Adsorptive separation and photocatalytic degradation of methylene blue dye on titanate nanotube powders prepared by hydrothermal process using metal Ti particles as a precursor

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ABSTRACT

Titanate nanotube powders (TNTPs) with the twofold removal ability, i.e. adsorptive separation and photocatalytic degradation, are synthesized under hydrothermal conditions using metal Ti particles as a precursor in the concentrated alkaline solution, and their morphology, structure, adsorptive and photocatalytic properties are investigated. Under hydrothermal conditions, the titanate nanotubes (TNTs) with pore diameter of 3–4 nm are produced on the surface of metal Ti particles, and stacked together to form three-dimensional (3D) network with porous structure. The TNTPs synthesized in the autoclave at 130 °C for 24 h exhibits a maximum adsorption capability of about 197 mg g^{-1} in the neutral methylene blue (MB) solution (40 mg L^{-1}) within 90 min, the adsorption process can be described by pseudo second-order kinetics model. Especially, in comparison with the adsorptive and the photocatalytic processes are performed in turn, about 50 min can be saved through synchronously utilizing the double removal ability of TNTPs when the removal ratio of MB approaches 95% in MB solution (40 mg L^{-1}) at a solid–liquid (S/L) ratio of 1:8 under ultraviolet (UV) light irradiation. These 3D TNTPs with the twofold removal properties and easier separation ability for recycling use show promising prospect for the treatment of dye pollutants from wastewaters in future industrial application.

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1. Introduction

The presence of dyes in wastewaters has been recognized as one of the most important environmental hazardous substances, and the discharge of dyes in the wastewaters is a matter of concern for both toxicological and esthetical reasons [1,2]. By now, several physical, chemical and biological decolorization processes have been reported [1–4]. Thereinto, the adsorption technique is a typical physical process, which is widely used to remove those pollutants that are not easily biodegradable from waters. The commercial activated carbon and those alternative non-conventional and low-cost materials, including agricultural wastes, industrial solid wastes, biomass, clays minerals and zeolites, are extensively investigated as adsorbents for color removal [1,2]. On the other hand, the photocatalytic degradation is an important chemical process, which utilizes the photo-generated holes and electrons to decompose the organic pollutants. Titanium-based nanomaterials, i.e. titanium oxides (TiO$_2$) and titanates, as the most promising photocatalysts, have obviously attracted extra attention in the

degradation of dye pollutants originating from their unique properties of chemical inertness, high photoreactivity, non-toxicity, and photostability [3,4].

The crystal phase and particle size of titanium-based photocatalysts are well known key factors to their photocatalytic activity. Among the several reported preparation routines, the hydrothermal method has been considered to be an effective technique to fabricate titanium-based nanomaterials with ordered-nanostructures and high photoreactivity [3,4]. Several authors demonstrated that the multi-phases TiO$_2$ nanorods could be selectively synthesized by the thermohydrolysis of titanium salts, such as TiCl$_4$, Ti(OCH(CH$_3$)$_2$)$_4$, or Ti(OBu)$_4$ (Bu refers to –C$_4$H$_9$), in the acidic aqueous media, wherein the selectivity was strongly dependent on the medium acidity [4–7]. Recently, the anatase TiO$_2$ single crystals with exposed {0 0 1} facets were also prepared by using hydrofluoric acid (HF) as a capping agent from different raw materials under hydrothermal conditions [8,9]. Correspondingly, the titanate nanotubes (TNTs) were synthesized by using TiO$_2$ powders as precursor in the concentrated alkaline solution [10–12]. The TNTs composed of corrugated ribbons of edge-sharing TiO$_6$ octahedral are of a multilayered structure and nanometer-scale inner-core cavity, and the surface of TNTs is also easily negatively charged after treatment with weak bases because of the protonic by nature

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structure of $H_2Ti_3O_7$. Thus, an increasing interest is being focused on possible applications of TNTs as the substrate to decorate with different active catalysts such as enzymes, nanoparticles and metal ions over the last few years [11,12].

Besides the precursor materials of titanium salts and oxides, it is noted that titanium-based photocatalysts were also synthesized recently using metal Ti particles as raw materials under hydrothermal conditions [13–16]. For example, the flower-like TiO_2 nanostructures with exposed {0 0 1} facets were synthesized by a low-temperature hydrothermal process from Ti powders in hydrofluoric acid solution, and they exhibited enhanced photocatalytic degradation of methylene blue (MB) under ultraviolet (UV) light [13,14]. In addition, the three-dimensional (3D) network TiO_2 nanowire film, which exhibited high photoelectrochemical performances, was directly produced on the surface of Ti foil through the reaction of metal Ti and concentrated alkaline solution under a hydrothermal condition [15,16]. In this article, we synthesized titanium-based photocatalysts by using metal Ti particles as a precursor in the concentrated alkaline solution under hydrothermal conditions. It was observed that the TNTs could be synthesized on the surface of Ti particles with large specific area, good adsorptive capability, easily separating ability, and good photocatalytic activity under UV light irradiation. The as-synthesized TNTPs possess the twofold removal ability of adsorptive and photocatalytic on the treatment of MB dye.

2. Experimental

2.1. Synthesis of titanate nanotube powders

The metal Ti powders (−325 mesh, 99.5% purity) purchased from Beijing Yitianhui Metal Institute, other chemicals were of analytical grade and used as received without further purification. In a typical synthesis, 0.5 g metal Ti powders and 40 mL NaOH ($10\,mol\,L^{-1}$) were poured into a Teflon-lined stainless steel autoclave (50 mL), and a magnetic stirring rod was also added into the system to facilitate the intermittent stirring, i.e. 2 min in every 3 h, during the hydrothermal process. Then, the autoclave was kept in an oven at 130 °C for different reaction time [10–12]. After completion of the reaction, the products were collected through centrifugation and thoroughly washed with high-purity water until pH = 7.0 was reached, and then dried in the vacuum at 80 °C.

2.2. Characterization of titanate nanotube powders

The phase composition of the as-synthesized TNTPs samples was identified by powder X-ray diffractometer (XRD; D/Max-IIIA, Rigaku, Japan) with Cu Kα radiation ($\lambda = 0.154$ nm), at 30 kV and 30 mA. The morphology of samples was characterized by scanning electron microscopy (SEM; LEO 1530 VP, Oberkochen, Germany) and by transmission electron microscopy (TEM; JEM-2100HR, JEOL, Japan). The specific surface area of samples was measured by nitrogen adsorption–desorption isotherms at 77 K according to the Brunauer–Emmett–Teller analysis (BET; ASAP 2020, Micromeritics, USA). A desorption isotherm was used to determine the pore size distribution using the Barrett–Joyner–Halenda (BJH) method.

MB dye was used as the target pollutant to evaluate the adsorptive and photocatalytic performances of TNTPs. The MB solutions were prepared by dissolving MB in distilled water, and their pH values were then adjusted by adding HCl ($0.1\,mol\,L^{-1}$) or NaOH ($0.1\,mol\,L^{-1}$) and determined using a pH/mV meter (pHSJ-3F, LeiCi, China). The adsorption experiments were carried out in 250 mL glass beakers with magnetic stir at room temperature (~25 °C). 25 mg as-prepared sample was poured into 200 mL MB solution (a typical: $40\,mg\,L^{-1}$) under dark and constant magnetic stirring
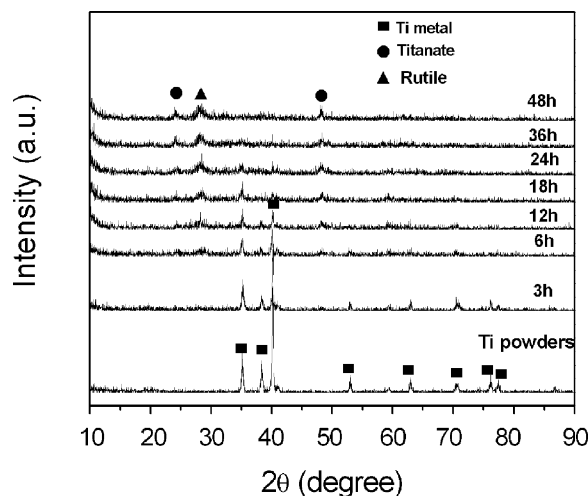

Fig. 1. The XRD patterns of metal Ti powders and the samples synthesized in the autoclave for 3 h, 6 h, 12 h, 18 h, 24 h, 36 h, and 48 h, respectively.

conditions. Photocatalytic degradation experiments were carried out in a photochemical reactor (XPA-1, XuJiang, China) equipped with a medium mercury lamp (300 W) at room temperature. All photocatalytic reactions were performed using identical initial conditions: 200 mL MB solution ($40\,mg\,L^{-1}$) was mixed with 25 mg TNTPs under constant magnetic stirring. During the adsorption or photocatalytic process, 5 mL solution was timely taken out and subsequent the solids were removed from the solution using a 0.45 μm nitrocellulose filter, and then detected by a Shimadzu UV-1800 UV-Vis spectroscopy ($\lambda = 665$ nm) to obtained MB content in the solution.

3. Results and discussion

3.1. Morphology and structure of titanate nanotube powders

With increasing the hydrothermal time, it was observed that the color of products was transferred from gray of metal Ti powders into offwhite, and their total volume was enhanced as well, indicating new substances being produced on the surface of metal Ti particles. The XRD patterns of the samples synthesized under different hydrothermal time are shown in Fig. 1. Obviously, the diffraction peaks of metal Ti steadily decreased and then nearly disappeared after 24 h, whereas the diffraction peaks of sodium titanate ($Na_2Ti_6O_{13}$; JCPDS no. 21-1272) and rutile TiO_2 appeared after 6 h and became stronger, which validated the formation of sodium titanate layer on the surface of Ti particles under hydrothermal conditions in the concentrated alkaline solution. It was known that TiO_2 could be used as the precursor to synthesize titanate, and titanate was also easily transferred to TiO_2 [15,17]. So, considering the preparation conditions and succedent SEM experimental results, the products are nominated as titanate structure in this paper. Equal molar sodium titanate or TiO_2 has a larger volume than that of metal Ti particles, and the as-prepared products are porous structures, thus the volume of products is enhancing with increasing the hydrothermal time.

The low-magnification SEM image of metal Ti powders, high-magnification images of metal Ti powders and the samples synthesized in the autoclave for 3 h, 24 h, and 36 h are shown in Fig. 2. It can be seen that metal Ti particles (−325 mesh) have an irregular morphology, broad particle size, and polished surface layer, whereas, the nanowire-like products, which stick together to form 3D structure, are produced on the surface of Ti particles under hydrothermal conditions, and correspondingly lead to
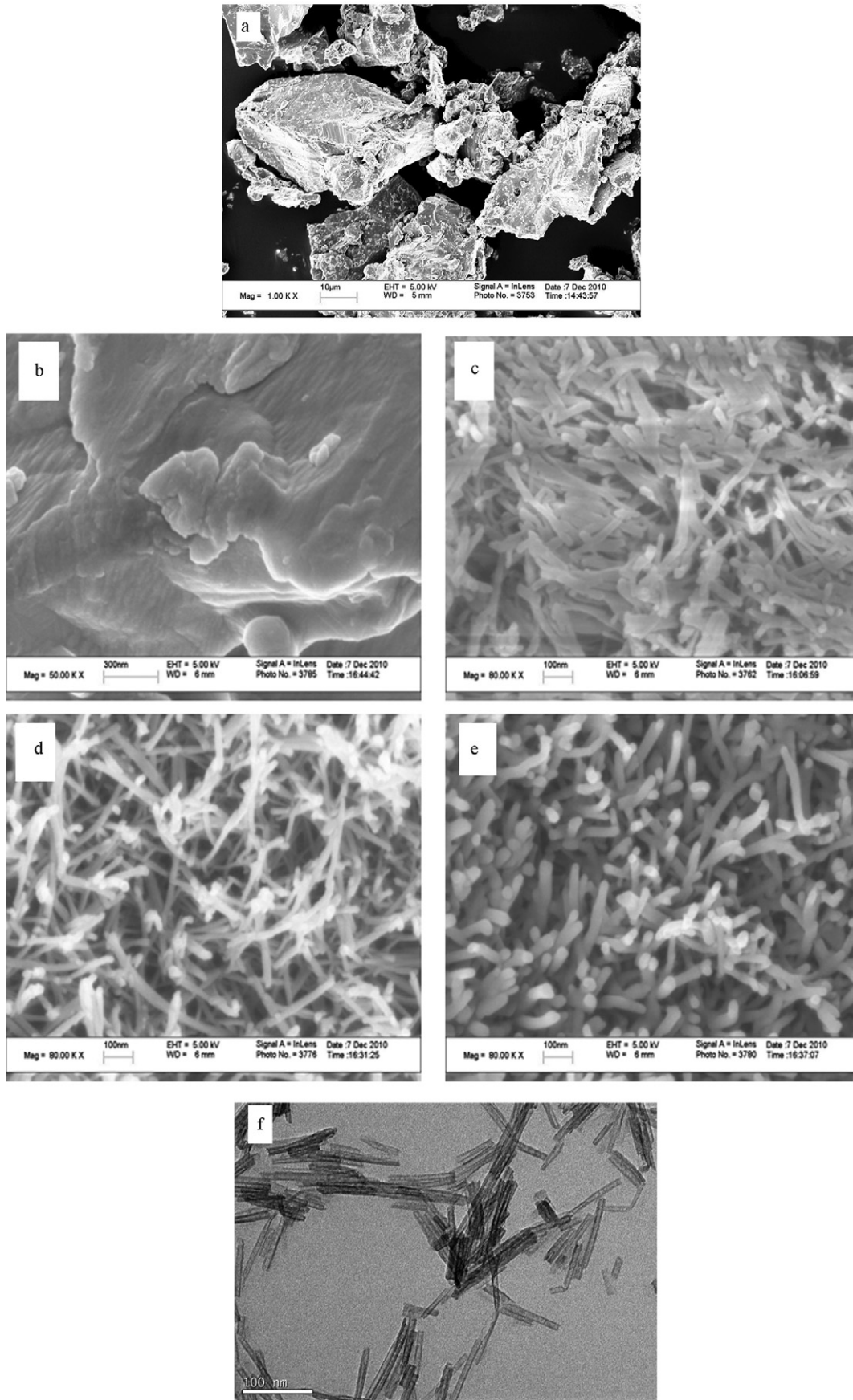
Fig. 2. (a and b) The low- and high-magnification SEM images of metal Ti powders, the high-magnification images of the samples synthesized in the autoclave for (c) 3 h, (d) 24 h, and (e) 36 h, respectively, and (f) the TEM image of nanoproducts on the powders.
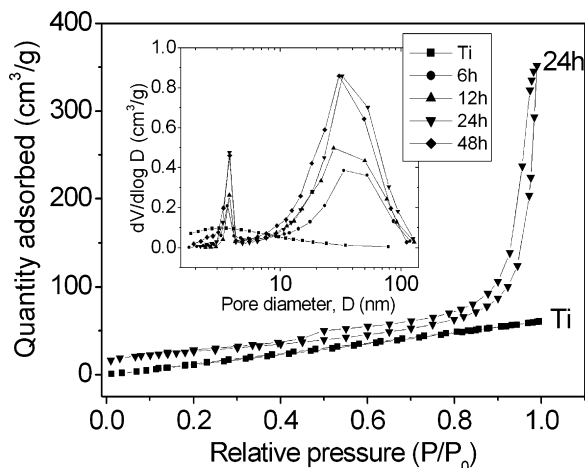
Fig. 3. The nitrogen adsorption–desorption isotherms and Barret–Joyner–Halenda (BJH) pore size distribution of the samples synthesized in the autoclave for different hydrothermal time.

Fig. 4. The time dependent of adsorption ratio on the titanate nanotube powders synthesized in the autoclave with different time in MB solution ($40 \, \text{mg L}^{-1}$) at a solid-to-liquid (S/L) ratio of 1:8 and room temperature.

enlarged particle sizes. What's more, the SEM results revealed that the influences of hydrothermal time on the surface morphology of products. The nanowire-like products were observed on the surface of Ti particles treated in the autoclave for 3 h, and more products could be obtained with increasing the hydrothermal time. Thereinto, the majority of nanowire-like products lied down and formed 3D network on the surface of particles for the samples synthesized for 3 h and 6 h, which is similar to the results obtained on the Ti foil [16]. Afterwards, the nanowire-like products were growing longer, thicker, and more independent for the samples synthesized in longer time. Under hydrothermal conditions, metal Ti reacted with the NaOH aqueous solution and many sodium titanate nanocrystallines were created and covered the particle surface, then these nanocrystallines began to grow vertically on the substrate through a dissolution–recrystallization process. Therefore, the length of the nanowire-like products increased with increasing reaction time [15].

In the other experiment, it was observed that some nanowire-like products dropped from the powders and formed a suspension when they was poured into the water and subsequently treated under ultrasonic condition (100 W, 15 min). Thus, the suspension was used to perform TEM test to characterize the microstructure of the nanowire-like products (Fig. 2f). It is clearly indicated that the nanowire-like products are nanotubes. Therefore, the as-synthesized samples are shown as titanate nanotube powders (TNTPs).

The nitrogen adsorption–desorption isotherms and Barret–Joyner–Halenda (BJH) pore size distribution were carried out to characterize the surface layer of the as-synthesized samples. Only the nitrogen adsorption–desorption isotherm of the sample synthesized in the autoclave for 24 h is shown in Fig. 3 with that of metal Ti powders due to the restriction of plotting, the other samples have similar isotherm characteristics. The inset of Fig. 3 shows the pore size distribution plots of metal Ti powders and the samples synthesized for different time. It can be observed that the adsorption capacities of the sample synthesized in the autoclave for 24 h are much higher than that of metal Ti powders. There is hardly any adsorption for the metal Ti powders, while the as-synthesized sample displays type BDDT-IV adsorption–desorption isotherms. And the pore size distribution curve, as shown in the insert figure, exhibits type H3 hysteresis loops that can be associated with the mesoporous structure. In addition, the BJH method gave two pore size distributions that a narrow pore-size distribution of 3–4 nm and a broad range of pore
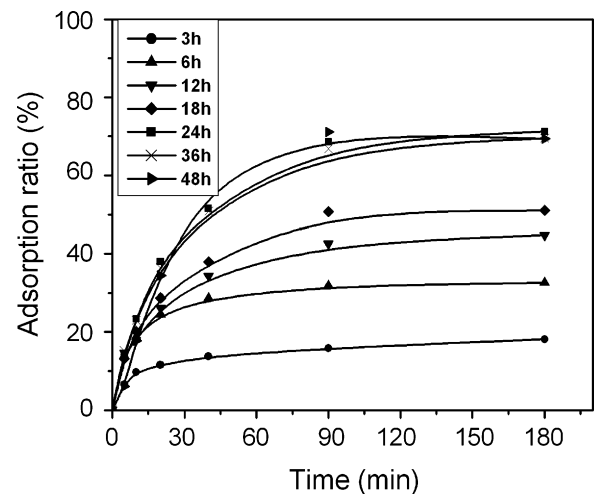
diameter from 10 nm to 100 nm. The pore diameter of 3–4 nm is attributed to the inner diameter of TNTs, while the broad range of pore diameter is ascribed to the interaggregation of TNTs on the surface of particles [18]. Especially, with the formation of 3D TNTs on the surface of particles, the samples exhibit larger BET surface area and pore volume. In comparison with the apparent area of metal Ti powders ($2.5 \, \text{m}^2 \, \text{g}^{-1}$), the BET surface area of the samples synthesized in the autoclave for 6, 12, 24, and 48 h is respectively 57.3, 72.0, 91.7 and $122 \, \text{m}^2 \, \text{g}^{-1}$, and their pore volume is respectively 0.18, 0.22, 0.31 and $0.34 \, \text{cm}^3 \, \text{g}^{-1}$.

3.2. Adsorptive properties of titanate nanotube powders

As mentioned above, the as-synthesized TNTPs Exhibit 3D surface layer and a large specific surface area, thus, their adsorptive properties were firstly evaluated by using MB solution as the target pollutant. In practical, the adsorption process of pollutant on the adsorbent is usually related with various parameters such as adsorbent state, adsorption time, pH value of the solution, solid-to-liquid (S/L) ratio, and temperature and so on. Based on their importance to the separation of the target pollutant, the former three parameters were optimized using a series of experiments at room temperature and S/L = 1:8. Fig. 4 shows the time dependent of adsorption ratio of MB on the TNTPs synthesized in the autoclave with different time.

More amounts of MB were separated from the solutions with the increase of adsorption time after the addition of TNTPs adsorbent in all cases, and finally approach their maximum capacity at about 90 min. With the increasing of hydrothermal time, the adsorptive ratio of the corresponding samples enhanced steadily, and the sample synthesized in the autoclave for 24 h exhibits a maximum adsorption capability. Although there is lager BET surface area for the samples synthesized in the autoclave for 36 h and 48 h than that of 24 h, no more adsorption ratio can be obtained, showing about 24 h is needed to form an optimized microstructure in these conditions. In the succedent photocatalytic experiments, it was also demonstrated that no obvious difference occurred in their photocatalytic reactivity for the as-synthesized samples, thus the apparent difference is practically related with their adsorption ability.

The sample synthesized in the autoclave for 24 h is chosen to perform the adsorption experiments on the effects of solutions with different MB concentrations and pH values. Fig. 5 shows the effects of MB concentrations on the adsorption ratio. It can be seen that almost all of MB was adsorbed when the concentration of MB was
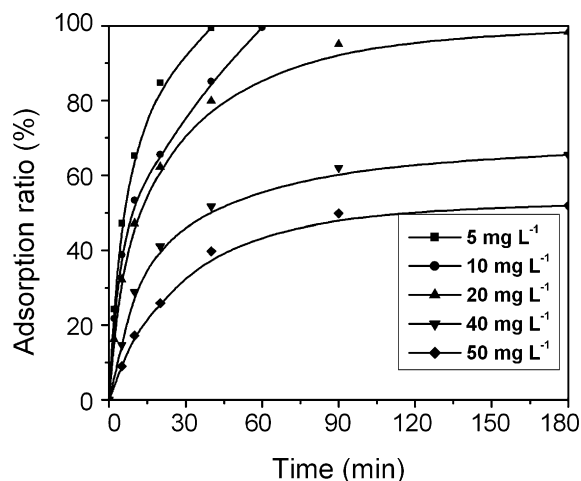
Fig. 5. The time dependent of adsorption ratio on the titanate nanotube powders synthesized in the autoclave for 24 h in MB solutions with different concentrations.

less than 20 mg L^{-1}, while about 60% and 48% MB was adsorbed when the solutions with concentration of 40 mg L^{-1} and 50 mg L^{-1} were respectively used after 90 min. Because the adsorption ratio in 90 min is approaching their maximum, the adsorption quantity on the TNTPs can be calculated based on the adsorption ratio and the solution concentration. Almost equal adsorption quantity of MB, i.e. ca. 197 mg g^{-1}, in two solutions can be obtained, showing 197 mg g^{-1} is the maximum adsorption quantity of the TNTPs within 90 min. Moreover, from the data presented in Fig. 6, it is clearly shown that adsorption capacity is affected by the acidic degree of MB solution. In the acidic medium, the adsorption capacities are enhanced with increasing pH value from 2 to 7, while no obvious difference between the basic and neutral solutions. Since the initial pH value of MB solution is around 7.0, the adsorption differences of MB at pH value of 2, 5 and 7 can be explained by the fact that MB molecules compete with hydrogen ions on the TNTs. In addition, when pH increases, there is an increase of the positive surface charge, which results in a lower electrostatic repulsion between the positive charged metal ions and the surface of the TNTPs, and it is in favor of the adsorption process.

The adsorption kinetic of MB on the TNTPs synthesized in the autoclave for different time in MB solution (40 mg L^{-1}, pH = 7) was also investigated, and their adsorption kinetic curves are shown in
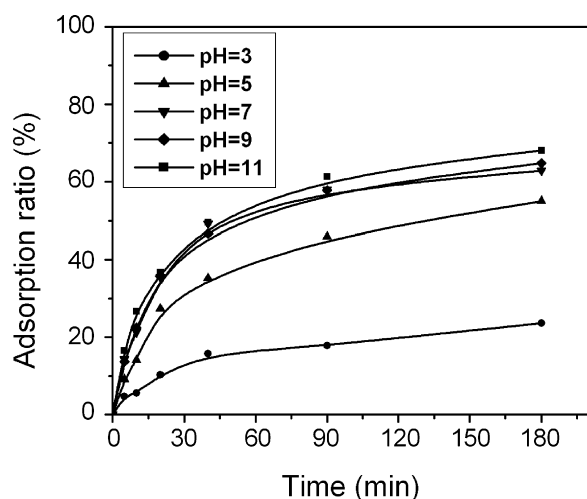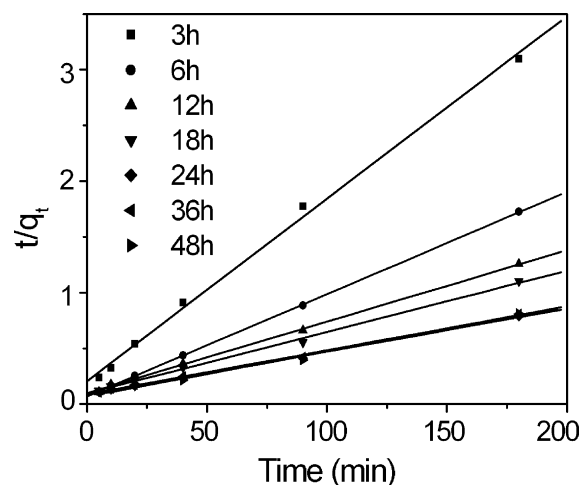

Fig. 7. The adsorption kinetic curves of MB on the titanate nanotube powders synthesized in the autoclave for different time in MB solution (40 mg L^{-1}, pH = 7).

Fig. 7. A pseudo-second-order kinetics model was used as follows:

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{t}{q_e}$$

where q_e is the equilibrium adsorption capacity, q_t is the adsorption capacity at t, t is the reaction time, and k is the pseudo-second-rate constant. For all samples, the linear relationship of t/q_t vs. t shows that the adsorption of MB molecules on the TNTPs can be described well by the pseudo second-order rate model with high correlation coefficients ($R > 0.995$). The equilibrium adsorption capacity of the TNTPs synthesized in the autoclave for 3, 6, 12, 18, 24, 36, and 48 h are 61.1, 109.1, 156.0, 181.5, 260.4, 252.5, and 248.1 mg g^{-1}, respectively. In agree with the results obtained in Fig. 4, the sample for 24 h exhibits a maximum equilibrium adsorption capacity. The equilibrium adsorption capacity is not a linear function of the specific surface area of samples, for which is attributed to the porous microstructure formed on the powders besides their specific surface area. In addition, it is considered that the adsorption process is agreed with chemisorption as the rate-limiting mechanism through the electron exchange between sorbent and sorbate [19].
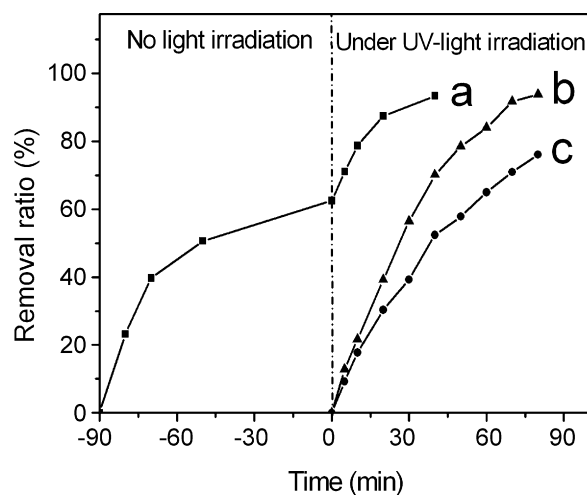

Fig. 6. The time dependent of adsorption ratio on the titanate nanotube powders synthesized in the autoclave for 24 h in MB solution (40 mg L^{-1}) with different pH values.

Fig. 8. The removal ratio of MB vs. irradiation time using the titanate nanotube powder photocatalysts synthesized in the autoclave for 24 h under (a) adsorption/UV-light irradiation, (b) UV-light irradiation only, and (c) the removal ratio for recycle particles under UV-light irradiation only.
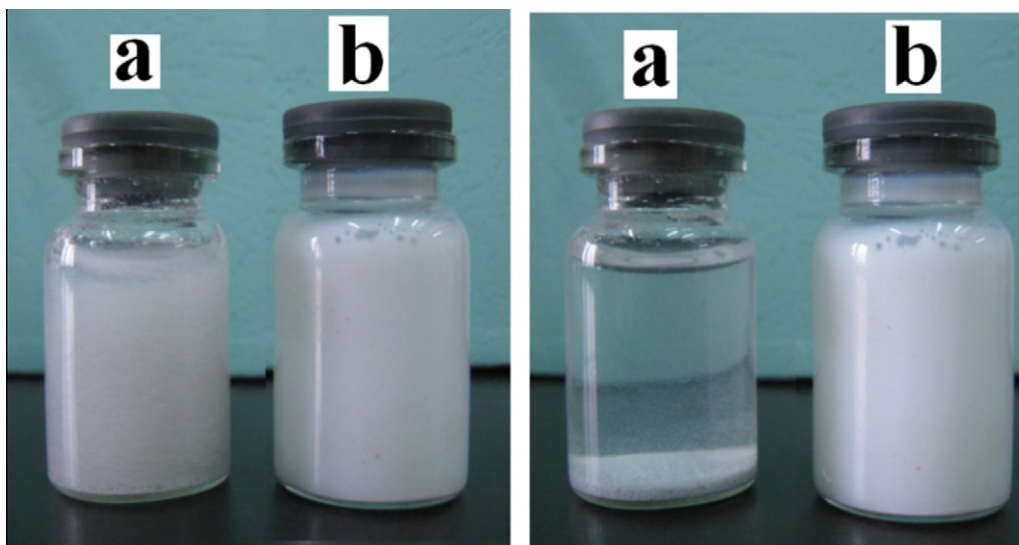
Fig. 9. The sedimentation of (a) the titanate nanotube powders and (b) TiO$_2$ nanopowders for 2 min in aqueous suspensions.

3.3. Photocatalytic activities of titanate nanotube powders

Two series of experiments were performed to evaluate the photocatalytic activities of TNTPs and synchronously distinguish the effect of adsorption on the removal ratio. The first one was carried out with an adsorption process for 90 min in dark to allow the system to reach adsorption equilibrium prior to the light on, while the second was exposed directly to the UV-light irradiation. It was observed that no obvious differences occurred in the photocatalytic reactivity for the samples synthesized with different hydrothermal time, the removal abilities were generally direct proportion of their adsorption capability. Thus, only the curves of removal ratio vs. irradiation time using the TNTPs synthesized in the autoclave for 24 h are shown in Fig. 8. It can be seen that the removal ratio of MB in the solution approaches about 95% (curve a) when UV-light irradiation was applied for 40 min after the adsorption process. On the other hand, the same removal ratio was obtained (curve b) when the system was performed under UV-light irradiation for 80 min, showing the removal ratio can be improved using the double removal properties of TNTPs, i.e. adsorptive separation and photocatalytic degradation.

Moreover, the removal ability of the recycle particles was also evaluated and their photocatalytic data are given in Fig. 8 (curve c). The TNTPs were collected through centrifugation after the photocatalytic experiment and subsequently recycled with washing and UV-light irradiation for 30 min. Afterwards, the photocatalytic degradation experiment was performed under same conditions. Compared with the removal ratio of the fresh TNTPs, i.e. 95%, a lower value is obtained for the recycle particles, i.e. 77%. As mentioned above, there is strong adsorptive ability for the as-prepared TNTPs, the residue sorbates on the recycle particles will hinder not only their adsorption but also their photocatalytic degradation.

In comparison with TiO$_2$ nanomaterials reported in other literatures [4,10–13,20], the photocatalytic reactivity of the-synthesized TNTPs is somewhat lower. The micron level particle size and lower light irradiation area are attributed to these differences. In our other experiment, it was indicated that the adsorption capacity of TNTPs was decreased when they were washed with diluted HCl (0.1 mol L^{-1}) according to the literatures [10,15,16], and their removal ability of MB was also decreased correspondingly. However, these TNTPs have taken an advantage over other nanostructure catalysts due to their particle size and separability. It is well known that the photocatalysts with nanorange present superior activities due to their large surface-to-volume ratios [3,4], while the separation of small size photocatalysts from suspended solution after reaction is very difficult for the nanomaterials. One of the advantages of TNTPs is that they may be conveniently separated to recycle the catalysts, i.e. the natural sedimentation or filtration treatment can separate TNTPs from the MB solution. As shown in Fig. 9, the TNTPs were almost completely deposited in the bottom of bottle from an aqueous suspension after 2 min, while the aqueous suspension of TiO$_2$ nanopowders is still relatively turbid. So, using their separability and adsorptive ability, it is possible to adsorb the hazardous substances from wastewater by using the TNTPs as sorbent and then enrich the sorbent and degradate the sorbate.

4. Conclusions

In summary, the titanate nanotube powders (TNTPs) with three dimensional (3D) network surface layer have been synthesized by a simple hydrothermal method using metal Ti particles as a precursor. The obtained nanowire-like products on the Ti particle surface are validated to be titanate nanotubes with pore diameter of 3–4 nm. As expected, the 3D TNTPs exhibit a very high capability for the adsorptive separation and photocatalytic degradation of MB. In addition, the 3D TNTPs are also easy to separate from MB solution. Thus, it is possible to remove dye pollutants from wastewaters through a process, for which includes pollutants adsorption, photocatalysts separation, photocatalytic degradation, and photocatalysts regeneration steps. The as-prepared 3D TNTPs with the properties of higher photocatalytic activity and easier separation for recycling use show promising prospect for the treatment of organic pollutant from water in future industrial application.

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