Photocatalytic Degradation of Phenol in Aqueous Solutions Using TiO2/SiO2 Composite

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Photocatalytic degradation of phenol in aqueous solutions was investigated using TiO_2/SiO_2 composites with different Ti/Si molar ratios (95/5−75/25) and calcined at 500 °C. The synthesized composites were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and N_2 adsorption–desorption isotherms. Their photocatalytic activities for phenol degradation were evaluated in a batch reactor under simulated visible light using a special 26 W compact lamp. The results showed that all synthesized composites consist of pure anatase phase with high crystallinity and exhibit high photocatalytic activities for phenol degradation. At the initial concentration 10 ppm phenol and catalyst dose 0.10 g/L, the highest photocatalytic activity for phenol degradation was observed with the synthesized TS05 composite (Ti/Si molar ratio of 95/5), resulting in 53.5 % phenol degradation yield after 4 h. The corresponding phenol degradation yields using the synthesized composites TS15 (Ti/Si molar ratio of 85/15) was ~ 40.0 % and TS25 ((Ti/Si molar ratio of 75/25) was ~ 36.0 %. The TS05 composite could be a promising photocatalyst for the removal and degradation of organic pollutants.

1. Introduction

The presence of phenolic compounds in water solutions has caused several serious problems. A representative of these compounds is phenol (Chiou and Juang, 2007), which is a precursor in many manufacturing processes like the petrochemical, pharmaceutical, plastic, biotechnology and dye industries (Hao et al., 2015). Because of their toxicity (Kim et al., 2017) and stability, phenolic compounds often remain in the environment for long periods, so they remain dangerous to human health when exposed to phenol-polluted water (Trinh et al., 2016).

Removing phenolic compounds from waste waters has received widespread attention recently. Phenol from wastewater can be removed by traditional methods such as chemical oxidation, adsorption and biotechnology (Sacco et al., 2018). The conventional waste-water treatment technologies have some disadvantages and limitations (Royaee and Sohrabi, 2010). The common chemical oxidation method is suitable for removing high concentrations of organic pollutants but not mineralizing all organics. Activated carbon adsorption includes phase transfer of pollutants without degradation, which causes another pollution problem. Biochemical technology is slow and requires controlling pH, temperature and the problematic disposal of activated sludges. The current trend of phenol treatment is tending towards complete mineralization of the final products to CO_2 and H_2O (Royaee and Sohrabi, 2010). Consequently, advanced oxidation processes (AOPs) are preferred methods to handle phenolic compounds in wastewater (Trinh et al., 2016).

In recent years, AOPs are considered as promising methods for phenol degradation (Hao et al., 2015). Among the AOPs, semiconductor photocatalysis has been recognised as an efficient strategy for the elimination by transforming environmental pollutants into friendly products. The most commonly used photocatalyst is TiO_2 due to its non-toxicity, low cost (Tahir, 2018), as well as its physical and chemical stability (Yilleng et al., 2018). TiO_2 is limited by the low photocatalytic activity in applications because its energy gap is wide (3.2 eV) (Moradi et al., 2019) and low specific surface area (Cui et al., 2019). Hence, many attempts have been made to improve TiO_2 photoactivity by modifying its structure with metals and non-metals (Tahir, 2018). For example, $N-TiO_2$ was prepared by acid-catalysed hydrolysis, showed higher phenol degradation compared

with pure TiO₂ (Wu et al., 2014). Au−Pd nanoparticle-doped TiO₂ was also prepared, resulting in low band-gap energy (Yilleng et al., 2018). Some research results indicate that increasing the specific surface area of the aimed materials might play an important role in their photocatalytic activity (Guo et al., 2014). For this purpose, silica, one of the most common adsorbents, was used to prepare TiO_2/SiO_2 (Guo et al., 2014). TiO_2/SiO_2 mixed oxide has higher activity than pure TiO₂ when being used as a photocatalyst (Dong et al., 2019). The added SiO2 strengthens the thermostability of anatase TiO₂, increases its specific surface area and enhances its photocatalytic activity (Feng et al., 2019). Regarding the composite of silica-supported TiO2 particles, the probability of electron−hole recombination will reduce and the photocatalytic performance of TiO2 can be enhanced (Cetinkaya et al., 2013). Most importantly, there are few reports discussing the factors affecting the synthesis of TiO_2/SiO_2 composite, so a research is necessary.

In this work, TiO_2/SiO_2 nanoparticles were synthesized using the sol−gel method and the effect of TiO_2/SiO_2 molar ratio on phenol photocatalytic degradation was investigated. The effects of H_2O, polyethylene glycol, titanium n-butoxide and acetylacetone heating time were also studied. The results obtained will be a basis for further development of TiO_2/SiO_2 composite photocatalysts for application in waste-water treatment.

2. Experimental

2.1 TiO₂/SiO₂ synthesis

Titanium *n*-butoxide (TNB-Acros 99 %) was used as the precursor of TiO₂ and tetraethylorthosilicate (TEOS-Merck 99 %) was used as the precursor of SiO₂. Acetylacetone (ACAC-Merck 98 %) was employed as a chelating agent during the sol–gel process. Polyethylene glycol (PEG-Merck, average MW of 20,000) was used to increase the mixture's viscosity. Ethanol (EtOH, 99.5%) and double distilled water were used in all experiments. TiO_2/SiO_2 composite was prepared as follows: TiO₂ solution was prepared by vigorous stirring of TNB, EtOH and ACAC (volume ratio 4 : 11 : 1) at 80 °C for 1 h, then cooled to room temperature for 30 min. SiO₂ solution was prepared by vigorous stirring of TEOS, EtOH and HNO₃ (molar ratio 1 : 14 : 1) for 1 h. Then, precise amounts of these two solutions were intensively mixed together at room temperature giving mixtures with Ti/Si molar ratios 95 : 5; 85 : 15; 75 : 25. The mixtures obtained were then aged 40 h at ambient temperature, dried at 120 °C for 3 h and calcined in air at 500 °C for 2 h. The synthesized TiO_2/SiO_2 were consequently denoted as TS05 (95 : 5), TS15 (85 : 15) and TS25 (75 : 25). Similar steps (ageing, drying, calcining) were applied to the TiO₂ solution itself to prepare TiO₂ without SiO₂.

2.2 TiO₂/SiO₂ characterization

The synthesized TiO_2/SiO_2 and TiO₂ were characterized with X-ray diffraction (XRD) using a D2 Phaser (Bruker) with Cu Kα radiation (λ = 0.154 nm) for crystallinity. Scanning electron microscopy (SEM) using JSM-6500F, JEOL was used for surface morphology. The band-gap energy of each sample was calculated from diffuse reflectance spectra (DRS) ranging from 850 to 220 nm, scanning step of 2 nm, at the rate of 400 nm/min using a Solid UV−vis JASCO V-550 instrument. Brunauer–Emmett–Teller (BET) measurements using a Quantachrome Instruments version 11.0 were used to calculate the specific surface area.

2.3 TiO₂/SiO₂ photocatalytic activity

Photocatalytic activities of the synthesized TiO_2/SiO_2 composites were tested monitoring phenol degradation in a laboratory-scale photoreactor. This 500 mL reactor was filled with 200 mL phenol solution (initial phenol concentration of 10 mg/L) and 200 mg synthesized TiO_2/SiO_2 composite. During the photocatalytic process, this mixture was constantly stirred at 30 ± 2 °C and illuminated by a special 26W compact lamp (Natural light PT 2191-ExoTerra) with wavelength region from 390 to 640 nm, in which the most intense wavelength is located at 540 nm. The lamp was placed above the reactor. The mixture was stirred in the dark for 60 min to ensure adsorption–desorption equilibrium before switching on the lamp. Experiments were performed for 4 h, and 5 mL samples were taken at each time interval (1 h). Each sample was subjected to filtration through a 0.45 µm Nylon syringe filter to remove particles and then added to 4-aminoantipyrine and potassium ferric cyanide at pH 10 to form a coloured complex (Medjor et al., 2015). This complex solution was determined using a Hitachi UV−vis spectrophotometer equipped with an Optics ISSUV/VIS light source with wavelength region from 400 to 600 nm. Degradation of the phenol was tracked by its absorption peak at 510 nm.

3. Result and discussion

3.1 Characteristics of the catalysts

The XRD patterns of different catalysts are shown in Figure 1. It is clear that all peaks on the patterns are assigned to the pure anatase phase TiO₂ (JCPDS 21-1272) at characteristic peaks 2θ 25.2° (101), 36.9°

(004), 48.24° (200), 54.86° (211) and 63.01° (213). No peaks of SiO_2 are seen in any of the samples, which indicates that SiO_2 is an amorphous phase. It is found that the crystallinity decreases and the peak widens by increasing silica content from 5.0 to 25.0 %. The increasing number of SiO_2 particles in the formation of TiO_2/SiO_2 composites means an increasing number of amorphous particles in the composites, consequently, the crystallinity will reduce, as confirmed by less intense XRD peaks of the composite. This result is in agreement with previous research.
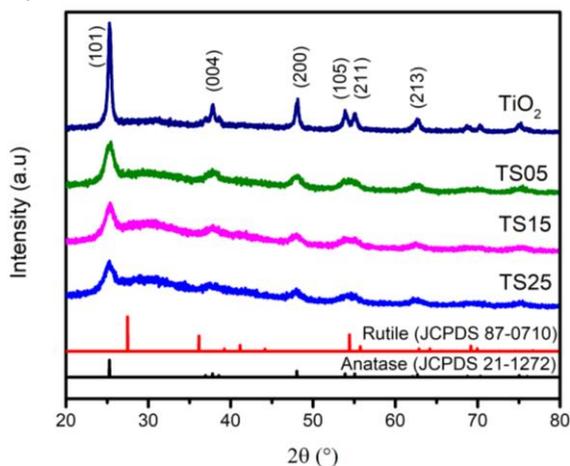

Figure 1: X-ray patterns of TiO₂, TS05, TS15 and TS25

The morphology of the catalysts was investigated using SEM as shown in Figure 2. It seems that the particles have a spherical shape with several fractal particles. The presence of fractal particles is explained as the particles that were formed in early precipitation due to the chelating process (Aji et al., 2017). It was observed that all of the samples show agglomerates and the TS15 particles are the smallest. The TS05 was seen to be similar in dimension of particles with diameter of 300 nm. It was proved that molar ratio $TiO_2:SiO_2$ = 95 : 5 has a higher pore volume than other samples (Table 1).

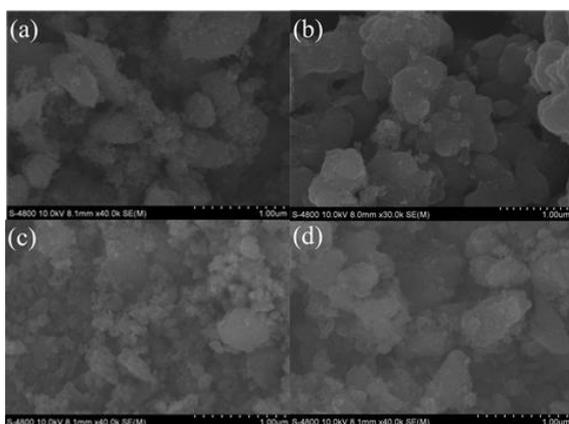*Figure 2: SEM images of (a)TiO₂; (b) TS05; (c)TS15; (d) TS25*

Nitrogen adsorption−desorption isotherms of TiO_2, TS05, TS15 and TS25 are shown in Figure 3a. It is noticeable that the N_2 adsorption−desorption isotherms obtained for the samples are type IV isotherms according to the IUPAC classification and are mesoporous materials. It can be seen that the TS05 presents a better capability of nitrogen adsorption, which is directly related to a higher pore volume (Table 1). The higher specific surface area of TS05 can undoubtedly provide reactant adsorption−desorption sites and more active sites for both adsorption and the photocatalytic reaction (Guo et al., 2014).

Textural properties and band-gap energy (Eg) for TiO_2, TS05, TS15 and TS25 samples are shown in Table 1. As the amount of SiO_2 in nanocomposites increases, the surface area also increases. Obviously, the pure TiO_2 displayed very low surface area in comparison with those of synthesized TiO_2/SiO_2. The specific surface area of TiO_2 was 46.412 cm^2/g, but with the addition of only 5.0 % SiO_2 the area was significantly increased,

demonstrating that SiO_2 helped improve the surface of catalyst material by creating more pores. By contrast, pore volume and pore diameter of TS05 is higher than the other samples. The presence of SiO_2 plays an important role in preventing the collapse of the hole channel and maintaining the mesoporosity of the prepared catalyst, which will provide more active sites in photocatalysis processes (Cui et al., 2019). It is also noticeable that the band-gap energy of TiO_2/SiO_2 samples is observed to be slightly increased in comparison with that of pure TiO_2. This increase in the band-gap energy with increasing content of silica can be attributed to structural interruption in the titania framework by Si atoms resulting in a larger energy gap between the valence band and conduction band, which reduces the recombination rate of electrons and holes at the time of irradiation (Smitha et al., 2010) (Figure 3b).

Table 1: Textural properties and band-gap energy (Eg) of TiO_2, TS05, TS15 and TS25 samples.

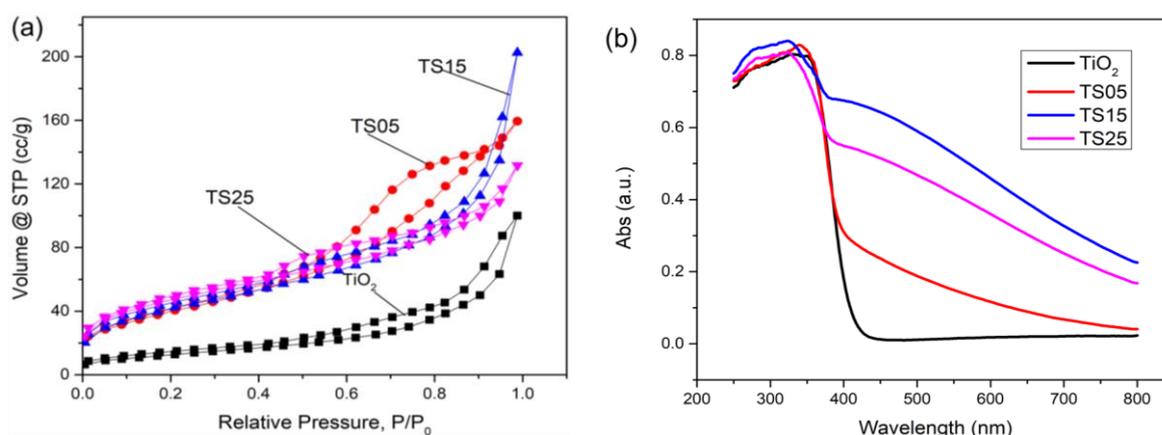| Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	Band gap (eV)
TiO_2	46.412	0.053	2.32	3.12
TS05	145.397	0.159	2.34	3.27
TS15	148.360	0.144	2.24	3.35
TS25	164.390	0.138	2.10	3.35

Figure 3: (a) N_2 adsorption–desorption isotherms; (b) The band-gap energy of TiO_2, TiO_2/SiO_2 samples

3.2 Photocatalytic degradation

Figure 4a shows the effect of molar ratio $TiO_2:SiO_2$ on phenol photocatalytic degradation. Clearly, the TS05 exhibited the highest photocatalytic activity in phenol degradation at a catalyst dose of 0.10 g/L. It reached 53.5 % after 4 h irradiation, which is higher than that of the TS25 sample (36.0 %), the TS15 sample (40.0 %) and the TiO_2 (33.0 %). This can be explained as the increase of silica increases the number of amorphous particles in the composites thereby increasing photocatalytic activity. When the amount of silica increased to 15.0 and 25.0 %, it showed low photocatalytic activity due to SiO_2 having no photocatalytic activity. The TS05 photocatalyst could be a promising photocatalyst for removal and degradation of organic pollutants. Thus, the TS05 catalyst sample is the optimal ratio of the carrier and investigates the effect of the agents on the catalytic synthesis using the sol−gel method.

The photocatalytic activity of the sample with various molar ratios $TNB:H_2O$ for degradation of phenol (10 ppm) under visible light is shown in Figure 4b. As can be seen from the graph, molar ratio $TNB:H_2O$ of 1 : 10 exhibited the highest photocatalytic activity in phenol degradation. It reached 53.5 % after 4 h irradiation, which is higher than that for the ratio of 1 : 4 (17.0 %) and 1 : 8 (38.0 %). This can be explained as the increasing amount of H_2O leads to increased amount of hydroxyl groups on the silica surface that hydrogen bonds between silanols can be formed (Hendrix et al., 2015). The titania precursor can react with multiple hydroxyl groups, forming perfect TiO_2/SiO_2 particles, which can improve the activity of the TiO_2/SiO_2 composite. When the amount of H_2O was increased with molar ratio 1 : 12, the titania precursor undergoes hydrolysis first to form $Ti(OH)_4$ before combining with TEOS, which could lead to the decrease of photocatalytic effectiveness. From the obtained results, the molar ratio of $TNB:H_2O$ as 1 : 10 was chosen to conduct further investigation of the following conditions.
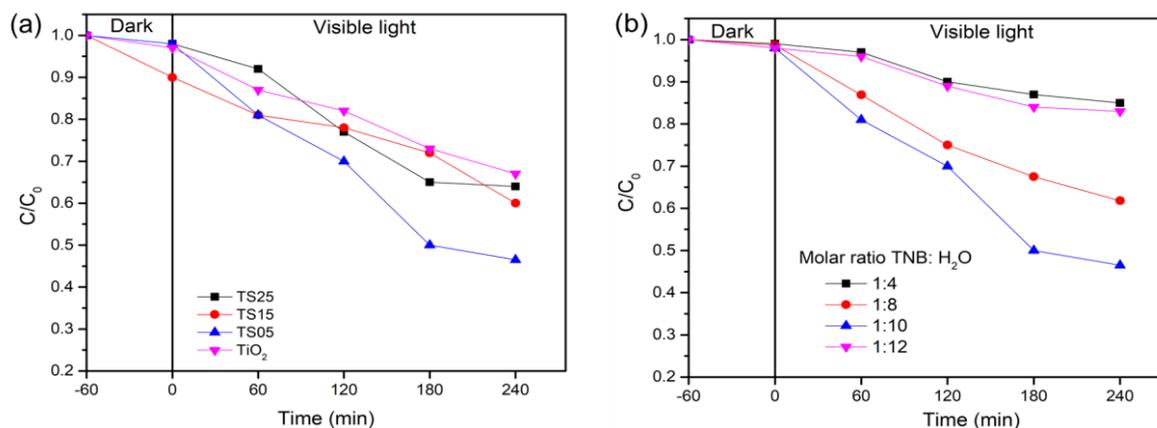
Figure 4: Photocatalytic degradation of phenol (a) Effect of molar ratio TiO2:SiO2; (b) Effect of molar ratio TNB:H2O over TS05

Figure 5a shows the photocatalytic activity of the sample with various molar ratios TNB:PEG for degradation of phenol. Overall, molar ratio TNB:PEG of 1 : 0.1 and 1 : 0.2 exhibited the same photocatalytic activity in phenol degradation. It reached 53.5 % after 4h irradiation, which is higher than that of the ratio of 1: 0.05 (25.0 %), 1 : 0.4 (40.0 %) and 1 : 0.8 (36.0 %). Because PEG was used as a catalyst for forming pores, increasing PEG leads to increasing photocatalytic activity. The photocatalytic activity of samples decreased when continuing to increase the amount of PEG with molar ratios 1 : 0.4 and 1 : 0.8. The PEG macromolecule inhibits the reaction of water and TEOS in solution so that the formation of hydroxyl groups is limited. From the obtained results, the molar ratio of TNB:PEG as 1 : 0.1 was chosen for the next study.
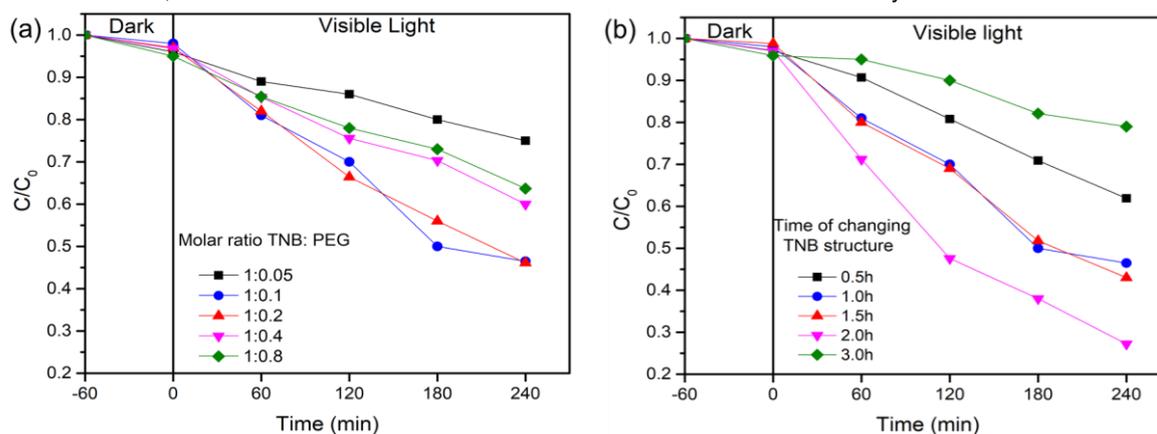

Figure 5: Photocatalytic degradation of phenol over TS05 (a) Effect of molar ratio TNB:PEG; (b) Effect of the time of heating TNB and ACAC

Figure 5b shows the effect of TNB heating time on phenol photodegradation. The results show the highest photocatalytic activity in phenol degradation when the heating time of TNB and ACAC is 2 h. After 4 h irradiation, it achieved 73 % which is higher than that of the heating times 0.5 h (38.0 %), 1 h (53.5 %), 1.5 h (57.0 %) and 3 h (21.0 %). Using ACAC to modify the structure of TNB, ACAC makes TNB more stable and harder to hydrolyse. Increasing the time of heating TNB precursor and acetylacetone leads to increasing photocatalytic activity. On the other hand, when the time of heating TNB was 3 h, phenol removal efficiency of this material decreased.

4. Conclusions

The TiO_2/SiO_2 composite was prepared by a sol–gel method. All synthesized samples are pure anatase phases with high crystallinity and high photocatalytic activities. In particular, the TS05 sample with the heating time of TNB and ACAC as 2 h achieved the highest efficiency of 73% after 4 h irradiation. The research shows that the heating time of TNB and ACAC plays an important role in changing the structure of TNB, it makes the TNB structure more stable. The TS05 photocatalyst could be a promising photocatalyst for removal and degradation of organic pollutants. The factors affecting synthesis of TiO_2/SiO_2 composite such as ACAC,

EtOH, hydrolysis time, ageing time, should be further studied in the future to improve photocatalytic activities for phenol degradation.

Acknowledgements

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