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Study of the end point of photocatalytic degradation of landfill leachate containing refractory matter

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Abstract

In a pilot scale shell and tube type photocatalytic reactor and a batch type lab scale photocatalytic reactor, the biologically pretreated landfill leachate from Kimpo landfill in Korea characterized to have low biodegradability (BOD/COD = 1.1%) was tested. The role of DO (dissolved oxygen) was important in photocatalysis, thus we monitored the DO at the inlet and outlet points of the pilot scale photocatalytic reactor. DO consumption in a pilot scale photocatalytic reactor was monitored as the index of reaction progress. However, complete mineralization could not be achieved due to the photocatalyst deactivation. After photocatalytic reaction, the residual species in the landfill leachate were identified with GC/MS. The residual materials were siloxane compounds, which might be adsorbed on photocatalyst. These adsorbed species would block the light source and the approach of DO to photocatalyst surface. Therefore, oxygen attachment onto the photocatalyst surface is difficult when no more degradation occurs.

Keywords: Photocatalysis; Landfill leachate; Deactivation; Dissolved oxygen

1. Introduction

The sanitary landfill method for the ultimate disposal of solid waste has been widely accepted and used. In Korea, the domestic wastes of 48,499 t/day, the industrial wastes of 204,428 t/day and the specific wastes of 7,831 t/day were, respectively, generated in 2001. The 43% of domestic wastes, 15% of industrial wastes and 12% of specified wastes were treated by landfill method [1]. After the solid disposal in landfill, there must be problems such as odor and leachate, especially since the landfill leachate caused by infiltrating rainfall can move into the surrounding soils and out of the landfill. The landfill leachate contains a high strength of organic matter such as humic, fulvic substances, inorganic matters and heavy metals [2,3]. To remove these materials, external treatment such as biological process [4,5], Fenton oxidation [6], filtration [3] and reverse osmosis [7,8] were required. Wastewaters produced from industrial processes and landfill containing large quantities of organic, inorganic matters and toxic materials are difficult to degrade by traditional biological processes. Biological treatment techniques are susceptible to toxic compounds which inactivate the waste-degrading microorganisms [9].

Research on heterogeneous photocatalytic oxidation processes has shown them as alternatives for the partial degradation and even total mineralization of various toxic and refractory organic matters [10–12]. Photocatalysis can oxidize a wide variety of organic compounds to harmless inorganics such as CO_2, H_2O and mineral acids, i.e., the pollutants are destroyed and not transferred to another phase; this technology seems to be a promising solution for environmental problems. This process can be also applied to the purification of gas phase pollutants such as VOCs [13]. Most of the research was carried out using pure compounds. Thus these results are insufficient to be applied in the field. However, only a few studies for treatment of landfill leachate by photocatalysis have been reported in the literatures [14,15]. Results in the present work can contribute to the purification of real wastewater under the field conditions.

Organic compounds in landfill leachate may be oxidized by photogenerated holes as well as by reactive free radical species. The hole by itself is either a very powerful oxidizing agent or it generates hydroxyl radicals in the presence of

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water and molecular oxygen [16]. In the production mechanism for reactive species, the role of oxygen becomes important. A widely accepted theory for the role of oxygen assumes that molecular oxygen can effectively scavenge the electrons in the conduction band, thus inhibiting the undesirable e^-/h^+ recombination process [17]. Oxygen can be a precursor for transformation into the various oxygen species such as $O_2^{\bullet -}$, HO_2^-, $HO_2^{\bullet}$ and H_2O_2, etc. [18,19]. Free radical $HO_2^{\bullet}$ and its conjugate $O_2^{\bullet -}$ are involved in degradation processes, but these radicals are much less reactive than free hydroxyl radical ($^{\bullet}OH$) which is the major reactive intermediate responsible for organic substrate oxidation [9].

The objectives of the present work were to assess the treatability of conventionally pretreated landfill leachate by photocatalytic oxidation, and to obtain the relationship of the end point of reaction and dissolved oxygen (DO). Reasons of incomplete mineralization will also be discussed with the deactivation of catalyst by residual non-photodegradable matters. Especially the deactivation of catalyst is very important because catalyst lifetime is an important factor of commercial catalyst.

2. Material and methods

2.1. Experimental procedure and apparatus

A pilot scale semi-batch mode photocatalytic system (System A) used for the degradation experiments included two UV lamps (254 nm), quartz-tubes and stainless steel tubes. This system is shown in Fig. 1(A). The suspension was continuously circulated with a slurry pump, stirred in the reservoir and could be considered as being constantly air equilibrated. The circulating flow rate was 6 l/min. Two drain ports were provided for the monitoring of inlet and outlet DO. The total volume of aqueous solution was 10 l and the illuminated volume was ca. 4 l. Illumination time could be calculated by the following equation:

$$t_{\mathrm{ill}} = t_{\mathrm{run}} \times \frac{V_{\mathrm{p}}}{V_{\mathrm{s}}} \quad (1)$$

where t_{ill} is the illuminated time, t_{run} the running time, V_{p} the illuminated volume in System A and V_{s} the volume of landfill leachate in System A.

In a preliminary study with landfill leachate, 3 g/l TiO_2 suspension in acidic solution (ca. pH 4–5) gave a relatively high removal rate [20]. Therefore, the initial pH of landfill leachate was adjusted to ca. 4 by H_2SO_4 and the landfill leachate was added to the reservoir with 3 g/l TiO_2 powders. The leachate was mixed with a paddle stirrer for ca. 1 h in order to evaluate the amounts of the leachate removed due to the adsorption by TiO_2 powder. The circulation rate was 6.24 l/min.

To investigate the reactive characters of photocatalysis, batch mode photocatalytic equipment (System B) was used. The light source (Philips, model G8T5, 8 W) was furnished with UVC light (equal to only 18.5 $M^{-1}\,cm^{-1}$) simulating, vertically lamps (16EA) were mounted around the quartz reactor and inside the wall of guide. A quartz photoreactor (190 ml) was equipped with an optical tube and top cover with provisions for gas and liquid inlet and outlet except the inlet air through a narrow tube from air generator to provide the DO in solution and outlet vented gas through the other tube which was connected the condenser to trap the water vapor by heating from the UVC lamps irradiation. After turning on the UV lamps, a small portion of the reacted leachate was withdrawn periodically and immediately centrifuged to remove TiO_2 at 3000 rpm for 10 min and stored in refrigerator under 4 °C.

The used photocatalyst which had reacted with the landfill leachate in System B for 48 h was separated by centrifuge at 3000 rpm for 20 min and washed with DI water, and then was dried in an oven (ca. 24 h at 103 °C). The dried photocatalyst was regenerated by sonication. The photocatalyst slurry was also prepared by sonication (40 kHz for 1 h). The photocatalyst prepared by sonication was separated by centrifuge at 3000 rpm for 20 min. The treatment was repeated seven times, and the photocatalyst was dried in an oven (ca. 24 h at 103 °C). Both photocatalyst samples were placed in a closed vial in the dark after two different treatments.

2.2. Reagents and analytical procedures

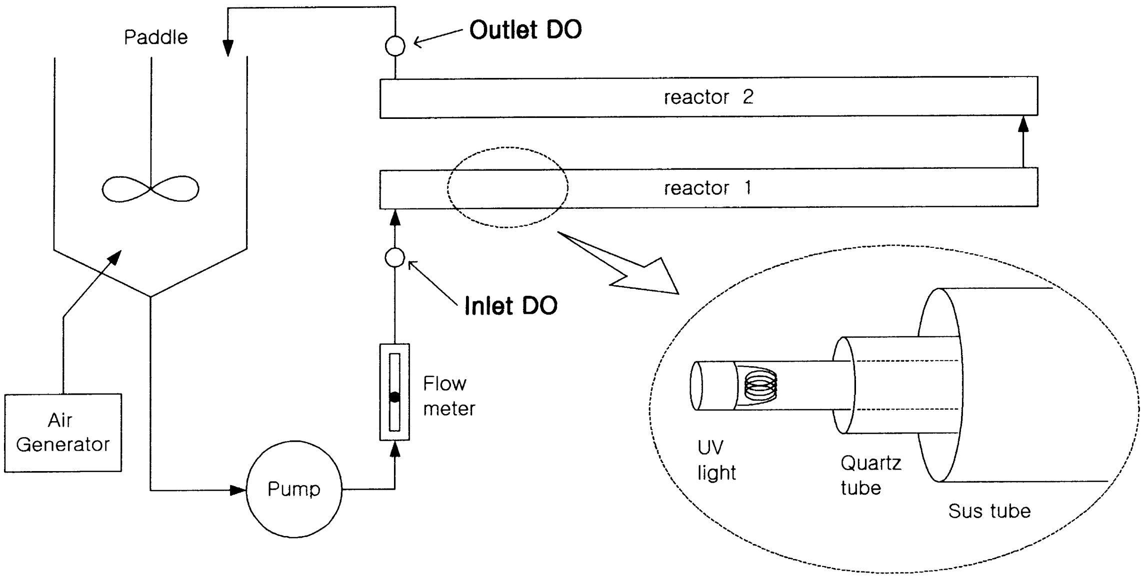
In the present work, Degussa P-25 TiO_2 was used and its crystal phase was about 70% anatase. According to the manufacture's specification, the elementary particle in dry powder was approximately spherical in shape with a particle size of 20 nm. All chemicals were reagent grade and were used without further purification.

DO was measured by DO meter (YSI Model 58). The chemical oxygen demand (COD) was measured by the open reflux method. The total organic carbon (TOC) was determined by TOC analyzer (Rosemount DC-180). The value of TOC was obtained by the elimination method (i.e., TOC = total carbon − inorganic carbon). A Hewlett-Packard GC/MS was used to identify and quantify the components and intermediates in landfill leachate.

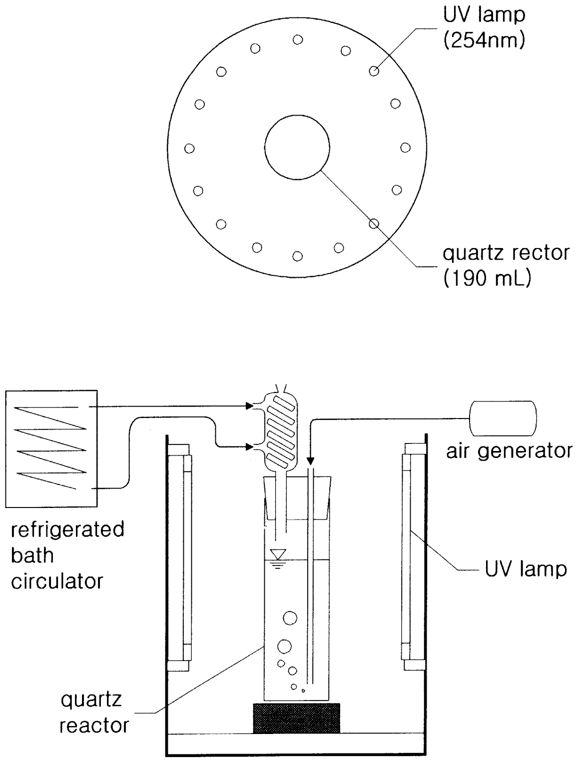
3. Results and discussions

3.1. Characteristics of landfill leachate

The characteristics of landfill leachate from the Kimpo landfill in Korea are represented in Table 1. Pretreated landfill leachate by biological anaerobic digestion and aerobic oxidation was characterized as low biodegradability (BOD/COD = 1.1%). Therefore, a physicochemical purification process seems to be appropriate for the treatment of the landfill leachate. The concentration of chloride, which can poison the catalyst, was higher than 4 g/l.



(A) System A; pilot scale semi-batch mode photocatalytic system.



(B) System B; Lab scale batch mode photocatalytic system

Fig. 1. Schematic diagram of photocatalytic oxidation system.

3.2. Photocatalyzed degradation of landfill leachate

As can be shown in Fig. 2, it was found that the landfill leachate was photocatalytically degraded efficiently in the presence of DO and in the acidic solution. The experiments were taken place in System A.

At pH 4, the removal efficiency was higher than at neutral pH (ca. 8.8). The degradation was lower at neutral pH because landfill leachate had high concentration of alkalinity that could be reacted with hydroxyl radical with high reaction rate. Therefore, alkalinity must be removed by pH adjustment before photocatalytic reaction.

Table 1
Characteristics of landfill leachate from Kimpo landfill in Korea

Parameters	Concentration
pH (–)	8
Alkalinity (mg/l as $CaCO_3$)	1225
SS (mg/l)	36
BOD (mg/l)	7.9
COD (mg/l)	706
TOC (mg C/l)	203
Cl^- (mg/l)	4235

Under optimum conditions, the dark-adsorption of landfill leachate on the TiO_2 was conducted in System A for 1 h before the photocatalytic oxidation experiments were commenced. COD of ca. 102 mg/l (12.4% of COD) and TOC of ca. 38 mg C/l (19.8% of TOC) were adsorbed onto the photocatalyst surface for 1 h. During the adsorption, the pH was raised to 5.26 from 4.45.

Fig. 3 illustrates the decrease in COD and TOC values of landfill leachate samples as a function of illumination time. The COD and TOC values of landfill leachate decreased exponentially as a function of illumination time. Only 52% COD, 79% TOC removal after 5 h illumination time was observed. After ca. 10 h of photocatalytic oxidation, 56% COD and 88% TOC were removed. From the results, the concentrations were COD of ca. 315 mg/l and TOC of ca. 21 mg C/l when the photocatalytic reaction was steady state. From the environmental viewpoint, the overall photomineralization is important. In this study the photocatalytic oxidation of landfill leachate was stopped at 5–6 h, i.e., no further degradation occurred. In the case of real wastewater, complete mineralization by photocatalysis was difficult [21]. Fig. 3 gives two questions. First, when does the reaction stop? The finding out of the ending point of reaction was necessary without COD or TOC analysis. Secondly, why does the reaction stop? For this question, the stable and non-photocatalytic degradable intermediates and deactivation will be discussed.

3.3. End point of photocatalytic oxidation

An important key for the answer of first question can be found in Fig. 4. The experiment was conducted with System A. Variations of inlet and outlet DO were monitored by DO meter. Those changes of consumed amounts are shown in Fig. 4. The DO levels of the reaction solutions were measured at the point of inlet to the photoreactor and outlet from the photoreactor. The inlet DO levels were maintained in 5–6 mg/l with the air feeding rate of 20 l/min.

In Fig. 4, it was found that the DO consumption was very low and/or was close to zero after 5 h photocatalysis. It is known that DO was readily adsorbed on the TiO_2 surface and could be reduced by e^- to produce a superoxide ion radical $O_2^{\bullet-}$ and/or $O_2^{\bullet 2-}$ [22], i.e., the major role of DO in photocatalysis was the conduction band electron scavenging and the trapping of the organic radicals and hydroxyl radicals intermediates [19,23]. Other reasons why no more degradation occurred included the possibility that the electron/hole pair could not be photogenerated and, that DO could not absorb onto the TiO_2 surface.

To investigate the relationship between COD removal and DO consumption, changes in COD removal with illumination time and the accumulated DO consumption in System A are shown in Fig. 5. Total DO consumption during the photocatalytic reaction, DO_{accu} is

$$DO_{accu} = \int \frac{v}{V_p} \frac{d(DO_i - DO_o)}{dt_{ill}} \quad (2)$$

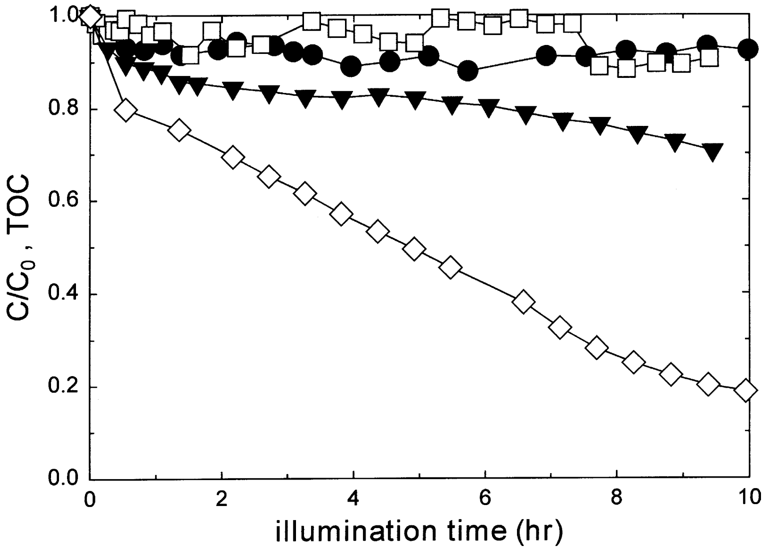


Fig. 2. Time-course of TOC in landfill leachate treated by photocatalytic oxidation with 3 g/l TiO_2 under the different experimental conditions: (●) without aeration and without pH adjustment; (□) with aeration and without pH adjustment; (▼) without aeration and initial pH ca. 4; (◇) with aeration and initial pH ca. 4.

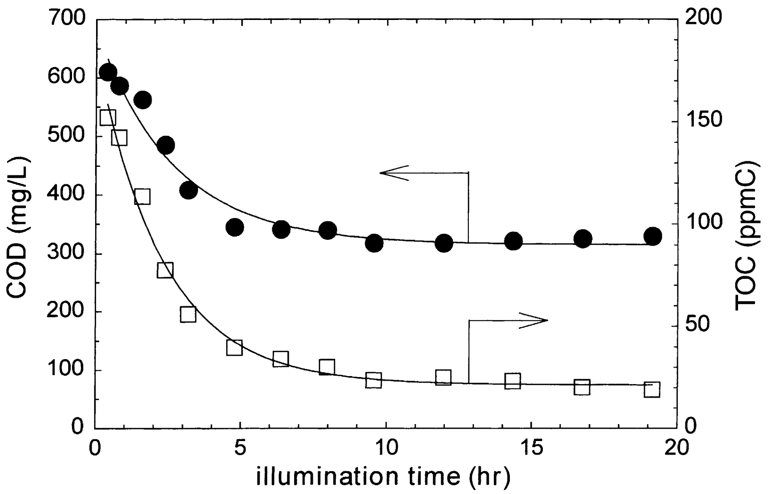


Fig. 3. Decrease in COD and TOC of landfill leachate treated by photocatalytic oxidation as a function of illumination time. Experimental conditions were 3000 mg/l TiO_2; initial pH ca. 4.

where v is the flow rate, DO_i the DO at inlet point and DO_o the DO at outlet point.

In Fig. 5(A), the pattern of the data clearly indicates Langmuir adsorption kinetics. The COD removal and the DO_{accu} first increased linearly and then reached a maximum level at 300, and 400–500 mg/l, respectively. If a higher oxygen partial pressure was supplied, disappearance of landfill leachate appeared to be quicker [19]. From the COD and DO monitoring results, it could be found that progression of COD removal and of DO_{accu} were similar and the differential change was nearly zero or very low after 5 h. The result that the photocatalytic oxidation rate was nearly zero, when the amount of DO consumption was quite low, and it agrees with Ku and Jung's report [24]. From this result that simultaneous differential change occurred in both characteristics, the DO consumption could be the index of reaction progress.

Concerning the DO_{accu}, however, COD was not removed stoichiometrically (see Fig. 5(B)). The removal rate of COD was 1.5 times as large as the rate of accumulation of DO_{accu}.

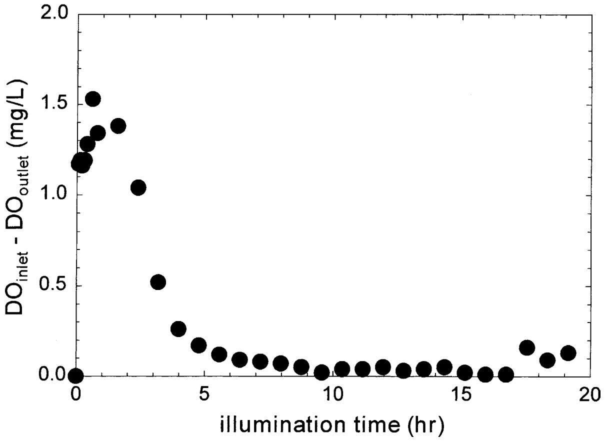


Fig. 4. Consumed DO in photocatalytic reactor vs. UV illumination time during photocatalyzed oxidation.

Nevertheless, the hole scavengers could be water or could be organic impurities in solution [19], COD removal rate was lower than the rate of consumed DO accumulation. Thus it was supposed that a part of DO and these oxygen radical species would not participate in the oxidation reaction, and the energy to generate these species was an irreparable loss.

3.4. Adsorption of non-photodegradable matters

Experiments for the evidence of non-photocatalytic degradable materials in sample treated by photocatalytic oxidation were carried out. As have been mentioned in Section 2.1, landfill leachate mixed with 3 g/l TiO_2 was photodegraded in System A for 48 h (running time). Photocatalytically oxidized solution and used TiO_2 were separated from suspension. Earlier photocatalytically oxidized landfill leachate in semi-batch photoreactor was photocatalytically oxidized in System B mixed with new fresh TiO_2. After more irradiations, little change in COD and TOC were found and it can be seen in Fig. 6.

As can be shown in Fig. 3, the rate of photocatalytic decomposition slowed down considerably. Fig. 6 shows the continuous reaction of landfill leachate that has been earlier treated by photocatalytic oxidation. In photocatalysis with new fresh TiO_2, COD removal was not found after 8 h. Further increases in treatment time caused no significant change in COD and 52% COD reduction was finally obtained. In the case of TOC, however, a second addition of new fresh TiO_2 caused an increase in removal rate. The lowest TOC value achieved after ca. 8 h with secondary new fresh TiO_2 was 6.2 mg C/l.

It is possible that the adsorption onto TiO_2 occurs in the absence of light. When UV light was turned on, adsorbed species were separated from the surface by photocatalysis. After a while adsorption–desorption approached the steady state, i.e., the rate of adsorption became equal to the rate of

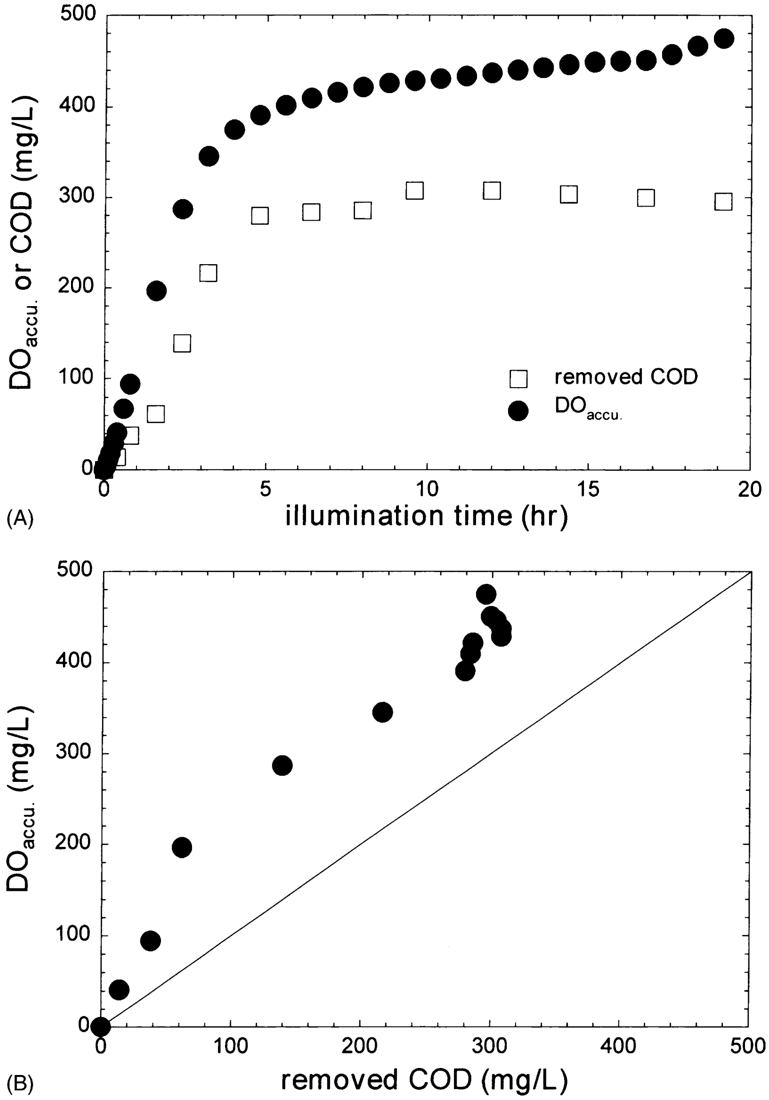


Fig. 5. The relationship of removed COD and accumulated DO in System A.

redissolution. Consequently, it seems to be that the greater part of residual COD consisted of inorganic compounds, which are difficult to decompose by photocatalysis. However, TOC that is a small portion of total COD can be partially removed.

However, complete mineralization could not be reached even with fresh TiO_2. Formation of intermediates in landfill leachate treated by photocatalytic oxidation may produce imperfect mineralization. Thus the incomplete oxidized compounds to inhibit the degradation of materials might present in the irradiated solution [25]. To detect the unknown intermediates, GC/MS was used. The disappearance of parent materials and the formation of its end products in samples were monitored by GC/MS. Cyclotetrasiloxane, cyclopentasiloxane and cyclohexasiloxane, etc. left after the photocatalysis and these materials may be suggested as the non-photocatalytic degradable matters. It is inferred from the existence of the landfill leachate in soils which contain SiO_2, etc. that generation of siloxane compounds in landfill leachate may be possible.

These inactive species might also deposit onto the photocatalyst surface. These phenomena can disturb the UV transmittance and block the adsorption of O_2. Thus, in Fig. 6, the deactivation observing in the second photocatalysis with fresh TiO_2, having high adsorption potential, is not surprising since the materials in landfill leachate are easily adsorbed onto TiO_2. Before UV illumination, many molecules in landfill leachate were impartially detected. Among the materials, the oxidized species such as 4-trimethylsilyl-9,9-dimethyl-9-silafluorene, tetracosamethylcyclododecasiloxane and benzene, etc., could not be detected after photocatalytic reaction for 48 h. Similar species were also detected in landfill leachate treated in twice with fresh TiO_2. But sensitivity was lower due to decreased concentration of the intermediates by photocatalysis. Some of these detected compounds often have a

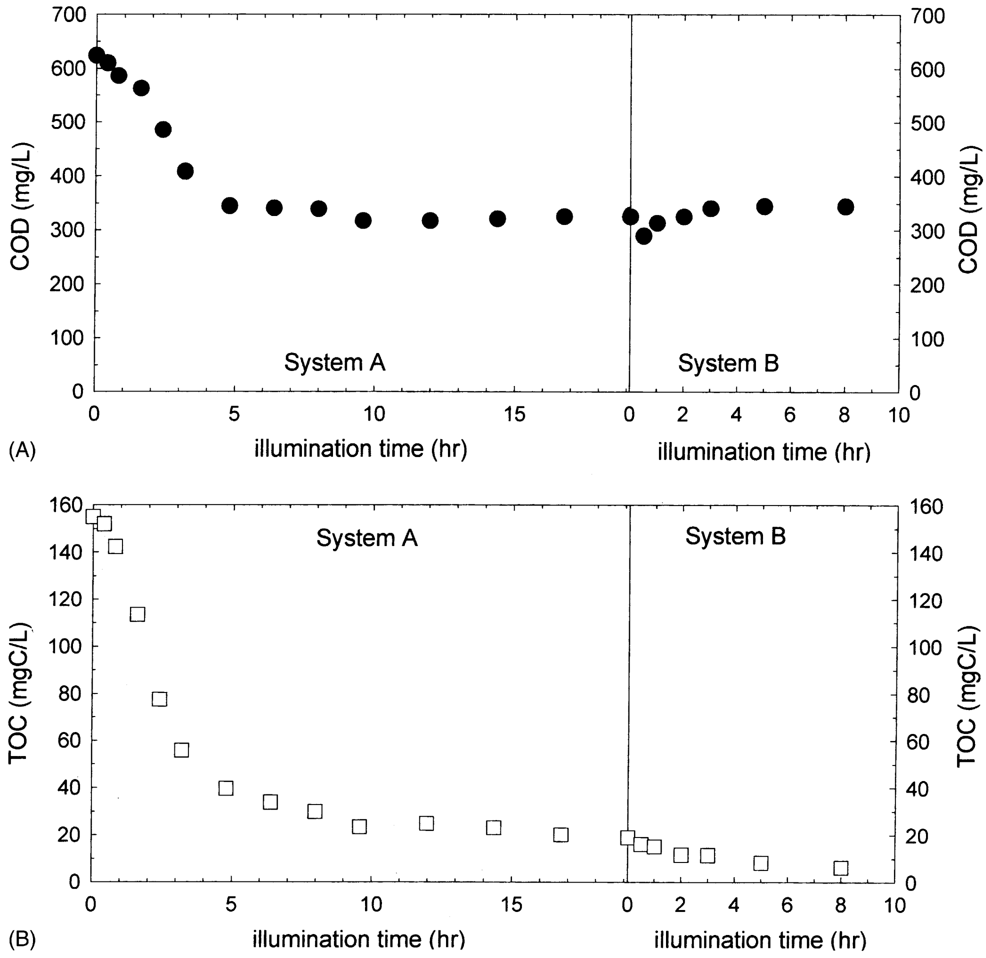


Fig. 6. Photocatalytic degradations of landfill leachate simultaneous reactions.

very similar chemical structure, which renders their identification difficult. Anyway it is supposed that these species could inhibit the reaction.

3.5. Deactivation of photocatalyst

Deactivation is a very critical problem in photocatalytic reaction. Many studies of photocatalyst deactivation were published for the last years [26,27]. To investigate the possibility of using deactivated catalyst, System B and regenerator (i.e. sonicator, washing, centrifuge and oven dry, etc.) was operated. The results in this section compared with the results discussed in the previous section.

In the regeneration of photocatalyst, it is supposed that yield depend on the kind of treatment method. In order to reinforce the result of deactivation, photocatalytic reactions with regenerated photocatalyst by washing and/or sonication and used photocatalyst without further treatment were carried out. From the viewpoint of application of the process, the regeneration by UV illumination [27] appears difficult to apply. Sonication produces shock waves and cavitation in solution [29], energy which can remove the adsorbents from the surface. Thus adsorbed compounds also can be separated from TiO_2 by the physical process of sonication. Sonication gives rise to the generation of cavitation, which is connected with an extreme temperature and pressure increase of some 5000 K and 500 kPa. The temperature within the short-lived cavitations is sufficiently enough to split water into H and OH radicals [28].

The relevant experiment was a comparison of the behavior for landfill leachate photocatalysis TiO_2 regenerated by sonication with that of used TiO_2. Fig. 7 shows the removal of COD and TOC as a function of the illumination time for the two experiments (with regenerated TiO_2 by sonication and used TiO_2 without treatment). The initial concentration, C_0, was the original concentration of landfill leachate. COD and TOC removal by reaction in the absence of illumination is listed in Table 2.

These data show that the photocatalyst regenerated by sonication could reduce the COD in landfill leachate more

Table 2
COD and TOC removal by adsorption with different TiO_2

	COD (mg/l)	TOC (mg C/l)
Fresh TiO_2	104	36.83
Regenerated TiO_2	59	16.93
Used TiO_2	96	24.35

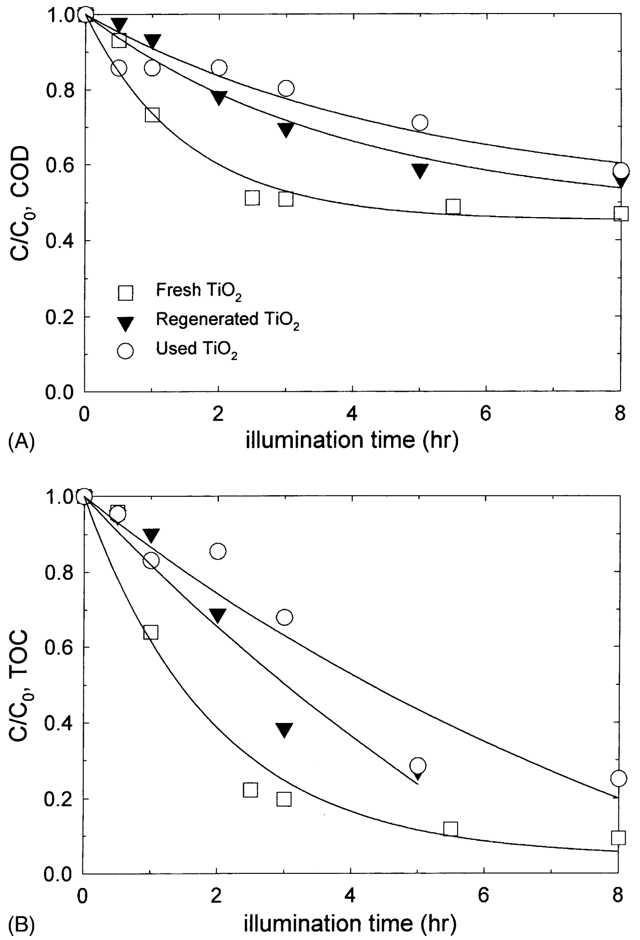


Fig. 7. Comparison of the behavior for landfill leachate photocatalysis between used TiO_2, regenerated TiO_2 by sonication and fresh TiO_2.

effectively than the used photocatalyst treated only by water washing. Simultaneous TOC variations are also shown as function of the UV illumination times. From this result, it was confirmed that sonication was a suitable regeneration method for the deactivated photocatalyst with landfill leachate. However, this result did not agree with Ameen and Raupp [30] result. The difference of behavior may be due to the characteristics of adsorbents on photocatalyst surface. Hydroxyl radicals generated by cavitation and sonication can also destroy any organic materials due to their high oxidation potential [28]. Therefore, the adsorbents on photocatalyst could be decomposed by these radicals. It is suggested that sonication can physically separate the absorbents from the surface of catalyst, and it can degrade the adsorbents and materials in landfill leachate. Therefore, the landfill leachate could be partially degraded by sonication. Thus it was found that the removal rate of photocatalysis with TiO_2 regenerated by sonication was higher than that of photocatalysis with used TiO_2. It was noted that photocatalysis with used TiO_2 could be partly produced. It was an indirect evidence that the stopping of photocatalytic degradation was not only deactivation of photocatalyst but also the presence of non-photodegradable matters such as siloxane compounds.

These results suggest that the adsorbed species may block light from entering TiO_2. Thus the attachment of DO onto the photocatalyst surface is difficult when no more degradation occurs.

4. Conclusions

From the results, the complete mineralization of real wastewater by photocatalysis was difficult. Therefore, we have investigated when and why did incomplete mineralization occur. The reason for incomplete mineralization was a deactivation of catalyst by adsorption of non-photodegradable materials in landfill leachate. The DO consumption in photocatalytic system was very low and/or was close to zero when no more photocatalysis was progressed. A part of consumed DO and these oxygen radical species did not somewhat participate the oxidation reaction. Non-photodegradable materials such as cyclotetrasiloxane, cyclopentasiloxane and cyclohexasiloxane, etc. left after the photocatalysis. These inactive species might also deposit onto the photocatalyst surface, and block the adsorption of O_2. To overcome the deactivation of catalyst, a sonication was suggested as suitable regeneration method for the deactivated photocatalyst with landfill leachate.

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