O_2 and/or ozonation, Fenton's reagent (aerobic biological treatment), or ozonation (biological treatment) [7].

In our group, special attention has been given for combining the PCO and biofilm processes to degrade dyestuff wastewater. Two kinds of combined systems are developed in all cases: the one is the immobilized TiO_2 system followed by the aerobic biofilm process and the other is the aerobic biofilm process followed by the immobilized TiO_2 system. The main aim of this study is to propose a general strategy that can be used to develop a combined PCO and biological process for dyestuff wastewater treatment using batch experiments and continuous experiments for 180 days.

2. Materials and methods

2.1. Materials

The dye, Rhodamine B (RhB, reagent grade, 95% pure), was used as a test pollutant. RhB consists of green crystals or reddish-violet powder and the molecular formula is $C_{28}H_{31}CN_2O_3$ (mol. wt. 479.00). It is highly soluble in water and its color is fluorescent bluish-red. RhB has been found to be potentially toxic and carcinogenic and this compound is now banned from use in food and cosmetics [8]. The photocatalyst employed in this study was Degussa P-25 TiO_2 powder of which the particle size is 30 nm containing 70% anatase and 30% rutile. Its BET surface area is 50 m^2/g.

2.2. Preparation of immobilized photocatalyst

Immobilized TiO_2 was formulated by a procedure described earlier [9]. Immobilized TiO_2 was formulated as follows: (1) Degussa P-25 TiO_2 powder was mixed well with oxime type silicone sealant (TiO_2 weight percentage: 15.0%), (2) putting the mixture of silicone sealant and TiO_2 powder on a glass slide, spreading the mixture like a film, (3) drying for 24 h at room temperature, (4) cutting the film (length, 1–3 mm; width 1–3 mm; thickness, 0.5–2 mm).

2.3. Batch photocatalytic experiment

Immobilized TiO_2 (87.0 g/l) was put into a photocatalytic reactor (reactor volume, 1.75 l). In order to mix the immobilized TiO_2, air was introduced for 5 l/min. Batch experiments consisted of three parts. The first batch experiment was conducted to compare the performance of the adsorption, UV and photocatalytic oxidation at RhB concentration 2.5, 5, 10 and 15 mg/l. Adsorption was conducted by using a jar-tester at 200 rpm in a dark condition. The second experiment was conducted to determine the effect of the initial RhB concentration on the RhB decolorization and COD removal efficiency at a constant COD concentration of 200 mg/l (RhB concentration, 0, 2.5, 5, 10, 15 and 20 mg/l,). The last experiment was done to determine the effect of the initial COD concentration on the decolorization of RhB and COD removal efficiency at a constant RhB concentration 15 mg/l (COD concentration, 0, 200, 400 and 800 mg/l). All experiments were conducted with the pH 7 and 20 ± 1 °C. All batch experiments were conducted three times and mean values were showed.

2.4. PCO reactor and biofilm reactor

The reactor systems consisted of a PCO reactor and a biofilm reactor (Fig. 1). The systems were divided into two systems by the sequence of reactor arrangement. The R1 system used a PCO reactor as a pretreatment followed by a biofilm reactor. In the R2 system, a biofilm reactor was installed before a PCO reactor. The detailed dimensions of reactor systems are shown in Table 1. A biofilm reactor and PCO reactor were made of acrylic sheet and glass, respectively. An air-distribution device was installed in the lower part of PCO reactor for the fluidization of the immobilized TiO_2 and air was controlled by a rotameter. A 32 W UV lamp (G30T5VH, Lighttech), which basically emits 254 nm, was used as an artificial light source. The intensity of the incident light was 3.6 mW/cm^2. The optimum amount of the immobilized TiO_2 in the reactor known as 87.0 g/l in a previous study [9] was put into the PCO reactor.

An air diffuser was installed in the center of the biofilm reactor. The support media were web-type polypropylene (Fig. 2). The seeding sludge was the recycled sludge in paper manufacturing wastewater treatment system and the synthetic wastewater (Table 2) was fed to the biofilm reactor after seeding.

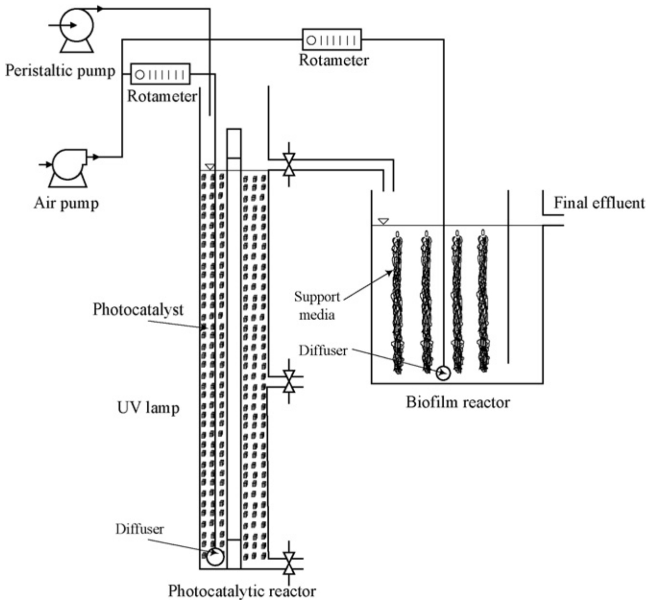

Fig. 1. Schematic diagram of photocatalytic oxidation and biofilm reactor system (basis: R1 system).

Table 1
Dimensions of reactor system

	Reactor system			
	R1 (PCO-biofilm)		R2 (Biofilm-PCO)	
	R1-1	R1-2	R2-1	R2-2
Volume (l)	1.75	5.73	5.73	1.75
Area of support media at biofilm reactor (m^2)	–	0.228	0.228	–
Volume fraction of media at biofilm reactor (%)	–	19.9	19.9	–

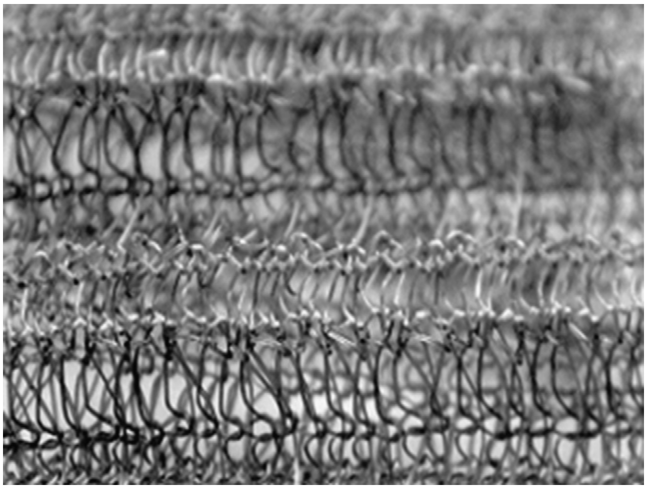

Fig. 2. Photograph of the support media of web-type.

2.5. Biofilm formation and continuous experiment

The COD_{cr} of influent synthetic wastewater was 200 mg/l and the hydraulic retention time (HRT) was maintained for 8 h. The overall organic loading rate was 0.6 kg COD/(m^3 day). After 20 days, the formed biofilm was not detached from the media and RhB of 2.5 mg/l was fed to the biofilm reactor for 3–4 days interval in order to ensure acclimation to RhB.

After the biofilm formation and RhB acclimation periods for 2 months, HRT based on the biofilm reactor such as R1-2 and R2-1 was maintained for 32 h (R1-1, 9.8 h; R1-2, 32 h; R2-1, 32 h; R2-2 9.8 h) and the synthetic wastewater of COD 200 mg/l containing RhB (2.5 mg/l) was flown into the first reactor of R1 and R2 system. HRT was changed when the color and COD concentration in the biofilm reactor reached a steady state. All experiments were conducted with the pH 7 and 20 ± 1 °C.

Table 2
Compositions of synthetic wastewater (unit: mg/l)

Item	Concentration
Glucose	200
Urea	50
$NaHPO_4$	50
NaCl	15
KCl	7
$MgSO_4$	7
Rhodamine B	2.5

2.6. Fenton's oxidation experiment

Fenton's oxidation experiment was conducted in order to compare the performance of immobilized photocatalytic oxidation system. At the steady state of HRT 4 h, the effluent pH of biofilm reactor (R2-1) was controlled to pH 3 using H_2SO_4, which was known as the optimum pH in Fenton's oxidation. After the Fenton's oxidation experiment was done, the pH was adjusted to 7 again, using NaOH solution [10]. All experiments were conducted three times and mean values were showed.

2.7. Measurement and analysis

The color of RhB was measured using the absorbance of 30 wavelengths by UV–vis spectrophotometer (UV-1201, Shimadzu) and it was shown as ADMI (American dye manufactures Institute) color using the Adams–Nickerson color difference formula [11]. The COD measurement followed the procedures described in the Standard Methods [12].

3. Results and discussion

3.1. Batch experiments

Fig. 3 shows the decrease of color with different initial RhB concentrations using UV irradiation, adsorption and photocatalytic oxidation (immobilized TiO_2 + UV irradiation). The adsorption onto the inside of reactor was neglected. The initial decolorization rate was calculated using the data during the first 30 min and are shown in Fig. 3 and listed in Table 3 [13]. As shown in Fig. 3 and Table 3, the initial decolorization rate was increased with the increase of initial RhB concentration. The rate increase of photocatalytic oxidation is the highest among the three decolorization mechanisms (adsorption, photolysis, photocatalytic oxidation).

It is obvious that the order of color removal rate is photocatalytic oxidation > adsorption > photolysis at the three decolorization activities [13]. The fast decolorization of RhB occurred in the presence of both photocatalyst and UV irradiation. Bhatkhande et al. [14] reported that when the adsorption of nitrobenzene on the TiO_2 surface is the greatest, the photocatalytic degradation is effectively the highest and a large decrease in the concentration is observed at the beginning of the photocatalytic degradation experiments. Zhu et al. [15] reported that the most important factor among the supports for TiO_2 is the adsorption ability. Judging from the above reports and results,

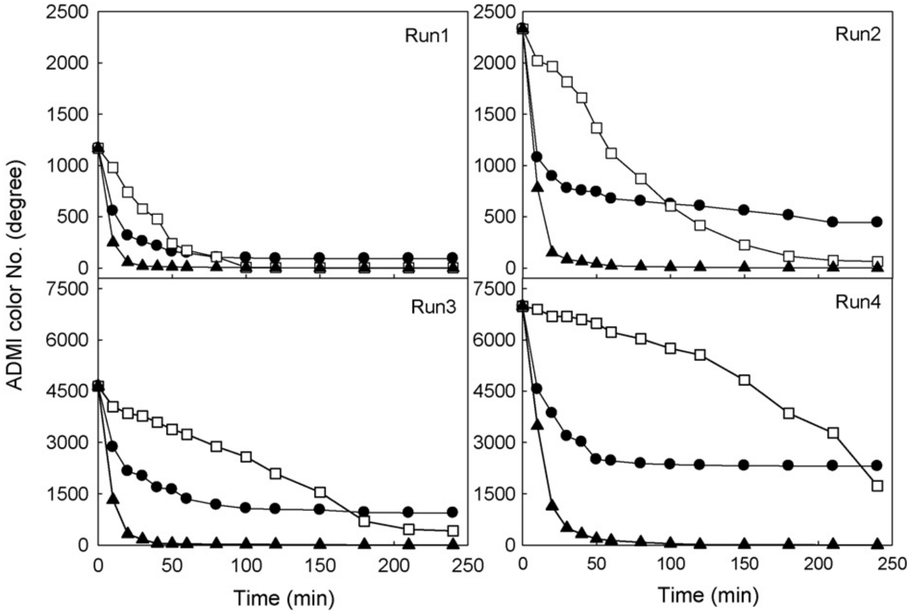

Fig. 3. Effect of initial RhB color on the RhB decolorization. (●) Adsorption, (☐) UV irradiation, (▲) immobilized TiO_2 + UV irradiation Run1, initial ADMI color No. 1167 (RhB concentration, 2.5 mg/l); Run2, initial ADMI color No. 2330 (RhB concentration, 5 mg/l); Run3, initial ADMI color No. 4645 (RhB concentration, 10 mg/l); Run4, initial ADMI color No. 6982 (RhB concentration, 15 mg/l).

the adsorption onto the immobilized TiO_2 may be an important factor in RhB photocatalytic decolorization and assisted the photocatalytic oxidation by an increase of light penetration [16]. We had already reported that the immobilized TiO_2 had high adsorption ability and the decolorization of the immobilized TiO_2 was higher than that of the powdered TiO_2 [13,16].

Based on the COD 200 mg/l, the variation of color and COD by the variation of RhB concentration as 0, 2.5 (ADMI color No., 1167°), 5 (ADMI color No., 2230°), 10 (ADMI color No., 4645°), 15 (ADMI color No., 6982°) and 20 mg/l (ADMI color No., 9312°) were observed and shown in Fig. 4. According to Fig. 4(a), almost all color was removed within 100 min even though the high RhB color of 9312° (RhB concentration, 20 mg/l). Therefore, the color removal ability of the photocatalytic reactor was shown as high. When only COD of 200 mg/l were supplied as shown in Fig. 4(b), the COD concentration was shown as 24 mg/l after 240 min. The COD removal rate was low at the initial reaction state when the RhB concentration was 20 mg/l, however, the COD removal rate increased at 100 min when the color removal was completed. Comparing the color and COD removal, the color removal was relatively faster than the COD removal. It indicates that, in general, the decolorization rate of the RhB solution was more rapid than the mineralization rate of the COD removal. The latter will take a longer time for further oxidation [17].

The effect of COD concentrations on the RhB color removal was observed at the RhB concentration of 15 mg/l (Fig. 5). The initial decolorization rate was decreased by the increase of the initial COD concentration (Fig. 5(a)). The COD removal rate was decreased by the increase of initial COD concentration (Fig. 5(b)). In the report of Quan et al. [18], the increase of organic and inorganic concentration inhibited the photocatalytic degradation rate of lindane (γ-hexachlorocyclo hexane). Also, Rincon and Pulgarin [19] reported that photo disinfection of *Escherichia coli* was greatly inhibited by the organic matters. Shifu and Gengyu [20] reported that adding the organic compounds into reaction solution, the conversion of nitrate decreases rapidly and organic compounds are effectively trapped matter of $^{\bullet}OH$ radicals, when there are organic compounds in the reaction solution, the organic compounds compete with the nitrate for the $^{\bullet}OH$ radicals, so that through the addition of organic compounds, the photocatalytic oxidation of nitrate is inhibited. Therefore, we can see that the initial COD concentration in the solution affected the color removal rate.

Table 3
Initial decolorization rate of RhB (°/min)

	Rate			
	Run1	Run2	Run3	Run4
UV irradiation only	17.0	19.1	19.6	22.1
Adsorption by immobilized TiO_2	30.2	54.3	87.6	126.5
Immobilized TiO_2 + UV irradiation	38.3	74.9	149.3	216.1

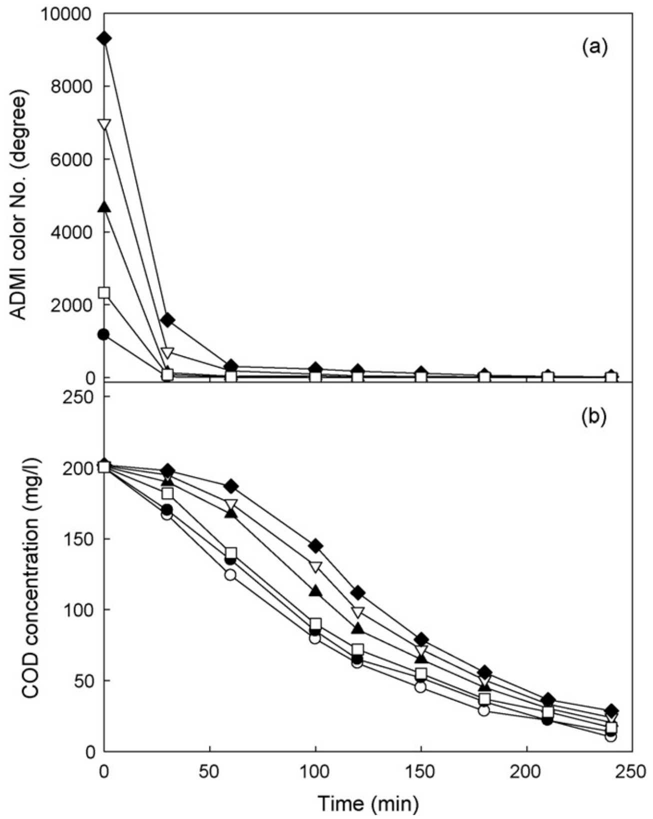

Fig. 4. Effect of initial RhB color on the RhB decolorization (a) and COD removal (b). (a) Color removal and (b) COD removal. Initial COD concentration, 200 mg/l; (◯) ADMI color No. 0 (RhB concentration, 0 mg/l), (●) ADMI color No. 1167 (RhB concentration, 2.5 mg/l), (□) ADMI color No. 2330 (RhB concentration, 5 mg/l), (▲) ADMI color No. 4645 (RhB concentration, 10 mg/l), (□) ADMI color No. 6982 (RhB concentration, 15 mg/l), (□) ADMI color No. 9312 (RhB concentration, 20 mg/l).

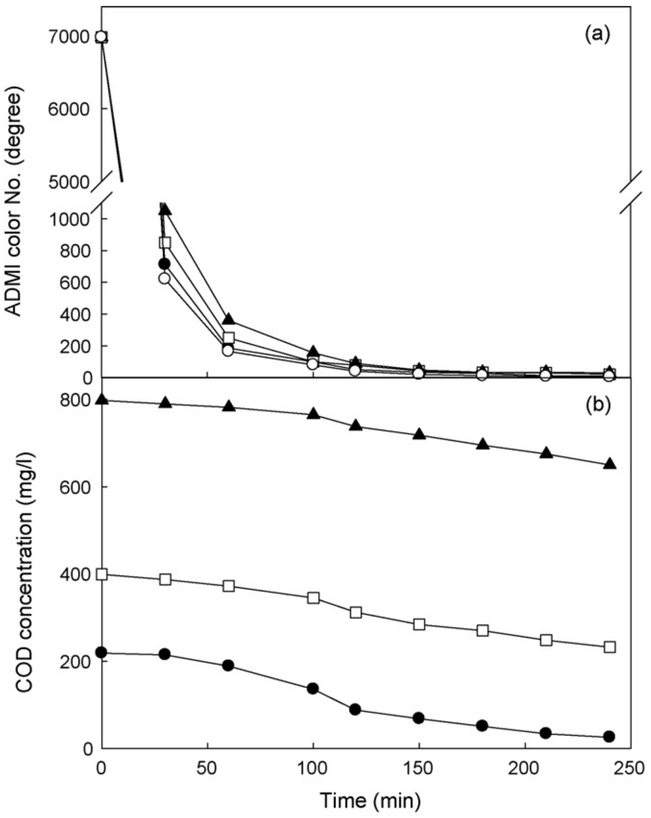

Fig. 5. Effect of initial COD concentration on the RhB decolorization (a) and COD removal (b). Initial ADMI color No. 6982 (RhB concentration, 15 mg/l), COD concentration (◯) 0 mg/l, (●) 200 mg/l, (□) 400 mg/l, (▲) 800 mg/l.

3.2. Continuous experiment

The variations of HRT in R1 and R2 systems are shown in Table 4. In continuous experiments, the influent and effluent ADMI colors of each reactor in R1 and R2 systems were shown in Fig. 6. The influent ADMI color was in the range of 1210–1245°. In the R1 system (PCO + biofilm), at the case of R1-1, almost all color was removed and the color was shown as 22–25° at a steady state until stage C and the remaining color was removed to 5–6° at R1-2 (Fig. 6(a)). As the HRT in the biofilm reactor decreased to 8 h (PCO reactor, 2.4 h), the color was shown in the effluent of post-biofilm reactor. And it was shown as 160–180° when the HRT was 4 h (PCO reactor, 1.2 h). At this point, the effluent color was 50–60° at the pre-PCO reactor; however, it increased to 160–180° at the post-biofilm reactor. We can see that the color was apparently removed by the breakdown of chromophore at the pre-PCO reactor; the incomplete broken down RhB was reorganized and formed the color in the post-biofilm reactor even though the reason was not distinct yet.

In pre-PCO and post-biofilm reactor systems, the limiting HRT of the pre-PCO reactor and the biofilm reactor should be higher than 2.4 and 8 h, respectively, in order to satisfy the water standard at clean area in Korea [21].

The effluent ADMI colors of the pre-biofilm reactor and the post-PCO reactor in the R2 were shown in Fig. 6(b). In the pre-biofilm reactor, the color was shown as about 860° and the color removal efficiency was 30.6% until HRT 12 h. However, the one was 1167° and the other was 5.8% after HRT 12 h, which showed that the color removal was limited in the pre-biofilm reactor. The effluent color at the post-PCO reactor was a little influenced by the effluent color at the pre-biofilm reactor at the high HRT condition and the effluent color at the post-PCO reactor increased as the HRT was decreased. The effluent color at the post-PCO reactor was about 30° at the stage E, which was much lower than that of the R1 system.

The absorbance of influent and effluent of each reactor at a steady state in HRT 1.2 was shown in Fig. 7. In the R1 system, in the case of the pre-PCO reactor, the peak was not noticeable at 554 nm, which was the peak wavelength of RhB. However, at the post-biofilm reactor, the peak appeared again at 554 nm. In the R2 system, the peak at 554 nm was high at the pre-biofilm reactor, but was not noticeable at the post-PCO reactor. Also, in this system, a new peak, which meant a color change, was not visible. The color removal of RhB was caused by the breakdown of chromophore, because a new peak was not shown [22]. Pulgarin et al. [23] reported that if the pre-treatment (photochemical) time in photochemical-biological treatment of *p*-NTS (*p*-nitrotoluene-*ortho*-sulfonic acid) is too short, the intermediates in the solution are still structurally close to the initial compound and the effi-

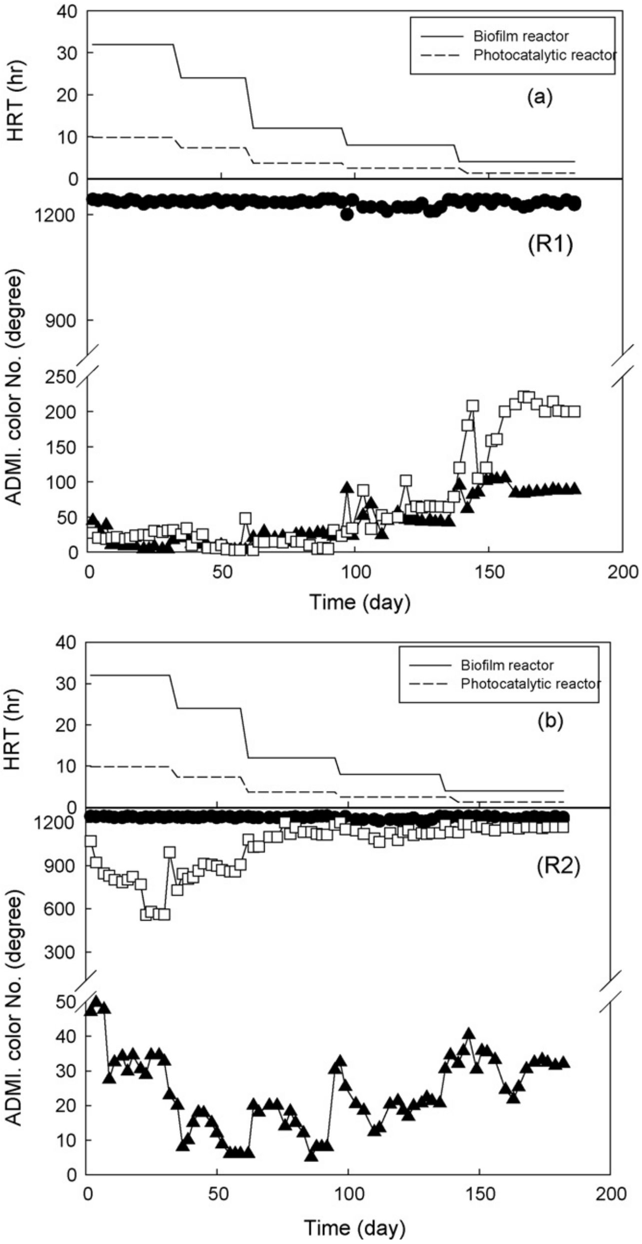

Fig. 6. Variation of color with operation time in R1 (a) and R2 (b) systems. (●) Influent, (☐) biofilm effluent, (▲) PCO effluent.

ciency of both the biological and the whole coupled process is dramatically diminished.

In the results in Fig. 7 and Pulgarin et al. [23], the untreated RhB was reorganized and the color was shown again at the post-biofilm reactor in the R1 system because of the short HRT of the pre-PCO reactor.

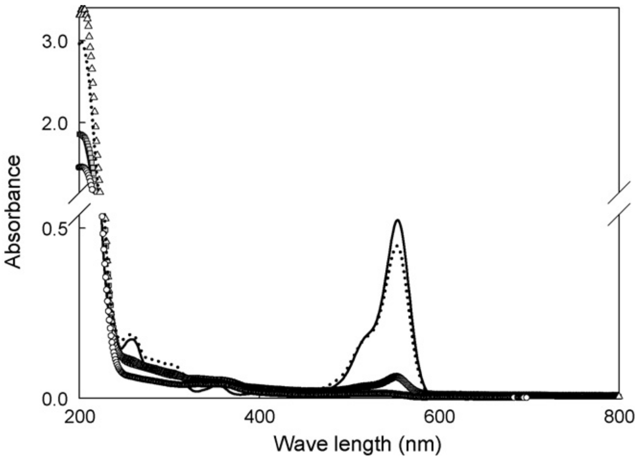

Fig. 7. Absorption spectrum of an influent and R1and R2 at HRT 1.2 h (basis: PCO reactor). (—) Influent, (▨) R1-1 (PCO), (☐) R1-2 (biofilm), (· · ·) R2-1 (biofilm), (◯) R2-2 (PCO).

3.3. COD removal

The variations of influent and effluent COD concentration in R1 and R2 systems were shown in Fig. 8. The influent COD was in the range of 204–216 mg/l. The effluent COD in the pre-POC reactor in the R1 system was low, below 20 mg/l at stage A, B and C, so the remaining COD to be treated at the post-biofilm reactor was very low. When the stage was turned to E (low HRT), the effluent COD of the pre-PCO reactor and the post-biofilm reactor increased to 64.5 and 14.3 mg/l, respectively, and the overall COD removal efficiency at this HRT was 93.3%. The COD value at this HRT was lower than the water standard; however, the color value was over the standard in Korea. The optimum operation condition should be determined by the color value, so it was D stage.

In the R2 system, the effluent COD concentration at the pre-biofilm reactor and post-PCO reactor were 33.4 and 17.5 mg/l at stage E, respectively. Comparing the COD removal in R1 and R2, most COD was removed at the pre-PCO reactor in the R1 system; however, the variation of COD removal was low in R2, except HRT 4 h. At stage E, the final effluent COD concentration in R1 was similar to that in R2; however, the R2 was superior to R1 in color removal.

In many other studies, in order to treat a recalcitrant material such as dye, atrazine and olive mill in solution, the AOP process was preferentially selected as a pretreatment process at the coupled system with biological process [7,24–26].

Reviewing the results in Figs. 6–8, when the loading of biodegradable organics were increased by the decrease of HRT, the preferential COD removal was necessary because

Table 4
HRT conditions in continuous experiments

HRT	Stage				
	A	B	C	D	E
Biofilm	32	24	12	8	4
PCO	9.8	7.3	3.7	2.4	1.2

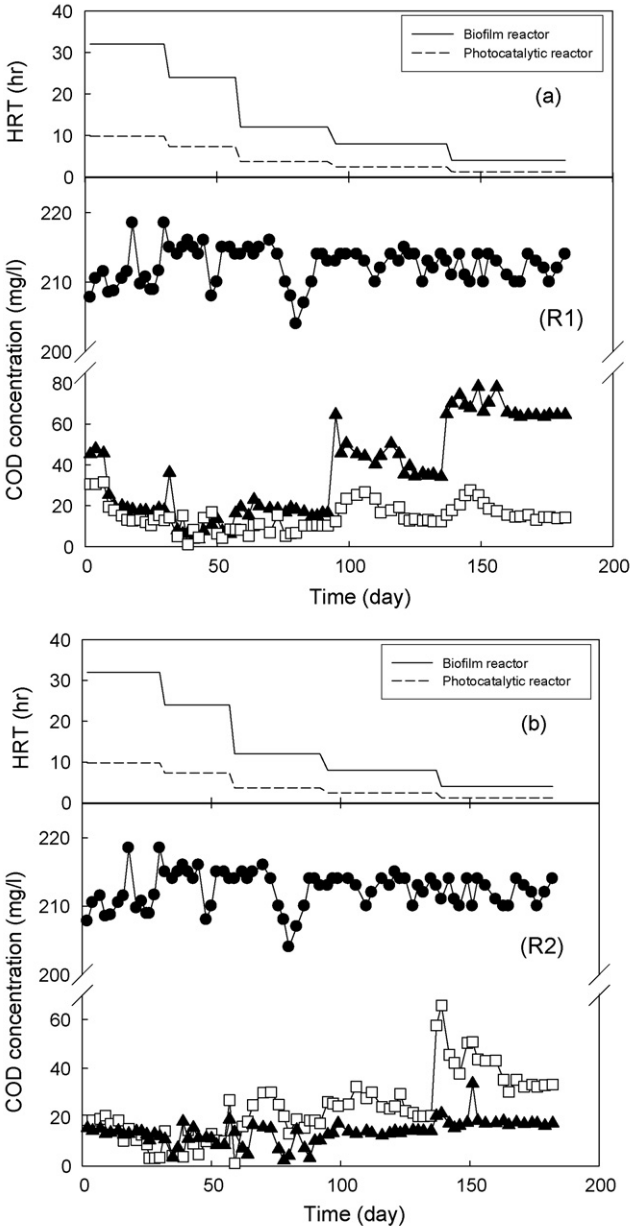

Fig. 8. Variation of COD with operation time in R1 (a) and R2 (b) systems. (●) Influent, (□) biofilm effluent, (▲) PCO effluent.

the COD concentration inhibited the color removal rate (Fig. 5). Therefore, the R2 system, using the biological process preferentially, was superior to the R1 system in the color removal.

3.4. Variation of UV_{254}

Most absorbance value occurring in the UV region of 200–400 nm has a close relation with the double-bond hydrocarbon and natural organic matter such as aromatic compounds and unsaturated aliphatic compounds, and it has been used as a parameter, which can substitute the dissolved organic carbon (DOC). And so, the absorbance value in UV_{254} has been used in determining the state variation of organic matter indirectly [27].

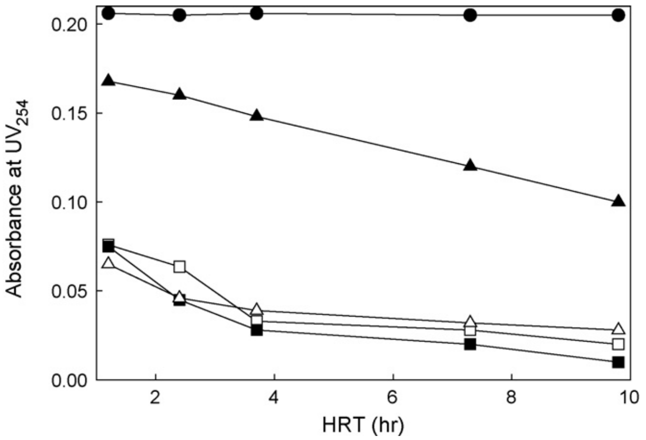

Fig. 9. Variance of UV_{254} in the influent and effluents at steady state (HRT basis: PCO reactor). (●) Influent, (□) R1-1, (■) R1-2, (▲), R2-1, (□), R2-2.

Based on the HRT of the PCO reactor, UV_{254} values of influent and effluent in each reactor were shown in Fig. 9. UV_{254} value in the influent was 0.205 and the UV_{254} values in the effluent were decreased by the increase of HRT. Especially, in the R1 system, the difference of UV_{254} values between the pre-PCO reactor and the post-biofilm reactor was not significant. However, in the R2 system, the difference between the pre-biofilm reactor and the post-PCO reactor was high. Therefore, we can assume that UV_{254} materials could not be degraded well in a biofilm reactor, irrespective of the order. At a higher HRT than 2.4, the UV_{254} values of final effluent in the R1 system were lower than those in the R2 system. However, at the low HRT of 1.2, the value in the R2 system was lower than that in the R1 system. Therefore, we can assume that the R1 system is more efficient for the removal of DOC at the high HRT (low loading rate), but the R2 system is efficient at a low HRT (high loading rate).

3.5. Fenton oxidation

The dyestuff wastewater in Korea has been treated mainly by the coagulation-activated sludge process and pure oxygen-activated sludge-Fenton oxidation process [28,29]. The activated sludge-coagulation process and their combination are widely used in textile wastewater treatment. However, the combination process is not sufficient in textile wastewater and sludge produced from both processes becomes more difficult to dispose [10]. A method of treating dye or textile wastewater with a hydrogen peroxide-ferrous ion system, known as Fenton's reagent, has been reported by many investigators. The Fenton reaction is known as a viable technique for the treatment of dye wastewater [30].

In order to investigate the oxidation ability of the PCO reactor, the Fenton oxidation process was compared using the effluent from the pre-biofilm reactor (R2-1, HRT 4 h) at a steady state. Fenton oxidation was conducted by varying $Fe_2SO_4 \cdot 7H_2O$ and H_2O_2 (30%) concentration at the optimum pH 3 and mixing rate of 250 rpm. The experiment conditions and the results of PCO and Fenton oxidation for the removal of color and COD are in

Table 5
Comparison between PCO and Fenton oxidation

	Raw wastewater	PCO	Fenton
H_2O_2 dosage (mmol)	–	–	12.5
$Fe_2SO_4 \cdot 7H_2O$ dosage (mmol)	–	–	0.0005
ADMI color No.	1167	32.1	48.1
COD (mg/l)	33.4	17.5	26.7

Table 5. All experiment results were lower than the allowing limit. And the experiment results of color and COD removal in the POC reactor were superior to any Fenton oxidation's results.

Arslan et al [31] reported that the initial reaction rate constant for decolorization and COD removal efficiency was shown as photo-Fenton > Fenton > UV/TiO_2 in AOP for Remazol Black B4. However, in Remazol Turquoise Blue G 133, the color removal and COD removal were in the order of photo-Fenton > Fenton > UV/TiO_2 and photo-Fenton ≧ UV/TiO_2 > Fenton, respectively. Also, Hsing et al [32] studied the AOP of Acid Orange 6 (AO6) and reported as follows: among the investigated AOPs, the ranking of AO6 decolorization was in the order of Fenton > $O_3/UV/TiO_2 \geqq O_3/UV > O_3 > UV/TiO_2 \geqq$ UV and the performance of AOPs on TOC removal was in the order of $O_3/UV/TiO_2 > O_3/UV >$ Fenton = $O_3 > UV/TiO_2 >$ UV.

Moreover, in the comparative study for the removal of 15 mg/l RhB [33], the order of RhB decolorization and COD removal were shown as photo-Fenton > $UV/TiO_2/H_2O_2$ > Fenton > $UV/H_2O_2 > UV/TiO_2$ and photo-Fenton > $UV/TiO_2/H_2O_2 > UV/TiO_2$ > Fenton > UV/H_2O_2, respectively.

Comparing these results with other researchers' results, we can see that the optimum AOP should be selected cautiously after the fundamental study because the removal efficiencies of color and COD can be changed by the object removal materials.

4. Conclusions

Batch experiments using the immobilized photocatalyst and two coupled continuous experiments with the PCO-biofilm and biofilm-PCO were conducted. When the color was 9312°, almost all color was removed at 100 min by the batch experiments of immobilized photocatalysis. The COD removal rate decreased as the increase of color and the initial color removal rate decreased by the increase of the COD concentration. The PCO reactor was good for color removal but it was not for COD removal. The color and COD removal efficiencies in the R2 system (pre-biofilm + post-PCO) were higher than those in the R1 system (pre-PCO + post-biofilm). The optimum HRT in the R1 system was 2.4 h of pre-PCO reactor and 8 h of post-biofilm reactor. And the optimum HRT in the R2 system was 4 h of the pre-biofilm reactor and 1.2 h of the post-PCO reactor. So, the HRT in R1 was twice as high as that in R2. The PCO process was superior to Fenton oxidation in the color and COD removal.

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