

Degradation characteristic of TiO₂-chitosan adsorbent on Rhodamine B and purification of industrial wastewater

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Abstract—Based on biosorption and photodegradation coupling technology, a novel adsorbent, which not only adsorbs the heavy metal ions but also degrades organic compound, was prepared by immobilization of nano-TiO₂ on chitosan matrix. Degradation characteristic of Rhodamine B (Rh.B) was investigated by TiO₂-chitosan adsorbents. The results showed that degradation ratio reached 94.3% by 0.2 g adsorbents under ultraviolet radiation light (UV) at initial Rh.B concentration of 10 mg/L and optimal pH of 9.0. Degradation and adsorption behavior characteristics were discussed in the presence of binary pollutants (Rh.B and Ag⁺). The coexistence of Ag⁺ intensely inhibited the degradation ability of Rh.B. Higher Ag⁺ concentration weakened the degradation ability. However, Rh.B did not affect the adsorption capacity of Ag⁺. Moreover, TiO₂-chitosan adsorbent contributed to a higher degradation ability of organic pollutants in practical wastewater. Degradation capacity of contaminants in paper-making wastewater reached 60.8 mg/g at the initial COD concentration of 2,000 mg/L.

Key words: TiO₂, Chitosan, Photodegradation, Rhodamine B, Wastewater

INTRODUCTION

With the development of dye, paper and electroplating industries, the water pollution caused by toxic dyes and heavy metal ions is threatening to humans and the surrounding environment [1]. Many traditional methods such as ion-exchange and active carbon adsorption, which were applied to remove these two kinds of pollutants, have been investigated and applied to industry [2]. These methods showed favorable purification effect of wastewater, but they also had some shortcomings. For example, an ion-exchanger is an efficient method, but it could not only remove the heavy metal ions but also absorbed Ca²⁺, Mg²⁺ [3]. So the fast adsorption equilibrium required high frequencies of desorption and regeneration. Despite activated carbon having great adsorption capacity for organic compounds, desorption and regeneration were difficult under common conditions [4].

Recently, TiO₂ photocatalytic materials are very promising for application of the water purification and environmental treatment. This is because TiO₂ can be irradiated to produce electron-hole pairs with ultraviolet radiation which is equal to or greater than its band gap energy ($E_G=3.2$ eV). In an aqueous system, the holes (h⁺) are subsequently trapped by H₂O to yield •OH radicals, while the electrons (e⁻) are trapped by preadsorbed O₂ molecules to yield superoxide radicals O₂⁻ species which could interact with protons to generate •OH radicals. The •OH radicals have strong oxidation activity and completely degrade most of the organic pollutants into CO₂, H₂O and inorganic acid correspondingly, having no secondary pollution [4,5].

However, one of the bottlenecks in using TiO₂ as a photocatalyst is its difficulty for separation and regeneration after being used, especially in the wastewater treatment system [6,7]. Therefore, many researchers undertook some attempts to immobilize TiO₂ particles on some supports, such as mounting TiO₂ on SiO₂ [8], activated carbon [9], glass, pumice, zeolites, aluminum, polymers, etc [10,11].

Chitosan, as a new kind of biosorbent, has been widely used in the wastewater treatment because of its high adsorption capacity for heavy metal ions [12,13]. A novel method of immobilization of nano-TiO₂ on chitosan was achieved by Su and co-workers [14,15]. This new double functions TiO₂-chitosan adsorbent resolved the re-collection and reuse limitation of nano-TiO₂, and was used not only in degradation of dyes, but also in adsorption of heavy metal ions. Degradation studies of acidic dyes (such as Methyl Orange, MO; Methylene Blue, MB; Sunset Yellow, SY) by TiO₂-chitosan adsorbents were referred to in the previous work of our lab [16,17]. And heavy metal ions (such as Ag⁺ and Ni²⁺) always played a stimulative role in degradation of those dyes [18]. However, there were no researches reported about the degradability of alkaline dyes by TiO₂-chitosan adsorbents and the effects of the heavy metal ions on degradation.

In this work, biosorption and photodegradation technology were coupled through immobilization of TiO₂ on chitosan. Since Rhodamine B (Rh.B), one of the most common alkaline dyes, was found to be potentially toxic and carcinogenic [19-21], the degradability of Rh.B using TiO₂-chitosan adsorbent was studied. Then, effects of pH and presence of Ag⁺ on TiO₂-chitosan adsorbent were investigated. TiO₂-chitosan adsorbent also provided a higher degradation ability of organic pollutants in practical alkaline wastewater, which had the vital significance to reduce the pressures of worldwide environmental pollution.

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EXPERIMENTAL

1. Reagents and Apparatus

In this work, titanium dioxide was used as the photocatalyst (Degussa P25, 80% anatase, 20% rutile, 50 m²/g, primary particle size 25-30 nm, agglomerate size 100 nm); Chitosan with 90% degree of deacetylation was extracted from shrimp shells from Jinan Haidabei Marine Bioengineering Co. Ltd. Rhodamine B, epichlorohydrin, silver nitrate and acetic acid were of analytical grade.

2. Preparation of Adsorbent

2-1. Preparation of TiO₂-chitosan Adsorbent

0.5 g chitosan was dissolved in 10 mL acetic acid (10% (v/v)). 0.2 g TiO₂ was added in the above solution, then dispersed with ultrasonic for 15 min. 1.6 ml epichlorohydrin was added, reacting for 4 h at room temperature. Then the mixture solution was dropped into 0.25 mol/L NaOH (as the solidifying solutions), and the spheres were formed instantaneously. The formed TiO₂-chitosan beads (particles size: 0.970±0.050 mm) were stirred in the alkaline solutions for 3 h. At last, the TiO₂-chitosan beads were washed with distilled water and dried at 60 °C.

2-2. Preparation of Chitosan Adsorbent

0.5 g chitosan was dissolved in 10 mL acetic acid (10% (v/v)), then 1.6 ml epichlorohydrin was added, reacting for 4 h at room temperature. Then the mixture solution was dropped into 0.25 mol/L NaOH (as the solidifying solutions), and the spheres were formed instantaneously. The formed chitosan beads (particles size: 0.720±0.050 mm) were stirred in the alkaline solutions for 3 h. At last, the TiO₂-chitosan beads were washed with distilled water and dried at 60 °C.

2-3. Preparation of SDS-modified TiO₂-chitosan Adsorbent

Four parts of chitosan (0.5 g/part) and TiO₂ (0.2 g/part) were dissolved in 10 mL acetic acid (10% (v/v)). Four parts of SDS (the volume of SDS in each tube was 0.05 ml, 0.10 ml, 0.15 ml and 0.20 ml, respectively) were added in the above solutions, then dispersed through ultrasonic for 15 min. 1.6 ml epichlorohydrin was added in each tube, reacting for 4 h at room temperature. Then the mixture solution was dropped into 0.25 mol/L NaOH (as the solidifying solutions), and the spheres were formed instantaneously. The formed SDS-modified TiO₂-chitosan beads remained in the alkaline solutions for 3 h and then were washed with distilled water dried at 60 °C.

3. Analysis

The morphology of the adsorbent surface was obtained with scanning electron microscope. The concentration of Rh.B was analyzed by an adsorption spectrophotometer under 554 nm.

4. Photodegradation of Rh.B

0.2 g adsorbent (dry) was added into a dish (9 cm) containing 40 ml Rh.B (10 mg/L) and the mixtures were shaken in a shaker (50 rpm). The mixtures were shaken in a reciprocal shaker (50 rpm) at 20-25 °C for 8 h. An ultraviolet lamp (20 W, and the lamp is 0.5 m long and has a diameter of 0.02 m with a maximum UV irradiation peak of 365 nm) was available in the shaker which was placed at a distance of 10 cm above from the dish. Furthermore pH of the solution was regulated by HNO₃ and NaOH.

$$\text{Degradation of Rh.B (\%)} = (C_m - C_d) / C_m \times 100 \quad (1)$$

where C_m and C_d are the initial and equilibrated concentrations of Rh.B (mg/L).

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Table 1. Characteristics of wastewater for purification process

Items	Value
COD (mg/L)	1830±50
BOD (mg/L)	820±30
pH	5.0-6.0

5. Characteristics of Wastewater

Paper-making wastewater was provided by Beijing Hongxing printing house and its characteristics summarized in Table 1.

6. Purification of Wastewater

0.2 g adsorbent (dry) was added into 40ml paper-making wastewater, other cases same as 2.4. The wastewater with different initial COD values was prepared by dilution with distilled water.

$$\text{Removal ratio of COD (\%)} = (\text{COD}_m - \text{COD}_d) / \text{COD}_m \times 100 \quad (2)$$

Where COD_m and COD_d are the initial and equilibrated COD value of wastewater, respectively.

RESULTS AND DISCUSSION

1. Degradation Characteristic of TiO₂-chitosan Adsorbent

The removal abilities on Rh.B of pure nano-TiO₂, TiO₂-chitosan adsorbent, chitosan adsorbent under UV and TiO₂-chitosan adsorbent in dark are illustrated in Fig. 1. Compared with the pure nano-TiO₂, a slight decrease of the degradation ability of TiO₂-chitosan adsorbent on Rh.B was observed. The total removal ratio of Rh.B by TiO₂-chitosan adsorbent could reach 83.2%, which was almost 90% of the pure nano-TiO₂. Comparison of COD value treated with pure nano-TiO₂, chitosan adsorbent, TiO₂-chitosan adsorbent and TiO₂-chitosan adsorbent in dark is shown in Table 2. Obvious degradation or adsorption of Rh.B was not observed by TiO₂-chitosan adsorbent in dark and chitosan adsorbent under UV. It can be con-

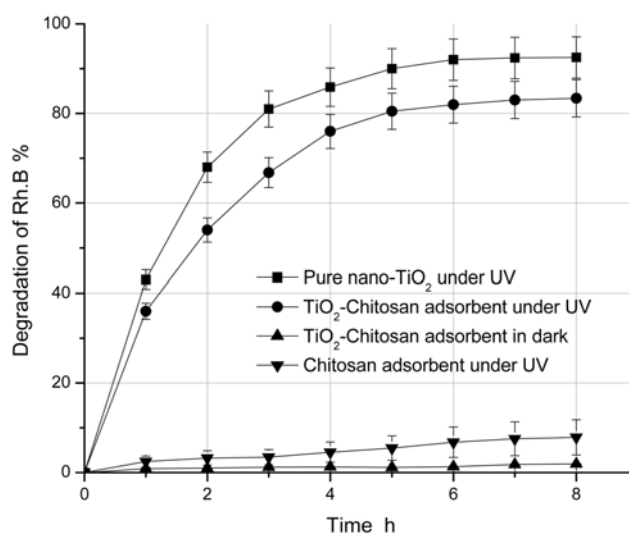
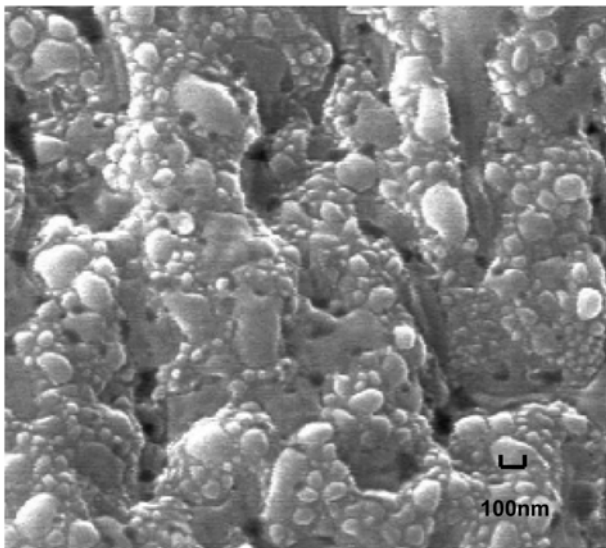


Fig. 1. Comparison of the degradation ratio of Rh.B with pure nano-TiO₂, chitosan adsorbent, TiO₂-chitosan adsorbent and TiO₂-chitosan adsorbent in dark: 40 mL Rh.B solution (10 mg/L) was contacted with 0.2 g adsorbent at about pH 7.0 and room temperature (25.0-27.0 °C).

Table 2. Comparison of COD value treated with pure nano-TiO₂, chitosan adsorbent, TiO₂-chitosan adsorbent and TiO₂-chitosan adsorbent in dark

	COD before treating	COD after treating
Pure nano-TiO ₂ under UV		184±10
TiO ₂ -Chitosan adsorbent under UV	526±10	236±10
TiO ₂ -Chitosan adsorbent in dark		521±10
Chitosan adsorbent under UV		508±10

W=0.2 g V=40 ml pH=7 t=8 h

**Fig. 2. SEM photo of TiO₂-chitosan adsorbent.**

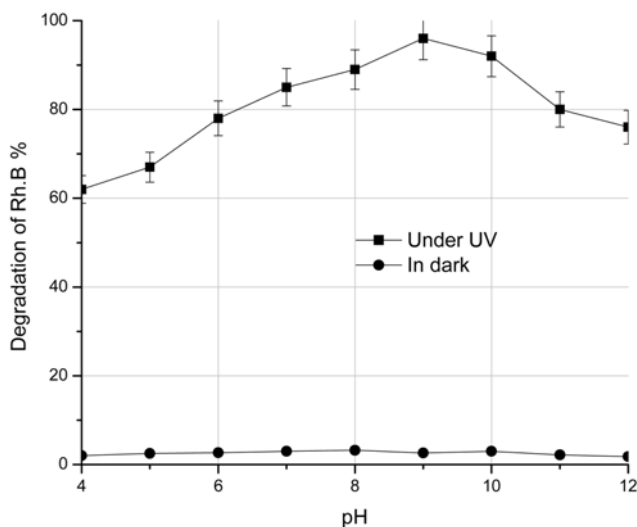
cluded from this experiment that the removal of Rh.B by TiO₂-chitosan beads is mainly the result of degradation, not the adsorption by chitosan.

The morphology of the adsorbent surface investigated with SEM is shown in Fig. 2. The surface of TiO₂-chitosan adsorbent was very unsmooth with many minute granules, which led to adsorbent having a large specific surface area. So, unsmooth structures could provide more adsorption sites for Rh.B with TiO₂ catalyst on the adsorbent surface.

2. Effect of pH on Adsorption

The pH of solution was a significant parameter during the adsorption process. It was known to all that weak-acid condition was an advantage for the photocatalytic reaction of methyl orange, which is a kind of acidic dye [22]. In this test, degradation of Rh.B was carried out under different pH values from 4.0 to 12.0. The degradation ratios of Rh.B under UV and in the dark at various pH values are shown in Fig. 3, respectively. The pH of aqueous solution had an optimal value of 9.0 and the maximum degradation ratio of 94.3% at the initial Rh.B concentration of 10 mg/L under UV. However, there was no obvious degradation by adsorbent in the dark. In light of simple operation, we maintained a neutral environment as our experimental conditions.

The explanation for this behavior was probably that the pH value in the solution affected the surface properties of the photocatalyst.

**Fig. 3. Effect of pH on the degradation of Rh.B: 40 mL Rh.B solution (10 mg/L) was contacted with 0.2 g adsorbent at room temperature (25.0-27.0 °C), reacting 8 hours.**

The zero-point charge is pH 6.25 for TiO₂ [23]. So it was more positive in acidic medium (pH<6.25), whereas it was negatively charged in the alkaline medium (pH>6.25). Rh.B was a univalent cation in aqueous solution, hence electrostatic repulsion between the positive TiO₂⁺ and Rh.B⁺ retarded adsorption in acidic pH range while TiO₂ surfaces acquired negative charges in alkaline condition. Electrostatic interactions between TiO₂ and Rh.B⁺ led to strong adsorption and resulted in the corresponding high degradation ability. As pH value was more than 9.0, the surface of the adsorbent would be covered with negative charge, which would obstruct the transfer of photoelectron (e⁻) to catalyst surface, and reduce the yield of •OH. And therefore, the circumstance of alkalescence was of advantage to degradation of Rh.B, which was consistent with the results reported by Rajeev Jain [24].

3. Effect of Presence of Ag⁺ on Degradation

The adsorption behavior of heavy metal ions and removal ability of organic pollutants in the presence of binary pollutants have been seldom studied. Thus, it is meaningful for removal behaviors on binary pollutants by TiO₂-chitosan adsorbent. Hongyan Huo [14,15] confirmed that the degradation ability of dye (such as methyl orange) could be improved with the increase of the adsorption capacity on metal ions (such as Ni²⁺, Ag⁺ and Cu²⁺) of adsorbent, which showed the adsorption of heavy metal ions and the degradation of dye should be synergic action.

As shown in Fig. 4, Ag⁺ adsorption capacity increased from 48.5 mg/g to 169.4 mg/g at the increase of Ag⁺ initial concentration from 200 mg/L to 1,000 mg/L. Under the presence of Rh.B in the solution, Ag⁺ adsorption capacity increased from 31.9 mg/g to 165.4 mg/g at the same condition. Adsorption capacity of TiO₂-chitosan adsorbent only slightly decreased and had no significant effect on the removal of Ag⁺ in the presence of Rh.B. This phenomenon attributes to the strong binding force between amino groups of chitosan and Ag⁺, which is consistent with the result of the literature [25].

Based on photocatalytic technology, the degradation effects of TiO₂-chitosan adsorbent on Rh.B in the absence of Ag⁺ in the solution were very attractive (see Fig. 5(a)). However, in the presence

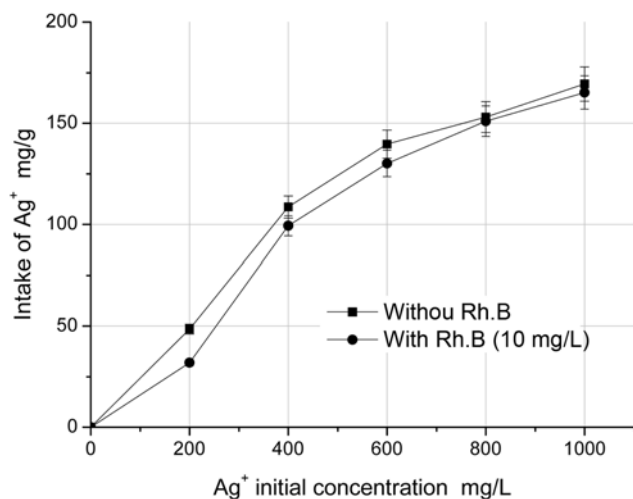


Fig. 4. Effect of Ag^+ initial concentration on adsorption capacity: 40 mL Ag^+ solution (200–1,000 mg/L) was contacted with 0.2 g adsorbent at about pH 7.0 and room temperature (25.0–27.0 °C).

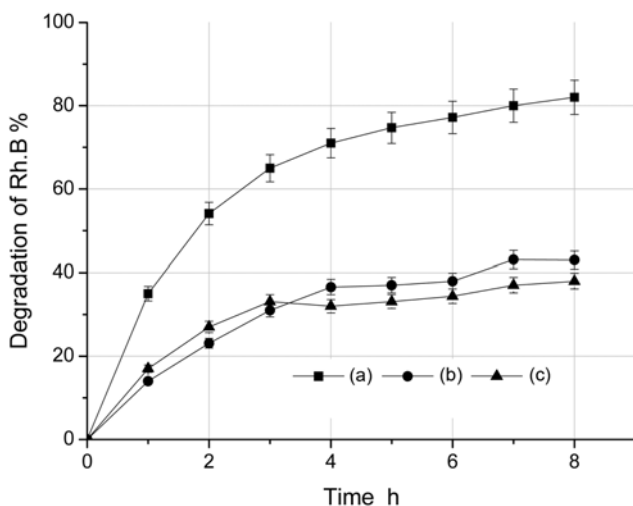


Fig. 5. Effect of Ag^+ -coexistence on the degradation of Rh.B: 40 mL Rh.B solution (10 mg/L) at about pH 7.0 and room temperature (25.0–27.0 °C). (a) with 0.2 g adsorbent (b) with 0.2 g adsorbent when Ag^+ (200 mg/L) was presented. (c) with 0.2 g adsorbent when Ag^+ (1,000 mg/L) was presented.

of Ag^+ , the removal ability of Rh.B by TiO_2 -chitosan adsorbents was strongly inhibited. And the adverse effect on the removal ability of Rh.B was not obviously enhanced with the increase of Ag^+ concentration in the solution from 200 mg/L to 1,000 mg/L.

The degradation process of Rh.B would be divided into two stages: first, Rh.B⁺ was adsorbed on the surface of the adsorbent; second, Rh.B⁺ reacted with photocatalyst of TiO_2 [14,15]. However, Ag^+ could take priority of adsorption and receive the photoelectron (e^-) from TiO_2 surface, and then restrain the adsorption of Rh.B. Finally it further retarded the degradation on Rh.B.

4. Effect of Surfactant in Preparation

Considering that SDS is a kind of negative ion surfactant which could enhance the degree of dispersion of nano- TiO_2 in chitosan

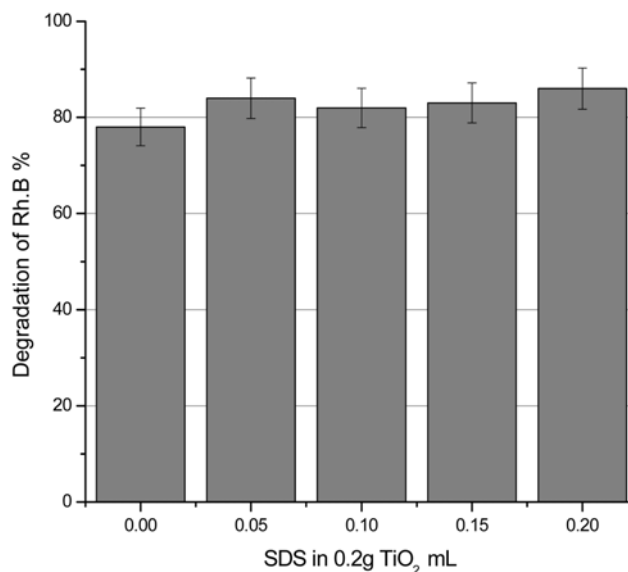


Fig. 6. Effect of loading SDS on the degradation of Rh.B: 40 mL Rh.B solution (10 mg/L) was contacted with 0.2 g adsorbent at about pH 7.0 and room temperature (25.0–27.0 °C), reacting 8 hours.

coating, increase the TiO_2 specific surface area of photocatalytic and reduce the chance of nano- TiO_2 being embedded to chitosan coating inside [26], SDS-modified TiO_2 -chitosan adsorbent was prepared (as shown in 2.2.2). To gain the optimum amount of SDS, series amounts of SDS were investigated from 0.05 mL to 0.20 mL. Comparison of the degradation capability of the TiO_2 -chitosan adsorbent and SDS-modified TiO_2 -chitosan adsorbent is shown in Fig. 6.

The degradation capability of modified TiO_2 -chitosan adsorbent with SDS was enhanced. As indicated in Fig. 6, the degradation ratio of Rh.B increased from 78% to 84% after adding 0.05 mL SDS at the initial Rh.B concentration of 10 mg/L at about pH 7.0 in solution. Air bubbles in the preparation process of modified TiO_2 -chitosan adsorbent by adding SDS were observed, which would be one reason to increase the specific surface area of adsorbent and then improve the photocatalytic efficiency. However, If SDS amount increased from 0.05 mL to 0.20 mL, the degradability and degradation speed would remain at a steady level. The reason is that a thimbleful of SDS would make the TiO_2 diffuse adequately in chitosan coating, and excessive SDS would not contribute to dispersion of TiO_2 .

5. Degradation Characteristic of Adsorbent in Practical Wastewater

Since the basic component of paper-making wastewater is lignin, which has the same aromatic group as Rh.B, the removal ability of TiO_2 -chitosan adsorbent on organic pollutant in practical wastewater was displayed in Fig. 7. The results showed that the degradation by TiO_2 -chitosan adsorbent on COD in paper-making wastewater was enhanced with the increase of the initial COD value, and then COD removal reached 60.8 mg/g at the initial COD concentration of 2,000 mg/L, which also showed a high removal capability of organic pollutant in practical wastewater, although degradation of macromolecules (such as lignin) was more difficult than small molecules (such as Rh.B).

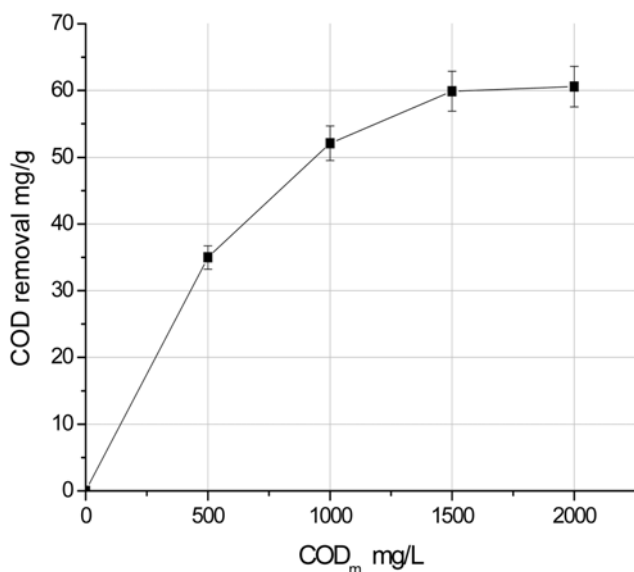


Fig. 7. Effect of initial COD of wastewater on COD removal. 40 mL paper-making wastewater was contacted with 0.2 g adsorbent at about pH 7.0 and room temperature (25.0-27.0 °C), reacting 8 hours.

Table 3. Comparing the removal ability of COD with literature

Photocatalyst	TiO ₂ -zeolite	TiO ₂ -chitosan
Dosage/(g/L)	50	5
COD _m /(mg/L)	1080	2000
Removal rate of COD/%	82	15.2
Removal capacity of organic pollutants/(mg/g)	17.7	60.8

W=0.2 g V=40 ml pH=7 t=8 h

Comparing the removal capacity of contamination with the TiO₂-zeolite photocatalyst prepared by Zhongliang Shi [27], TiO₂-chitosan adsorbent showed a more effective degradation ability of organic pollutants. As indicated in Table 2, the removal capacity on organic pollutants of TiO₂-chitosan adsorbent was about three times that of TiO₂-zeolite.

Furthermore, TiO₂-chitosan adsorbent could not only degrade organic pollutants, but also selectively adsorb the heavy metal ions, which would be more promisingly applied in the wastewater treatment from electroplating, dyeing, paper-making and other heavily polluting industries.

CONCLUSIONS

Due to the reciprocity of loading TiO₂ and chitosan, the TiO₂-chitosan adsorbent prepared showed high photoactivity for the photodegradation of Rh.B and adsorption of Ag⁺. The degradation ratio on Rh.B of TiO₂-chitosan adsorbent reached 94.3% under UV irradiation at the initial Rh.B concentration of 10 mg/L and optimal pH of 9.0. Intake of Ag⁺ by the same adsorbent could also reach 165.4 mg/g at Ag⁺ initial concentration of 1,000 mg/L. However, in the presence of Ag⁺, Rh.B and TiO₂-chitosan adsorbents, the removal ability of Rh.B was strongly inhibited. The reason was probably that

Ag⁺ could be competitive active site on the surface of the adsorbent with Rh.B⁺ in solution, and then the degradation ability of Rh.B was inhibited. Nevertheless TiO₂-chitosan adsorbent also provided a higher degradation ability of organic pollutant in practical wastewater. COD removal in paper-making wastewater reached 60.8 mg/g at the initial COD concentration of 2,000 mg/L. It showed that the TiO₂-chitosan adsorbent would have more potential applications in wastewater treatment.

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