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A novel preparation approach and denitrification performance of TiO_2/Fe^0 photocatalysts

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ABSTRACT

Chemical vapor hydrolysis deposition (CVHD), a novel method for preparation of TiO_2/Fe^0 is presented. In the method, tetrabutyl titanate (TBT) and sponge iron (Fe_s) are used as precursor and carrier, respectively. Especially, TBT was hydrolyzed slowly with the thin water vapor to create TiO_2 nanoparticles on the Fe_s carrier. The experiment showed that the optimal preparation conditions for TiO_2/Fe^0 via CVHD were calcination temperature of 723 K and TiO_2-loading amount of 7.57%. The as-prepared TiO_2/Fe^0 catalysts were evaluated by the catalytic reaction of nitrate reduction, and exhibited a higher catalytic activity and selectivity than the similar catalysts prepared with the typical methods of sol–gel or alkoxide hydrolysis precipitation. The present results demonstrate that the selective nitrate reduction over TiO_2/Fe^0 catalysts with HCOOH as the hole scavenger, highlighting the validity of removal of aqueous nitrate by photocatalysis.

Keywords: Chemical vapor hydrolysis deposition (CVHD); Nitrate; Photocatalysis; TiO_2/Fe^0

1. Introduction

Nitrate contamination in groundwater has become more and more serious in many countries because of the excessive use of fertilizers. Drinking water containing high concentration of nitrates can cause methemoglobinemia or blue baby syndrome in infants [1]. The efficient methods of the aqueous nitrate removal are very urgent. Some processes like physicochemical, chemical, biological, and photocatalytic reduction have been attempted for nitrate removal [2–4]. Conventional physicochemical or biological methods are mostly ineffective to remove nitrate due to the high solubility and stability of nitrate. In this regard, the application of photocatalysis appears to be a more appealing access than many conventional methods for the conversion of nitrate compounds. Photocatalysis has attracted considerable attention owing to its potential in environmental cleaning and energy regeneration. The TiO_2 photocatalysts were involved in numerous researches because of their low cost, non-toxicity, high stability, and easy preparation [5–8]. However, pure TiO_2 could be activated only by UV light due to its energy gap (3.0–3.2 eV). Besides, pure TiO_2 also exhibits low quantum efficiency due to easy recombination between photoelectrons and holes. Loading on surface is a promising way to reduce the recombination of photo induced electrons and holes. In previous studies, Ag, Fe, Pt, Pd, Ru, and Rh [9,10], as electron trapper, have been added into TiO_2 to suppress the recombination. Ranjit and Viswanathan [11] further indicated that the amount of metals loaded on TiO_2

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and the synthesis method have had great impact on the photocatalytic reduction of nitrate. Among various monometallic carriers, Fe_s has porous, cheap, and reduction features. Moreover, Fe^{3+} is most frequently employed owing to its unique half-filled electronic configuration [6,12,13], which might narrow the energy gap through the formation of new intermediate energy levels and also diminish recombination of photoinduced electrons and holes by capturing photoelectrons. At present, the TiO_2 nanoparticles loaded on Fe_s (TiO_2/Fe^0) can be prepared by sol–gel or alkoxide hydrolysis-precipitation methods. Although these methods are easier to realize metal doping, the particle size of the obtained TiO_2 is not uniform and the particle agglomeration rises frequently in the calcining process. Therefore, a fine type of TiO_2/Fe^0 catalyst with a uniform structure based on these methods is difficult to be obtained.

In this work, TiO_2/Fe^0 catalysts were prepared by a novel method Chemical vapor hydrolysis deposition (CVHD). The method uses tetrabutyl titanate (TBT) as the precursor of TiO_2 and anhydrous ethanol as dispersant. Since TBT was hydrolyzed slowly by water vapor in the air, catalyst particles are small and uniform. In the water vapor treatment process, grain size, particle morphology, and crystalline phase can be easily controlled via processing conditions. The CVHD method could have obtained nanoparticles with ultrahigh surface areas and negligible agglomeration, and enhanced photocatalytic nitrate reduction. Such work has not been reported so far. As an application, the prepared TiO_2/Fe^0 catalysts will be evaluated for the performance in the photocatalytic nitrate reduction reaction in groundwater.

2. Materials and methods

2.1. Catalysts preparation

2.1.1. CVHD method

TiO_2/Fe^0 catalyst was prepared by the CVHD. Briefly, 10 ml anhydrous ethanol was added slowly to a certain amount of TBT with stirring for 2 h until forming a homogeneous and transparent liquid. The obtained liquid was dripped on a filter paper in a glass dish to reach saturation. The pretreated 0.147–0.42 mm Fe_s particles were evenly placed on the treated filter paper and were sealed. The TBT was evaporated from the paper and hydrolyzed slowly by the water vapor in the air for 48 h to create TiO_2 precipitate on the Fe_s subsurface. After hydrolysis reaction, the solid materials were taken out and aged for 24 h, and then washed thoroughly with distilled water and fast dried finally. TiO_2/Fe^0 catalysts were subsequently obtained by 2 h calcination at different temperatures under N_2 protection.

2.1.2. Alkoxide hydrolysis-precipitation method

Known amount of TBT was dropped slowly into a mixture of 20 ml anhydrous ethanol and 1 ml glacial acetic acid with vigorous stirring to get a solution, called as Solution-I. Another solution (Solution-II) was prepared by adding 1 ml glacial acetic acid to the mixture of 1.1 ml H_2O and 20 ml anhydrous ethanol under stirring. The obtained Solution-II was added dropwise into Solution-I at a velocity of about 45 drop/min, and then the TiO_2 sol was formed after 1 h stirring. Fe_s particles were dipped into the above-prepared TiO_2 sol to load TiO_2 on the Fe_s surface. TiO_2/Fe^0 catalysts can be obtained by calcining at 723 K under the protection of N_2.

2.1.3. Sol–gel method

Known amount of TBT were added drop wise into 20 ml anhydrous ethanol with vigorous stirring for 30 min. Then 2 ml of diethanolamine was added to get transparent TiO_2 gel. The Fe_s particles were dipped into the above-prepared gel to load TiO_2 load on the Fe_s surface. TiO_2/Fe^0 catalyst can be obtained by calcining at 723 K under the protection of N_2.

2.2. Photocatalytic reaction

The experimental apparatus is shown in Fig. 1. The photocatalytic reactor, main part of the setup, is constructed of a double-layer tube. The tube contains

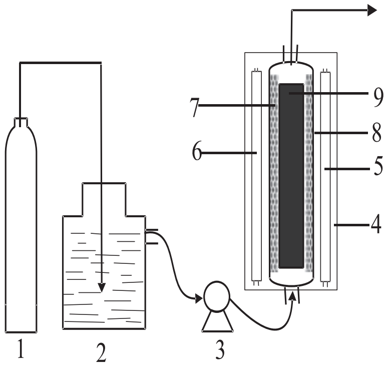

Fig. 1. Schematic of photocatalytic reactor: (1) nitrogen cylinder, (2) raw water tank, (3) peristaltic pump, (4) reflecting shade, (5, 6) UV lamp, (7) catalyst bed, (8) quartz window tube, and (9) solid glass column.

a solid glass column in the inner layer (Φ: 12 mm) and a quartz tube as the outer layer (H: 110 mm, Φ: 15 mm). The catalysts were filled in the space between the two layers. Two UV lamps (20 W) were located on both sides of the quartz window tube. The aluminum cap reflector was used to cover the outside of the reactor. TiO_2/Fe^0 of 20.0 g was filled into the reactor. When running, potassium nitrate solution was used as the synthetic wastewater and keeps a flow rate of 1.0 mL/min to pass through the catalysts bed from the bottom (the reactor was kept 338 K). Especially, the system is oxygen-free by filling with nitrogen gas. A certain amount of formic acid (0.027 mol/L) was added into synthetic wastewater (50 mg/L NO_3^--N) as the hole scavenger and the pH was adjust. When the TiO_2/Fe^0 catalysts were irradiated with UV lamps, the outflow was sampled every 2 h and filtered with 0.22 μm membrane to measure the concentration of NO_3^--N, NO_2^--N, NH_4^+-N.

2.3. Characterization and analysis

The as-prepared TiO_2/Fe^0 catalysts and the raw Fe_s particles were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD measurements were carried out on a D/Max-3c X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154056$ nm). SEM images were taken using a Quanta 200 electron microscopy. The concentrations of nitrite, nitrate, and ammonia were analyzed with spectrophotometry (UV-2000). The conversion rate of nitrate and N_2 selectivity can be calculated as follows:

$$\gamma = \frac{C_{01} - C_1}{C_{01}} \times 100\% \tag{1}$$

$$\beta = \frac{C_{01} - C_1 - C_2 - C_3}{C_{01} - C_1} \times 100\% \tag{2}$$

where γ is the percentage of nitrate conversion, β is the N_2 selectivity, %. C_{01} is the initial nitrate concentration, and C_1, C_2, and C_3 are the residual concentrations of nitrate, nitrite, and ammonia after reaction for 2 h, respectively, mol/L.

3. Results and discussion

3.1. Characterization of catalysts

The prepared TiO_2/Fe^0 catalysts were characterized to reveal the changes of the morphology and composition on the surface. Fig. 2 shows the SEM images of the raw Fe_s particles and the synthesized TiO_2/Fe^0 via CVHD (calcined temperature at 723 K, loading amount of 7.57%). As can be seen from Fig. 2(b), the raw Fe_s surface was covered with obvious wrinkles and micropore. On TiO_2/Fe^0 surface, there was part of b are surface and pore structure, and some TiO_2 can be observed on the surface and internal pore of the carrier. These morphologic changes provided beneficial conditions for the photocatalytic reduction reaction in water.

XRD patterns for Fe_s, pure TiO_2, and TiO_2/Fe^0 are given in Fig. 3. In the patterns of Fe_s (Fig. 3(a)), there were not only the diffraction peaks of zero-valent iron (ZVI), but also other complex peaks derived from the Fe_s oxides. It can be seen from Fig. 3b that the diffraction peaks at 25.1°, 37.6°, 47.9°, 54.5°, and 62.7° in the pure TiO_2 agree well with that of anatase (JCPDS file No. 21-1272) [14]. Moreover, the ZVI phase structure has little change (Fig. 3(c)).

The calcination temperature regulates the mineral species on the surface of the prepared materials. XRD patterns of TiO_2/Fe^0 catalysts calcined at different temperatures are shown (Fig. 4). The characteristic diffraction peaks of typical anatase phase all appeared at the temperatures of 623, 723, and 823 K. Both 623 and 723 K consisted of the characteristic diffraction peak of anatase phase, while for 723 K, narrow diffraction peaks and high peak intensity were observed, suggesting a higher content of anatase phase in 723 K. This was because crystal growth and crystallinity increased (the sample of TiO_2) with increasing temperature. At 823 K, the peak intensity of anatase phase decreased and the diffraction peak of rutile phase appeared. This was because further increasing the calcination temperature of TiO_2 from 723 to 823 K led to the transformation of TiO_2 crystalline phase from anatase to rutile phase. The XRD results show that the content of anatase phase increased with the increase in calcination temperature, but the anatase phase was transformed into rutile phase gradually when above a certain temperature. Therefore, in order to get high catalytic activity of anatase phase (TiO_2), the calcination temperature was determined as 723 K.

3.2. Preparation methods and conditions' influence on the photocatalytic performance

3.2.1. Preparation methods

With the catalytic performance, we evaluated three kinds of TiO_2/Fe^0 photocatalysts prepared with CVHD, alkoxide hydrolysis-precipitation, and sol–gel methods, respectively. The nitrate conversion rate (CR) and nitrogen selectivity (NS) were mainly selected to testify the catalytic performance. Fig. 5

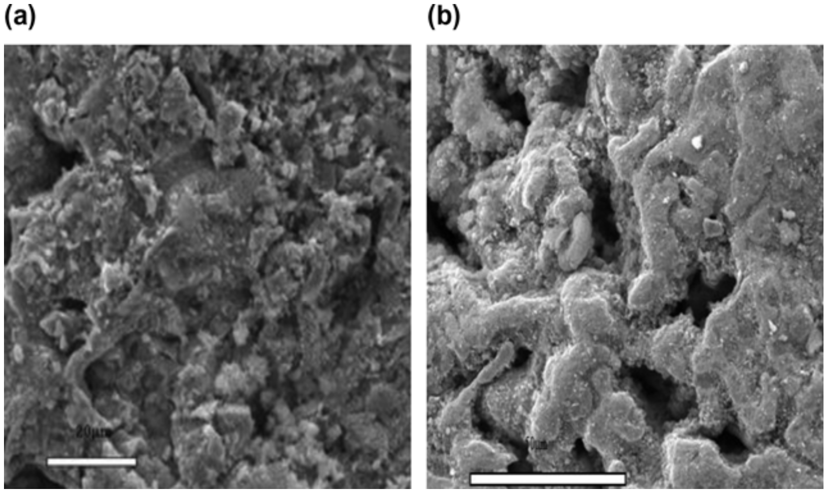

Fig. 2. SEM images of (a) TiO_2/Fe^0 catalyst and (b) Fe_s particles treated with acid-washed.

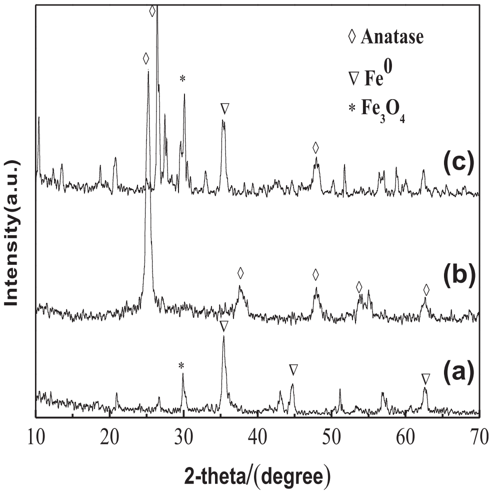

Fig. 3. XRD patterns of (a) Fe_s particles, (b) pure TiO_2 particles, and (c) TiO_2/Fe^0.

shows CR and NS with three catalysts. In contrast to the alkoxide hydrolysis-precipitation or sol–gel methods, the catalyst prepared with CVHD exhibited a better activity in the photocatalytic reaction of nitrate reduction, thereinto CR and NS are highest, and up to 87.3 and 60.9%, respectively. The reasons for this phenomenon come from two aspects. On one hand, in the method of CVHD, the TBT were hydrolyzed slowly by water vapor of the air, which was a chemical hydrothermal processing. The produced TiO_2 particles were small, uniform, and highly dispersible, which provides large specific surface area and more reactive sites for the photocatalytic reaction system. On the other hand, compared with other two methods, without the use of the glacial acetic acid as hydrolysis inhibitors, Fe_s in CVHD process was not oxidized on the surface. So the active reaction sites do not reduce distinctly. For the reasons given above, the catalysts prepared from CVHD method showed a better denitrification performance than the other two methods.

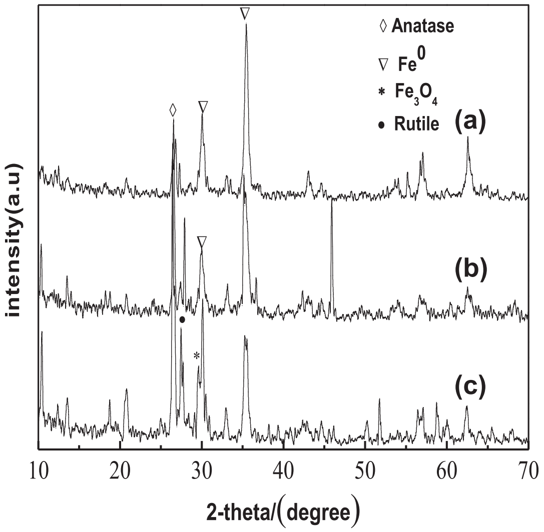

Fig. 4. XRD patterns of the TiO_2/Fe^0 catalysts calcined at (a) 623, (b) 723, and (c) 823 K.

3.2.2. *Calcination temperature*

The calcination temperature is crucial to form the proper TiO_2 crystals. CR and NS were investigated in various reactions with catalysts were prepared in three calcination temperatures. As can be seen from Fig. 6, CR and NS were the highest for the catalyst prepared

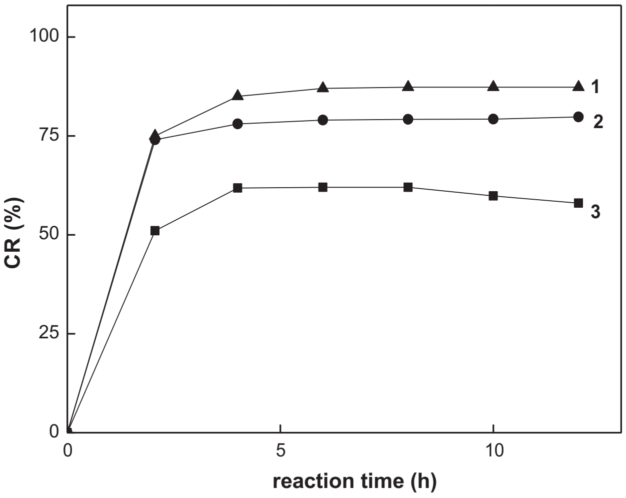

Fig. 5. Catalytic performance with TiO_2/Fe^0 catalysts prepared in various preparation method: (1) CVHD, $\beta = 60.9\%$, (2) Sol–gel method, $\beta = 28.3\%$,(3) Alkoxide hydrolysis-precipitation, $\beta = 40.5\%$. β is the N_2 selectivity. Reaction conditions: 20 g of TiO_2/Fe^0 catalyst, 5.84% TiO_2 loading, UV (254 nm), solutions purged with N_2, and reaction period 12 h.

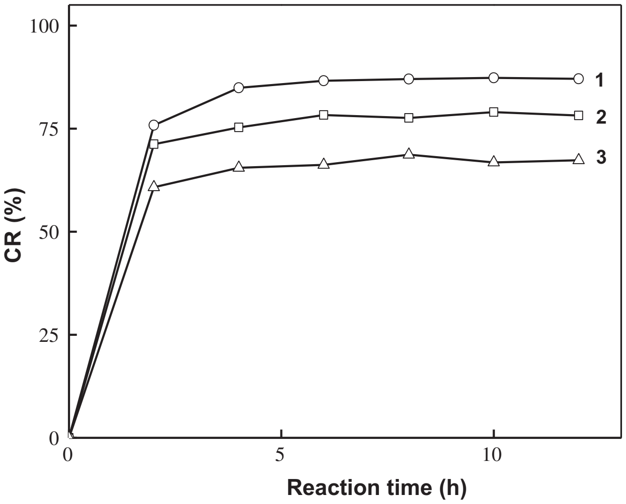

Fig. 6. Catalytic performance using TiO_2/Fe^0 catalysts prepared under different calcination temperatures: (1) 723 K, $\beta = 55.9\%$, (2) 623 K, $\beta = 43.4\%$, (3) 823 K, and $\beta = 39.2\%$. β is the N_2 selectivity. Reaction conditions: catalysts prepared by CVHD, 20 g of TiO_2/Fe^0 catalyst, 7.57% TiO_2 loading, UV (254 nm), solutions purged with N_2, and reaction period 12 h.

at 723 K. The reasons are, firstly, the anatase crystal structure, the efficient TiO_2 catalyst utilized in photocatalytic reaction, has not yet formed fully at low temperature such as 623 K. Secondly, the phase transformation of TiO_2 particles was from anatase to rutile gradually with the increasing temperature, but the rutile structure was not conducive to the reaction. This transformation agreed with the XRD results (Fig. 5). Thirdly, a much higher temperature (823 K) aggravated the agglomeration of nanoparticles on the surface, and then reduced the specific surface area. Therefore, in our study, the optimal calcining temperature was selected as 723 K, which agreed with some other researches [15].

3.2.3. Effects of TiO_2 loading amount

The denitrification reaction catalyzed by TiO_2/Fe^0 is significantly dependent on TiO_2 loading amount on substrates (Fig. 7). Increasing the TiO_2 load from 5.84 to 7.57%, the denitrification efficiency was increased from 82.3 to 88.2%. But in our experiments, the denitrification efficiency was decreased to 81.2% with further increasing the TiO_2 amount to 10.25%. The following reasons can explain the phenomenon. On one hand, with the increase in TiO_2 load, the density of photoelectrons will increase under UV irradiation, thus improving the efficiency of nitrate reduction, Moreover the Fe_s oxides (Fe^{2+}) can also prevent the recombination of electrons and holes in the surface of TiO_2. But higher TiO_2 load, such as 10.25%, reduced the exposed surface area of Fe_s and slowed down the oxidizing reaction of ZVI into Fe^{2+} under acid (HCOOH) condition, decreased the density of electrons and the concentration of Fe^{2+}. Thereby the

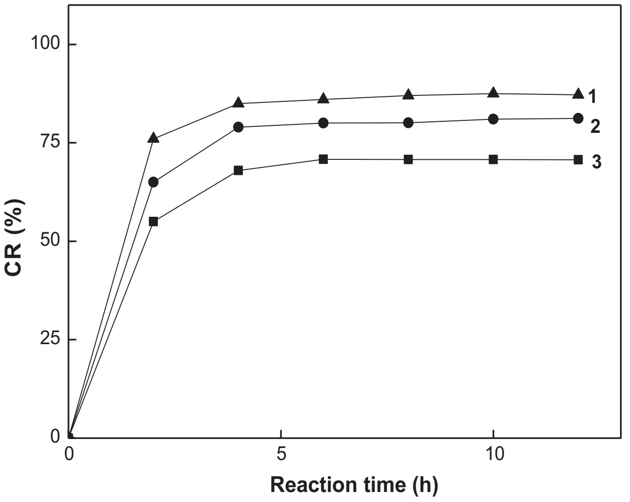

Fig. 7. Catalytic performance using different amounts of catalyst: (1) 7.57% TiO_2, $\beta = 60.9\%$ (2) 10.52% TiO_2, $\beta = 34.5\%$ (3) 5.84% TiO_2, and $\beta = 40.1\%$. β is the N_2 selectivity. Reaction conditions: catalysts prepared by CVHD and calcined at 723 K, 20 g of TiO_2/Fe^0 catalyst, UV (254 nm), solutions purged with N_2 and reaction period 12 h.

insufficient amount of electrons and Fe^{2+} repressed the transformation of nitrate [1]. On the other hand, too little TiO_2 load can reduce the electronic production in the system. So the appropriate TiO_2 load played a key role in the conversion of nitrate. The optimum loading of TiO_2 is 7.57% in our experiments.

3.3. Running conditions

3.3.1. Dissolved oxygen

Since the photocatalytic reaction of denitrification was mainly a reduction reaction, dissolved oxygen has negative effects on the process. In order to uncover the effect, the tests with and without bubbling N_2 through the wastewater were carried out (Fig. 8). The results show that catalytic activity of TiO_2/Fe^0 without dissolved oxygen was higher than that with the existence of dissolved oxygen. This is mainly due to that, the existence of dissolved oxygen, will oxidize Fe^{2+} to Fe^{3+} and promote NO_2^- transforming to NO_3^-.

3.3.2. UV wavelength

To verify the effect of different UV wavelengths in photocatalytic reaction, the denitrification reactions assisted with UV of 365 nm, 254 nm, and without UV were carried out (Fig. 9). The results show that catalytic activity of TiO_2/Fe^0 was highest under the 254 nm UV. It may be explained by the fact that the power of 254 nm UV and the band gap of TiO_2 is a good match [16,17], and the efficiency of photocatalytic reduction of nitrate was improved accordingly. In addition, the catalytic efficiency of 365 nm UV light was lower than that of 254 nm, and higher than that without UV irradiation. This is because the ultraviolet lamp provided energy to improve the catalytic efficiency of reaction [18]. On the basis of this description, it can be concluded that there is a significant effect of UV wavelength on the reduction of nitrate.

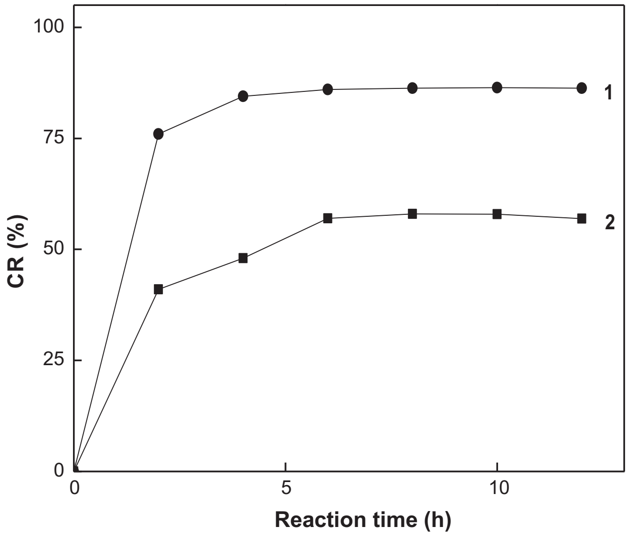

Fig. 8. Catalytic performance (1) solution purged with N_2, $\beta = 60.9\%$ (2) in the presence of dissolved oxygen, $\beta = 21.7\%$. Reaction conditions: catalysts prepared by CVHD and calcined at 723 K, 7.57% TiO_2 loading, 20 g of TiO_2/Fe^0 catalyst, UV (254 nm), and reaction period 12 h.

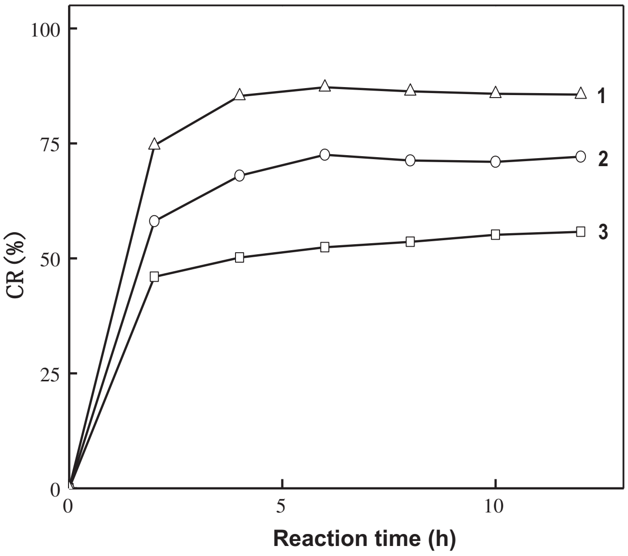

Fig. 9. Catalytic performance using different UV wavelengths: (1) $\lambda = 254$ nm, $\beta = 60.9\%$ (2) $\lambda = 365$ nm, $\beta = 30.2\%$ (3) Without UV irradiation, $\beta = 19.6\%$. Reaction conditions: catalysts prepared by CVHD and calcined at 723 K, 7.57% TiO_2 loading, 20 g of TiO_2/Fe^0 catalyst and reaction period 12 h.

4. Conclusion

TiO_2/Fe^0 photocatalysts with a uniform microporous structure are obtained by a novel preparation approach of CVHD. In contrast to the alkoxide hydrolysis-precipitation or sol–gel methods, the obtained TiO_2/Fe^0 catalysts exhibit higher photocatalytic activity on the denitrification performance, with the nitrate CR and NS up to 87.3 and 60.9%, respectively. The photocatalytic nitrate reduction of the TiO_2/Fe^0catalysts prepared by CVHD is strongly associated with calcination temperature, TiO_2 loading amount, dissolved oxygen, and UV wavelength. In our reactor, the best denitrification performance is achieved with TiO_2/Fe^0 catalysts at calcined temperature of 723 K, TiO_2 loading amount of 7.57%. The important running conditions include bubbling N_2 through the wastewater tank and using 254 nm UV lamp.

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