



Investigation on solar photocatalytic activity of TiO₂ loaded composite: TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP

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ABSTRACT

The TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP composites were prepared by sol–gel method. X-ray diffraction (XRD) and scanning electron microscope (SEM) were carried out to characterize them. Their photocatalytic activities were evaluated by degradation of Acid Red B under solar light irradiation. The results showed that the photocatalytic activity of the TiO₂ catalyst can be greatly enhanced by using appropriate amount of loaded biomaterials or biomimetic material. Otherwise, the influencing factors, such as TiO₂ loaded content, heat-treated temperature and heat-treated time on the photocatalytic activity of TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP were reviewed. Meanwhile, the effect of solar light irradiation time and dye initial concentration on the photocatalytic degradation of Acid Red B dye in aqueous solution were also investigated in detail.

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1. Introduction

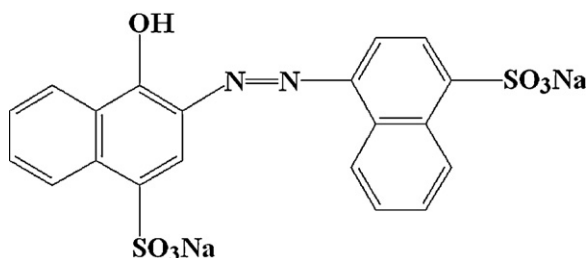
In recent years, TiO₂ is widely used for the degradation of many organic pollutants due to its physical and chemical stability, relative high catalytic reactivity and cheapness and so on [1–3]. When TiO₂ is irradiated by ultraviolet light, the powerful reactive oxygen species (ROS) can be generated on its surface, which can decompose most organic compounds [4–7]. However, as a kind of industrially produced inorganic material, TiO₂ exhibits low identifiability and selectivity for dye molecules in aqueous solution [8,9]. Since the ROS generated on the surface of TiO₂ have very short half-lives [10], a large number of ROS will disappear during diffusion in aqueous media without participating in any degradation reactions [11]. Therefore, the poor selection for dye molecules reduces the photocatalytic efficiency of TiO₂. In order to enhance the identification capacity of TiO₂, a variety of support materials such as activated carbon [12–17], zeolite [18–20] and mesoporous silica [21–23] were once been used. By using these support materials with super adsorption capacity or large surface area, the selectivity of the TiO₂ composites was enhanced to a certain extent. Nevertheless, these support materials have no proprietary selectivity for the dye molecules except strong adsorption. When the adsorption

was too strong, the over-adsorbed dye molecules may inhibit the subsequent photocatalytic reactions [13].

Deriving from the organism, biomaterial should identify the most of organic dye molecules effectively due to their good biocompatibility and structural complementarity. Skeleton and Dens are nature biomaterials with good biological activity, excellent biocompatibility and feature surface structure [24–26]. As a biomimetic material, hydroxyapatite (HAP) is the principal inorganic materials constituent of Skeleton and Dens, which also exhibits the excellent biocompatibility to a certain extent [24,27]. Therefore, the composite catalysts made from biomaterials or biomimetic material and TiO₂ will behave the advantages of good biocompatibility and relative high catalytic reactivity. They could identify and select the dye molecules onto the surface of TiO₂ and then effectively oxidize them.

In this study, the Skeleton, Dens and HAP were chosen as support materials, and TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP composites were prepared by sol–gel method. For comparison, pure TiO₂ was also prepared under the same condition. Their photocatalytic activities were studied by destructing Acid Red B. The results indicated that composites catalysts had much higher photocatalytic activity than pure TiO₂. Meanwhile, the catalysts supported by nature biomaterials exhibited much higher photocatalytic activity than that by biomimetic materials. Molecular structure of Acid Red B dye is given in Scheme 1.

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Scheme 1. Molecular structure of Acid Red B dye.

2. Experimental

2.1. Treatments of Skeleton, Dens and HAP powders

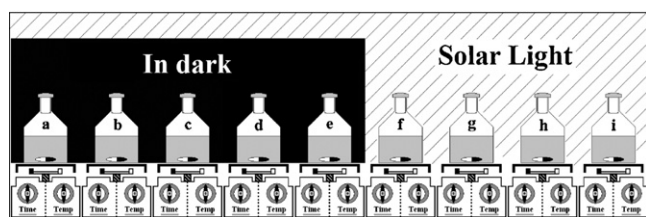
The Skeleton and Dens were first cleaned in water and then soaked in HCl (0.50%) for 30 min. After washing and drying, the Skeleton, Dens and HAP were calcined at 500 °C for 120 min, and then ground to obtain the exiguous powder.

2.2. Preparation of TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP composites

The TiO₂ loaded composites were prepared through sol-gel method. (C₄H₉O)₄Ti, C₂H₅OH, CH₃COOH and H₂O with the volume ratio of 1.0:1.7:0.17:0.10 were homogenized by a magnetic stirrer until uniform sol was formed. Three kinds of biomaterial (Skeleton, Dens and HAP) powders were put into the prepared sol, respectively. And the mass ratios of TiO₂ and biomaterial were 10 wt%, 30 wt% and 50 wt%, respectively. At the same time, the mixture was stirred by a magnetic stirrer for 3.0 h. The sol solution was placed in a culture dish to finish the sol-gel transition, and then dried at 100 °C for 24 h to get a dried gel. The dried gel was ground and a light-yellow powder was obtained. The separated deposit was put into a crucible and heated in a muffle furnace at the calefactive rate of 2.0 °C min⁻¹. And then the temperature was controlled at 300 °C, 500 °C and 700 °C for different lengths of time (30 min, 60 min and 90 min, respectively). Finally, the TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP composites were obtained using a series of mass ratios of TiO₂ to TiO₂ loaded composite (10 wt%, 30 wt% and 50 wt%). For comparison, the bare TiO₂ was prepared under the same procedure.

2.3. Experiments of photocatalytic degradation

The experimental setting drawing is shown in Scheme 2. And the experimental conditions such as 100 mL total volume, 10 mg/L Acid Red B initial concentration and 1000 mg/L catalyst (heat-treatment at 500 °C for 50 min) addition amount and natural pH



Scheme 2. The apparatus of solar light irradiation. (a: Acid Red B solution without any catalyst in the dark (original solution); b: Acid Red B solution with TiO₂ composite in the dark; c: Acid Red B solution with TiO₂/HAP in the dark; d: Acid Red B solution with TiO₂/Dens in the dark; e: Acid Red B solution with TiO₂/Skeleton in the dark; f: Acid Red B solution with TiO₂ under solar light irradiation; g: Acid Red B solution with TiO₂/HAP under solar light irradiation; h: Acid Red B solution with TiO₂/Dens under solar light irradiation; i: Acid Red B solution with TiO₂/Skeleton under solar light irradiation.)

value (pH 5.91) were kept constant throughout this work unless a special requirement was involved. The various catalysts were well mixed into Acid Red B solutions in conical flasks. The mixture solutions were placed in the dark for 30 min with adequate agitation to determine the percentage of dye adsorption. After that the solutions were sampled every 20 min under solar light irradiation (light irradiation intensity is 3×10^4 J/m² min on July when did the experiment) to determine the percentage of degradation reduction. The sampled suspensions were then centrifuged at 4000 rpm for 20 min to remove the catalysts and then analyzed by UV-vis spectrophotometer. The ratios of dye adsorption and reduction were determined from the change in absorbance of the Acid Red B solution at $\lambda_{\max} = 514$ nm using the following equation:

$$\text{adsorption ratio (\%)} = \frac{C_0 - C_a}{C_0} \times 100$$

$$\text{absolute degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

$$\text{relative degradation (\%)} = \frac{C_a - C_t}{C_a} \times 100$$

where C_0 is the initial concentration of Acid Red B solution, C_a is the dye concentration after adsorption by catalysts and C_t is the instant concentration after a certain time solar light irradiation.

3. Results and discussion

3.1. XRD and SEM of TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP composites

The different biomaterials (Skeleton, Dens and HAP) (heat-treated at 500 °C for 120 min) and catalysts (TiO₂/Skeleton, TiO₂/Dens, TiO₂/HAP and TiO₂) (heat-treated at 500 °C for 50 min) were characterized by powder X-ray diffractometer (D8 ADVANCE, Bruker, Germany) using Ni-filtered Cu K α radiation in the range of 2θ from 10° to 70°. As shown in Fig. 1, the characteristic diffraction peaks of Skeleton, Dens and HAP are basically the same. It confirms that the main constituent of Skeleton and Dens is HAP. For the TiO₂ loaded composites (TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP), only the most intensive peak ($2\theta = 25.4^\circ$) belonging to TiO₂ is visible in the XRD pattern. And the other peaks of TiO₂ are covered by the XRD pattern of biomaterials (Skeleton, Dens and HAP). The results indicated that the TiO₂ particles and the biomaterials integrate well. In addition, at the heat-treated temperature of 300 °C, the diffraction peaks of anatase phase are only present. When the heat-treated temperature reaches 500 °C, it can be seen in Fig. 1, a new peak belonging to rutile phase ($2\theta = 27.5^\circ$) appears, which indicates that the phase transformation of anatase to rutile happens. Meanwhile, the rutile phase becomes more and more with the increase of heat-treated time (30 min, 50 min and 70 min). Finally, when the heat-treated temperature reaches 700 °C, the rutile phase becomes the main crystal phase in the TiO₂ loaded composites.

The external surface of TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP composites were characterized by scanning electron microscopy (SEM) (JEOL JSM-5610LV, Hitachi Corporation, Japan). As is shown in Fig. 2, the grayish surface reveals that the biomaterials (Skeleton, Dens and HAP) are covered with TiO₂ film. In addition, according to the SEM photographs, it can be seen that there are different morphologies on the surface of nature biomaterial and biomimetic material. That is, the TiO₂/Skeleton and TiO₂/Dens composites have the irregular and uneven surfaces, respectively, while the TiO₂/HAP composite has a regular sphere surface.

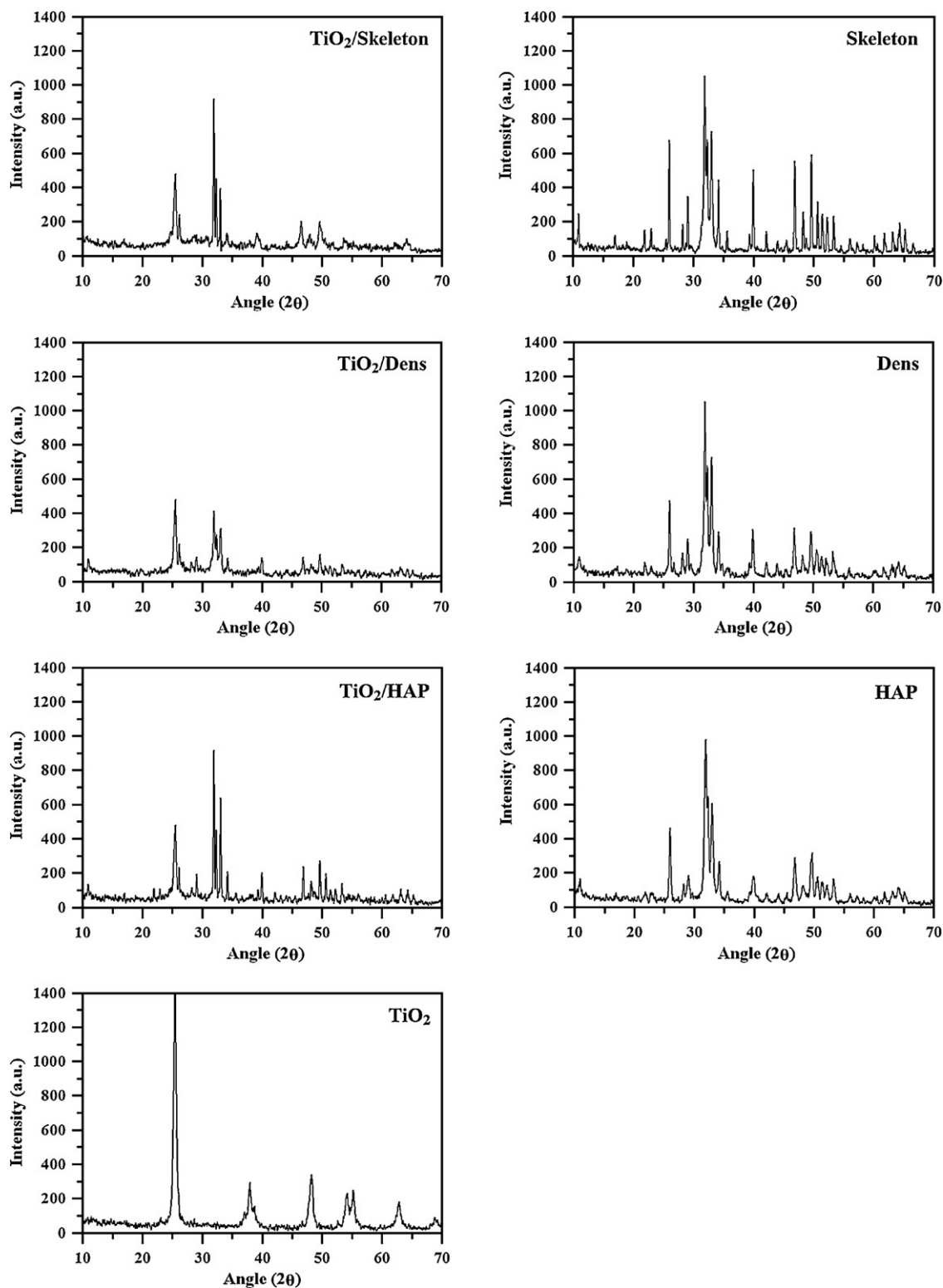


Fig. 1. XRD patterns of TiO_2 , $\text{TiO}_2/\text{Skeleton}$, TiO_2/Dens , TiO_2/HAP (at 500°C for 50 min heat-treatment) and Skeleton, Dens, HAP (at 500°C for 120 min heat-treatment).

3.2. Photocatalytic activity of $\text{TiO}_2/\text{Skeleton}$, TiO_2/Dens and TiO_2/HAP composites

As shown in Fig. 3, the UV–vis spectra of Acid Red B solutions under different conditions were recorded by UV–vis spectrophotometer (LAMBDA-17, PerkinElmer Company, USA). The maximum

absorption peak at 514 nm in the visible region corresponds to the azo bond ($-\text{N}=\text{N}-$), while the absorption peaks at 295 nm and 320 nm in ultraviolet regions are related to the naphthyl ring. In the dark, owing to the compatibility and selectivity, the TiO_2 loaded composites ($\text{TiO}_2/\text{Skeleton}$, TiO_2/Dens and TiO_2/HAP) exhibited a slightly higher adsorption than the bare TiO_2 . Among them, the

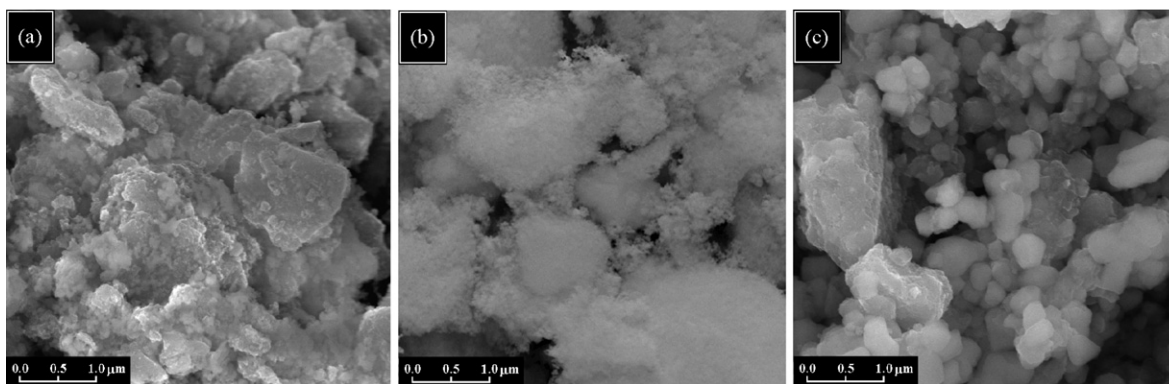


Fig. 2. The SEM of TiO₂/Skeleton (a), TiO₂/Dens (b) and TiO₂/HAP (c) (with 30 wt% TiO₂ under 500 °C and 50 min heat-treatment).

TiO₂/Dens composite exhibited the highest adsorption. Under solar light (SL) irradiation, the degradation (%) using the TiO₂ loaded composites was obviously higher than that using the bare TiO₂. This revealed that the TiO₂ loaded composites showed much higher photocatalytic activity than the bare TiO₂ powder. Within 80 min solar light irradiation, the degradation (%) of Acid Red B based on the maximum absorption peak reaches to 81.14% in the presence of TiO₂/Skeleton composite. It was obviously higher than the corresponding that (63.15%) in the presence of bare TiO₂ powder. The high reactivity of the TiO₂ loaded composites may attribute to the biocompatibility and structural complementarity of biomaterials and biomimetic materials with organic pollutants. That is, the biomaterials or biomimetic materials can identify the Acid Red B molecules and selectively absorb them to the surface of the TiO₂ loaded composites, and then decompose them effectively. In addition, the TiO₂/Skeleton and TiO₂/Dens composite exhibited the higher photocatalytic activity than the TiO₂/HAP composite. This result indicates that the Skeleton and Dens as biomaterials exhibit a better structural compatibility and biocompatibility than the HAP.

For evaluating the photocatalytic activities of TiO₂ loaded composites, the total organic carbon (TOC) removals of Acid Red B solutions were also performed by TOC analyzer (TOC 1200, Thermo Electron Corporation, The Netherlands). Based on the TOC removals of Acid Red B solutions, the calculated degradation (%) are 80.21%, 73.26%, 69.54% and 53.45% for TiO₂/Skeleton, TiO₂/Dens, TiO₂/HAP and TiO₂, respectively. That is, the trend of TOC removals was perfectly consistent with ones determined by using UV–vis spectra. The results prove again that the Acid Red B dyes in aqueous solu-

tion were degraded mostly adopting the TiO₂ loaded composites as the photocatalysts under solar light irradiation. Otherwise, the UV–vis absorbance analysis is a credible method to perform measurement and get preliminary information on the degradation of organic pollutants fast and easily, and it was used in all our later works.

3.3. Effect of TiO₂ loaded content, heat-treated temperature and heat-treated time on photocatalytic activity of TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP composites

The effect of different TiO₂ content (10 wt%, 30 wt% and 50 wt%) for the biomaterials (Skeleton, Dens and HAP) on the photocatalytic activities of the TiO₂ loaded composites was investigated under 80 min solar light irradiation, and the results are shown in Fig. 4a. It can be seen that the 30 wt% TiO₂ content behaves the highest photocatalytic activity for three TiO₂ loaded composites. For any biomaterial, the reduction (%) of Acid Red B dye increases with the increase of TiO₂ content (from 10 wt% to 30 wt%), and then slightly falls with the further increase. The hoist of reduction (%) in the presence of TiO₂ loaded composites may attribute to the fact that the proper high TiO₂ content results in the more light absorption. It is noteworthy that 50 wt% TiO₂ loaded amount shows a lower photocatalytic activity than that of 30 wt%. It is because that, when the TiO₂ content is too high, such TiO₂ loaded composites, just like bare TiO₂ powder, will not behave the advantages of the supports (biomaterials). That is, it could not identify and select the organic dye molecules effectively.

The heat-treated temperature and heat-treated time play an important role for the activity of many semiconductor photocatalysts, because they decide the crystallization, particle size and surface properties as well as crystal form. Hence, the photocatalytic activities of a series of a 30 wt% TiO₂ loaded composites (TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP) and bare TiO₂ at different heat-treated temperatures for 50 min were investigated as shown in Fig. 4b. It is clear that the best degradation (%) is obtained when the heat-treated temperature is 500 °C. This phenomenon can be explained by the XRD data. The calcination at lower temperature (e.g., at 300 °C) leads to a lower crystallization grade of TiO₂ powder, and the TiO₂ loaded composites are not well formed yet. When the temperature is up to 700 °C, a mass of TiO₂ particles congregate together and the anatase phase of TiO₂ begins to transform into the rutile phase debasing the photocatalytic activity of TiO₂ loaded composites.

In Fig. 4c the effect of heat-treatment time on photocatalytic activity of a 30 wt% TiO₂ loaded composites was reviewed at 500 °C heat-treated temperature. It was found that the best degradation (%) of Acid Red B was obtained for 50 min heat-treated time.

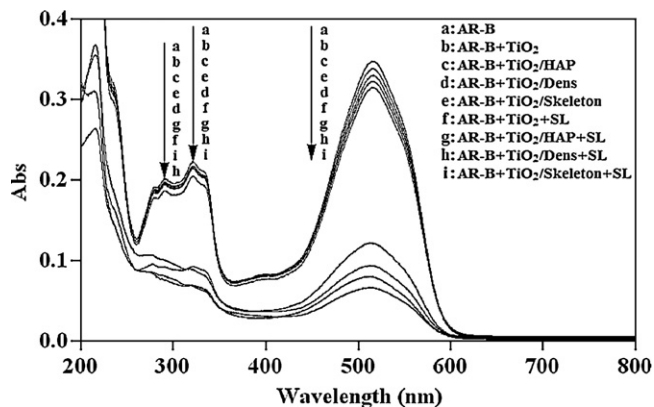


Fig. 3. UV–vis spectra of Acid Red B solutions under different conditions (SL: solar light).

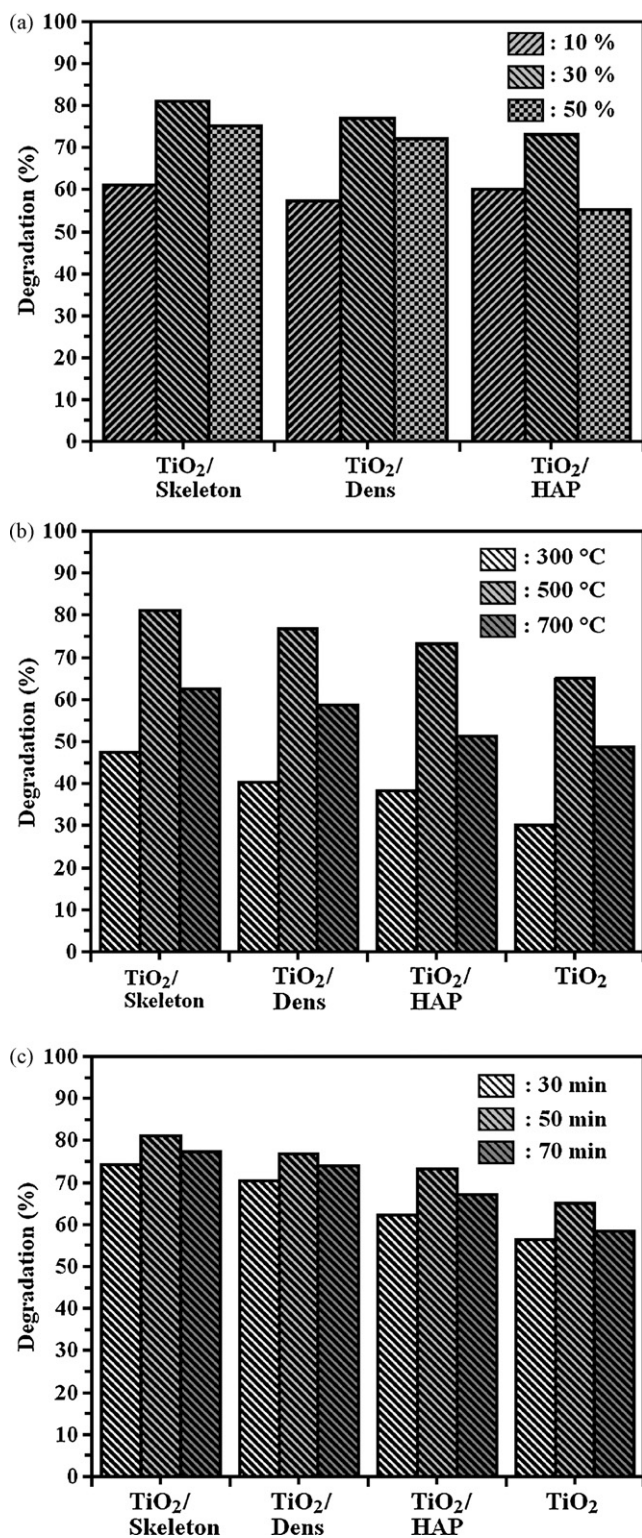


Fig. 4. Effect of TiO₂ content (a), heat-treated temperature (b) and heat-treated time (c) on the photocatalytic activities of TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP (with 30 wt% TiO₂ under 500 °C and 50 min heat-treatment).

The reasons can be explained as follows. When the heat-treated temperature was determined at 500 °C as a possible critical temperature between anatase and rutile phases of TiO₂, along with the increase of heat-treated time the crystal phase of anatase TiO₂ gradually transformed to the rutile phase. For short heat-treated time

(e.g., 30 min), only a spot of the anatase phase (3.4%) transformers into the rutile phase form. However, beyond 50 min, the rutile phase (4.5%) becomes more and more and exists as a self-existent crystal phase at last. It is well known that a suitable proportional mixed crystal phase redounds to the increasing of photocatalytic activity of TiO₂ catalyst [28,29]. So, in order to get high photocatalytic activity, the proper heat-treatment temperature and heat-treatment time are necessary.

3.4. Effect of irradiation time and reaction kinetics on photocatalytic degradation of Acid Red B

Considering the treatment life cycle cost, shortening time or heightening rate for any pollutant treatment is a necessary goal. Hence, the effect of solar light irradiation time on degradation of Acid Red B dye was reviewed within 100 min irradiation at 20.0 min intervals. As shown in Fig. 5a, it could be seen that the reduction ratios of Acid Red B dye for all cases increased along with the increase of irradiation time. Apparently, the degradation (%) using TiO₂ loaded composites (TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP) was higher than that using the bare TiO₂. After 100 min irradiation, the degradation (%) using TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP composites achieves 92.41%, 87.25% and 83.12%, respectively, while the degradation (%) using pure TiO₂ only achieve 74.32%.

In order to determine the reaction kinetics of photocatalytic degradation, the relationship between $-\ln C_t/C_0$ and solar light irradiation time (t) is plotted as shown in Fig. 5b. It is found that the degradation reactions of Acid Red B dye under different conditions basically obey to the first-order reaction kinetics. The rate constants were calculated from the plots of the natural logarithm of the dye concentration as a function of irradiation time. The rate constants (k) are 0.0248 h⁻¹, 0.0194 h⁻¹, 0.0168 h⁻¹ and 0.0132 h⁻¹, respectively, for TiO₂/Skeleton, TiO₂/Dens, TiO₂/HAP and TiO₂. The high rate constant indicates that the loaded Skeleton composite has high photocatalytic activity during degradation of Acid Red B dye.

3.5. Effect of initial concentration on photocatalytic degradation of Acid Red B dye

Because of considerable wide concentration range of organic pollutants in factual wastewaters, it is needed to consider the effect of dye concentration on the photocatalytic degradation under solar light irradiation. Fig. 6 illustrates the degradation percentage as a function of dye initial concentrations within 25.0 mg/L at 5.0 mg/L intervals after 80 min solar light irradiation. It is noteworthy that within the certain time period, as the dye initial concentrations increase, for all four courses the degradation (%) firstly ascends until up to the maximum whose corresponding concentration is about 10.0 mg/L. And then they decline following the increase of initial concentrations. Being similar to general photocatalytic degradation, as the initial concentrations of the dye increase, the probability of the reaction between dye molecules and oxidizing species also increases, leading to an increase of the degradation (%) [5]. On the contrary, the increase of initial concentrations is bound to weaken the transmission ability of solar light for the solution and then subsequently decrease the light intensity that arrived at the surface of TiO₂ articles. In the case, the TiO₂ powder in solution cannot operate adequately, which is just the reason why degradation (%) declines for high concentration dye wastewater [30]. Therefore, a proper initial concentration should be chosen in order to get an ideal degradation (%).

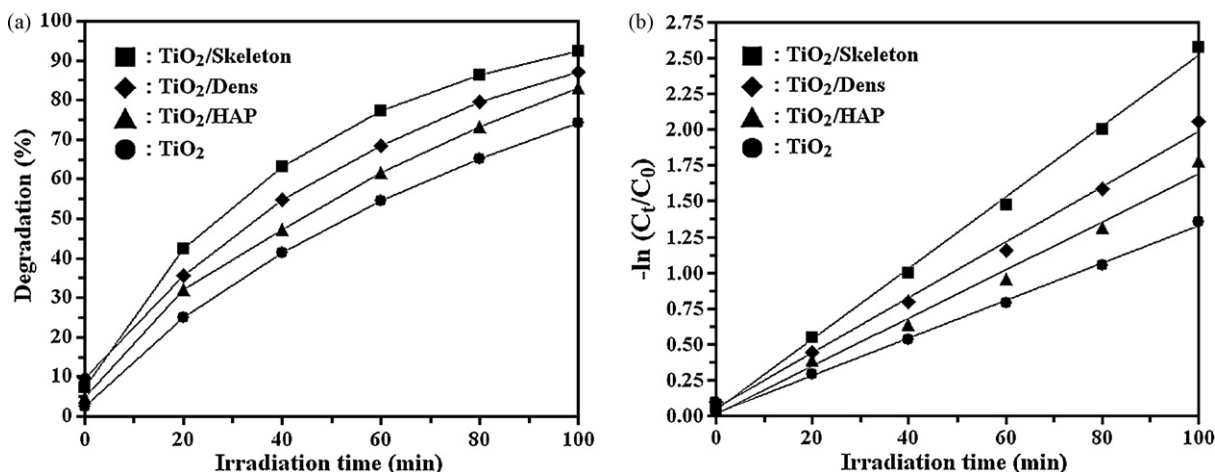


Fig. 5. Effect of solar light irradiation time (a) and reaction kinetics (b) on photocatalytic degradation of Acid Red B.

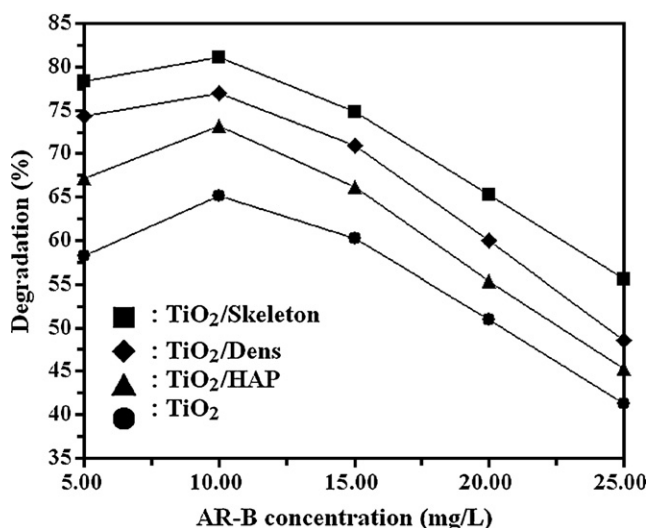


Fig. 6. Effect of initial concentration on the photocatalytic degradation of Acid Red B.

4. Conclusions

Photocatalytic activities of supported TiO₂ catalyst on three types of biomaterials (Skeleton, Dens and HAP) were compared with that bare TiO₂ synthesized by sol–gel method. The experiment results indicated that the composites with 30.0 wt% TiO₂ content treated at 500 °C for 50 min exhibited the highest photocatalytic activity under solar light irradiation. The TiO₂ loaded composites (TiO₂/Skeleton, TiO₂/Dens and TiO₂/HAP) behave high activity due to the synergistic effect of biomaterial identification and TiO₂ photocatalysis. Hence, this method is feasible for the treatment of wastewater using solar energy.

Acknowledgements

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