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Preparation and properties of a composite quartz sand catalyst with supported TiO_2 nanoparticles

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A composite catalyst based on quartz sand with TiO_2 nanoparticles supported was prepared by the sol-gel method with using tetrabutyl titanate (TBOT) and quartz sand as raw material, and a photocatalytic degradation test of methylene blue (MB) was performed. The microstructure of the prepared composite catalyst was characterized by X-ray diffraction (XRD) and scanning electronic microscope-energy dispersive spectrometer (SEM-EDS). The effects of TiO_2 loading, calcination temperature, and pH value on the photocatalytic degradation efficiency were studied. The results showed that the degradation rate of MB increased with an increase of TiO_2 loading, and decreased with an increase of calcination temperature and pH value. The microstructure analysis showed that nano-TiO_2 particles were homogeneously dispersed on the surface of the quartz sand, and the quartz sand has a strong adsorption effect towards MB. The efficiency of photocatalytic degradation of MB is significantly increased due to the synergistic effect of a composite catalyst based on quartz sand with nano-TiO_2 supported.

Keywords: quartz sand, nanoparticle, methylene blue, photocatalytic degradation.

Приготування та властивості композитного каталізатора з кварцового піску з нанесеними наночастинками TiO_2. *J. Jianhua, L. Gang*

Композиційний каталізатор на основі кварцового піску з нанесеними наночастинками TiO_2 був приготований золь-гель методом з використанням тетрабутілтітаната і кварцового піску в якості сировини. Проведено фотокаталитический тест на деградацію метилен синього. Досліджено мікроструктура приготованого композитного каталізатора. Вивчено вплив кількості TiO_2, температури прожарювання і значення pH на ефективність фотокаталітичної деградації. Результати показали, що швидкість розкладання метилен синього збільшується зі збільшенням кількості TiO_2 і зменшується зі збільшенням температури. Ефективність фотокаталітичної деградації метилен синього була значно підвищена завдяки синергетичного ефекту композитного каталізатора на основі кварцового піску з нанокристалічним TiO_2.

Композиционный катализатор на основе кварцевого песка с нанесенными наночастицами TiO_2 приготовлен золь-гель методом с использованием тетрабутилтитаната и кварцевого песка в качестве сырья. Проведен фотокаталитический тест на деградацию метилен синего. Исследована микроструктура композитного катализатора . Изучено влияние количества TiO_2, температуры прокаливания и значения pH на эффективность фотокаталитической деградации. Результаты показали, что скорость разложения метилен синего увеличивается с увеличением количества TiO_2 и уменьшается с увеличением температуры. Эффективность фотокаталитической деградации метилен синего была значительно повышена благодаря синергетическому эффекту композитного катализатора на основе кварцевого песка с нанокристаллическим TiO_2.

1. Introduction

Since Fujishima and Honda discovered the photo-induced decomposition of water on theTiO_2 electrode [1], TiO_2 has been widely investigated in water purification due to its high efficiency, non-toxicity, and high chemical stability [2–3]. However, there are still few reports on the large-scale engineering application of TiO_2 in sewage treatment. The main reason is that nano-TiO_2 particles are easy to agglomerate in water, thus impairing the photocatalytic degrading performance. In practice, it is common to add TiO_2 additive to achieve engineering-grade degradation efficiency, and it's also hard to reuse powder TiO_2, which will inevitably lead to higher cost of the pollution control and limit the wide application of TiO_2 [4]. In recent decades, the TiO_2 immobilization technology has triggered worldwide attention; this can improve the photocatalytic efficiency of TiO_2 by loading less nano-TiO_2 particles on carriers, e.g. active carbon [5], zeolite [6], and glass fibers [7] etc. This technology can reduce the loading of TiO_2 and improve the recycle rate of the TiO_2, which is of significance to promote the utilization of TiO_2 in environment purification.

Quartz sand is a common mineral of abundant reserves on the earth and low price, which is widely used as fillers and fine aggregates. The main component of quartz sand, crystal silica dioxide (SiO_2), has stable chemical properties and rough surface, which makes it an ideal support for TiO_2. In this paper, quartz sand was used as the carrier and TBOT as the precursor. The composite catalyst based on quartz sand with nano-TiO_2 supported was prepared by the sol-gel method. The photocatalytic degradation efficiency of the composite catalyst was studied by degrading MB.

2. Experimental

2.1 Raw material and apparatus

Natural quartz sand (75 ~ 150 μm) was derived from Sichuan province, China. TBOT (AR), MB (AR), and nitric acid (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. A muffle furnace (SG-XL600, Shanghai institute of optics and fine mechanics, China), a magnetic stirrer (JB-3, Jiangsu jintan instrument factory, China), a drying oven (TX-11, Shanghai medical equipment factory, China), a water bath (SY-1, Jiangsu jintan instrument factory, China), an UV-visible spectrophotometer (UV765, Shanghai precision scientific instrument Co. LTD, China), an X-ray diffractometer (D/max2550, Rigakud, Japan), and a scanning electron microscope (Quanta 200F, FEI, America) were used.

2.2 Sample preparation

A certain amount of TBOT was added into deionized water drop by drop (2–3 drops/sec) with stirring, and a small amount of nitric acid was also added to inhibit hydrolysis. The mass ratio was: TBOT: deionized water: nitric acid = 1: 8: 0.08. After finishing the addition, a milky white suspension was obtained. Then, the suspension was placed in a water bath of 50°C for about 1 h with stirring to obtain a light blue TiO_2 sol. Subsequently, a certain amount of quartz sand (QS) was added into the prepared TiO_2 sol, and the mixture was treated by ultrasonic for 30 min and then put in an oven at 100°C until the mixture weight was constant (TiO_2 mass fraction were 2.5 %, 5.0 %, 7.5 %, and 10.0 %). Finally, the solid particles was calcined in a muffle furnace at different temperatures (200°C, 300°C, 400°C, and 500°C) for 4 h and then naturally cooled to room temperature. The samples were labeled as QS-*n*-*m* (*n* is the percentage of TiO_2 and *m* is the calcination temperature). For controlled trial, the TiO_2 sol was dried at 100°C and then calcined in a muffle furnace at 200°C to obtain TiO_2 powder, which was labeled as S–TiO_2.

2.3 Photocatalytic degradation test

The schematic diagram of the photocatalytic reaction device is shown in Fig. 1. The reactor is a glass petri dish with a diameter of 15 cm and the light source is a high-pressure mercury lamp (main wavelength 300 nm). The 500 mL MB solution (50 ppm) and 1 g of the composite catalyst were added together in the reactor, and then the whole system was treated in the dark envi-

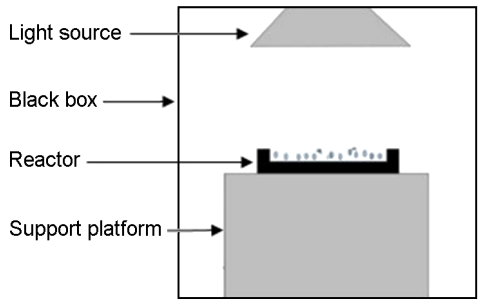

Fig. 1. Schematic diagram of the photocatalytic reaction device.

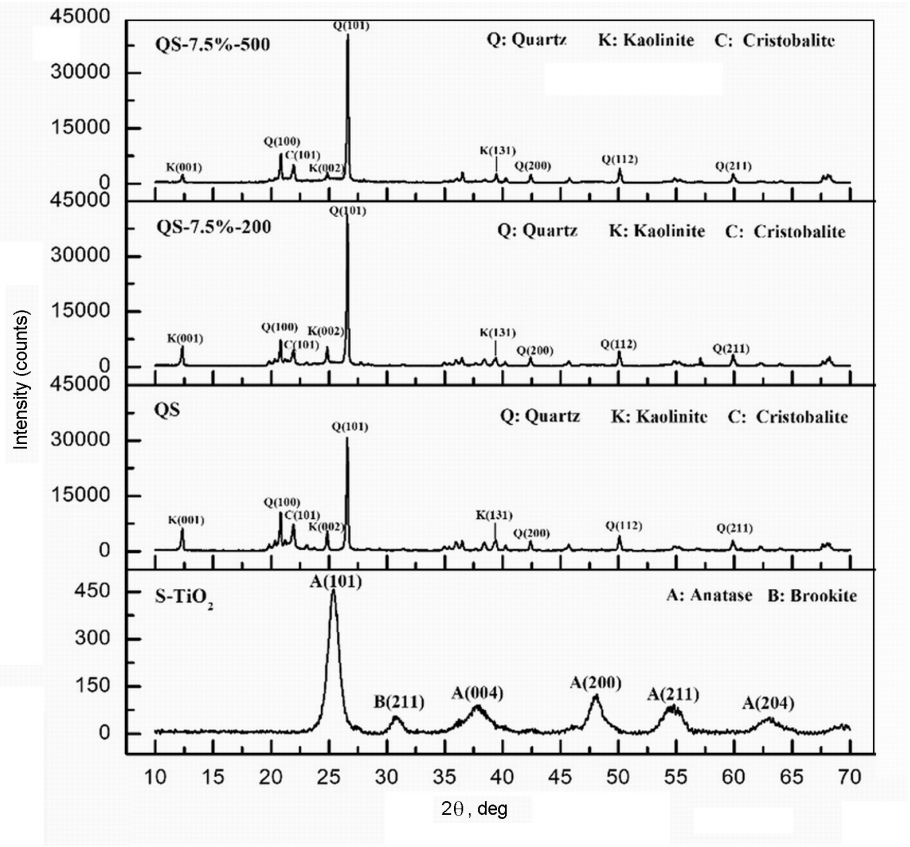

Fig. 2. X-ray diffraction patterns of S–TiO_2, QS, QS-7.5 %-200, and QS-7.5 %-500.

ronment for 1 h to establish adsorption equilibrium. Afterwards, the light source was turned on to excite the photocatalytic reactions. During the reaction, 5 ml of the MB solution were sampled by a pipette every 1 h (4 times in total), and then the absorbance of the MB solution sample was measured at the wavelength of 660.5 nm by using a spectrophotometer. The degradation rate of MB is calculated according to the following formula:

$$d = \frac{A_0 - A_t}{A_0} \cdot 100\%, \quad (1)$$

where d is the degradation rate, A_0 is the initial absorbance, and A_t is the absorbance after degradation.

3. Results and discussion

3.1 X-ray diffraction analysis

X-ray diffraction patterns of S–TiO_2, QS, QS-7.5 %-200, and QS-7.5 %-500 are shown in Fig. 2. For S–TiO_2, characteristic diffraction peaks of anatase TiO_2 were observed at 2θ (25.4°, 37.9°, 48.2°, 55.2°, and 62.9°) according to PDF# 73-1764, indicating that the main crystal phase of S–TiO_2 was anatase that was of high photocatalytic activity. In the diffraction pattern of QS, according to PDF#86-2237, the characteristic diffraction peaks of quartz were detected at 2θ (20.9°, 26.6°, 42.5°, 50.2°, and 60.0°), and the diffraction intensity was great. Besides, the characteristic diffraction peaks of kaolinite (2θ = 12.4°, 25.0°, and 39.4°) as well as α-cristobalite (101) can be observed. The result showed that the main component of the natural quartz sand used in this paper was quartz, containing a small amount of kaolinite and α-cristobalite impurities. According to the diffraction patterns of QS-7.5 %-200 and QS-7.5 %-500, it can be seen that the main crystal phase of composite catalysts was still quartz and no diffraction peaks of anatase were observed. This is because the loading of TiO_2 was very low, and in addition, the strongest diffraction peak intensity of S–TiO_2 (about 450) was much smaller than that of quartz (about 30,000).

Consequently, the characteristic diffraction peaks of anatase were most likely overlapped by quartz ones. However,

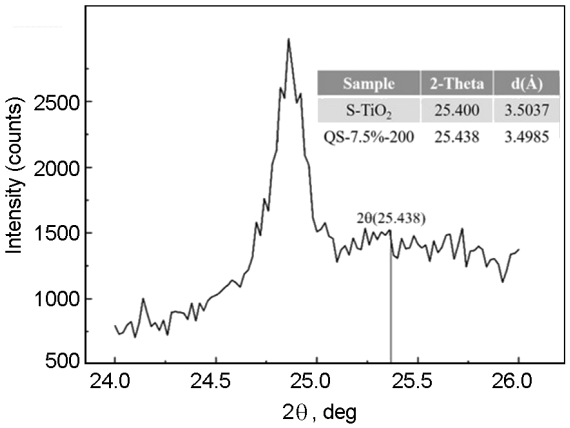

Fig. 3. X-ray diffraction pattern of QS-7.5 %-200 (24° < 2θ < 26°).

through a fine analysis of the diffraction pattern of QS-7.5%-200 (24° < 2θ <26°), a weak diffraction peak was found at 2θ (25.4°), and the interplanar spacing corresponding to this diffraction peak was approximately the same as that of anatase (101), as shown in Fig. 3. It can be concluded that QS-7.5 %-200 contained a trace amount of anatase. With the increase of the calcination temperature, the intensity of diffraction peaks of kaolinite crystal plane (001) gradually weakened, indicating that the calcination treatment promoted the transition of kaolinite from the crystalline state to the amorphous state. After calcination, the intensity of the diffraction peak of quartz (101) crystal plane was stronger, indicating that the purity of quartz was improved.

3.2 Micromorphology

As shown in Fig. 4(a), S–TiO_2 had a compact block structure. From the magnified image, it can be observed that spherical particles aggregated into worm-like basic units, which were closely packed and interlocked with each other to form a dense TiO_2 block. It's indicated that TiO_2 crystal particles with poor dispersion tended to agglomerate under the calcination treatment. Fig. 4(b) shows the morphology of natural quartz

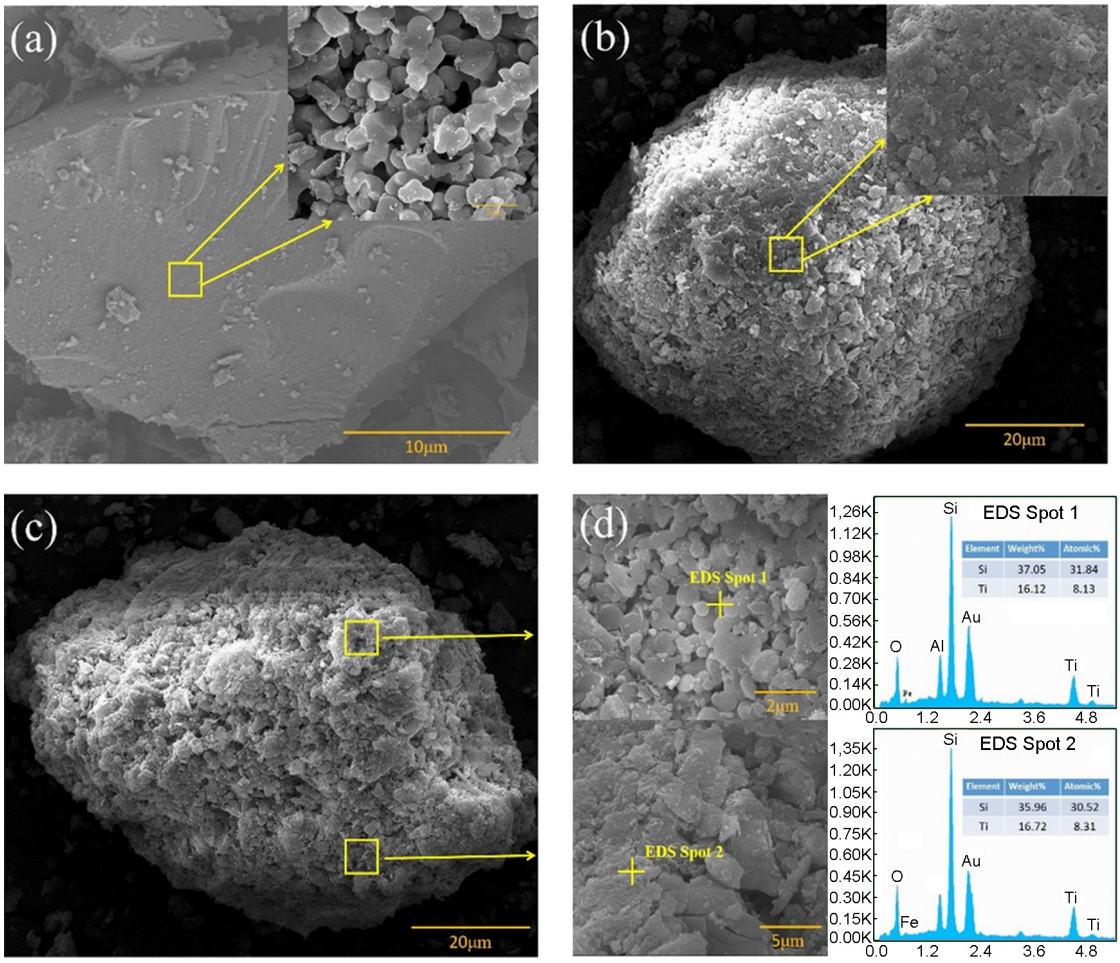

Fig. 4. SEM images: (a) S–TiO_2; (b) QS; (c) QS-7.5 %-200; (d) QS-7.5 %-200(EDS).

sand. The quartz sand particles were spherical and its particle size was about 60 μm. The surface of quartz sand was stacked with plate or sheet units, forming a mass of rough micro-nano synapses. This structure contributed to the uniform distribution of TiO_2 particles on the surface of quartz sand. Fig. 4(c) displays the microstructure of QS-7.5 %-200. The results show that the calcination treatment posed no effect on the particle size and shape of quartz sand, but the surface of QS-7.5 %-200 was covered with a flocculent layer, and the edges and corners gradually disappeared. This is because the TiO_2 particles were anchored by micro-nano synapses of quartz sand and homogeneously dispersed on its surface, and after calcination, a loose TiO_2 film was formed over quartz sand. Fig. 4(d) shows the micro-area morphology of QS-7.5 %-200 and the corresponding element composition spectrum (two micro-areas were randomly selected). The mass fraction of Ti in spot 1 (16.12 %) was close to that of spot 2 (16.72 %), indicating that the TiO_2 particles were homogeneously dispersed on the surface of quartz sand.

3.3 Photocatalytic degradation performance

Fig. 5 shows the degradation rate of MB by using 1 g QS-10 %-200, 0.9 g QS, and 0.1 g S–TiO_2. The results show that under dark condition, all samples had a certain adsorption effect towards MB, and the adsorption equilibrium was reached within 1 h. The adsorption rate of QS as well as QS-10 %-200 towards MB was about 10%. Due to the small dosage of S–TiO_2, its adsorption effect was weak. After illumination, the QS degradation rate towards MB was still maintained at about 10 %. This is because MB was stable under ultraviolet light and the number of available adsorption sites on QS was limited, and the system was in the state of adsorption equilibrium. For QS-10 %-200 and S–TiO_2, MB can be continuously degraded, but the degradation rate for QS-10 %-200 was significantly higher than that for S–TiO_2. The degradation rate of QS-10 %-200 towards MB reached 68 % in 5 h, which was higher than the sum of these for S–TiO_2 (54 %) and QS (10 %), suggesting that the composite catalyst of quartz sand supported with TiO_2 showed synergistically enhanced effect. This is owing to the rough texture of quartz sand, on which TiO_2 particles were homogeneously fixed. And when the composite catalyst was placed in an aqueous solution, TiO_2 particles were not agglomerated, thus

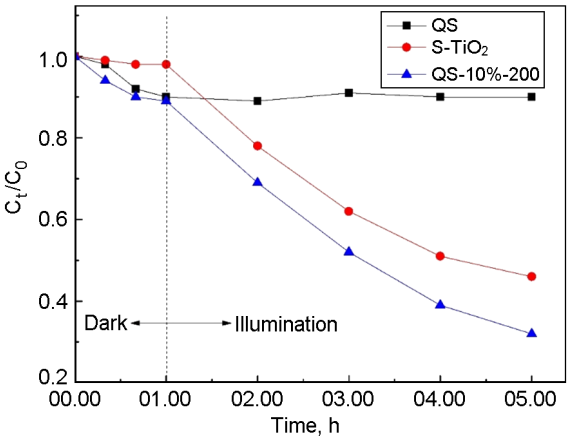

Fig. 5. Photocatalytic degradation rate of MB by QS-10 %-200 (1 g), S–TiO_2 (0.1 g), and QS (0.9 g).

increasing the photocatalytic degradation efficiency. Besides, quartz sand had a strong adsorption effect on MB molecules; thus, a high-concentration MB molecular layer can be formed on the surface of TiO_2, increasing the reaction rate. When MB was decomposed by the active oxidative species on TiO_2, the adsorption equilibrium of the system was broken; this promoted the adsorption of free MB molecules on quartz sand. The adsorption effect of quartz sand and the photocatalytic degradation effect of TiO_2 together facilitated the mass transfer process of the photocatalytic degradation reaction, which can synergistically improve the photocatalytic performance.

Fig. 6(a) shows the effect of calcination temperature on the degradation rate of MB. As the calcination temperature increased, the photocatalytic degradation efficiency continued to decrease. This is because the calcination treatment contributed to the increase of the TiO_2 crystal size and the decrease of the surface area. Hence, the absorption efficiency of photons was reduced and hole-electron pair recombination efficiency may be increased, thereby reducing the quantum efficiency. Fig. 6(b) shows the effect of TiO_2 content on the degradation rate. With the increase of TiO_2 content, the photocatalytic degradation efficiency continued to increase, but the change was nonlinear. This can be explained that when TiO_2 loading is high, nano-TiO_2 particles would overlap and agglomerate with each other, reducing the dispersity of TiO_2. Therefore, the effect of increasing the loading of TiO_2 on improving the efficiency of photocatalytic degradation was weakened. Fig. 6(c)

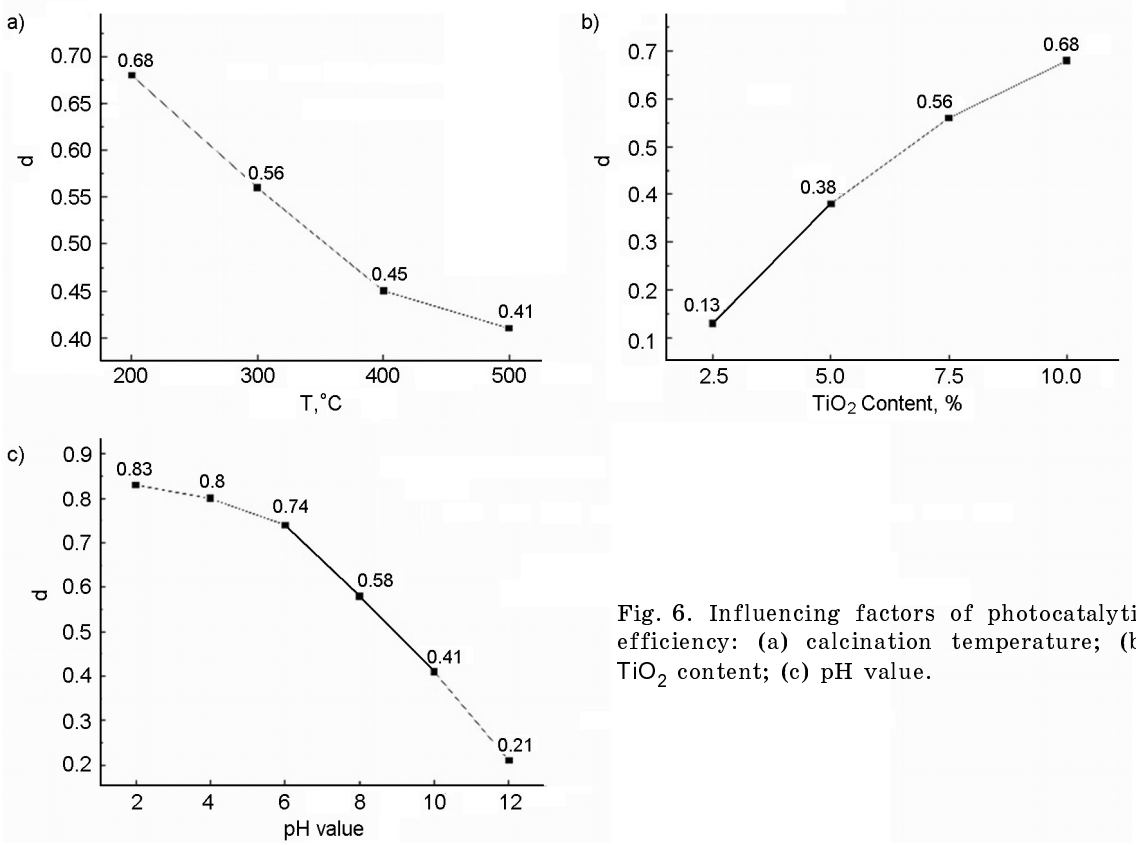

Fig. 6. Influencing factors of photocatalytic efficiency: (a) calcination temperature; (b) TiO_2 content; (c) pH value.

shows the effect of pH value on the degradation rate. As the pH value rose, the degradation rate declined rapidly. This phenomenon was mainly related to the adsorption of MB molecules. The research shows that the average point of zero charge of TiO_2 is at pH = 5.6 [8] and the color rendering of MB is mainly due to the presence of anions. In the case of low pH value, the composite catalyst with positive charges will have a strong adsorption effect towards the anions of MB, accelerating the reaction rate, so the photocatalytic efficiency is enhanced.

4. Conclusions

– Through the sol-gel method, a TiO_2-supported quartz sand composite catalyst was successfully prepared. SEM images showed that quartz sand had micro-nano synapses and its surface was rough. Nano-TiO_2 particles were homogeneously dispersed on the surface of quartz sand.

– The synergistic effect of the surface adsorption of quartz sand and the photocatalytic degradation of TiO_2 can significantly improve the photocatalytic degradation performance of the composite catalyst.

– The degradation rate of MB by the composite catalyst increased with the increase of TiO_2 content, and decreased with the increase of calcination temperature and pH value.

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