

Composite Paper Sheet Containing TiO₂-diatomite for Removing Phenol in Aqueous Solution

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Composite paper sheet containing titanium dioxide and diatomite (TiDI) was prepared *via* a papermaking technique. The composite sheet was applied to remove phenol from aqueous solution. The composite sheet with a 2:1 mass ratio of cellulosic-fiber to TiDI removed phenol more effectively under UV irradiation than the composite paper sheet that utilized titanium dioxide (TiO₂) alone. Composite paper sheets that contained TiDI with a TiO₂/diatomite mass ratio of 1:2 removed phenol most effectively. The results showed that the TiDI composite paper could serve as a functional material to photodegrade phenol from aqueous solution under UV irradiation effectively.

Keywords: Titanium dioxide; Diatomite; Photodegradation; Phenol

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INTRODUCTION

Water pollution by different hazardous compounds has raised global concerns (Huang *et al.* 2008, 2009; Chakraborty *et al.* 2012). Phenol is a toxic organic compound. It is commonly used as an industrial additive and can be easily released into air and water streams during its processing and application across many fields (Michalowicz *et al.* 2007; Alkaram *et al.* 2009). Phenol is harmful to aquatic life and human beings even at low concentrations (Luttrell 2003; Rudel *et al.* 2011). Therefore, various approaches, such as solvent extraction (Kujawski *et al.* 2004), biodegradation (Annadurai *et al.* 2002; Li *et al.* 2010), treatments with adsorbents (Yang *et al.* 2001; Özkaya 2006), and chemical oxidation (Alejandre *et al.* 2002; Pérez *et al.* 2002), have been used to remove phenolic compounds from wastewater. However, these methods present some drawbacks, including the need of post-treatment to recover the adsorbents, the secondary pollution caused by discarding the adsorbents, and the environmental problems that result from the solvents used in the solvent-extraction method. In addition, costs of common oxidizers used in the chemical oxidation treatments are high. The conventional biodegradation method cannot treat non-biodegradable wastewater even though it is considered an environmentally friendly method with reasonable cost. Moreover, large amounts of microorganisms and long residence time are usually required to degrade the phenol by biodegradation treatments.

An alternative for phenolic pollutant removal is the advanced oxidation process (AOP), in which the oxidation process takes place by exploiting highly active hydroxyl radicals for the mineralization of pollutants (Andreozzi *et al.* 1999; Bauer *et al.* 1999;

Matilainen *et al.* 2010; Oller *et al.* 2011). Photocatalytic oxidation is an example of an AOP. The degradation of phenol by using titanium dioxide (TiO₂) as a photocatalyst has received much attention because TiO₂ can catalyze the oxidation of organic molecules with a low energy cost (Mahmoudi *et al.* 2007; Chiou *et al.* 2008; Laoufi *et al.* 2008; Hafizah *et al.* 2009). In the meantime, it offers other advantages, such as high photosensitivity, nontoxicity, and chemical stability (Hara *et al.* 2000; Neppolian *et al.* 2002; Konstantinou *et al.* 2003; Senthilkumaar *et al.* 2005). However, the powder form of TiO₂ can cause secondary pollution. Therefore, many attempts have also been devoted to immobilizing TiO₂ onto a suitable supporting matrix, such as activated carbon, zeolite, glass, *etc.*, for specific application (Ichiura *et al.* 2003; Iguchi *et al.* 2003; Portjanskaja *et al.* 2004). TiO₂-diatomite composite systems have been already investigated by several researchers for the photodegradation of organic compounds (Sun *et al.* 2014; Zuo *et al.* 2014; Zhang *et al.* 2016)

In this work, TiO₂-diatomite (TiDI) is adhered to cellulosic paper to form a composite-paper sheet. The composite-paper sheet containing TiDI was prepared *via* a papermaking technique and applied to the degradation of phenol in aqueous solution under UV irradiation. The ability of the composite sheets containing TiDI on the photocatalytic decomposition of phenol was investigated.

EXPERIMENTAL

Materials

Phenol (C₆H₅OH, Sigma-Aldrich, 99%, Shanghai, China), TiO₂ powder (Tianjin Fucheng Chemical Reagents, Tianjin, China), diatomite (AG-WX3#, BET: 30.2 m²/g to 47.8 m²/g, particle size: 10 μm to 150 μm, Guangdong Geology and Mineral Products, Guangdong, China), and *Eucalyptus exserta*. M. pulp slurry (35 °SR) were used as received. Two types of flocculants, polydiallyl dimethylammonium chloride (PDADMAC; molecular weight (*M_w*), *ca.* 8 × 10⁴; Sigma-Aldrich, Shanghai, China) and anionic polyacrylamide (A-PAM, HH-351, *M_w*, *ca.* 2.25 × 10⁶, self-prepared) were used as retention aids in a dual polyelectrolyte system. Phenol and other chemicals were of reagent grade and used without further purification.

Methods

Preparation of composite paper sheet (Chen et al. 2006)

Handmade paper sheets with a pulp grammage of 110 g/m² were prepared according to TAPPI T205 sp-12 (2012) with a ZQJ2 – B papermaking machine (Machinery Plant of Northwest Light Industry Institute, Xi'an, China). Pulp slurry (the weight of the dry pulp was 4.17 g) was mixed with PDADMAC (0.3 wt.% of the dry pulp) and A-PAM (0.9 wt.% of the dry pulp weight) to prepare the neat paper sheet. Then, the mixture was pressed at 500 kPa for 5 min to form a wet sheet. The wet sheets were oven-dried at 105 °C for 30 min.

The composite paper sheet containing TiO₂ (35 wt.%, 1.45 g) was also prepared by the above method. Pulp slurry (65 wt.%, the weight of the dry pulp was 2.72 g) was mixed with PDADMAC (0.3 wt.% of the dry pulp), followed by the sequential addition of inorganic suspensions containing TiO₂ (35 wt.%, 1.45 g) and A-PAM (0.9 wt.% of the dry pulp weight). Thus, the composite paper sheet contained three main components, *i.e.*, TiO₂ (0 wt.% to 35 wt.%), diatomite (0 wt.% to 35 wt.%), and pulp (65 wt.%). Four types

of composite paper sheet were prepared with different mass ratios of TiO₂ to diatomite, including 2:1, 1:1, 1:2, and 1:4. The above paper sheets obtained were conditioned at 23 °C in an atmosphere with 50% relative humidity for more than 24 h before use in experiments.

Adsorption of phenol in the solution by paper sheet

To investigate the adsorption of phenol by the composite paper sheet in water, three paper sheets (sheet dimension: 25 mm × 25 mm) were coated with TiO₂, TiDI, and diatomite, respectively. Then, each paper sheet was placed in a 250-mL reaction vessel. A piece of uncoated paper sheet (sheet dimension: 25 mm × 25 mm) was used as the control. Phenol solution (50 mL) with a phenol concentration of 10 mg/L was injected into the vessel. Also, powdered TiO₂ (0.024 g) or powdered TiDI (0.024 g) was added to the sample solution to compare their ability of adsorbing phenol in solution with paper sheets. The pH value of the phenol solution was adjusted to 6 *via* 0.5 M of NaOH solution. After adjusting the pH, the solution was kept in the dark and magnetically stirred with a constant rotation rate of 30 *r/min*; the aliquots of the suspensions were collected from the reactor at the given time intervals.

Photocatalytic decomposition of phenol in water solutions

Each one of the aforementioned paper sheets (per sheet dimension: 25 mm × 25 mm) was placed in a 250-mL reaction vessel (90 mm in internal diameter and 120 mm in height). Phenol solution (100 mL) with a phenol concentration of 10 mg/L was injected into the vessel with a syringe. After being soaked in the phenol solution for 2 h in the dark, the paper sheet was taken out and placed into another 250-mL reaction vessel filled by 100 mL of phenol solution with a concentration of 10 mg/L. Then, a UV lamp (19 W, $\lambda = 253.7$ nm) irradiated the sheet to investigate the photocatalytic decomposition of the phenol in aqueous solution.

Effect of solution pH value on the photocatalytic decomposition of phenol

The pH value of the solution was adjusted by 0.5 M NaOH solution or 0.5 M HCl solution and maintained at various values between 2 and 8 during the test. Before the test, the mixture was kept in the dark and magnetically stirred (30 *r/min*) for 2 h to ensure the sample would reach its adsorption equilibrium before UV irradiation. After the dark adsorption period, the sheet was irradiated for 1 h to 24 h. The aliquots of the suspensions were collected from the reactor at the given time intervals. Before characterization, particles were removed from the aliquots by centrifugation (4000 *r/min*, 5 min). When the irradiation was finished, the paper sheet was removed from the solution and oven-dried at 105 °C for 30 min. After drying, the sheet was weighted. The weight retention ratio of the paper sheet was calculated as the weight of dried paper sheet after use in solution divided by the weight of original dried paper sheet before use in the phenol solution.

Durability of TiDI sheet during repeated use for decomposing phenol

To assess the durability of a composite sheet during repeated use for removing phenol in aqueous solution, samples were soaked in phenol solution (100 mL) with a concentration of 10 mg/L for 5 h under UV irradiation, and then the phenol concentration of residual solution was measured. The same procedure was repeated eight times using

the same composite paper sheet; the residual phenol concentration was recorded after each time of soaking.

Characterization of paper sheets

Scanning electron microscopy (SEM, JSM-5600LY, Nidec Corporation, Tokyo, Japan) examined the surface morphology of the prepared sheets with 15 kV electron acceleration voltage. The chemical composition of the sheets was analyzed by X-ray diffraction (XRD) using a Xpert MPD Pro (PANalytical B.V., Almelo, Netherlands) with Cu-K α radiation (wavelength = 1.54 Å). The powder diffraction patterns were collected by a 2-h scan from 10° to 80° with an increment of 0.02°.

Analytical methods

Two methods of measurements monitored the change of phenol concentration in each photodegraded phenol solution. The first was the adsorbance of phenol that was measured at $\lambda_{\max} = 270$ nm with an ultraviolet–visible spectrometer (TU-1800PC, Beijing General Instruments, Beijing, China); and the second was the chemical oxygen demand (COD) of the same solution that was measured to investigate the mineralization degree of the substrate based on the dichromate method (Sun *et al.* 2006).

RESULTS AND DISCUSSION

Adsorption of Phenol from Aqueous Solution

The adsorptions of phenol with different materials from aqueous solution in the dark are shown in Fig. 1. The materials included powdered diatomite, powdered TiO₂, neat paper sheet, TiO₂ paper sheet, diatomite paper sheet, and TiDI composite sheet. Clearly, across all materials, the adsorption of phenol from aqueous solution in the dark reached equilibrium for approximately 30 min. However, only approximately 5 wt.% aqueous phenol could be adsorbed by powdered TiO₂, while approximately 40 wt.% phenol in the solution could be removed by the powdered diatomite after 30 min of soaking adsorbents in the solution.

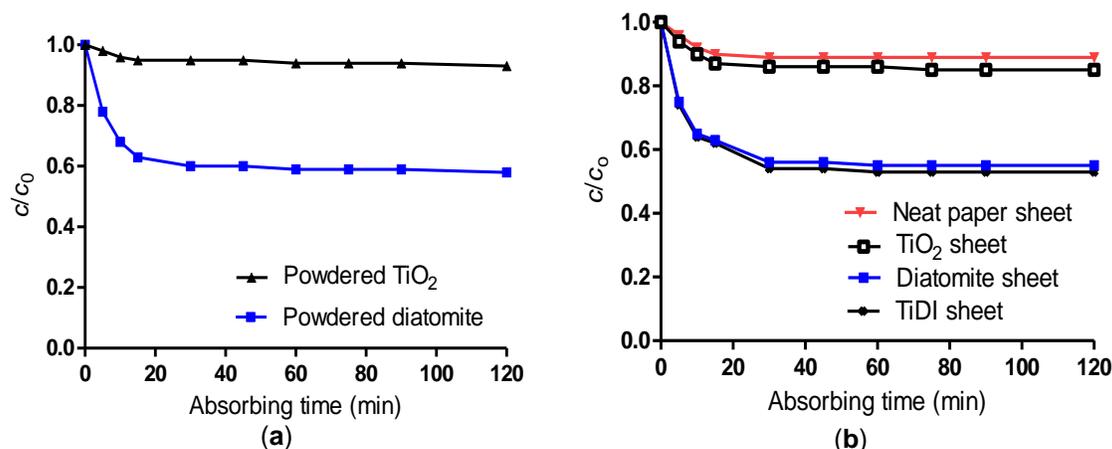


Fig. 1. The adsorption of phenol in aqueous solution by different materials; where c_0 (mg/L) is the original concentration of phenol in solution, and c (mg/L) is the phenol concentration after treatment with adsorbent materials

As for the paper sheets, the neat paper sheet adsorbed only 11 wt.% phenol after 30 min. The adsorption ratios of phenol by the sheets that had TiO₂, diatomite, and TiDI were 14.5%, 42.3%, and 45.6%, respectively, after soaking the sheets in the solution for 30 min. These results indicated that diatomite and its composite-paper sheet could adsorb substantially more phenol than the others, which can be due to the high porosity of diatomite (Sun *et al.* 2015; Tang *et al.* 2016; Zhang *et al.* 2016). The diatomite paper sheet adsorbed a comparable amount of phenol to the powdered diatomite, which indicated that the function of diatomite for adsorbing phenol was substantially maintained when it was coated onto the sheets.

Photocatalytic Degradation of Phenol in Aqueous Solution

To investigate the effect of TiDI sheets on the photocatalytic degradation of aqueous phenol, the paper sheets that already reached the adsorption equilibrium in phenol solution formerly were used to further adsorb the phenol from solution; thus, their decomposition ability of phenol was evaluated. As shown in Fig. 2 and Fig. 3, after irradiating the solution for 5 h without TiDI sheet, there were no obvious changes in phenol concentration (Fig. 2) and COD value (Fig. 3).

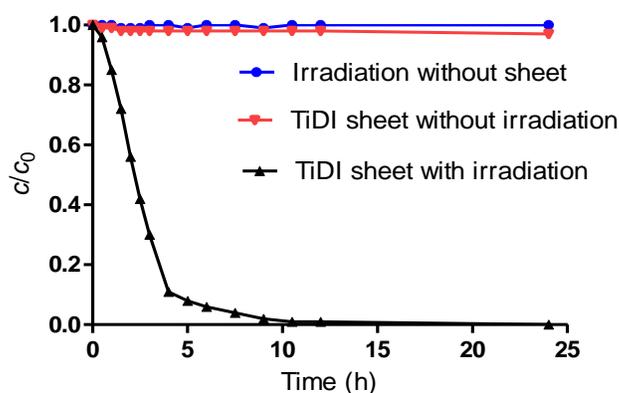


Fig. 2. The phenol concentration ratios of the aqueous solution after treatment with sheets under different conditions

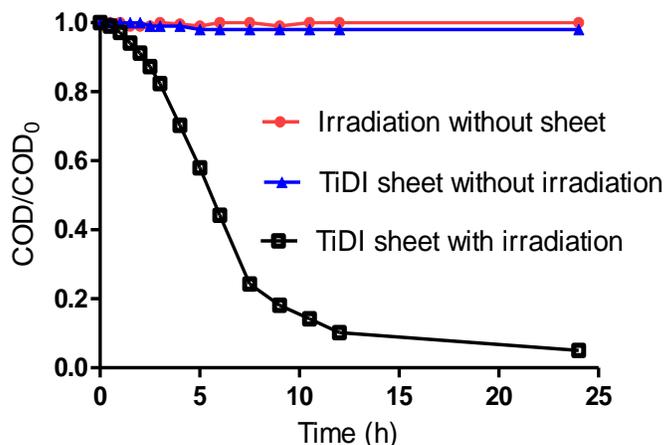


Fig. 3. The COD value ratios of the solutions before and after treatments; where COD₀ (mg/L) is the chemical oxygen demand of phenol solution before treatment, and COD (mg/L) is the chemical oxygen demand of phenol solution after treatment

The same lack of effect was observed in the solution with the TiDI sheet without irradiation (Figs. 2 and 3). However, the phenol concentration and the COD value of the solution reduced by 99% (Fig. 2) and 90% (Fig. 3), respectively, after 24-h UV irradiation on the solution containing TiDI sheet. This indicated that the TiDI sheet could effectively catalyze the degradation of phenol in aqueous solution under UV irradiation. This may have been due to the high photosensitivity of TiO_2 powders in the sheet, which effectively decomposed the phenol adsorbed by diatomite. The porous materials were involved in the adsorption of pollutants on the surface sites, which then improved the photocatalytic degradation of pollutants (Özkaya 2006). Diatomite, which consists of amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), has a large specific surface, a specific porous structure, and a strong adsorption ability, resulting in an attractive force toward many pollutants (Zuo *et al.* 2014). Clearly, the reduction of COD values was inconsistent with the phenol concentration decrease measured by an ultraviolet–visible spectrometry (UV–Vis) method. It is well known that phenol degradation could lead to the formation of several byproducts including oxalic acid, catechol, benzoquinone, resorcinol, and hydroquinone, *etc.* These byproducts can further react with hydroxyl radicals in the solution (Fan *et al.* 2006; Kamble *et al.* 2006; He *et al.* 2011; Mino *et al.* 2016). Therefore, it was understandable that the thorough degradation of phenol would be time-consuming. Due to the uncertainty introduced by the intermediate products from the photodegradation of phenol, the UV–Vis method used in this experiment could only measure the concentration change of the phenol in aqueous solution, but could not accurately determine the ratio of complete decomposition of phenol. However, this method was suitable for predicting the degradation trend of phenol in aqueous solution. In contrast, the COD value change could describe the complete decomposition ratio of phenol, which was the indicator of the byproducts amount of the phenol decomposition.

The Influence of the Initial pH Value of Solution on the Phenol Removal

Phenol solutions (10 mg/L) with pH values of 2, 4, 6, and 8 were prepared before conducting the experiments of phenol degradation by TiDI composite sheets. As shown in Fig. 4, the highest photocatalytic degradation efficiency was observed at pH = 6.0.

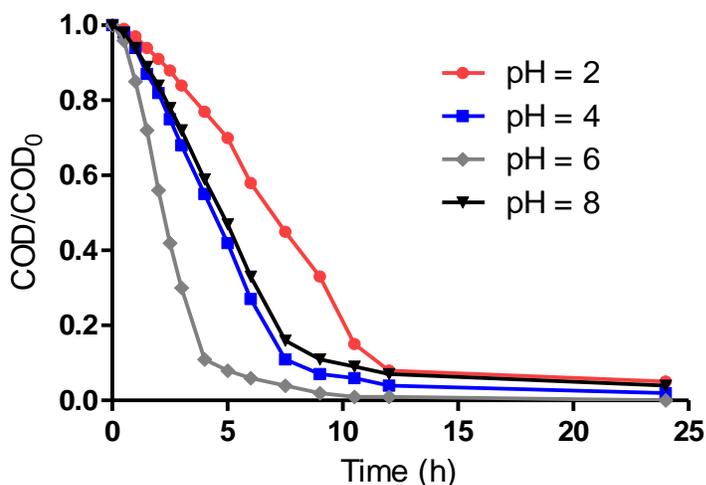


Fig. 4. Effect of pH value on the photocatalytic phenol degradation efficiency described by COD value ratios before and after treatments

The COD value in the solution was decreased by over 90% after UV irradiation for 4 h by TiDI sheet with the solution of pH 6.0; for solutions with pH of 4.0 and 8.0, the same reduction degree of COD value took more than 8 h. Moreover, it took 12 h to reduce the COD value 90% when the initial pH of the solution was 2.0.

It is well known that the degradation by AOPs is based on the generation of hydroxyl radicals ($\bullet\text{OH}$) with a strong oxidizing ability (Andreozzi *et al.* 1999). During the AOP catalyzed by TiO_2 , the pH value of the solution could affect the surface charge of the TiO_2 powder (Lin *et al.* 2015). It has been found that the pH value that corresponded to the point of zero charge for TiO_2 was approximately 6 (Lin *et al.* 2015). When $\text{pH} < 6.3$, the positively charged surface state of TiO_2 could benefit the immigration of photo-generated electrons to the surface, then the electrons combine with O_2 to generate $\bullet\text{OH}$, thus contributing to the photodegradation process. When $\text{pH} > 6.3$, the negatively charged surface state of TiO_2 could benefit the immigration of photo-generated holes to the surface, then the holes combine with H_2O to generate $\bullet\text{OH}$, thus also contributing to the photodegradation process. However, if the pH level is much higher or lower than 6, the $\bullet\text{OH}$ generation could be suppressed (Chen *et al.* 2016). When the pH value increased to more than 8, the negatively charged surface of TiO_2 particles prevented them from adsorbing the hydroxide ions, thus reducing the formation of hydroxyl radicals and the photo-oxidation efficiency (Matilainen *et al.* 2010; Lin *et al.* 2015). Therefore, the optimum pH value for the phenol degradation could be around 6 when using TiO_2 as photocatalyst.

The Influence of TiO_2 /Diatomite Mass Ratio on the Degradation of Phenol

As shown in Fig. 5, the residual phenol concentrations increased with the decreased TiO_2 /diatomite mass ratios of the sheets when the ratio was higher than 1:2. Namely, the decomposition of phenol occurred more effectively with a larger amount of diatomite. The initial decomposition rate of phenol ($-dc/dt$, where c is the concentration of phenol (mg/L) and t is the reaction time (h)) showed the same trend as that of the phenol concentration (Fig. 6).

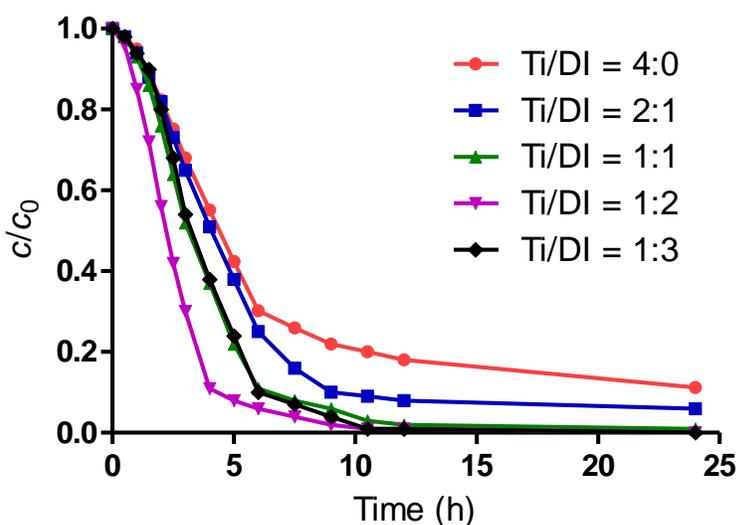


Fig. 5. Effect of the mass ratios of TiO_2 to diatomite on the photodegradation efficiency described by the phenol concentration ratios before and after treatments

Moreover, the decomposition rates of phenol for all samples reached their highest values at approximately 2 h, which was in agreement with the time for reaching the adsorption–desorption equilibrium of the sheets in the phenol solution. The TiO₂ and diatomite were almost uniformly distributed on the composite sheet, and the TiO₂ particles were located near the diatomite. Therefore, phenol in the solution could first be adsorbed by diatomite, and then decomposed by TiO₂ particles near the diatomite, *i.e.*, the photocatalytic decomposition of phenol was promoted by the higher concentration of phenol captured by the diatomite (Sun *et al.* 2014; Zuo *et al.* 2014; Sun *et al.* 2015; Tang *et al.* 2016; Zhang *et al.* 2016). Thus, a composite sheet that contained TiO₂ powder and diatomite powder could photodegrade the phenol more effectively than sheets that solely contained TiO₂ powder or diatomite powder.

It is worth noticing that the maximum value of $-dc/dt$ for the composite TiDI sheet with a 1:2 mass ratio of TiO₂/diatomite was approximately two times that of the sheet that had solely TiO₂ powder (TiO₂:DI = 4:0), as shown in Fig. 6.

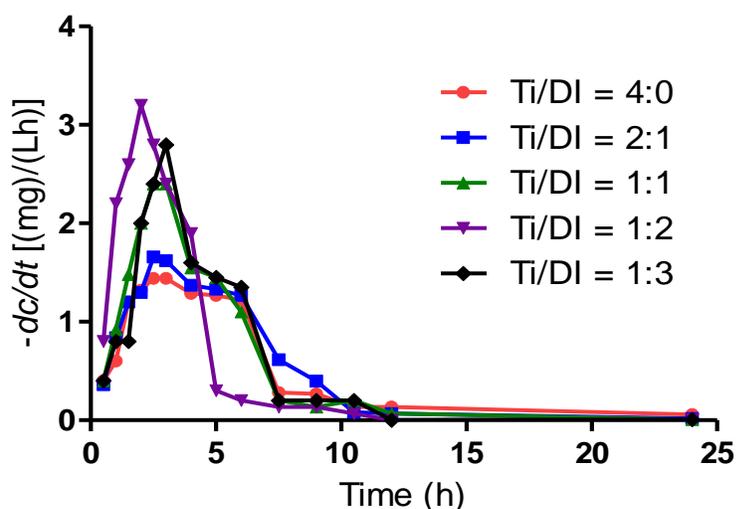


Fig. 6. Effect of the mass ratios of TiO₂ to diatomite on the photodegradation rate

This indicated that the high adsorption capability of diatomite greatly promoted the photocatalytic decomposition of phenol by TiO₂, and that the TiDI composite could effectively decompose phenol with low concentrations. However, when the mass ratio of TiO₂:DI decreased from 1:2 to 1:3, the value of $-dc/dt$ also decreased. Therefore, two factors likely controlled the degradation rate of phenol, the adsorbing rate of phenol by diatomite powder and the true photodegradation rate by TiO₂ powder. The amount of the diatomite powder controlled the adsorbing rate, *i.e.*, the adsorbing rate increased with increased diatomite powder amount. The amount of the TiO₂ powder controlled the true photodegradation rate of phenol. An increased TiO₂ powder amount increased the true photodegradation rate. However, the total amount fraction of the inorganic powder on the TiDI sheet was constant (35 wt.% based on the total weight of sheet). If the amount fraction of diatomite powder decreased, the amount fraction of TiO₂ powder should increase, which would lead to the reduced adsorbing rate of phenol and the increased true photodegradation rate. A balanced composition would help to achieve the best performance in phenol removal. The optimal TiO₂:DI mass ratio was 1:2.

The Performance of the Repeatedly-used Composite Sheet for Phenol Degradation

The performance of the composite sheet that was repeatedly applied to remove phenol in aqueous solution is shown in Fig. 7. With the increased times of TiDI utilization in the solution, the residual phenol concentration increased, which meant that the adsorption and decomposition ability of phenol by the TiDI sheet decreased. The main reason for this phenomenon could have been that some byproducts of phenol decomposition remained on the TiDI sheet. When this sheet was applied again in the new phenol solution, the sheet should first photocatalytically decompose the residual phenol, and thus decrease its ability for adsorbing and decomposing phenol. As shown in Fig. 7, after the sheet was utilized eight times in the solution, the residual phenol concentration increased to 11.8%, which was much higher than that at the first time (around 1.8%). In other words, the TiDI sheet reduced phenol concentration by approximately 90% after being applied in the solution for eight times. This showed its strong durability for adsorption and decomposition of phenol in solution. Furthermore, the remaining mass ratios of all the TiDI sheets were maintained at approximately 95% (Table 1), which indicated their stability of TiDI utilized in the phenol solution. Both results indicated that the TiDI sheet continuously removed the phenol in aqueous solution, which meant that the treatment cost was potentially low.

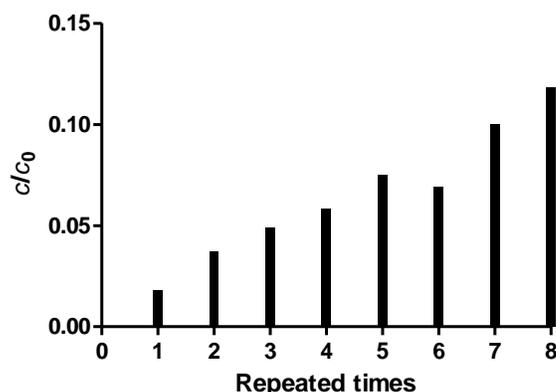


Fig. 7. The phenol concentration ratios of the solution after different repeated utilization times of TiDI composite sheet in solution

Table 1. Mass Retention Ratios of Sheet with Various Mass Ratios of TiO₂/DI

Mass Ratios of Ti:DI	Mass Retention Ratio of Sheets (%)
2:1	94.4
1:1	96.9
1:2	96.1
1:4	96.6

Characterization of Composite Sheets

The good durability of the composite sheet through its decomposition of phenol was confirmed by XRD and SEM analyses. The XRD patterns of different materials used for making the composite sheets are shown in Fig. 8. The diffraction peaks that corresponded to TiO₂ were positioned at 25.46°, 38.72°, and 48.18° (Fig. 8a), while the

diffraction peaks at 22.10° and 36.32° were attributed to that of diatomite (Fig. 8b). Figures 8c and 8d showed that the characteristic diffraction peaks of TiO_2 and diatomite still existed after applying in the composite sheets, which indicated that the crystal structure of TiO_2 and diatomite remained unchanged (Sun *et al.* 2014; Zhang *et al.* 2016). The above results proved that the TiO_2 powder and diatomite powder could retain their original function on the sheet.

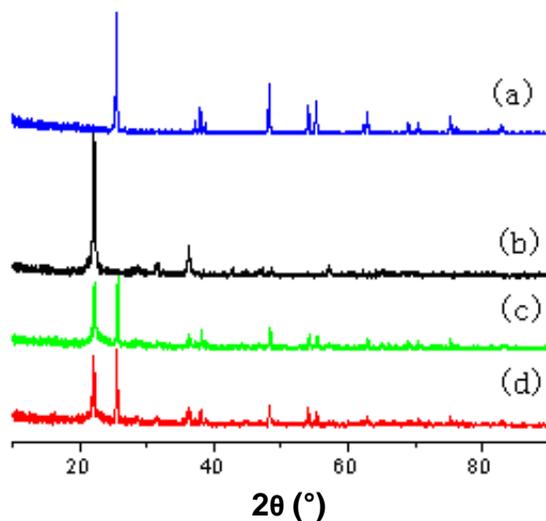


Fig. 8. XRD spectra of (a) TiO_2 powder, (b) diatomite powder, (c) TiO_2 -diatomite composite sheet before photocatalytic degradation, and (d) TiO_2 -diatomite composite sheet after eight times of utilization in phenol solution

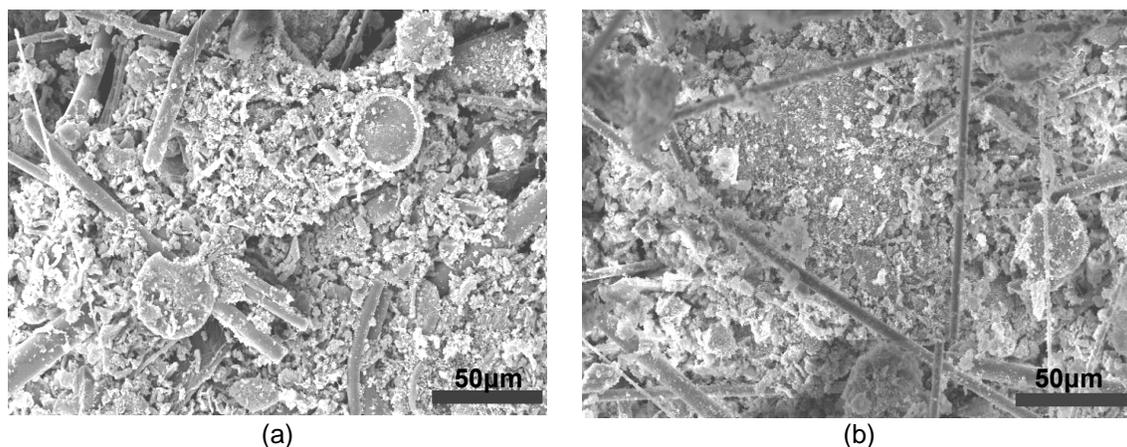


Fig. 9. Surface SEM images of composite sheet; (a) TiO_2 /diatomite (mass ratio of 1:2) composite sheet before utilization in phenol solution; (b) TiO_2 /diatomite (mass ratio of 1:2) composite sheet after eight-time utilization in phenol solution

Furthermore, after repeated utilization in phenol solution, the XRD pattern of the composite sheets did not show obvious change, which was an indication of good durability of the sheets. This could also be observed from the SEM images (Fig. 9) of the composite sheet, in which the TiO_2 powders adhered to diatomite powders and their morphology did not change noticeably after the sheets were used in the phenol solution for eight times.

CONCLUSIONS

1. The composite eucalyptus paper sheets that contained TiO₂ powder and diatomite powder were prepared by a papermaking technique and could be used to photodegrade phenol in aqueous solution effectively. It was found that TiO₂ powder and diatomite powder were firmly adhered to the eucalyptus fiber surface of the sheets. The phenol adsorbed by diatomite can be decomposed by TiO₂ photocatalysis. With a 1:2 mass ratio of TiO₂:diatomite, the composite paper sheet demonstrated the highest efficiency for decomposing phenol under UV irradiation. The pH value of the solution had effect on the removal efficiency of phenol by TiDI paper sheets. The optimum pH value for the phenol degradation could be around 6 when using TiO₂ as photocatalyst.
2. The TiO₂ powder and the diatomite powder could maintain their functionalities on the paper sheet and exhibited a good durability of TiDI composite paper sheet for the removal of phenol in aqueous solution.

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