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Novel low-cost Fenton-like layered Fe-titanate catalyst: Preparation, characterization and application for degradation of organic colorants

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ABSTRACT

Novel low-cost layered Fe-titanate catalyst for photo-Fenton degradation of organic contaminants was successfully developed by ion exchange of Fe^{3+} with Na^{+} layered nano Na-titanates which was prepared by alkali hydrothermal method. The as prepared materials were characterized by powder X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectrometer (EDX). The catalytic activity of the Fe-titanate catalyst was evaluated by the decolorization of three different dyes (rhodamine 6G (R6G), methyl blue (MB), and methyl orange (MO)) under UV irradiation at room temperature. Effect of several important factors such as Fe loading in the catalyst, initial solution pH, catalyst dosage, H_2O_2 amount, and reaction time was systematically studied. It was found that the decolorization was very efficient for all three dyes. The efficiency reached 98% for R6G, 98.5% for MB, and 97% for MO, respectively, under optimal conditions. The oxidation process was quick, and only 15 min is needed for all three dyes. Moreover, the Fe-titanate catalyst could be used in a wider and near neutral pH range compared with classic Fenton systems which need to be operated at around pH 3.0. Kinetic analysis results showed that the oxidation kinetics was accurately represented by pseudo-first-order model. More importantly, the catalyst was very stable and could be reused for at least four cycles when operated under near neutral pH. The Fe leaching from the catalyst measured was almost negligible, which not only demonstrated the stability of the catalyst, but also avoided the formation of secondary Fe pollution. Therefore, the reported Fe-titanates are promising nanomaterials which can be used as Fenton like catalyst for the degradation of organic contaminant in wastewater.

1. Introduction

Organic effluent containing wastewater has becoming an ever-increasing threat to the environment and the health of human beings [1–3]. Dyes released from different industries such as textiles, paper, plastics, leather, food, and cosmetic are major sources of the pollution due to their carcinogenic and mutagenic properties [4–8]. Many methods such as flocculation [9], reverse osmosis [10], precipitation [11], adsorption [4], and chemical oxidation [12], have been used for the removal of dyes released into aquatic environment. The chemical oxidation process aims at the mineralization of the chemical stable and non-biodegradable organic dyes to CO_2, H_2O and inorganics or, at least, at their transformation into harmless products [13]. Therefore, the oxidation method based on the chemical destruction may give the complete solution to the problem of dye pollutants compared with others in which only a phase separation is realized with the subsequent problem of the final disposal.

Especially, the Advanced Oxidation Processes (AOPs) with the generation of highly reactive radicals (e.g. hydroxyl free radicals) have attracted enormous attention in the dye wastewater treatment due to the reason that they can be operated at or near ambient temperature and pressure [14–16]. Homogeneous Fenton (H_2O_2/Fe^{2+}) and Fenton like (H_2O_2/Fe^{3+}) systems are commonly studied and reported AOPs in dye remediation [17–21]. However, such systems have significant disadvantages such as (i) narrow pH range (pH < 3.0) required, (ii) the production of iron-containing waste sludge which is difficult to dispose of, and (iii) high concentration of iron (50–80 mg/l) needed for successful mineralization which introduces secondary pollution in treated water [22,23]. To overcome these disadvantages, researchers have paid much attention to the development of heterogeneous Fenton-like catalysts such as Fe-containing mesoporous materials with similar catalytic activities as homogeneous Fe (II) ions [17,23–26]. In the literature, Fe-ions have been combined with many kinds of substrates such as membrane [27], zeolite [28], C-fabrics [29], and

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clays [30] to form Fe-containing Fenton like catalysts for dye remediation with similar catalytic activities as homogeneous Fenton systems. What is worth to be mentioned is that Fe leakage from the catalysts should be strictly controlled to avoid secondary Fe contaminants in water.

Recently, we have synthesized ion-exchangeable layered sodium titanate nanostructures through a simple alkali hydrothermal treatment of Ti precursor [31,32]. The morphology of the titanates can be easily controlled by the adjustment of synthesis conditions such as temperature, alkali concentration, and reaction time [31]. The titanates have the structures in which TiO_6 octahedra join each other to form layers with negative charges and sodium ions existing within the layers are ion exchangeable. Their ion exchange properties have been demonstrated to be highly efficient, irreversible and selective [32], which may provide the possibility of achieving a high loading of active catalyst with an even distribution and high dispersion. In this paper, layered titanates were synthesized via the alkali hydrothermal method using cheap industrial grade metatitanic acid as Ti precursor. Then Fe^{3+} ions were intercalated into the interlayer through an ion exchange process with Na^+ ions. The objective of this study was to investigate the possible use of Fe-containing titanates and H_2O_2 system as Fenton like catalyst for the remediation of organic dyes from wastewater. The obtained materials were characterized by powder X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectrometer (EDX). To evaluate the catalytic ability of Fe-titanates, decolorization experiments of three different dyes (rhodamine 6G, methyl orange and methyl blue) were conducted under UV irradiation at room temperature. The effect of different factors such as Fe loading in catalyst, initial solution pH, H_2O_2 and catalyst dosage, and reaction time on the decolorization process was investigated and the mechanisms of the dye decolorization were also proposed. Furthermore, the stability and reusability of the Fe-titanate catalyst was also studied.

2. Experimental

2.1. Materials

Metatitanic acid ($TiO(OH)_2$, TiO_2 content 80%) was purchased from Shanghai Mintchem Development Co. Ltd. and used as raw material in the hydrothermal synthesis of titanate nanostructures without any further purification. Methyl orange (MO), methyl blue (MB) and rhodamine 6G (R6G), NaOH, HCl, anhydrous $FeCl_3$ of analytical grade, hydrogen peroxide (H_2O_2, 30 wt%) were purchased from Alfa Aesar. All water used in this study had been treated by the deionized water equipment.

2.2. Catalyst synthesis

Fe-containing titanate catalyst was synthesized by the method combining an alkali hydrothermal treatment and a subsequent ion exchange process. In a typical synthetic procedure, 3 g metatitanic acid and 40 ml 10 M NaOH were mixed and stirred in a magnetic stirrer for 2 h to form a milk-like suspension. Then this mixture was sealed in an autoclave with an internal substrate of polytetrafluoroethylene (50 ml) and heated at 80 °C for 24 h. After the reaction, the precipitate was filtered and washed until pH neutral with deionized water. After drying at 80 °C for 24 h, the as-obtained product was characterized to be Na-titanates.

The Na-titanates were subsequently treated in Fe^{3+} solutions to obtain Fe-titanates through ion exchange. Different amounts of anhydrous $FeCl_3$ powders (0.2 g, 0.6 g and 1 g) were added, respectively, into three flasks containing 3 g Na-titanates and 100 ml deionized water and stirred for 6 h. The precipitates were then filtered, washed with deionized water for several times to remove unreacted Fe^{3+} ions and dried overnight at 80 °C in the air. Finally, three kinds of as-prepared Fe-titanates denoted, respectively, as FT-1, FT-2, and FT-3 were obtained.

2.3. Characterization

X-ray diffraction analysis was performed on a Philips X'Pert Pro MPD diffractometer with Cu Kα source (λ = 1.5406 Å). The morphologies of samples were characterized by field emission scanning electron microscopy (FESEM, FEI Sirion-200). The compositions of samples were analyzed on an energy-dispersive X-ray spectrometer (EDX, Inca Oxford) in conjunction with the FESEM. The optical absorbance of the colorant solutions with different concentrations was measured on a UV–vis spectrophotometer (Shimadzu, UV1750) in the wavelength ranged from 200 to 800 nm. The pH values were measured with Mettler Toledo pH meter (FG2/EL2). The zeta potential of samples was measured using the Zeta Meter (zetasizer 3000HSA, Malvern). Fe^{3+} concentrations in solutions were measured by Inductively Coupled Plasma Spectrometer (Thermo Scientific iCAP 6000).

2.4. Colorant decolorization experiments

The decolorization of three dyes using Fe-titanates/H_2O_2 system as catalyst was conducted in the photochemical reactor under UV irradiation (Hg lamp, 500 W, 305–387 nm) at room temperature (~25 °C). Thirty milliliter solutions with initial concentration of 1.25×10^{-5} M for R6G, 0.03 M for MB, 0.06 M for MO, were prepared to be used in the decolorization experiments. The influence of each important factor (Fe loading in Fe-titanates, initial solution pH, catalyst dosage, H_2O_2 amount, and reaction time) was studied separately while other factors were kept constant.

For the Fe loading effect in catalyst, Na-titanates, FT-1, FT-2, or FT-3 each with a dosage of 10 mg were allowed to react with 30 ml dye solutions for 15 min. H_2O_2 amount used was 15 μL H_2O_2 (1 M) for R6G, 300 μL for MB, 350 μL for MO. Initial solution pH of three dyes was adjusted to 6.5 for R6G, 5.6 for MB, 6.7 for MO, respectively. Only the catalyst with best decolorization efficiency (FT-3) would be used in the subsequent study.

For the initial solution pH effect, 10 mg FT-3 was allowed to react with 30 ml dye solutions for 15 min. H_2O_2 (1 M) amount used was 15 μL for R6G, 300 μL for MB, and 350 μL for MO, respectively. The solution pH ranged from 3 to 13 adjusted by 0.01 M HCl and 0.01 M NaOH was used in the experiments. Only the optimum pH would be used in the further study.

The effect of catalyst dosage, H_2O_2 amount, and contact time was investigated using the same method as mentioned above. All the experiments were duplicated and only mean values were reported. The maximum deviation observed was less than ±5%.

The concentration of dyes in the solution was measured by a UV–vis spectrophotometer. The measurement wavelength ranges from 200 to 800 nm. The residual concentration of the dyes was calculated by Beer–Lambert's law:

$$A = \varepsilon C l \tag{1}$$

where A is the absorbance, ε represents the extinction co-efficient at characteristic wavelength (λ_{max} = 520 nm (R6G), 664 nm (MB), 463 nm (MO)), C is the concentration, and l is the path length. The decolorization efficiency (%), i.e., the removal degree of dyes was calculated using the relation:

$$\%\ \text{Decolorization efficiency} = (1 - A_t/A_i) \times 100 \tag{2}$$

where A_i is the initial absorbance of the dye and A_t is the absorbance at the time t.

2.5. Stability and reusability of catalyst

To test the stability and recyclability of the Fe-titanates, FT-3 was first gathered via filtering method after the dyes were almost completely degraded. Then, the supernatant was centrifuged to collect the residual catalyst in it. The two parts of catalyst were put together, and used in a second cycle of decolorization experiment. This process was repeated for several times. All the experiments were operated under conditions which were best for the decolorization efficiency.

3. Results and discussion

3.1. Characterization of materials

The XRD patterns of as-prepared Na-titanates and Fe-titanates (FT-3) are shown in Fig. 1, respectively. As shown in Fig. 1, the main peaks of both are typical of layered titanates, especially the one at around $2\theta = 10°$, attributed to the interlayer distance in $Na_2Ti_3O_7{\cdot}nH_2O$ (JCPDs no. 72-0148) [32–36]. In the titanates, three edge-shared TiO_6 octahedra join at the corner to form stepped $Ti_3O_7^{2-}$ layers, sodium ions and water molecules located between the layers are exchangeable. The interlayer distance of Na-titanates is about 0.98 nm according to Fig. 1. XRD of FT-3 in Fig. 1 shows the change of (100) peak after the ion exchange treatment, and the interlayer decreases to 0.93 nm which implies that all Na^+ ions are substituted by Fe^{3+} ions. This result is consistent with EDX spectrum of Fe-titanates (FT-3, Fig. 2). From Fig. 2, clearly, in FT-3 only Fe, Ti and O elements exist, no Na element is observed. More details of the ion exchange process can be seen in our previous published paper. After the ion exchange, the decrease in the interlayer makes Fe^{3+} ions entrapped tightly in the interlayer, and no leakage will occur easily. The XRD patterns of FT-1 and FT-2 show no significant difference with FT-3.

Fig. 3 displays the SEM morphology of Na-titanates. Obviously, layered Na-titanate possesses the flower-like morphology, which is consisted of layered nanosheets [32]. This structure has large BET specific surface area, which is measured to be 403 m^2/g. As a result, this kind of titanates has very strong adsorption ability for substances. Moreover, this kind of micro–nano hierarchical structure also makes it easy to recover Fe-titanates from the reaction solutions by filtering method.

3.2. Decolorization experiments

3.2.1. Effect of Fe loading in the catalyst

Fig. 4 shows the decolorization efficiency of three dyes using Na-titanates, FT-1, FT-2, and FT-3 with different amounts of Fe loading as catalyst. The Fe loading of the four samples measured by EDX in atomic percent is 0%, 1.88%, 5.64%, and 9.41% respectively. The decolorization efficiency of all three dyes increases with the increasing Fe loading amount of the catalyst. This implies that Fe^{3+} ions play an important role in the decolorization of the dyes. The largest decolorization efficiency of dyes using FT-3 can reach 98% for R6G, 98.5% for MB, and 97% for MO, which demonstrates that FT-3 possess the potential to be an effective catalyst. In the subsequent experiments, only FT-3 was used.

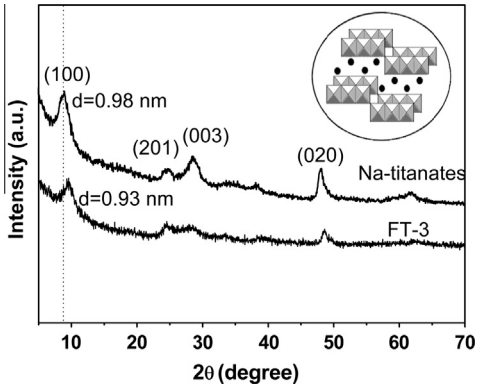

Fig. 1. X-ray diffraction patterns of Na-titanates and FT-3. Insert: schematic diagram of the structures.

3.2.2. Effect of initial solution pH

The Fenton's type reaction always shows a strong dependence of solution pH during oxidation [4,37–40]. Although the classic Fenton system is of high efficiency, it requires a narrow pH range ($pH < 3.0$) to prevent the precipitation of Fe^{2+} and Fe^{3+} [39]. It greatly limits the application of classic Fenton system. Heterogeneous Fenton-like catalysts have been extensively studied to overcome this disadvantage [39,41]. The effect of initial solution pH on decolorization efficiency of Fe-titanates is shown in Fig. 5. As can be seen, Fe-titanates can be used in a wide range of pH and the optimum pH is about 6.5 for R6G, 5.6 for MB, and 6.7 for MO. Compared with classic Fenton systems, the Fe-titanates will obviously possess a much wider application prospect due to the wide pH range and near neutral optimal pH required.

In Fig. 5, for each dye, the decolorization efficiency increases gradually with increasing pH values under acidic condition until the optimum pH arrives. This is caused by the change in surface charge of the catalyst. The zeta potential values of FT-3 suspended in aqueous solutions with pH ranged from 2 to 11 are presented in Table 1. With the pH increases, the surface charge of FT-3 becomes more and more negative. Dye molecules can be more easily adsorbed on the catalyst surface, which is beneficial to the subsequent oxidation process. While the pH values continue to increase, the decolorization efficiency decreases gradually. This can be ascribed to the lower oxidation potential of hydroxyl radicals, and decomposition of H_2O_2 [42]. As a result, there is an optimal pH for each dye under which the decolorization efficiency is largest.

In the meantime, the initial solution pH also plays an important role in the Fe leakage from the catalyst. As we discovered before, Fe^{3+} ions located in the interlayer of titanates can be exchanged out by H^+ in the solutions [32]. To measure the Fe leakage from the catalyst, FT-3 (10 mg) was suspended in aqueous solutions (30 ml) with a pH ranged from 2 to 7 for 2 h, respectively. After centrifugation, the supernate was sent to measure the Fe^{3+} concentration by ICP analysis. The results are also presented in Table 1. In lower pH, the Fe leakage is observable due to the ion exchange of Fe^{3+} with H^+. At pH above 5, the Fe leakage is almost negligible which means the secondary Fe pollution can be avoided and the catalyst is stable. Compared with the classic Fenton systems with the formation of large amounts of Fe sludge, this is of great significance. In considering of the decolorization efficiency and Fe leading, Fe-titanates as catalyst should be operated under near neutral pH. The subsequent experiments were conducted under the optimal pH.

3.2.3. Effect of catalyst dosage

The effect of variations in FT-3 dosage on the decolorization efficiency of three dyes in the Fenton like process is presented in Fig. 6, and corresponding conditions are as follows: initial pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; H_2O_2 (1 M) amount: 15 μL for R6G, 300 μL for MB, and 350 μL for MO; time: 15 min. The increase in FT-3 dosage from 0 to 10 mg enhanced the decolorization efficiency of all three dyes, which was mainly attributed to the increase in the number of active sites and improving H_2O_2 decomposition as well as the generation of more hydroxyl free

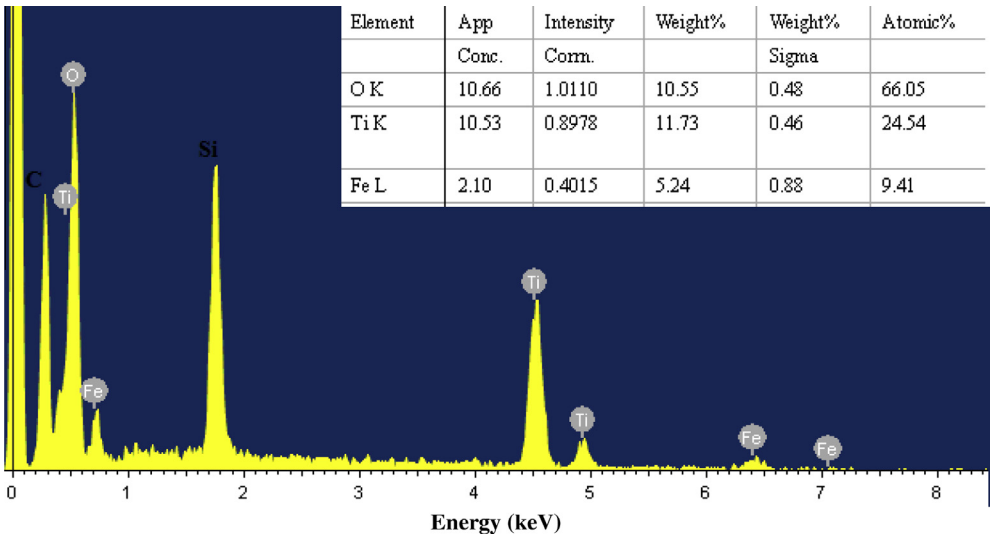

Fig. 2. The EDX spectrum of FT-3. Insert: the data obtained excluding data of C and Si which due to the substrate.

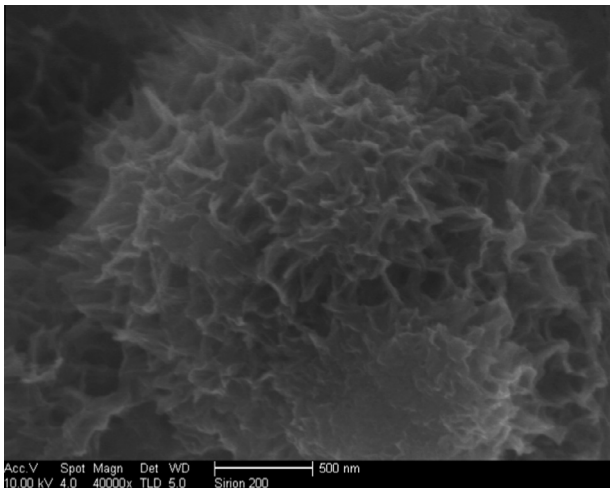

Fig. 3. The SEM morphology of Na-titanates.

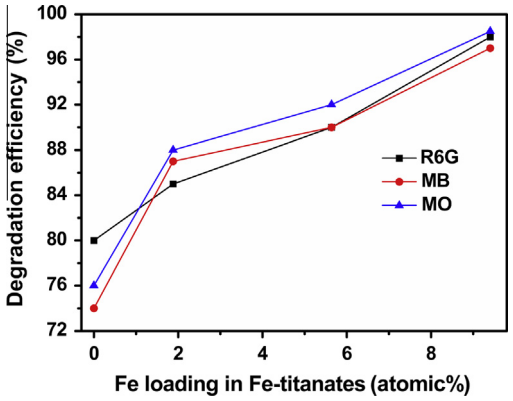

Fig. 4. The curves of DE versus Fe loading in the Fe-titanates for R6G, MB and MO. (Na-titanates, FT-1, FT-2, and FT-3 with different amount of Fe loading as catalyst: 10 mg; initial pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; H_2O_2 (1 M) amount: 15 μL for R6G, 300 μL for MB, and 350 μL for MO; time: 15 min).

radicals. However, when the dosage was more than 10 mg, the decolorization efficiency of all three dyes decreased with the increasing dosage. This may be due to the agglomeration of FT-3 particles and also the scavenging of hydroxyl free radicals because of excess amount of FT-3 [17,43]. Hence, 10 mg is the optimal FT-3 dosage, and will be used in the subsequent experiments.

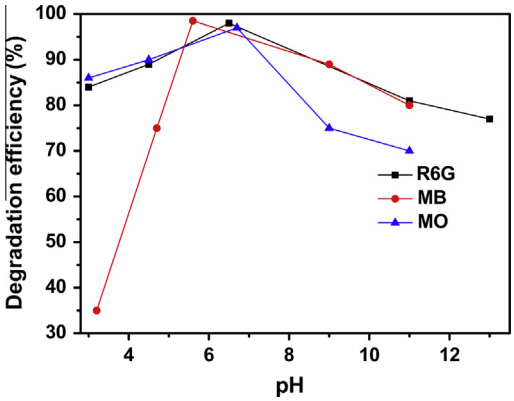

Fig. 5. The plots of DE versus pH for R6G, MB and MO. (FT-3 as catalyst: 10 mg; H_2O_2 (1 M) amount: 15 μL for R6G, 300 μL for MB, and 350 μL for MO; time: 15 min).

Table 1
Effect of pH on Zeta potential and Fe leakage concentration of FT-3.

pH	2	3	4	5	7	9	11
Zeta potential (mV)	19.7	7.3	1.1	−12.2	−19.2	−33.4	−40.3
Fe concentration (mg/l)	15.6	8.3	4.2	1.4	0.6	–	–

3.2.4. Effect of H_2O_2 amount

The amount of H_2O_2 used is another key factor that can significantly influence the decolorization of dyes in the Fenton like process [4,43] since it is directly related to the number of generated hydroxyl free radicals and hence to the decolorization efficiency. The effect of H_2O_2 amount on the decolorization efficiency of three dyes by FT-3 is shown in Fig. 7. Other conditions are set as follows: H_2O_2 concentration (1 M); initial solution pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; FT-3 dosage: 10 mg; time: 15 min. As shown in Fig. 7, for each dye, there is an optimal amount of H_2O_2, before which decolorization efficiency increases and after which decolorization efficiency decreases with the increasing H_2O_2 amount. The

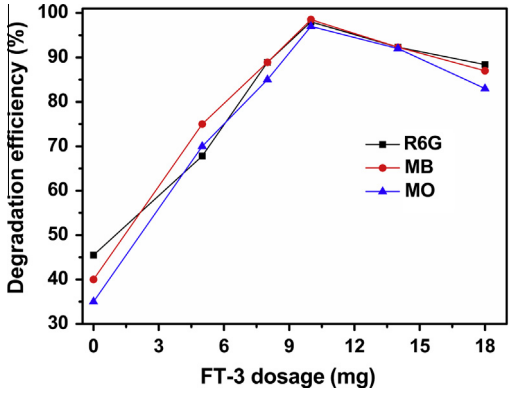

Fig. 6. The DE change with FT-3 dosage for R6G, MB and MO. (initial pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; H_2O_2 (1 M) amount: 15 μL for R6G, 300 μL for MB, and 350 μL for MO; time: 15 min.).

optimal amount of H_2O_2 is 15 μL for R6G, 300 μL for MB, and 350 μL for MO. While the H_2O_2 amount is less than the optimal amount, the decolorization efficiency increases because of insufficient hydroxyl free radicals in the solution. With the increasing of H_2O_2 amount used, more hydroxyl free radicals were generated in the solution, and thus more dyes are oxidized. While the optimal amount of hydroxyl free radicals in solution is reached, too much H_2O_2 is harmful to the oxidation process due to the scavenging effect based on the following equation [17]:

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2\cdot \quad (3)$$

Hence, 15 μL H_2O_2 (1 M) for R6G, 300 μL for MB, and 350 μL for MO is the optimal H_2O_2 amount for the dye decolorization on FT-3, respectively.

3.2.5. Effect of reaction time and kinetic study

The reaction time needed to reach equilibrium is another important parameter for the oxidation process. The effect of reaction time on the decolorization efficiency of three dyes by FT-3 is shown in Fig. 8, and other corresponding conditions are as follows: initial pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; H_2O_2 (1 M) amount: 15 μL for R6G, 300 μL for MB, and 350 μL for MO; FT-3 dosage: 10 mg. As can be seen, all three dyes were degraded quickly. The maximum decolorization efficiency can be reached in just 15 min, which is of great significance in the practical application.

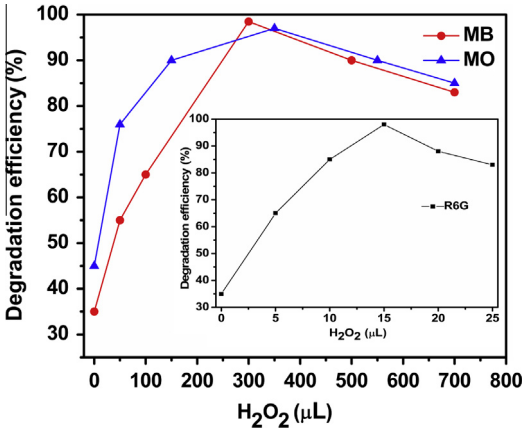

Fig. 7. Effect of initial H_2O_2 additional amount on DE for R6G, MB and MO. (FT-3 as catalyst: 10 mg; initial pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; time: 15 min.).

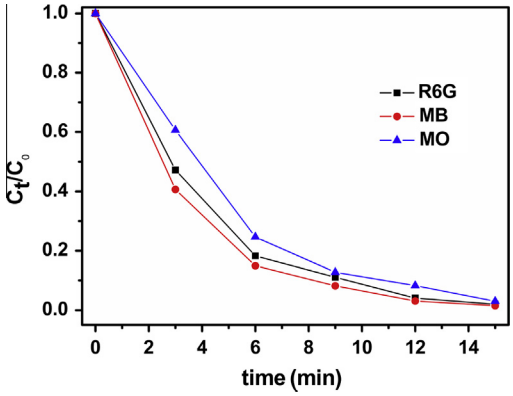

Fig. 8. C_t/C_0 of R6G, MB and MO change with time revolution (initial concentration (30 ml):1.25×10^{-5} M for R6G, 0.03 M for MB, 0.06 M for MO; FT-3 as catalyst: 10 mg; initial pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; H_2O_2 (1 M) amount: 15 μL for R6G, 300 μL for MB, and 350 μL for MO; time: 15 min.).

In general, the Fenton and photo-Fenton reaction rates on the degradation of organic pollution have been described well by the pseudo-first-order equation [44]:

$$\ln(C_0/C_t) = A + K_a t \quad (4)$$

where C_0 is the initial concentration of the dyes (M), C_t the concentration of the dyes at time t (M), t the reaction time (min), K_a the reaction rate constant (min^{-1}), and A an experimental constant. The fitted results using this model based on the data in Fig. 8 are shown in Fig. 9. As can be seen, the pseudo-first-order equation fits the experimental data well with a R^2 value at around 0.99 for all three dyes.

3.2.6. Stability and reusability of the catalyst

The stability and recyclability of FT-3 was evaluated by successive decolorization of three dyes. The amount of catalyst recovered through filtering and centrifugation was more than 95%. The recovered catalyst was subsequently used in another cycle of oxidation process. Table 2 shows the decolorization efficiency of three dyes by FT-3 in four cycles. As can be seen, FT-3 was able to be reutilized for at least four cycles without any significant decline of the catalytic ability under the optimal operation conditions. This obviously benefits from the negligible Fe-leakage under near neutral pH. Therefore, FT-3 is very stable and can be reused without loss of catalytic activity.

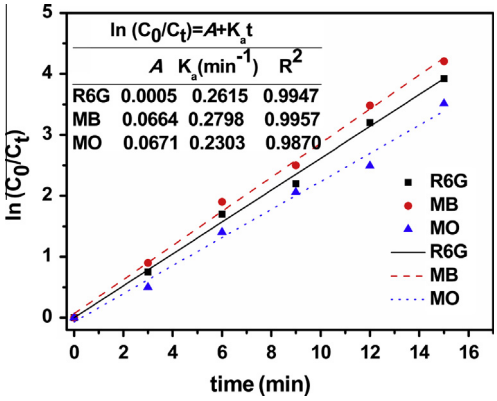

Fig. 9. ln (C_0/C_t) of R6G, MB and MO change with time revolution (initial concentration (30 ml): 1.25×10^{-5} M for R6G, 0.03 M for MB, 0.06 M for MO; FT-3 as catalyst: 10 mg; initial pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; H_2O_2 (1 M) amount: 15 μL for R6G, 300 μL for MB, and 350 μL for MO; time: 15 min.).

Table 2
Decolorization efficiency of three dyes by FT-3 in four cycles (initial H_2O_2 (1 M): 15 μL for R6G, 300 μL for MB, 350 μL for MO; initial solution pH: initial pH: 6.5 for R6G, 5.6 for MB, and 6.7 for MO; FT-3 dosage: 10 mg; time: 15 min).

	Cycle 1	Cycle 2	Cycle 3	Cycle 4
R6G	98.00%	96.80%	95.50%	93.00%
MB	98.50%	97.00%	96.50%	95.00%
MO	97.00%	96.40%	94.80%	94.00%

3.2.7. A possible catalytic mechanism

From the above experimental data, Fe^{3+} content and H_2O_2 content play decisive roles in the decolorization of R6G, MB, and MO under UV irradiation, which indicates that the decolorization is a Fenton like process ($Fe^{3+}/H_2O_2/UV$). In the heterogeneous UV-Fenton system, Fe^{2+} can be formed following Eq. (5), and then the dyes can be oxidized effectively by hydroxyl free radical which is generated from the decomposition of H_2O_2 with Fe^{2+} (Eq. (6)) [45]:

$$\equiv Fe^{3+} + UV \rightarrow \equiv Fe^{2+} + \cdot OH \quad (5)$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + \cdot OH + OH^- \quad (6)$$

$$H_2O_2 + UV \rightarrow \cdot OH + \cdot OH \quad (7)$$

where ≡Fe represents catalytic active sites on Fe-titanates. Under UV irradiation, hydroxyl free radical can also be formed from the directly photolysis of H_2O_2 following Eq. (7) [45]. All the formed hydroxyl free radical is ready to degrade and mineralize dyes. In the meantime, dye molecules in the solution can be excited by UV irradiation (Eq. (8)) [45,46]. Then, the excited dye molecules can be oxidized by $\equiv Fe^{3+}$ (Eq. (9)) and H_2O_2 (Eq. (10)).

$$Dye + UV \rightarrow Dye^* \quad (8)$$

$$\equiv Fe^{3+} + Dye^* \rightarrow \equiv Fe^{2+} + \text{organic intermediates} \quad (9)$$

$$H_2O_2 + Dye^* \rightarrow \text{organic intermediates} \quad (10)$$

As a result, with the combined action of UV light and H_2O_2, the decolorization efficiency of dyes on Fe-titanates can reach a high value of more than 97% at 15 min.

Finally, one should bear in mind that mechanisms associated with the photo-Fenton like ($UV/Fe^{3+}/H_2O_2$) process are not simple due to the amount of intermediates that can be formed in the progress of reaction. Researchers have proposed many possible routes, and many possible routes have not been yet elucidated [38]. Meanwhile, in this study and also in other reports of Fe/layered material hybrid Fenton like catalysts [21,30,38,46,47] whether the catalytic active sites (≡Fe) locate on the surface or in the interlayer of the layered materials is not very sure. This needs to be further investigated.

4. Conclusion

In summary, novel low cost Fenton like catalyst of Fe-titanates are prepared by a simple alkali hydrothermal treatment and a subsequent ion exchange of Fe^{3+} with Na^+. The Fe-titanates possess layered structures, and Fe^{3+} ions are located in the interlayer. The decolorization of three different dyes (R6G, MB, and MO) by the catalyst shows great efficiency. It is shown that the oxidation process strongly depends on the operation conditions, such as Fe loading in the catalyst, initial solution pH, catalyst dosage, H_2O_2 amount, and reaction time. Under optimal conditions, the decolorization efficiency can reach 98% for R6G, 98.5% for MB, and 97% for MO, respectively. The oxidation process is quick, and only 15 min is needed for all the three dyes. Unlike classic Fenton systems which need to be operated at pH around 3.0, Fe-titanates can be used at a wider and near neutral pH range. Thus, the costly initial acidification can be omitted. Moreover, the leakage of Fe is almost negligible when operated under optimal pH. As a result, Fe-titanates are very stable and can be reused for at least four cycles without significant decline of catalytic ability. These facts suggest that Fe-titanates possess the potential to be an ideal Fenton like catalyst.

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