Fabrication of Fe$_2$O$_3$-MnO$_2$ nanocomposite heterogeneous catalyst and advanced catalytic oxidation tannery wastewater

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ABSTRACT

Nanocomposite catalysts of Fe$_2$O$_3$-MnO$_2$ were prepared of by chemical coprecipitation method, and advanced treatment was performed on tannery wastewater with H$_2$O$_2$ as oxidant. The microstructure of the catalyst was tested by X-ray diffraction, field-emission scanning electron microscopy and high-resolution transmission electron microscope. The effect of molar ratio of MnO$_2$/Fe$_2$O$_3$, additive amount H$_2$O$_2$ oxidizer as well as pH value of the wastewater on the chemical oxygen demand (COD) removal rate of tannery wastewater was also investigated. The results showed that the catalyst mainly consisted of α-Fe$_2$O$_3$, β-MnO$_2$ and FeMn$_2$O$_4$. The catalysts were porous characteristic with size of about 60~100 nm. The nanocomposite catalyst of Fe$_2$O$_3$-0.4MnO$_2$ had good catalytic oxidation effect at pH of 3~5 and H$_2$O$_2$ of 0.6 mL/L wastewater, in which the COD removal rate of tannery wastewater reached 73.5%. In addition, the catalyst has good recycling performance in use.

Keywords: Nanocomposite heterogeneous catalyst; Catalytic oxidation; Chemical oxygen demand; Fe$_2$O$_3$-MnO$_2$

1. Introduction

With the development of pharmacy, leather, petrochemical and papermaking industries, the number and types of refractory organic compounds in wastewater are increasing gradually [1–4]. The high concentration organic wastewater has a great pollution to the environmental water, which has become a problem in wastewater control. In the process of leather-making, most of the protein and oil of raw leather were discarded and formed wastewater with high chemical oxygen demand (COD) and biochemical oxygen demand, which becomes the main organic pollution source of tannery wastewater. Meanwhile, the addition of dyes and tanning agents in the process of tanning increased the chroma of wastewater. As a result, tannery wastewater contains a large number of toxic substances, suspended pollutants and various organic substances [5–7]. Generally, the treatment of tannery wastewater was carried out in stages by combining physical, chemical and biochemical treatment. However, the effluent from the secondary sedimentation tank after

treatment still had high COD and chroma. In order to further reduce the COD and chroma in tannery wastewater, it was necessary to conduct advanced oxidation treatment. In the traditional advanced treatment of wastewater, two methods were often used. One is photocatalytic degradation technology; the other is Fenton reaction to catalyze the oxidation of pollutants in water (mainly organic matter). Fenton reaction is to use Fe^{2+} ions of FeSO$_4$ solution to catalyze H$_2$O$_2$ and form hydroxyl radical ($^{\bullet}$OH), which reacts with organic matter to destroy the structure of organic molecule and degrade it, so as to reduce COD and chroma of wastewater. Fenton process has great advantages for wastewater treatment because of its high efficiency and simplification. However, there also existed some problems for the Fenton reaction. On one hand, it is difficult to recover iron source, resulting in influence the quality of the effluent water, such as conductivity and chroma. On the other hand, the iron sludge formed by flocculation–sedimentation is easy to cause secondary pollution. Moreover, FeSO$_4$ could not be reused in the process of Fenton reaction, which also increased the cost of wastewater treatment.

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In recent years, the preparation of oxide catalysts, such as TiO_2 [8], Fe_3O_4 [9], MnO_2 [10], ZnO [11] and so on, to replace $FeSO_4$ solution has been attracted more and more attention to solve the problems in Fenton reaction. That is so called heterogeneous Fenton-like processes. Dutta et al. [12] prepared the nano-γ-Fe_2O_3 catalyst for the treatment of methylene blue wastewater from printing and dyeing enterprises under the photocatalytic effect. The results showed that nano-γ-Fe_2O_3 had good catalytic effect and significantly reduced the COD of wastewater. Yuan et al. [13] synthesized high catalytic activity of iron nanoparticles using $FeCl_3$ and aqueous plant extract to degrade methyl orange in a wide pH range. The results exhibited that iron nanoparticles could effectively degrade methyl orange dye molecule with a pronounced removal rate of 98.1%. The research of Chowdhury et al. [14] revealed that both combined physical (filtration) and chemical (Fe_2O_3, coagulants) treatment processes could be fruitful to reduce the toxicants load from tannery wastewater. Our previous research [15,16] showed that Fe_2O_3 could not only remove COD of pulping wastewater by heterogeneous Fenton-like reaction, but also remove COD and chroma of tannery wastewater. In addition to iron oxide, manganese oxide is also a very effective catalyst in advanced oxidation technology [17–19]. Niu et al. [17] designed a graphene/α-MnO_2 nanocrystals hybrid aerogel for catalytic ozonation of rhodamine B solution. The results revealed that the degradation rate constant of rhodamine B ozonation catalyzed by graphene/α-MnO_2 was about 1.2–2.3 times of that of UV/ozone. Valeika et al. [19] studied the oxidation of sulphides in tannery wastewater by MnO_2, showing that sulphides could be oxidized effectively when the size of MnO_2 particles was not exceed 0.1 mm. Literature indicated that many researchers have conducted research on heterogeneous deep catalytic oxidation of tannery wastewater, most of them were focusing on single oxide catalyst of Fe_2O_3 and MnO_2, however, there is limited research on the mixed phase of Fe_2O_3-MnO_2 nano-composite catalyst for advanced treatment.

The aim of this work is to prepare Fe_2O_3-$xMnO_2$ nano-composite by chemical coprecipitation method, advanced treatment was performed on tannery wastewater with H_2O_2 as oxidant. The influence of the molar ratio of MnO_2 to Fe_2O_3 on the catalytic performance of composite catalyst was also studied.

2. Materials and experiment process

2.1. Materials

All employed chemicals in the studies were analytical reagent grade, and they were used as received. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sodium carbonate ($NaCO_3$), polyvinyl alcohol, sodium dodecylbenzene sulfonate, manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) and polyacrylamide (PAM) were purchased from China National Pharmaceutical Group Chemical Reagent Co. Ltd., China.

2.2. Preparation of catalysts

To compare the performance of composite catalyst and single Fe_2O_3 catalyst, pure nano-Fe_2O_3 powders were synthesized. Firstly, $FeSO_4 \cdot 7H_2O$ and $NaCO_3$ were prepared to concentration of 0.7 and 0.4 mol/L solution, respectively. Then, 500 mL $NaCO_3$ solution, 12 g sodium dodecylbenzene sulfonate and 5 g polyvinyl alcohol were slowly poured into 500 mL $FeSO_4$ solution. Meanwhile, the magnetic stirrer was used to fully stir until the solid was completely dissolved. Subsequently, the blended solution was heated to 200°C and refluxed for stirring, and greyish green sediments were gradually precipitated in the blended solution. Thereafter, mixture solution with sediments was treated by filtration and centrifugal treatment to obtain solid powders. solid of sediments were then dried at 100°C for 12 h forming light brown powders. At last, the light brown powders were calcined at 500°C–600°C for 5 h and grinded to form F_2O_3 powders.

Fe_2O_3-$xMnO_2$ nano-composite powder were also synthesized by coprecipitation precipitation method. Based on different proportion of Fe_2O_3 and MnO_2 in composite catalyst of Fe_2O_3-$xMnO_2$ ($x = 0.2, 0.4, 0.6$ and 0.8, in which x is molar ratio of MnO_2/Fe_2O_3), the corresponding mass ratios of $FeSO_4 \cdot 7H_2O$ and $MnCl_2 \cdot 4H_2O$ were weighed. To prevent the aggregation of reaction products, 5 g of polyethylene glycol was added to a mixture of $MnCl_2$ and $FeSO_4$, and then they were poured into a beaker together. After that, a certain amount of deionized water and anhydrous alcohol were poured into the beaker and stirred by a magnetic stirrer at 50°C to form a solution. Subsequently, aqueous ammonia was gradually put into the mixed solution adjusting pH value to 9~10 and aging for 1 h. Thereafter, coprecipitation precipitates were filtrated, and they were washed by deionized water and anhydrous alcohol. At last, the solid precipitates were calcinated at about 550°C for 5 h and grinded to form different mass ratio of Fe_2O_3-$xMnO_2$ composite particles grinding.

2.3. Characterization of powders

Phase structures of powders were identified by D/max-2500 PC type X-ray diffractometers (XRD) with target of pure Cu-Ka operated at 50 kV and 100 mA. Microstructure was observed by a JEOL 7800F type field-emission scanning electron microscopy (FE-SEM) with energy-dispersive X-ray spectrometer (1-2 Musashino 3-chome, Showashima City, Tokyo, Japan). The morphology of the powders was further characterized by JEM-2100 type high-resolution transmission electron microscope (HR-TEM) with selected area electron diffraction.

2.4. Catalyst performance test

The raw wastewater with COD of 120 mg/L was the effluent from the secondary sedimentation tank after biochemical treatment of a tannery industry. The advanced oxidation of catalyst testing process is as follows: firstly, H_2SO_4 with concentration 1 g/L was added to 500 mL tannery wastewater sample and stirred with a magnetic stirrer for 1 min to completely dissolve the H_2SO_4. Then, a certain amount of H_2O_2 solution and Fe_2O_3 or Fe_2O_3-$xMnO_2$ powders were poured to the wastewater sample and stirred to be fully mixed for reaction at room temperature. After the reaction, poured out the liquid into another beaker and adjusted the alkali to neutral, and added PAM for flocculation and precipitation. Subsequently, 2.5 mL of the liquid supernatant was

transferred into a comparison tube to further test and then 0.7 mL CI and 4.8 mL CII reagents were poured into the test tube and blended them uniformly, in which CI and CII (provided by LianHua Environmental Science and Technology Company, China) are COD measurement reagents. After that, the test tube was put into a COD eliminator and digested. After the digestion, the test tube was cooled to room temperature and added with 2.5 mL deionized water. The solution was mixed and cooled in a water bath. Finally, the solution was poured to the comparison tube and COD was tested with LianHua Technology's COD analyzer.

3. Results and discussion

3.1. XRD characterization of catalyst

Fig. 1 shows the comparison of the XRD spectra of pure Fe_2O_3 and Fe_2O_3 + $0.4MnO_2$ powders. It can be seen from Fig. 1 that the α-Fe_2O_3 (PDF card No. 33-0664) with high purity is prepared by reacting of $FeSO_4 \cdot 7H_2O$ and $NaCO_3$. However, the powder prepared by $FeSO_4$ and $MnCl_2$ not only contains α-Fe_2O_3 and β-MnO_2 (PDF card No. 24-0735), but also a small amount of $FeMn_2O_4$ compounds (PDF card No. 750035).

3.2. Microstructure of the catalyst

Fig. 2a–f shows the HR-TEM image of Fe_2O_3-$0.4MnO_2$. Fig. 2c and e are a local enlargement of area A and B in Fig. 2a, respectively. Diffraction pattern of particles are shown in Fig. 2b, d and f. It can be found from Fig. 2 that not only nano-Fe_2O_3 and MnO_2 but also nano $FeMn_2O_4$ compound are produced during the powder preparation. In additionally, it is worth note that $FeMn_2O_4$ compound mainly presents strip or short rod shape. The scale of the nano-Fe_2O_3, MnO_2 and $FeMn_2O_4$ particles are about 60~100 nm.

Fig. 3a and b show the FE-SEM morphology of Fe_2O_3-$0.4MnO_2$ powder. It can be seen from Fig. 3 that Fe_2O_3 and MnO_2 powders do not show dispersed particles, and there is certain adhesion between them, forming porous honeycomb particles. Some particles also appear as hollow
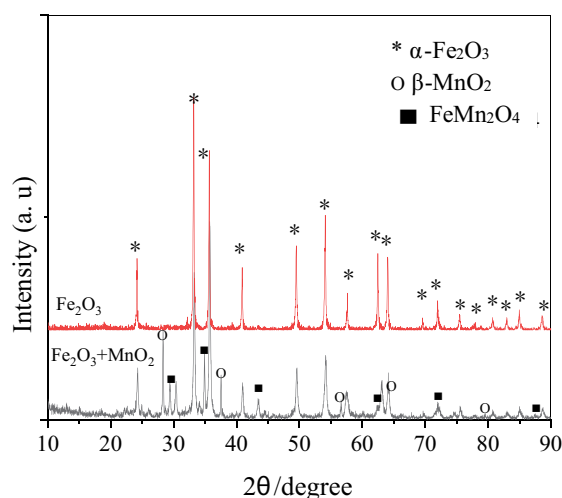
spheres, which is conducive to increasing the specific area of particles.

3.3. Effect of molar ratio of MnO_2/Fe_2O_3 and dosage of H_2O_2 on the COD removal rate

Fig. 4 shows the COD removal rate of wastewater at different molar rate of MnO_2/Fe_2O_3 in the composite catalyst and dosage of H_2O_2 under the pH value is about 5. It can be seen that the removal of COD from tannery wastewater first increases and then slowly decreases as the MnO_2 content in the composite catalyst increases. It can also be found that the composite catalyst of Fe_2O_3-$0.4MnO_2$ has the highest COD removal rate of wastewater at different dosage of H_2O_2, indicating that adding that content of MnO_2 has a good catalytic oxidation effect. Meanwhile, it can also be found form Fig. 4 that the amount of H_2O_2 addition has a significant impact on the COD removal effect. With the increasing of content of H_2O_2, the COD removal rate increases at certain amount co-catalyst. For the Fe_2O_3-$0.4MnO_2$ composite catalyst, when the amount of H_2O_2 addition exceeds 0.6 mL/L wastewater, the effect of H_2O_2 catalyst on COD removal rate is very small, meaning that the 0.6 mL of H_2O_2 for 1 L of wastewater is a good dosage.

3.4. Effect of the pH value

Fig. 5 shows the effect of pH value of water on the COD removal rate for the different molar ratio of MnO_2/Fe_2O_3 at H_2O_2 of 0.6 mL/L wastewater. It is indicated that with the increasing of pH value, the COD removal rate decreases at certain mass of composite catalyst. It can also be observed that pH value of 3–5 is the most effective pH value for treatment wastewater at a certain mass of catalysts and volume of H_2O_2. The main reason is that hydrogen peroxide can produce highly oxidizing free radicals such as $\cdot O$, $\cdot OH$, etc. at action of catalyst under pH of 3–5, which can rapidly oxidize pollutants in wastewater. In addition, it can also be found that when pH varieties from 3 to 5, COD removal rate of wastewater slightly decreased for Fe_2O_3-$xMnO_2$ ($x = 0.4~0.8$), but the decrease is not significant, meaning that when using a pH value of 5 for catalytic oxidation, not only does it not affect the COD removal rate obviously, but it can also reduce the use of concentrated sulfuric acid. Namely, the effluent salinity is relatively low and the introduction of SO_4^{2-} is less, which will beneficial to the combination with reclaimed water reuse process and zero discharge process.

3.5. Effect of reaction time

Fig. 6 shows the effect of reaction time on the COD removal rate at H_2O_2 of 0.6 mL, Fe_2O_3-$0.4MnO_2$ of 20 g for 1 L of wastewater and pH of 5. It can be found from Fig. 6 that the removal rate is relatively low when reaction time is less 30 min for Fe_2O_3-$0.4MnO_2$ catalyst. The low removal rate with a reaction time of less than 30 min may be due to the lack of reaction time and there is possible to exist a side reaction between the remaining H_2O_2 and potassium dichromate in the COD test solution. The COD removal rate reaches its peak at a reaction time of 30 min. However, the reaction time exceeds 30 min, further prolonging the reaction time
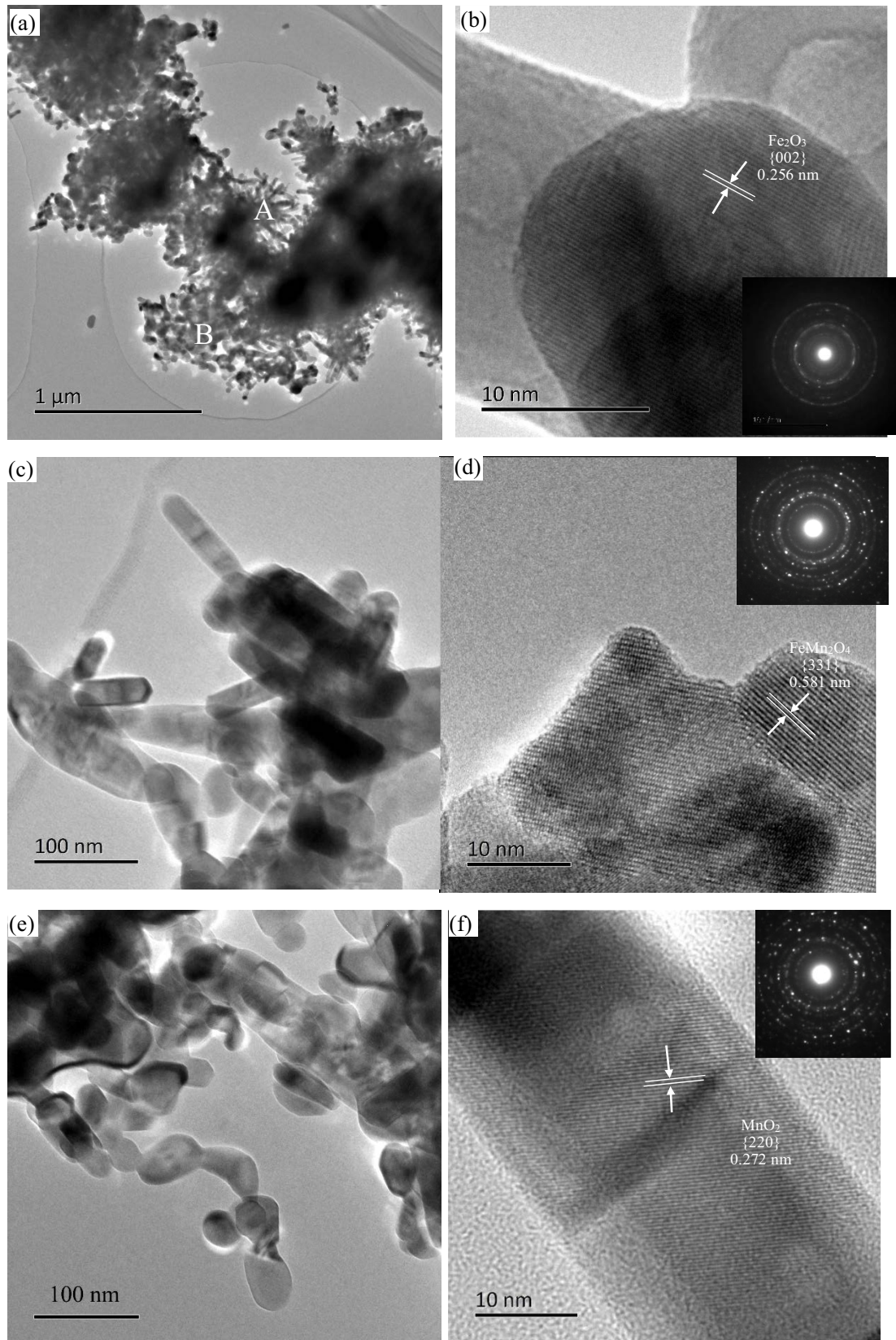

Fig. 1. X-ray diffraction spectra of the powders.

Fig. 2. High-resolution transmission electron microscope image of Fe_2O_3-0.4MnO_2 powder: (a) morphology of powder, (b) diffraction pattern of Fe_2O_3, (c) local enlargement of zone A in (a), (d) diffraction pattern of $FeMn_2O_4$, (e) local enlargement of zone B in (a), and (d) diffraction pattern of MnO_2.
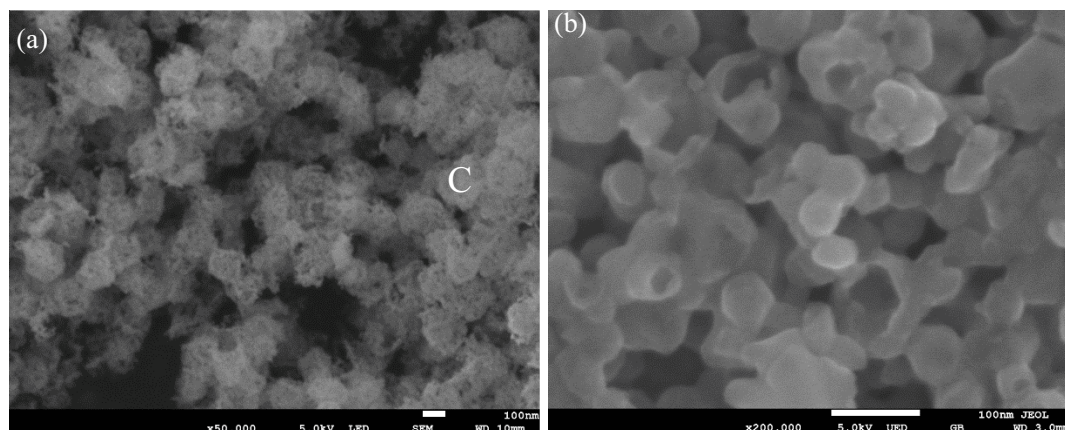
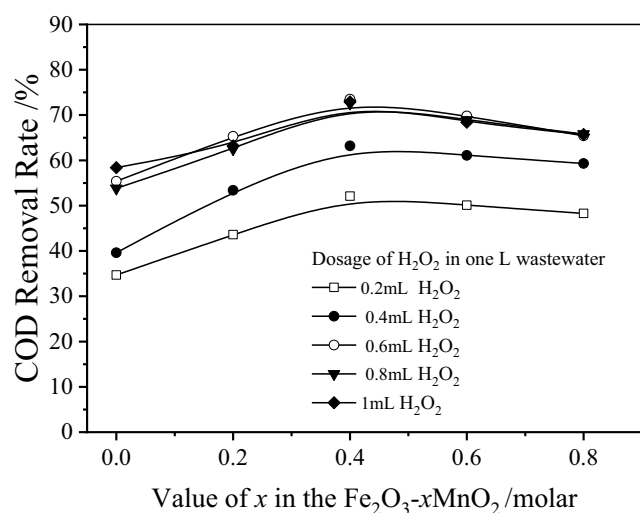Fig. 3. Morphology of Fe$_2$O$_3$-0.4MnO$_2$ powder: (a) morphology of powders and (b) local amplification of zone C.

Fig. 4. Chemical oxygen demand removal rate of catalysts with different molar ratio of MnO$_2$/Fe$_2$O$_3$ at different dosage of H$_2$O$_2$ (mass of Fe$_2$O$_3$-xMnO$_2$ was 20 g/L wastewater, pH value was 5 and the reaction time was 30 min).
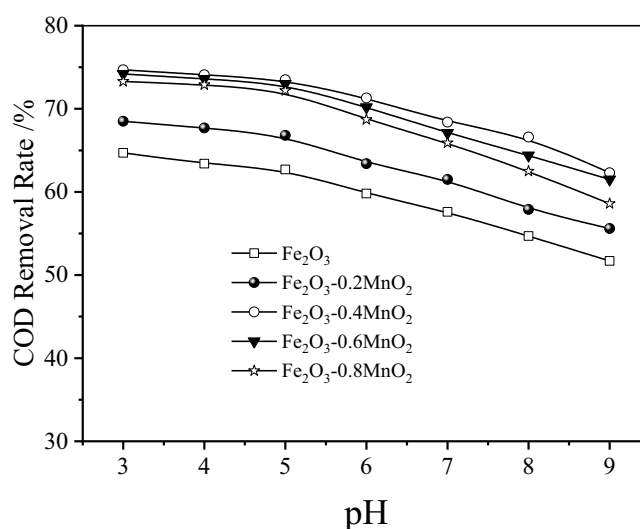

Fig. 5. Effect of pH value on the chemical oxygen demand removal rate of wastewater under the condition of 20 g catalyst for per liter wastewater, H$_2$O$_2$ of 0.6 mL for per liter wastewater and reaction time of 30 min.

does not significantly increase the COD removal rate. On the other hand, one can see that COD removal rate of wastewater has hardly changed for the comparison sample without adding catalyst. In a word, considering the COD removal rate and cost, reaction time of 30 min has good economic benefits.

3.6. Effect of adsorption

To analyze the effect of catalyst adsorption, different content catalysts without employing H$_2$O$_2$ are directly added into wastewater to test the COD removal rate, in which the reaction condition is reaction time of 30 min and pH value of 5 (as shown in Fig. 7). The result indicates that the COD of the wastewater slightly decreases, indicating that the catalyst has a certain adsorption effect. Because the catalyst cannot produce strong oxidizing hydroxyl radical without adding H$_2$O$_2$, the decrease in COD mainly depends on the

adsorption effect of the catalyst. The main reason for this adsorption effect is that the prepared catalyst is a porous nanocatalyst with a large specific surface area, and the pores also have adsorption. In addition, one can also see from Fig. 7 that effect of absorption on the COD is less that 10%, meaning that absorption effect is not the main contributor to the total tannery wastewater COD removal rate. Namely, oxidation of heterogeneous Fenton-like processes remains the dominant contribution to the COD removal effect.

3.7. Reuse test of the catalyst

To investigate of recycling and reuse for the composite catalyst, the used catalysts was poured out the liquid and rinsed the catalyst repeatedly and let it dry before repeated the next experiment after each experiment. Fig. 8 shows the effect of recycling and reuse catalyst to COD removal rate after certain reused number at 0.6 mL H$_2$O$_2$ per 1 L of

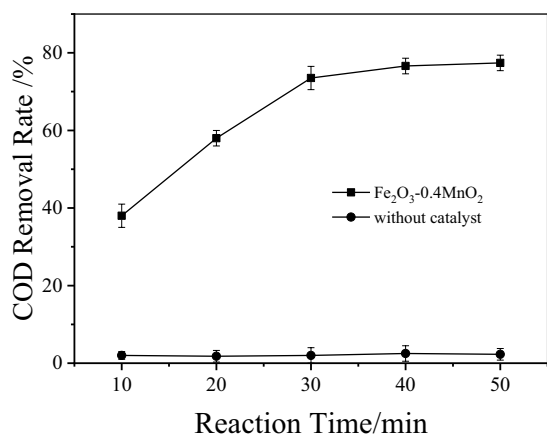Fig. 6. Effect of reaction time on the chemical oxygen demand removal rate under the condition of H_2O_2 of 0.6 mL and Fe_2O_3-$0.4MnO_2$ of 20g for 1 L of wastewater as well as pH of 5.
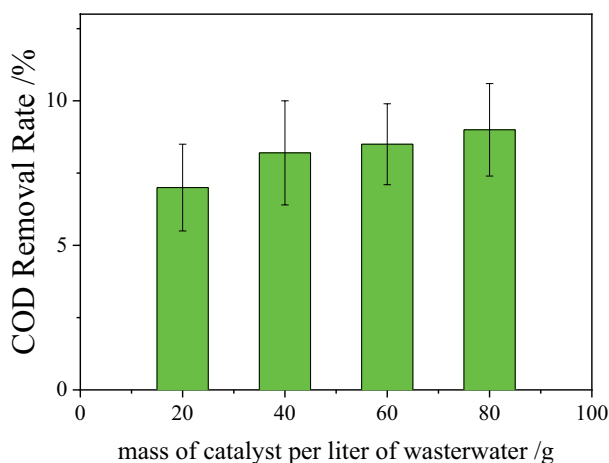

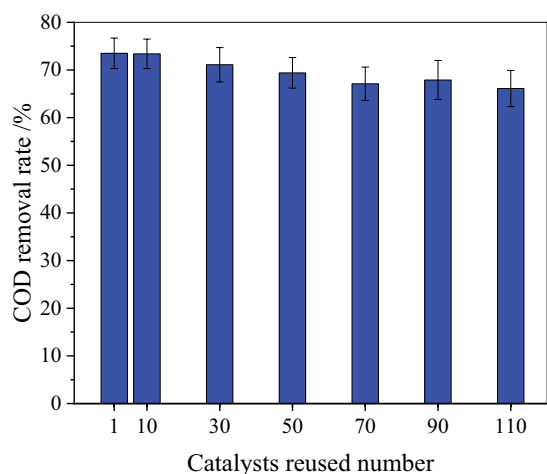Fig. 7. Adsorption test experiment of catalysts at reaction time of 30 min and pH of 5.

Fig. 8. The number of the reaction cycles to chemical oxygen demand removal rate under the condition of H_2O_2 and Fe_2O_3-$0.4MnO_2$ of 20 g for per liter wastewater, pH value of 5 and reaction time of 30 min.

wastewater, 20 g Fe_2O_3-$0.4MnO_2$, pH value of 5 and 30 min reaction time. It is seen from Fig. 8 that the COD removal rate is little changed after 110 times reused. The decrease rate to COD removal rate is approximately 8%, meaning that the composite catalyst still has a high COD removal rate. In other word, the catalyst has recyclable and reuse.

4. Conclusion

- Fe_2O_3-MnO_2 nanocomposite heterogeneous catalyst was prepared using chemical coprecipitation method. The composite catalyst was mainly composed of α-Fe_2O_3, β-MnO_2 and $FeMn_2O_4$. The composite catalysts had porous characteristic with size about 60~100 nm.
- Advanced treatment was performed on tannery wastewater, the molar rate of MnO_2 to Fe_2O_3 in the composite catalyst 0.4:1, catalyst had the best catalytic effect under the condition of mass of catalyst of 20 g per 1 L of wastewater, H_2O_2 of 0.6 mL for per 1 L of wastewater, pH of 5 and reaction time of 30min. The COD removal rate reached 73.5%.
- The catalyst had recyclable and reuse characteristic. It still had highly COD removal rate after 110 times reused.

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