Simultaneous Removal of Lignin and 2,4-Dichlorophenol in Pulp and Paper Mill Wastewater Using a Supervibration-photocatalytic Reactor

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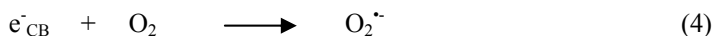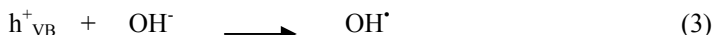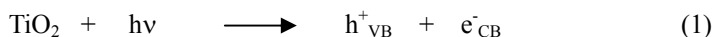Tel: 66-2-218-6678   E-mail: dr_chawalit@yahoo.com

Abstract

Advanced photocatalytic degradation of lignin and 2,4-dichlorophenol (2,4-DCP) was studied. The method used a newly developed supervibration-photocatalytic reactor based on the photocatalytic process combined with a supervibration agitator. Effects of operating conditions such as initial pH, UV intensity and supervibration frequency on removal efficiency were investigated. From the results obtained, removal efficiencies of lignin and 2,4-DCP were similar pattern. UV intensity and supervibration frequency in a low initial pH increased removal efficiencies of lignin and 2,4-DCP. The optimum operating condition for a supervibration-photocatalytic reactor was found at initial pH 5, 25.2mW/cm^2 UV intensity and 50Hz supervibration frequency. Under the optimum treatment condition, the reactor could simultaneously remove lignin and 2,4-DCP up to 75.1% and 94.1%, respectively within 420min.

Keywords: 2,4-Dichlorophenol, Lignin, Pulp and paper mill wastewater, Supervibration-photocatalytic reactor

1. Introduction

Pulp and paper mill has produced large volume of wastewater which are heavily loaded with organic maters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), chlorinated compounds, suspended solids, fatty acids, lignin and its derivatives, etc (Ali & Sreekrishnan, 2001, P175~196). Lignin is very complex and amorphous polymer which has been discharged from cooking and pulp bleaching processes as waste in effluent (Ksibi et al., 2003, P211~218). Pulp and paper mill effluent in Finland was found to contain 186~293mg/L of lignin material (Leiviskä et al., 2009, P3199~3206; Pessala et al., 2004, P319~330). The untreated wastewater causes a loss of aesthetic beauty in the receiving body of water (Pokhrel & Viraraghavan, 2004, P37~58). For instance, the dark brown color of these effluents inhibits the natural process of photosynthesis in streams due to absorbance of sunlight (Sahoo & Gupta, 2005, P1573~1578). Furthermore, many authors reported the presence of toxic species on aquatic organisms, such as growth inhibition and genotoxicity (Ali & Sreekrishnan, 2001, P175~196; Dekker et al., 2002, P374~380; Yakovleva et al., 2004, P242~246). Whereas, 2,4-DCP has been produced from pulp and paper making as a by-product of the chlorine pulp bleaching process (Pera-Titus et al., 2004, P219~256). It was found in aeration pond, treating pulp and paper mill wastewater in Selenga at 2.38mg/L (Batoev et al., 2005, P31~36). Previous studies reported the effects to organisms, such as growth inhibition in microorganisms (Matafonova et al., 2006, P209~212), growth inhibition (Scragg et al., 2003, P616~622) and physical changes (Sahinkaya & Dilek, 2009, P781~786) in aquatic organisms and effect on human erythrocytes (Bukowska et al., 2007, P238~244). Most wastewater treatments of pulp and paper mill are typically carried out using biological treatments but they can only remove small amounts of lignin (Leiviskä et al., 2009, P3199~3206) and 2,4-DCP (Kaigi et al., 2005, P191~196) and require long residence time. Therefore, powerful advanced oxidation processes are alternatives for effective treatment.

Photocatalysis involves the use of titanium dioxide (TiO$_2$) as a catalyst and ultraviolet light (UV) as an irradiation source. The UV light (wavelengths < 385nm) absorbed by the photocatalyst with energy higher than band gap energy of TiO$_2$ (3.2eV) excites an electron from the valence band to the conduction band, producing electron-hole pairs (e$^-$/h$^+$). During the process, hydroxyl radicals (OH$^•$) are generated on the surface of TiO$_2$. Mechanisms of photocatalytic reaction are shown in equations (1)~(6).

$$TiO_2 \ + \ h\nu \ \longrightarrow \ h^+_{VB} \ + \ e^-_{CB} \qquad (1)$$

$$h^+_{VB} \ + \ H_2O \ \longrightarrow \ OH^{\bullet} \ + \ H^+ \qquad (2)$$

$$h^+_{VB} \ + \ OH^- \ \longrightarrow \ OH^{\bullet} \qquad (3)$$

$$e^-_{CB} \ + \ O_2 \ \longrightarrow \ O_2^{\bullet-} \qquad (4)$$

$$O_2^{\bullet-} \ + \ 2H_2O \ \longrightarrow \ 2H_2O_2 \qquad (5)$$

$$H_2O_2 \ \longrightarrow \ 2OH^{\bullet} \qquad (6)$$

Due to the high oxidation potential (2.8V), $OH^{\bullet}$ are the principal agents responsible for the oxidation of numerous aqueous organic contaminants and mineralize them into carbon dioxide (CO_2), water (H_2O) and other small molecules (Chen et al., 2004, P329~337; Kaneko & Okura, 2002; Zhou & Smith, 2002, P247~264). The effects of the form of TiO_2, TiO_2 dosages, initial pH, UV light, and initial concentration on removal of lignin (Dahm & Lucia, 2004, P7996~8000; Ksibi et al., 2003, P211~218; Portjanskaja & Preis, 2007, P1~7; Tanaka et al., 1999, P287~294) and 2,4-DCP (Bayarri et al., 2007, P231~239; Bayarri et al., 2005, P227~236; Chen et al., 2004, P329~337; Pandiyan et al., 2002, P149~155) using UV/TiO_2 have been continuously studied. González et al. (2010, P3493~3499) reported that an increase in suspended TiO_2 from 0 to 20mg/L caused an increase in the 2,4-DCP removal initial rate. Effect of UV on 2,4-DCP degradation was studied by Bayarri et al. (2007, P231~239), UV-ABC radiation could be more efficient than UV-A. Furthermore, Dahm & Lucia (2004, P7996~8000) found that at the highest light intensity level (445mW/cm^2), lignin removal occurred much faster than that at the lower illumination intensity. However, it is difficult for TiO_2 powder to disperse and be recycled in aqueous solution. TiO_2 should be coated on some carriers before use (Bao-xiu et al., 2007, P1020~1024).

In this study, the effects of operating parameters on the performance of a novel supervibration-photocatalytic reactor for simultaneous treatment of lignin and 2,4-DCP were investigated, focusing on removal efficiency to determine the optimum treatment condition.

2. Materials and methods

2.1 Chemicals

The chemicals used in the experiments were phosphoric acid (H_3PO_4) (A.R.), hydrogen peroxide (H_2O_2) (A.R.), hydrofluoric acid (HF) (A.R.), lignosulfonic acid sodium salt (analytical grade) and 2,4-DCP (99%) (Aldrich); sulfuric acid (H_2SO_4) (A.R.), methanol (HPLC grade) and acetonitrile (HPLC grade) (LAB-SCAN); sodium hydroxide (NaOH) (analytical grade) (CARLO ERBA).

2.2 Experimental set-up

The experiments were conducted in laboratory scale. The supervibration-photocatalytic reactor, developed in this study, is based on the photocatalytic process combined with a supervibration agitator in order to provide faster reaction and higher removal efficiency. The schematic diagrams of the supervibration-photocatalytic reactor including an agitated tank, a supervibration agitator and an ultraviolet light source and the supervibration agitator containing an eccentric motor, a shaft and multistage blade were shown in figure 1. All experiments were carried out in batch-mode operation using a rectangular reactor of $26.3 \times 36.2 \times 26.3 cm^3$ with 25liters capacity, made of stainless steel. The supervibration equipment consists of a set of four multistage blades with each size of 5cm × 8cm × 1mm. Micro-structured TiO_2 film with thickness of approximately 1μm as photo-catalyst coated on the surface of the multistage blade (titanium plate) was produced by low-voltage anodization process of titanium plate, described by Portjanskaja et al. (2009, P26~30). The plate oxidation was conducted in a dual-electrode reaction chamber, in which the titanium plate was used as the anode and a stainless steel plate of the same size was used as the cathode. Both electrodes were submerged in a mixture of electrolyte solution (H_2SO_4 (1.0M)-H_3PO_4 (0.3M)-H_2O_2 (0.6M)-HF (0.03M)) and a direct-current source was used to provide electric current (150~200V) between electrodes. The illumination was provided using four low-pressure 6W mercury lamps (Philip TUV-G6T5, 254nm), which were attached at the top cover of the agitated vessel. The vertical vibration generated from eccentric motor is transferred to the multistage blade through the shaft and the generated supervibrational energy is converted to fluid energy. Consequently, this agitator generates a powerful 3-dimensional agitating flow in the tank and the flow rate produced by the supervibration agitator is higher than that produced by the conventional rotary pump in the same condition of the electrical power source.

2.3 Experimental procedures

Wastewater samples with 218~290mg/L of lignin and 111~152μg/L of 2,4-DCP were supplied by the pulp and paper mill located at Kanchanaburi province in Thailand. Before treatment, the wastewater was precipitated with gravity followed by filtration using glass microfiber filters, GF/C and then pH was adjusted with NaOH and
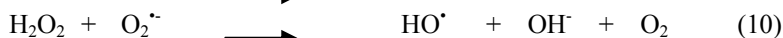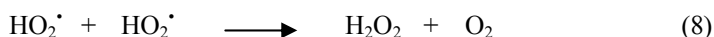
H_2SO_4. The temperature of wastewater was kept at room temperature (30°C). The removal efficiencies of lignin and 2,4-DCP were studied under different initial pH (5, 6, 7, 8, 9), UV intensity (0, 6.3, 12.6, 25.2mW/cm^2 and supervibration frequency (0, 20, 30, 40, 50Hz). The effluent samples were taken at 15, 30, 60, 90, 120, 180, 300 and 420min for lignin analysis on UV-Visible spectrophotometer and 2,4-DCP analysis on HPLC.

Lignin concentration was analyzed by UV-Visible spectrophotometer, Model Helios Alpha, with detection wavelength of 700nm (Eaton et al., 2005). Whereas, 2,4-DCP was detected by HPLC Varian Prostar with column C 18 (4.6mm di × 250mm) and UV-Visible detector at wavelength of 280nm. A mixture of 25% of acetonitrile, 30% of methanol and 45% of water adjusted at pH 3 with H_2SO_4 was used in the mobile phase (1ml/min of flow rate) (Kinakul, 2002).

3. Results and discussion

3.1 Effect of pH

Wastewater samples were treated under five different initial pH levels as 5, 6, 7, 8 and 9. The supervibration-photocatalytic reactor was carried out with 6.3mW/cm^2 of UV intensity and 30Hz of supervibration frequency. The experimental data depicted in figure 2 show that the effect of initial pH on the removal efficiency of lignin and 2,4-DCP was similar trend. The maximum removal efficiencies of lignin and 2,4-DCP were obtained at initial pH 5. The ultimate lignin removal efficiencies were 28.6% (pH 5), 25.1% (pH 6), 18.5% (pH 7), 13.2% (pH 8) and 10.1% (pH 9) within 420min. Whereas, 2,4-DCP removal efficiencies of the reactor were 65.6% (pH 5), 61.2% (pH 6), 56.8% (pH 7), 55.2% (pH 8) and 50.8% (pH 9) in the same time. The results indicate that both lignin and 2,4-DCP removal efficiencies were increased with the decrease in the initial pH. Several researchers obtained similar results in which more lignin removal (Chang et al., 2004, P1011~1017; Ma et al., 2008, P998~1004; Portjanskaja & Preis, 2007, P1~7) and more 2,4-DCP removal (Bayarri et al., 2005, P227~236; Pandiyan et al., 2002, P149~155) were achieved with samples of lower pH level thus, the acidic conditions favor the lignin and 2,4-DCP decomposition. It may be because, under acidic conditions, a superoxide radical ($O_2^{\bullet-}$) will react with a hydrogen ion (H^+) and produce a perhydroxyl radical ($HO_2^{\bullet}$). Consequently, the $HO_2^{\bullet}$ can form hydrogen peroxide (H_2O_2), which in turn gives rise to the $OH^{\bullet}$ as shown in equations (7)~(10) (De Lasa et al., 1992).

$$O_2^{\bullet-} + H^+ \longrightarrow HO_2^{\bullet} \qquad\qquad (7)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad\qquad (8)$$

$$H_2O_2 + e^- \longrightarrow HO^{\bullet} + OH^- \qquad\qquad (9)$$

$$H_2O_2 + O_2^{\bullet-} \longrightarrow HO^{\bullet} + OH^- + O_2 \qquad (10)$$

On the other hand, the point of zero charge (pzc) of TiO_2 is between pH 5.6 and 6.4. Therefore, depending on the pH, the TiO_2 surface will be charged positively (pH < pzc) and negatively (pH > pzc) that will have a significant effect on the adsorption properties of TiO_2. Molecules of lignin are negatively charge in alkaline solution, being repelled from the TiO_2 surface; which causes to reduce their adsorption. Also the accumulation of carbonate and bicarbonate ions, $OH^{\bullet}$ scavenger, could be the reason of decreased efficiency at alkaline pH (Portjanskaja & Preis, 2007, P1~7). In addition, 2,4-DCP is mostly in the un-ionized form under acidic pH values and then, it can be more easily adsorbed onto the TiO_2 surface, whereas for alkaline conditions, 2,4-DCP and TiO_2 surface are mostly charged negatively so can exist a repulsion between both compounds (Bayarri et al., 2005, P227~236; Pandiyan et al., 2002, P149~155).

3.2 Effect of UV intensity

In order to determine the effect of UV intensity, the experiments were performed by varying UV intensity as 0, 6.3 and 12.6mW/cm^2 at constant optimum initial pH 5 and 30Hz of supervibration frequency. Figure 3 reveals that lignin and 2,4-DCP removal efficiencies were increased greatly by the increase in UV intensity, thereafter it started decreasing slowly. Removal efficiencies of lignin with 6.3 and 12.6mW/cm^2 of UV intensity were 28.6% and 44.8%, respectively, and 65.6% and 73.2%, respectively for 2,4-DCP removal, after 420min. Whereas, the absence of UV light induced low lignin removal (6.2%) and 2,4-DCP removal (15.8%) in the same time of UV irradiation. It may be due to the photocatalytic degradation not occurring, but fluid energy converted from supervibration energy can break some molecules of the pollutants. The results indicate that an increase in UV intensity could enhance both lignin and 2,4-DCP removal. This is because when UV intensity is higher, the photonic flux irradiation will increase and the higher rate of hole production will occur. Thus, the rate of $OH^{\bullet}$ and the $O_2^{\bullet-}$ production increase, which would allow the degradation to be faster. Related results were previously observed by Dahm & Lucia (2004, P7996~8000). The results demonstrated lignin removal using a light intensity of 223~445mW/cm^2 and it was found that higher illumination intensity correlated well with higher initial

degradation rate and total lignin degradation. Furthermore, Bayarri et al. (2007, P231~239) reported that the photocatalytic degradation of 2,4-DCP was about 20% higher with UV-ABC than with UV-A. An increase in UV intensity always increases the reaction rate until the reaction is mass transfer limited (De Lasa et al., 1992).

3.3 Effect of supervibration frequency

The influence of supervibration frequency was also studied. Figure 4 illustrates the photodegradation efficiency of lignin and 2,4-DCP with five different supervibration frequency as 0, 20, 30, 40 and 50Hz in the presence of constant optimum initial pH (pH 5) and optimum UV intensity (12.6mW/cm^2). It indicated the effect of supervibration frequency on photocatalysis under the conditions used here. Although there was an absence of supervibration frequency (0Hz), the system could remove lignin and 2,4-DCP at 25.4% and 52.5%, respectively in 420min because of photocatalytic degradation (UV/TiO$_2$). When introducing the supervibration frequency into the system, the reactor was able to remove more lignin and 2,4-DCP. The removal efficiencies of lignin were 40.2% (20Hz), 44.8% (30Hz), 45.1% (40Hz) and 47.0% (50Hz) in the same time. For 2,4-DCP, the reactor could remove at 66.4% (20Hz), 73.2% (30Hz), 74.3% (40Hz) and 76.3% (50Hz), after 420min. Removal efficiencies of lignin and 2,4-DCP were increased as supervibration frequency increased. This is probably because, in the condition of higher supervibration frequency, the powerful 3-dimensional agitating flow in the reaction tank is higher. Therefore, the contact between pollutants and TiO$_2$ will be enhanced. In addition, the higher supervibration energy is converted to higher fluid energy and it may be more than chemical bond energy in pollutant structure; consequently, the breaking down of the lignin and 2,4-DCP molecules occurred. Additional experiment with increased UV intensity into the system was also performed. The results were found that, under conditions as UV intensity of 25.2mW/cm^2, initial pH 5, supervibration frequency of 50Hz, removal efficiencies of lignin and 2,4-DCP were up to 75.1% and 94.1%, respectively, after 420min. Portjanskaja & Preis (2007, P1~7) used mechanical agitation with magnetic stirrers in the UV/TiO$_2$ reactor for treatment of lignin. The system could degrade lignin not exceeding 50% after 25 hours when using 100mg/L of initial lignin concentration at pH around 8.0. Furthermore, Yang et al. (2008, P300~307) investigated degradation of 2,4-DCP in water using UV/TiO$_2$ and magnetic stirrers under conditions as 0.5mg/L of 2,4-DCP solution at initial pH 7 and 900μW/cm^2 of UV intensity. 2,4-DCP removal efficiency was around 53% within 120min, whereas present work using supervibration agitator could remove 2,4-DCP up to 77.9% in the same time. Therefore, the supervibration agitator in the present study has higher performance in lignin and 2,4-DCP removal than that of previous researches. This may be because the fluid flow rate produced by the supervibration agitator is higher than that produced by magnetic stirrers.

4. Conclusions

According to our study, a supervibration-photocatalytic reactor can effectively reduce pollutants as lignin and 2,4-DCP in wastewater and can be concerned as a new alternative technology for real world application. The optimum operating condition for a supervibration-photocatalytic reactor was found at initial pH 5, 25.2mW/cm^2 UV intensity and 50Hz supervibration frequency. Under the optimum treatment condition, the reactor could simultaneously remove lignin and 2,4-DCP up to 75.1% and 94.1%, respectively within 420min.

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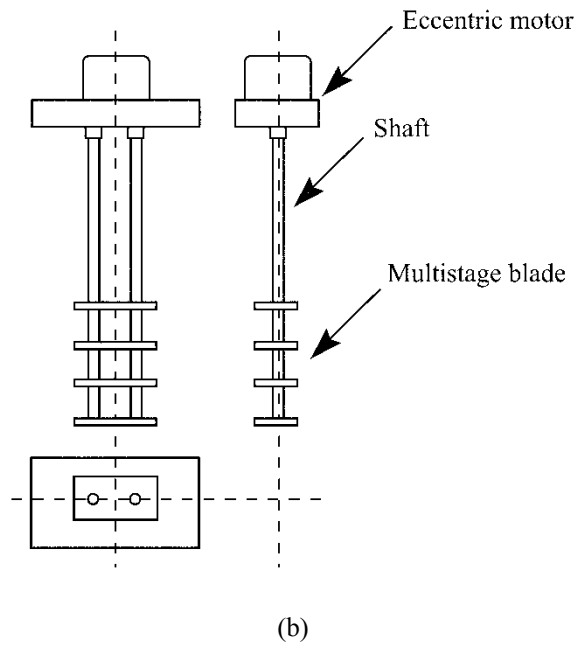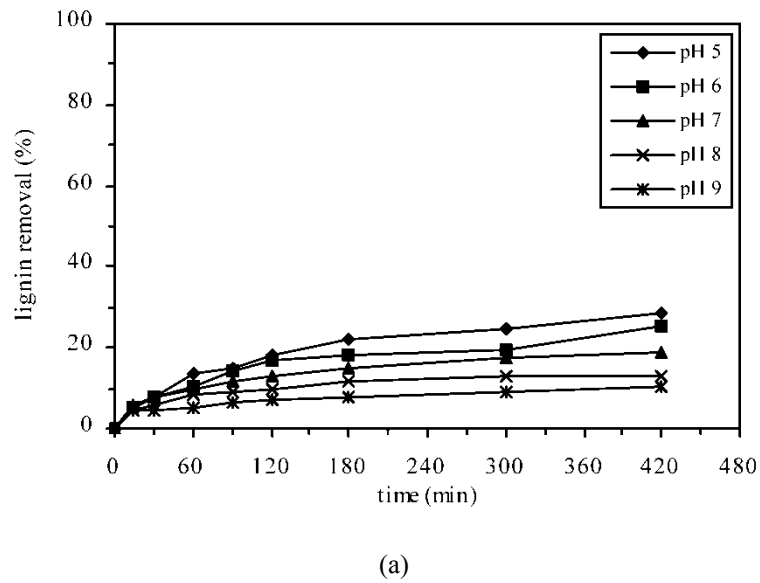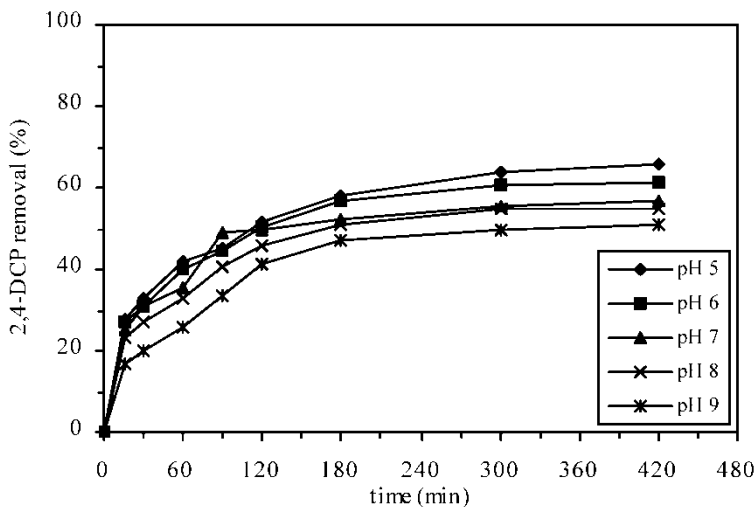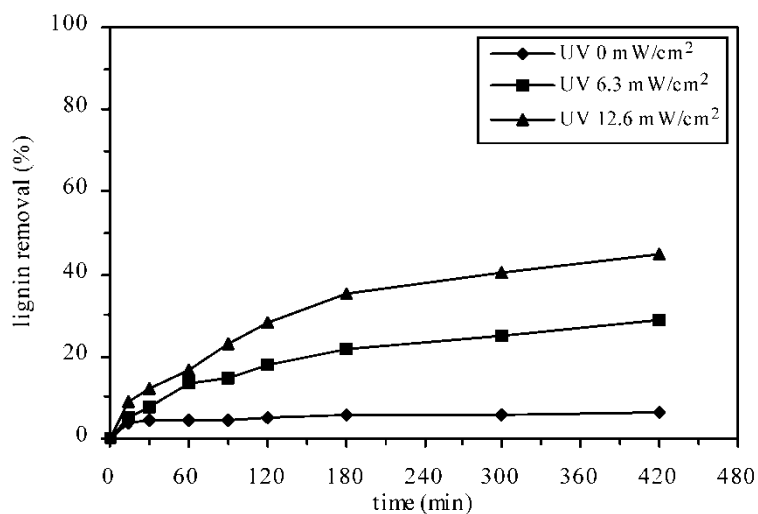

(a)

(b)
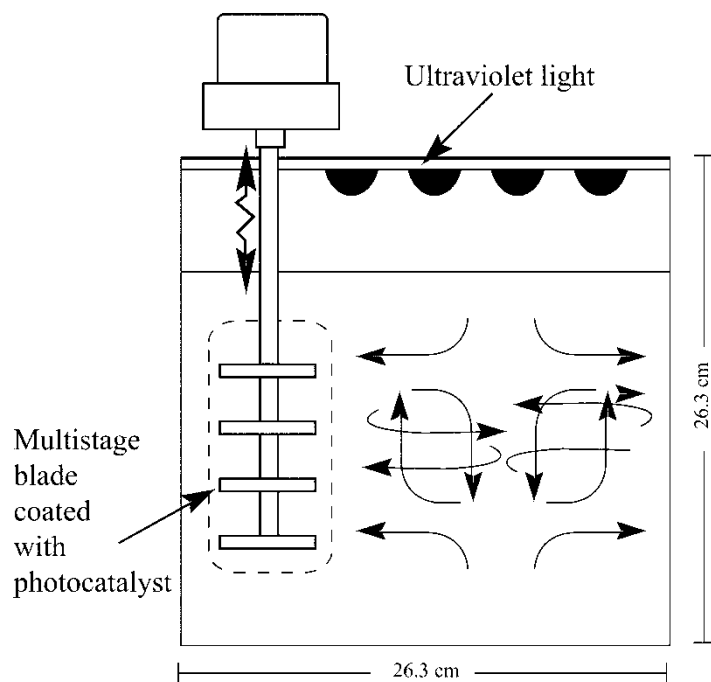
Figure 1. The schematic diagrams of the supervibration-photocatalytic reactor (a)
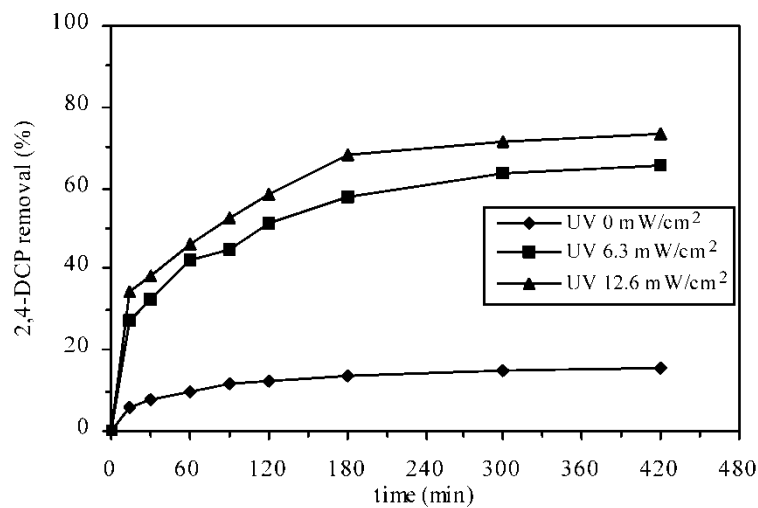and the supervibration agitator (b)

(a)

(b)

Figure 2. The effect of initial pH on removal efficiency of lignin (a) and 2,4-DCP (b)
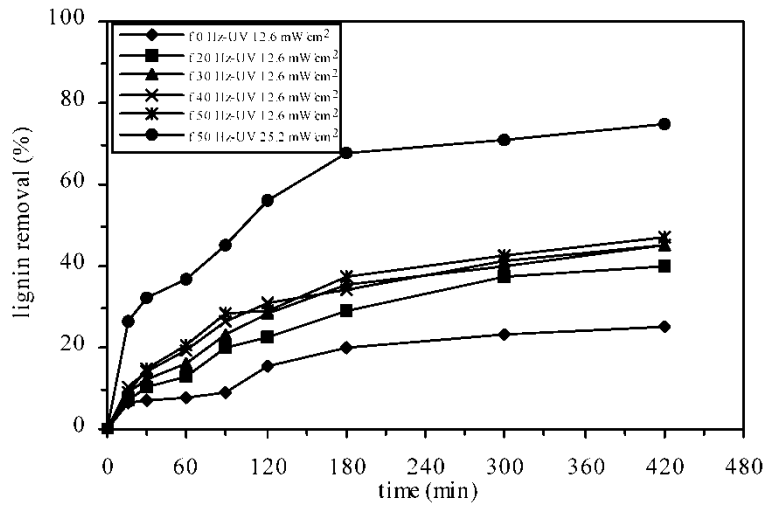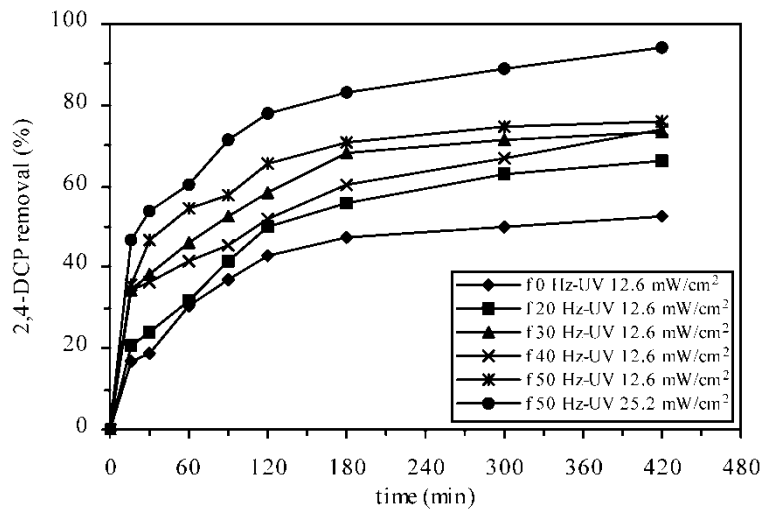

(a)

(b)

Figure 3. The effect of UV intensity on removal efficiency of lignin (a) and 2,4-DCP (b)

(a)

(b)

Figure 4. The effect of supervibration frequency on removal efficiency of lignin (a) and 2,4-DCP (b)