Effective degradation of tetracycline by magnetic palygorskite synthesized with different dosages of NaOH

Jintao Lian, Yunqiang Yi, Nuanqin Zhang and Zhanqiang Fang

ABSTRACT

In the process of preparing magnetic palygorskite from waste pickling liquor of the steel industry, the dosage of NaOH will affect the properties of the magnetic palygorskite. The experimental results showed that magnetic palygorskite can be effectively prepared when NaOH dosage is between 255 and 330 g/L. Vibration sample magnetometry proved that different NaOH dosages can affect the saturation magnetization of magnetic palygorskite. The catalytic performance of five catalysts synthesized with different NaOH dosages hardly changed after five cycles of Fenton-like catalytic degradation of tetracycline (TC). The magnetic palygorskite prepared by this method had good catalytic performance even when the catalyst preparation conditions were magnified ten times, which can provide a reference for large-scale preparation of magnetic palygorskite.

Key words | iron-based material, magnetic palygorskite nanocomposite, NaOH, steel pickling waste liquor, tetracycline

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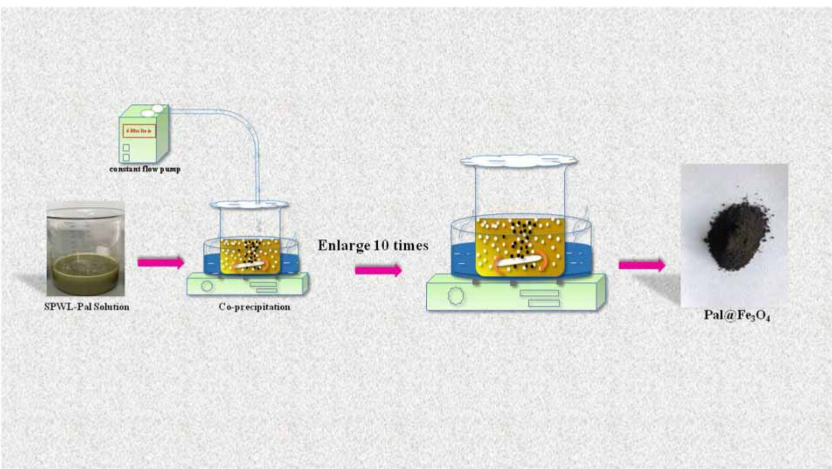
HIGHLIGHTS

- Catalytic degradation of 90% tetracycline by synthesis of magnetic palygorskite using different NaOH dosages.
- The saturation magnetization of magnetic palygorskite was affected by NaOH dosage.
- Catalysts were synthesized by enlarging the preparation conditions by ten times.

GRAPHICAL ABSTRACT



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INTRODUCTION

Pal@Fe_3O_4 has abundant hydroxyl groups (Si-OH) on the surface and is endowed with good hydrophilicity, which can be extraordinarily dispersed in aqueous solution (Wang *et al.* 2019). Moreover, Pal@Fe_3O_4 has excellent magnetic properties and has been widely used in the adsorption and catalytic degradation of pollutants. For example, Xie *et al.* (2018) used magnetic palygorskite to absorb U(VI), with a maximum adsorption capacity of 63.03 mg/g at pH = 6.0. Han *et al.* (2017) used magnetic palygorskite to degrade ethidium bromide and it maintained good catalytic activity after five cycles at pH = 2.0. But the application of magnetic palygorskite has been limited by complex preparation conditions and expensive raw materials. At present, many studies on the preparation of magnetic palygorskite need to use alkaline precipitant, but they do not consider the appropriate amount of precipitant, especially the influence of NaOH precipitant on the structure and properties of magnetic palygorskite (Han *et al.* 2017; Middea *et al.* 2018).

Chemical coprecipitation is the main method to synthesize Pal@Fe_3O_4 due to its simple process and short preparation time (Middea *et al.* 2017; Chi *et al.* 2018; Fu & Zhang 2018). The preparation process of Pal@Fe_3O_4 is as follows (Equation (1)):

$$Fe^{2+} + 2Fe^{3+} + 8OH^- + Pal \rightarrow Fe_3O_4 - Pal + 4H_2O \quad (1)$$

The addition of an alkaline precipitator was the key to the nucleation and growth of iron oxides on the Pal surface. Some of the Fe_3O_4 nanoparticles will agglomerate on the surface of Pal. On the one hand, the addition of an alkaline precipitator will make the local concentration of reaction solution too high; on the other hand, palygorskite is difficult to disperse uniformly in solvents (Rusmin *et al.* 2017; Fu *et al.* 2018). However, a series of studies only mentioned that when the precipitator was used to adjust the pH of the reaction solution to alkaline or when a black precipitate appeared in the reaction solution, the precipitator should be stopped during the synthesis of magnetic palygorskite (Saleh *et al.* 2018). Therefore, in order to understand the potential effect of alkaline precipitators on the properties of magnetic palygorskite, it is necessary to study how different NaOH dosages affect the structure and catalytic activity of magnetic palygorskite. Moreover, obtaining the most appropriate NaOH consumption will effectively reduce the industrial production cost. The utilization of hazardous waste resources made iron-rich steel pickling waste liquor the focus of current research. In previous research, the research group had successfully used iron pickling waste liquor as raw material to synthesize a variety of iron-based materials (Huang *et al.* 2014; Yi *et al.* 2019). However, the effect of NaOH dosage on the structure and catalytic performance of Pal@Fe_3O_4 using steel pickling waste liquor as raw material had not been reported.

In this paper, Pal@Fe_3O_4 was synthesized by coprecipitation of steel pickling waste liquor as raw material. After the preliminary experimental study, only when NaOH dosage was 255–330 g/L could magnetic palygorskite be prepared. Therefore, this paper sets NaOH dosage in the range of preparation of magnetic palygorskite. Because the steel pickling waste liquor contains a part of free acid, the basic precipitator should neutralize this part of free acid in the process of preparing magnetic palygorskite by coprecipitation, and then form Fe_3O_4 nanoparticles on the palygorskite surface by the following reaction (Equations (2) and (3)):

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe(OH)_2 + 2Fe(OH)_3 \quad (2)$$

$$nFe(OH)_2 + 2nFe(OH)_3 \rightarrow nFe_3O_4 + nH_2O \quad (3)$$

However, when the dosage of NaOH is less than 255 g/L, this means that the pH of the reaction system is too low, and the following side-reaction occurs (Equation (4)):

$$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4H_2 + 4FeOOH \quad (4)$$

Therefore, too-low NaOH content will lead to a failure to prepare magnetic palygorskite (Tang *et al.* 2009). When the dosage of NaOH is higher than 330 g/L, this means that the pH of the reaction system is too high, and the dosage of NaOH is much higher than the amount required for preparing magnetic palygorskite, which will eventually lead to the waste of precipitant (Zhang *et al.* 2015). The purpose of this study is: (1) to study the effect of NaOH dosage on the microstructures and magnetic properties of Pal@Fe_3O_4; (2) to study the effect of NaOH dosage on the catalytic performance of Pal@Fe_3O_4 for tetracycline; and (3) to study the amplification of preparation conditions of Pal@Fe_3O_4.

EXPERIMENT

Chemicals

Palygorskite with an average particle size of 325 mesh was provided by Jiangsu Xuyi Botu Aotu Co., Ltd. Steel pickling waste liquor was obtained from Foshan Kelang Environmental Protection Technology Co., Ltd (Foshan, China). H_2O_2 (30%, v/v), NaOH and potassium phosphate monobasic (KH_2PO_4) were provided by Tianjin Damao Company. Acetonitrile and methanol (HPLC) were provided by Tianjin Kermel Chemical Reagents Company. Tetracycline (TC) was provided by Energy Industrial (Shanghai, China).

Synthesis

Pal@Fe_3O_4 nanocomposites were synthesized by the coprecipitation method. In short, the mass ratio of Fe to Pal was 1:1 by adding Pal to steel pickling waste liquor (8 ml), and the heating temperature was 80 °C under anoxic conditions. NaOH solution (17–22 ml, 3 M) was added to the reaction solution. After three hours of reaction, the Pal@Fe_3O_4 nanoparticles were washed three times with deionized water and dried in a vacuum for 24 hours at 65 °C. In the scale-up preparation experiment, Pal was added to the steel pickling waste liquid (80 ml), the mass ratio of Fe to Pal was 1:1, and then NaOH solution (170–220 ml, 3 M) was added to the reaction solution. Reaction conditions and time were the same as above.

Characterization and analysis

The morphology and microstructure of the nanoscale materials were characterized by transmission electron microscopy (TEM, Tecnai G220, USA). The crystalline structure of the nanoscale materials was measured by X-ray diffractometry (XRD, Bruker D8 Advance, Germany). The magnetic properties of the nanoscale materials were measured by vibrating sample magnetometry (VSM, Lakeshore 7304, USA).

Catalytic activity testing

The experiments were performed in duplicate. The initial pH = 6.8 of the solution was adjusted using NaOH and KH_2PO_4. Quantities of 0.2 g/L catalyst and 100 mM H_2O_2 were added to 100 ml of TC solution (100 mg/L). The mixture was shaken at a speed of 250 r/min and a temperature of 30 ± 1 °C in a light-proof constant-temperature incubator; 0.05 ml t-butyl alcohol was added to terminate the reaction after a certain time interval, and then 1 ml of the reaction solution was taken out and passed through a 0.22 μm filter immediately. Five catalysts were separated by magnets in the Fenton-like catalytic test and then used in the next cycle test.

RESULTS AND DISCUSSION

Catalyst characterization

XRD

Other preparation conditions remained unchanged. The magnetic palygorskite prepared with NaOH dosage of 255 g/L, 270 g/L, 285 g/L, 300 g/L, and 330 g/L was labeled MP255, MP270, MP285, MP300, and MP330, respectively. As shown in Figure 1 for five composites, the reflections at $2\theta = 30.0°$, 35.4°, 37.0°, 43.0°, 53.4°, 56.9°, and 62.5° were in good agreement with the data of PDF#85-1436, corresponding to the (220), (311), (222), (400), (422), (511) and (440) diffraction planes of Fe_3O_4 crystals, indicating that the Fe_3O_4 in the composite had a cubic-tip crystal structure. These reflection points correspond to the characteristic reflection of Fe_3O_4 prepared by the coprecipitation method (Bao *et al.* 2019). The positions of the diffraction peaks of Fe_3O_4 in the five composites were almost the same, and there were no other impurity peaks in the five composites. And the crystalline structure of the Pal was

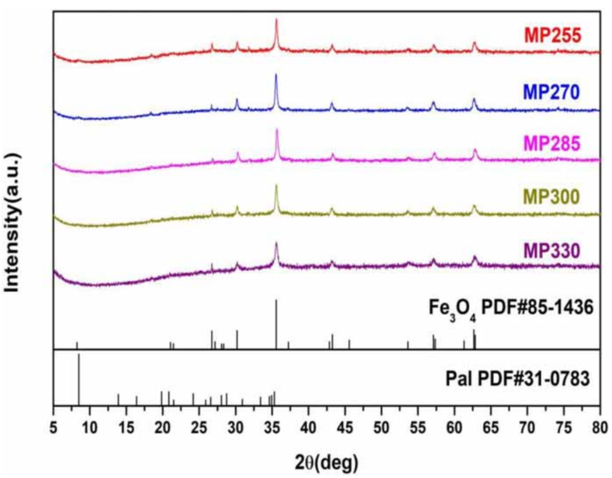

Figure 1 | XRD patterns of Pal@Fe_3O_4.

measured by XRD. The result showed Pal was in good agreement with the data of PDF#31-0783. The most characteristic diffraction peak of palygorskite was $2\theta = 8.4^\circ$ (Liu *et al.* 2018). However, the characteristic peak of Pal@Fe_3O_4 diffraction at about $2\theta = 8.4^\circ$ was not obvious. It was presumed that the Fe_3O_4 in the composites covered the Pal surface. From 270 g/L to 330 g/L, the peak strength of Pal@Fe_3O_4 decreased with the increase of NaOH dosage and the stronger the diffraction peak strength, which indicated that the crystallinity of the nanoparticles was higher. Therefore, MP270 has the best crystallinity among the five composites.

TEM analysis

As shown in Figure 2, Fe_3O_4 nanoparticles in the five kinds of magnetic palygorskite prepared by different NaOH dosage show approximately spherical morphology. It was clearly observed that Pal in the five nanocomposites had fiber morphology and rod structure, which were grouped in parallel and bonded into bundles (Liu *et al.* 2018). The diameter of Fe_3O_4 nanoparticles in MP255, MP270, MP285, MP300, and MP330 ranged from 10 to 80 nm. The size distribution of nanoparticles was uneven and very different. Although Pal as a carrier had greatly inhibited the agglomeration of Fe_3O_4 in the composites, Fe_3O_4 nanoparticles tend to aggregate into chained iron rings due to their strong magnetism and high surface energy (Bao *et al.* 2019; Zhao *et al.* 2019). Interestingly, a large number of black Fe_3O_4 nanoparticles were loaded onto the Pal, showing that Pal@Fe_3O_4 was very similar to the black corn-like structure. Of course, in the TEM maps of the five kinds of magnetic palygorskite, it can be observed that a small part of the palygorskite surface was not loaded with Fe_3O_4 nanoparticles, which was also one of the disadvantages of the chemical coprecipitation method. Due to the uneven distribution of Pal in the aqueous solution, the high local concentration of NaOH in the reaction solution resulted in a nucleation rate of nanoparticles higher than that of a crystal nucleus. On the one hand, the initial particle shape and the distance between particles were very small; on the other hand, the particle surface energy was very large, which eventually led to particle agglomeration (Xu & Zheng 2006).

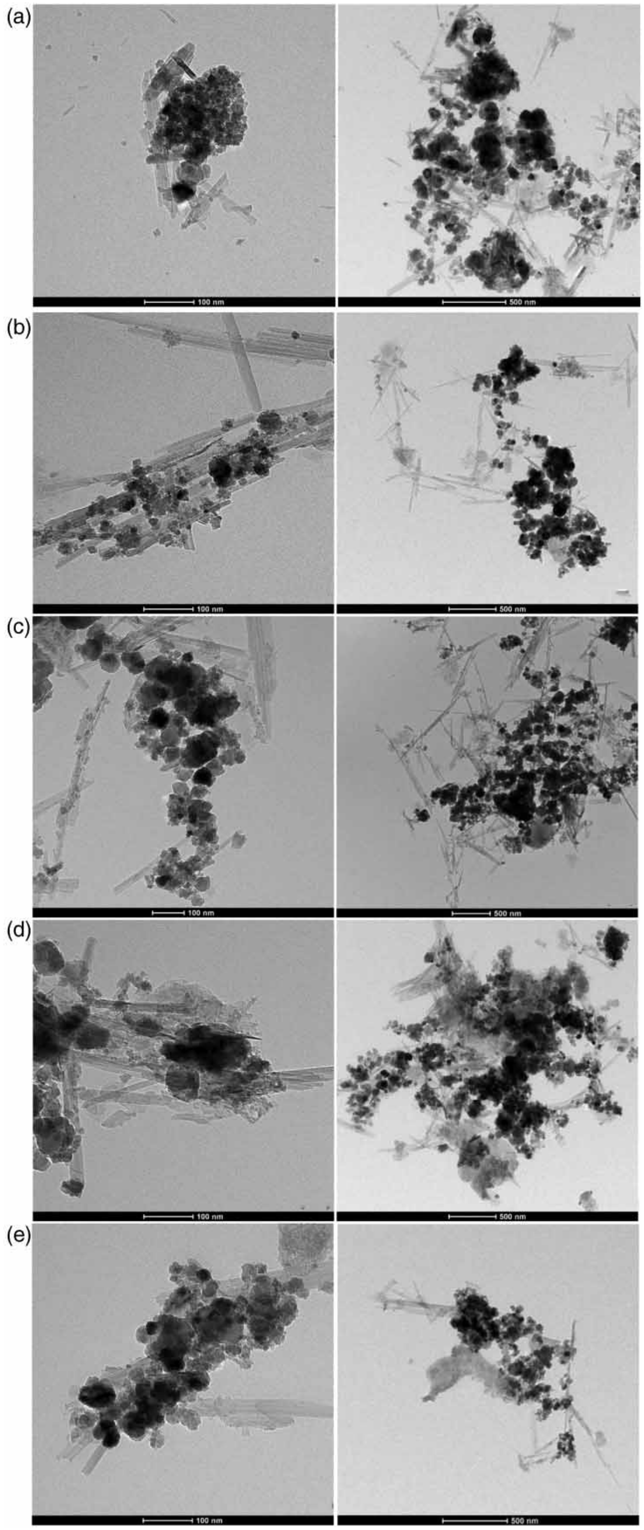

Figure 2 | TEM images of (a) MP255 (b) MP270 (c) MP285 (d) MP300 (e) MP330.

Magnetic property

Figure 3 shows the hysteresis loops of nanocomposites MP255, MP270, MP285, MP300, and MP330 measured at 300 K. The coercivity of the five nanocomposites was zero, which proved that they were superparamagnetic and could

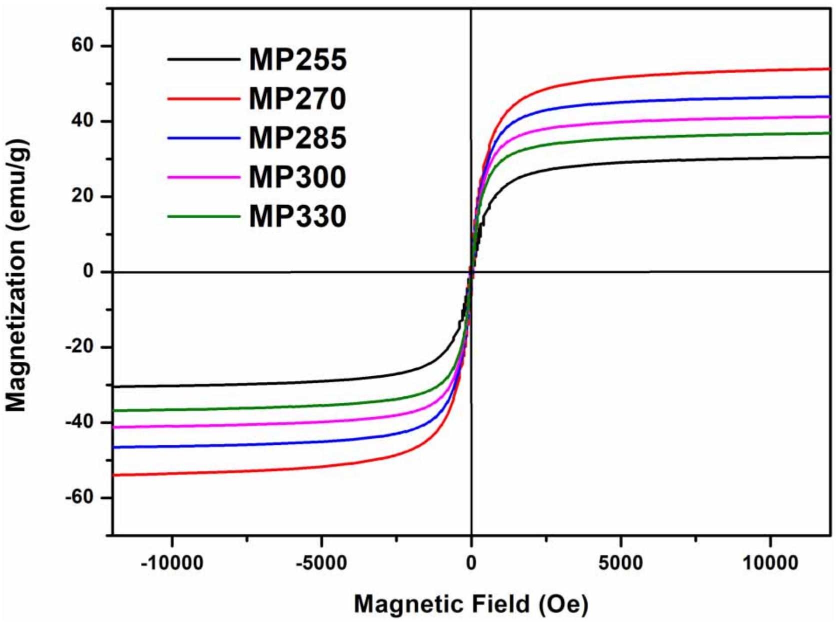

Figure 3 | The magnetic hysteresis loops of Pal@Fe_3O_4.

avoid self-agglomeration of the carrier materials caused by residual magnetism (Yuan *et al.* 2017). The saturation magnetization of the nanocomposites MP255, MP270, MP285, MP300, and MP330 reached 30.49 emu/g, 53.93 emu/g, 46.55 emu/g, 41.22 emu/g, and 36.86 emu/g, respectively. Nanocomposite MP270 had the strongest saturation magnetization, and when the NaOH dosage exceeded 270 g/L, that is 270 g/L–330 g/L, the saturation magnetization of the magnetic palygorskite decreased with the increase of NaOH dosage. The reason may be that with the increase of the pH of the reaction solution, the magnetic domains of the crystal structure were aligned due to the better crystallinity of the nanoparticles, thus enhancing the magnetic properties. It was also confirmed that the magnetic properties of magnetic palygorskite were not only affected by the carrier Pal, but also related to the preparation process. It was noteworthy that all the five nanocomposites had excellent magnetic properties, which indicated that Pal@Fe_3O_4 nanocomposites prepared in a suitable range of NaOH dosage can respond rapidly to an external magnetic field. These results are very important for magnetic separation and recycling of nanocomposites.

Catalytic performance testing

In order to evaluate the catalytic activity of magnetic palygorskite prepared by different NaOH dosages, the degradation efficiency of TC by the nanocomposites MP255, MP270, MP285, MP300, and MP330 in a buffer system ($pH = 6.80$) was compared. As shown in Figure 4, the rate of degradation of tetracycline by magnetic palygorskite prepared with different NaOH dosages was not significantly different. The degradation rate of tetracycline by the five catalytic materials was analyzed: after one hour of reaction, the degradation rate of tetracycline was MP255 (72%) > MP330 (69%) > MP300 (67%) > MP285 (63%) > MP270 (60%); after two hours of reaction, the degradation rate of tetracycline was MP255 (87%) > MP330 (86%) > MP300 (84%) > MP285 (82%) > MP270 (81%); after three hours of reaction, the degradation rate of tetracycline was MP330 (91%) > MP255 (90%), MP300 (90%) > MP285 (88%) > MP270 (86%). The nanocomposites MP255, MP270, MP285, MP300, and MP330 all exhibited excellent catalytic performance in Fenton-like catalytic degradation of TC. However, MP255 maintained the maximum degradation efficiency of TC in the first two hours of the reaction. The concentration of leached iron ions in the five kinds of reaction solution of magnetic palygorskite was determined. It was found that the maximum concentration of leached iron ions was 0.316 mg/L after the reaction of MP255, because the homogeneous Fenton reaction of Fe^{2+} and Fe^{3+} dissolved in the reaction solution with H_2O_2 resulted in more •OH attacking TC (Feng *et al.* 2004). However, there was no significant difference in the catalytic degradation efficiency of TC by the five magnetic palygorskites throughout the reaction. This

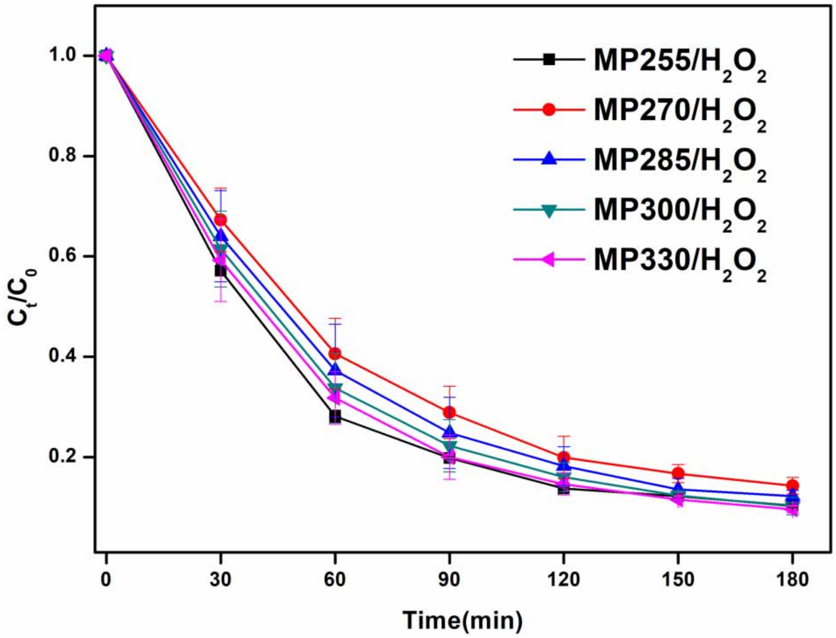

Figure 4 | Degradation efficiency of TC by different systems (pH: 6.8, TC: 100 mg/L, H_2O_2: 100 mM, catalysts: 0.2 g/L and $T = 30 \pm 1$ °C).

showed that during the reaction, the conversion of Fe(II) and Fe(III) on the surface of the five magnetic palygorskites while catalysing H_2O_2 to generate active free radicals to attack TC was still the main process (Hou *et al.* 2017; Li *et al.* 2020).

Evaluation of the stability and recyclability of the nanocomposite

Stability was an important index to evaluate the performance of Fenton-like catalysts. As shown in Figure 5, the

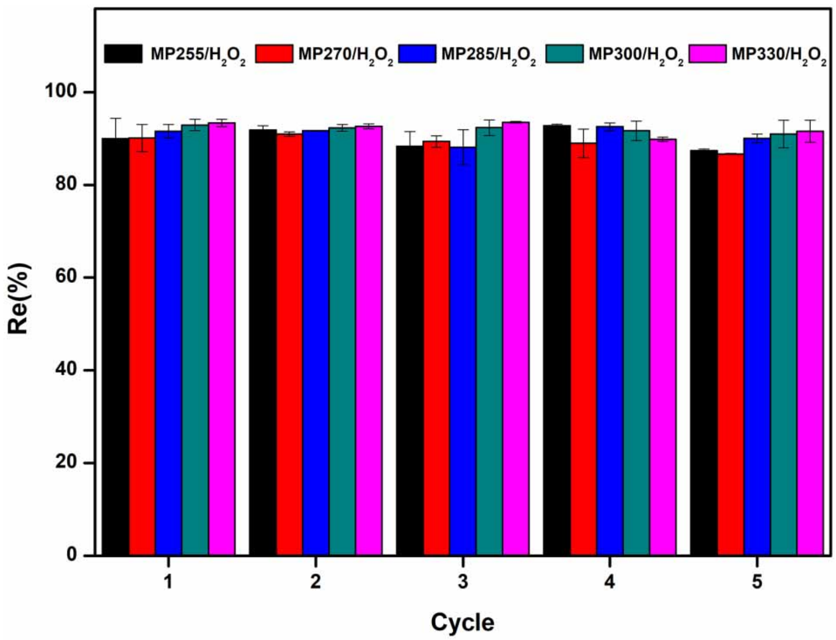

Figure 5 | Degradation rate of tetracycline by Pal@Fe_3O_4 in five cycles (pH: 6.8, TC: 100 mg/L, H_2O_2: 100 mM, catalysts: 0.2 g/L and $T = 30 \pm 1$ °C).

catalysts MP255, MP270, MP285, MP300, and MP330 can still degrade tetracycline stably after five cycles in a buffer system (pH = 6.80), and the degradation rate can reach about 90% in three hours. In addition, the leaching of iron ions in magnetic nanocomposites was the main factor leading to the destruction of catalyst structure and the decrease of catalyst usage. In order to evaluate the stability of the five magnetic palygorskite catalysts, iron ions precipitated during the reaction were detected (Zhang *et al.* 2019). In MP255, MP300, and MP330 they can be detected only after the first reaction. The concentration of iron ions in solution was 0.316 mg/L, 0.032 mg/L and 0.076 mg/L, respectively. In addition, in the following four reactions, the concentrations of iron ions in solution after MP255, MP300, and MP330 reactions were all lower than 0.03 mg/L. Interestingly, the concentration of iron ions in MP270 and MP285 in five reactions was lower than 0.03 mg/L, which indicated that the structures of MP270 and MP285 were more stable than those of MP255, MP300, and MP330. The low iron ion concentration of the five kinds of magnetic palygorskite after reaction also showed that surface Fenton was the main process of TC degradation (Hou *et al.* 2016). In addition, compared with the acid condition, it was difficult for the catalyst to form iron oxide with the dissolving tendency in the reaction process of the buffer system. Fe_3O_4 in Pal@Fe_3O_4 hardly enters the reaction solution in the form of soluble iron ions. At the same time, the low concentration of iron ions also showed that the five catalysts MP255, MP270, MP285, MP300, and MP330 had only slight changes in the degradation rate of tetracycline in five cycles, which indicated that the structure of magnetic palygorskite prepared by different NaOH dosages was quite stable.

Experiments on the magnified fabrication of the nanocomposite

In order to verify the feasibility of preparing Pal@Fe_3O_4 by chemical coprecipitation after enlarged production and explore the change of its catalytic performance, the preparation conditions of Pal@Fe_3O_4 were enlarged by ten times. That was to say, 170 ml, 200 ml, and 220 ml NaOH (3 M) solution were added to 80 ml steel pickling waste liquor, respectively. The prepared Pal@Fe_3O_4 nanocomposites were expressed as FMP255, FMP300, and FMP330. In the buffer system, TC was degraded by nanocomposites FMP255, FMP300 and FMP330 respectively. As shown in Figure 6, the catalytic degradation rates of these three materials to TC for three hours were 86%, 87%, and 87%, respectively. However, in the previous experiments, the catalytic degradation rates of MP255, MP300 and MP330 composites for three hours on TC were 90%, 90%, and 91%, respectively. It was proved that magnetic palygorskite with better catalytic properties can still be prepared under

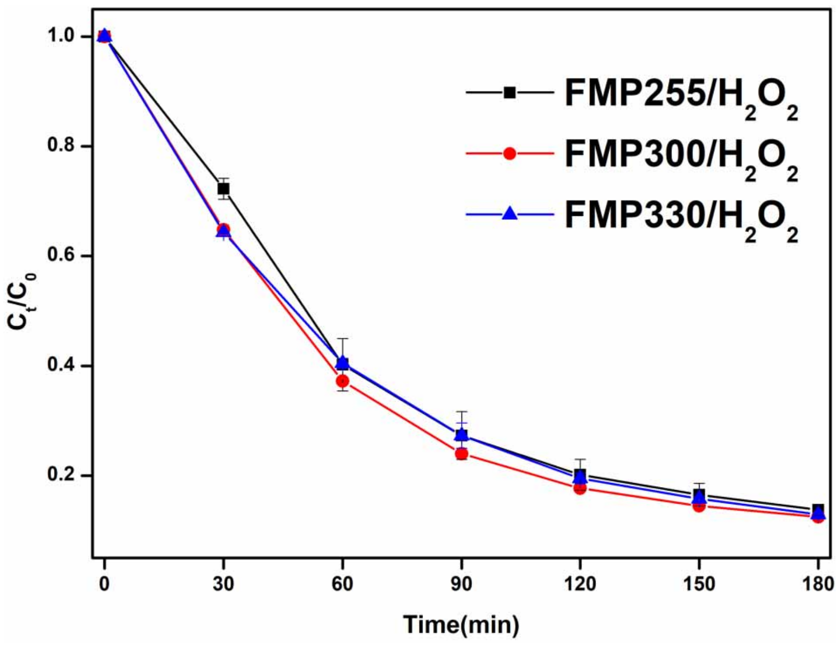

Figure 6 | Degradation rate of tetracycline by Pal@Fe_3O_4 prepared by enlarged experiment (pH: 6.80, TC solution: 300 ml (100 mg/L), H_2O_2: 100 mM, catalysts: 0.2 g/L and $T = 30 \pm 1\ ^{\circ}C$).

ten times magnification. The dosage of 3 M NaOH in the range of 170–220 ml will not significantly affect the catalytic performance of the catalyst. It was further proved that the dosage of NaOH can be selectively reduced and the cost of preparation can be reduced in the process of preparing magnetic palygorskite by chemical coprecipitation. Through calculation and analysis, it was assumed that MP255 and MP330 can be synthesized by using 1 ton of steel pickling waste liquor, and 0.625 t of industrial water and 75 kg of sodium hydroxide can be saved by synthesizing MP255.

CONCLUSIONS

Five kinds of magnetic palygorskite nanocomposites were successfully synthesized by controlling the dosage of NaOH. The surface of the nanocomposites was loaded with black nanoparticles of Fe_3O_4 with a diameter of 10–80 nm, but the saturation magnetization decreased with the increase of NaOH dosage. Five cycles of catalytic degradation of tetracycline showed that magnetic palygorskite prepared with different NaOH dosages had stable structure and good catalytic performance. The magnification experiment provided strong proof for the application of the coprecipitation method in industry to adjust the dosage of the alkaline precipitator NaOH in a certain range, and to synthesize magnetic palygorskite nanocomposites from steel pickling waste liquor.

ACKNOWLEDGEMENTS

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