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Enhanced photo-Fenton activity of Fe_3O_4 spheres/ montmorillonite under visible light

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Abstract— *In this work, a magnetically separable montmorillonite/Fe_3O_4 sphere composite (MMT/Fe) was synthesized by a simple polyol thermal method. The characteristics of the as-preparation composites were checked by XRD, SEM, PL technologies. In addition, the photocatalytic activities of the composite products were checked by degradation of Rhodamin B (RhB) under visible light. The results showed that MMT/Fe composite exhibited the high photocatalytic activity for RhB removal under visible light irradiation. The improved photocatalytic activity of MMT/Fe can be ascribed to the low combination rate of photoinduced electron/hole pairs. Especially, MMT/Fe can be recovered easily by using an external magnetic field and posse the high stability after six runs. These properties of the MMT/Fe composites as prepared could be a promising photocatalyst for the degradation of organic dye contaminants.*

I. INTRODUCTION

The growing industrialization has genered a large hazardous substances as organic dyes [1]. AOP (advanced oxidation processes) are considered as water treatment route at nearly ambient conditions which can generate various active radicals for removal of pollutants. AOPs are regarded as high efficient approach for degradation of the organic containment in water/wastewater because of their strong capability for removing non-slective contaminant, which conventional methods cannot [2].

Photo-Fenton reaction is one of most efficient process due to potential of resulting in more active radicals. It can be considered as combination of Fenton reaction and light irradiation. However, the photo-Feton still remain some disadvantage such as generation of large sludge, difficult for recovery catalyst and high leaching iron [3]. Recently, magnetic nanoparticles of spinel ferrite have been a field of intensity study and application due to their unique optical, interesting magnetical properties [4]. The preparation of magnetic structure have been paid more and more attention by researchers. Spinel ferrite with the general formula MFe_2O_4, where M represent to the metal, which could be regarded as a cubic close-packed attachment of oxygen atoms, in which M(II) and Fe(III) located at tetrahedral (A-sites) or octahedral sites (B-sites). Among the spinel oxides, Fe3O4 nanoparticles with a cubic spinel structure where a half of Fe3+ ions occupy in all the tetrahedral sites, a half of the Fe3+ ions and all the Fe2+ ions local on the octahedral sites, are considered as promising materials in many fields owing to its abundant, low-cost, friendly-environment, easy controllable synthesis and interesting magnetic properties [5].

Several natural materials has been used for adsorbent of contaminated organic. When a comparison is made with other low-cost adsorbents, the clays and their modified composites have been found as a promising adsorbents. Clays have been used for catalyst field because of their low-cost, high adsorption capacity from water [6, 7]. Additionally, clays expose the outstanding advantages for photo-Fenton catalyst loading as large specific surface area, rich pores structure [8]. So, combining the advantages of montmorillonite clay material and spinel oxides, Fe_3O_4 may open new possibilities to achieve desirable adsorption and effective magnetic separability.

In this work, heterogeneous catalys Fe_3O_4 spheres/montmorillonite was prepared, characterized and employed for the photo-Fenton degradation of rhodamine B (RhB) under visible light irradiation. The effects of operating parameters such as initial pH, catalyst dosage on the degradation of RhB were investigated systematically. The experimental results show that the photocatalysts as-prepared exhibited a high activity and stability for dye removal.

II. EXPERIMENTAL

2.1 Materials

All chemicals were analytical reagent grade and used without additional purification or treatment. De-ionized water was used as the solvent throughout the experiment.

2.2 Preparation of MMT/Fe catalyst

Fe_3O_4 sphere were synthesized by a simple solvothermal approach. Typically, $FeCl_3.7H_2O$ (4mmol) firstly dissolved in 60 mL of ethylene glycol, followed by stirring for 0.5 h. Successfully, 20 mmol of natri acetate then added to solution keeping stirring for another 0.5h, .Sequently, the solution tranfered into the 80 ml autoclave and treated at 180^0 C for 24h. After natural cooled at room temperature, the resulting product was collected by a magnet, rinsed with ethanol and de-ionized water several times and dried at 80 °C for 12 h.

The MMT/Fe sphere composite was prepared by simple impregnation method. 0.5 g Fe_3O_4 was added into 50 ml of ethanol under ultrasonic treatment for 30 min. Then, a certain amount of MMT added into the Fe_3O_4 suspension under vigorously stirring for four hours. The mixture was separated from the solution by an internal magnet, then washed and dried at 80^0C for 12h in an electric oven. In this work, MMT/Fe composite with 20 wt% of Fe_3O_4 were synthesized.

2.3 Characterization

X-ray diffraction (XRD analysis was carried out an X-ray powder diffractometer with Cu Kα radiation at 40 kV and 40 mA. The morphology and internal structure of the prepared samples were further checked by transmission electron microscopy (TEM) using a JEM 2100F electron microscope operated at a voltage of 200 kV. The specific surface areas (BET) of products were examined by nitro adsorption on an Autosorb-1 (Quantachrome Instruments, Boynton Beach Florida). The element composition of the as prepared samples was investigated by Energy dispersive X-ray (EDX) method.

2.4 Heterogeneous photo-Fenton degradation of RhB

To evaluate the photocatalytic activity of the sample, the reaction was set up by the photocatalytic decolorization of RhB under visible light. The light irradiation source consists of a 500 W Xe lamp with a 420 nm cutoff filter. A mount of 0.3 g MMT/Fe was introduced into 50 mL RhB solution (10^{-5} mol/L), pH=5, under stirring for ensuring the establishment of adsorption-desorption equilibrium between the photocatalyst and RhB. Then the solution was irradiated with continuous stirring and 4ml of suspension was collected after every 10 minutes. The RhB degradation effect was measured by checking the absorbance at 553 nm during the photodegradation process with a Hitachi U-3010 UV-vis spectrophotometer.

III. RESULTS AND DISCUSSION

3.1 XRD analysis

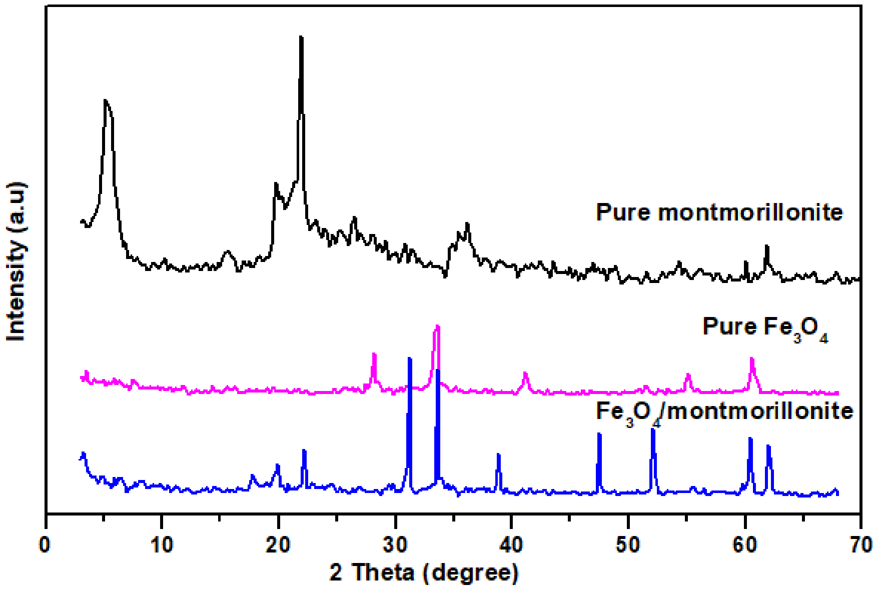

Fig. 1. XRD pattern pure Fe_3O_4; Pure montmorillonite and 20 wt % MMT/Fe composite

The XRD patterns of Fe_3O_4, montmorillonite, Fe-MMT samples are shown in Fig. 1. There were strong peaks observed at 5.38°, 19.82° 26.5°, 35.98° and 61.8° which could be attributed to montmorillonite [9]. The peak at around $2\theta = 5°$ is typical signal for montmorillonite dioctahedral or octahedral structure which is known as Keggin structure. Peaks at around $2\theta = 19.8°$ and 35.98° ascribed to quartz as impurities in the material [10]. The Fe_3O_4 pattern show that the reflection peaks ascribed to the crystal planes, (220), (311), (400), (422), (511), and (440), respectively, which matches well with the standard patterns of cubic spinel structure (JCPDS 77-1545)[11]. From Fe-MMT XRD patterns, it is clearly seen that a lower shift of $d_{(0\ 0\ 1)}$ reflection angle and new peaks at 45.6° and 62.42° observed, corresponding to (222) and (440) of Fe_3O_4 respectively, showing incorporation of Fe metal to the clay structure.

The appearance and morphology of original MMT and MMT/Fe catalyst was observed by SEM. The morphologies of pure montmorillonite, pure Fe_3O_4 and MMT/Fe3O4 composite, are illustrated in Fig. 2. SEM images of montmorillonite in Fig. 2a show typical layered structures. SEM images of Fe_3O_4 ireveal that the products has uniform microsphere shape (shown in Fig 2b). The SEM image of montmorillonite–Fe_3O_4 composite in Fig. 2c shows that Fe_3O_4 nanoparticles are dispersed evenly on the surface or inserted between layers of the montmorillonite plates. The average size of Fe_3O_4 loaded on bentonite was found to be 500 nm. The higher initial loading metal concentration, the more metal oxide particles uniformly distributed on the surface of MMT/Fe without any aggregation.

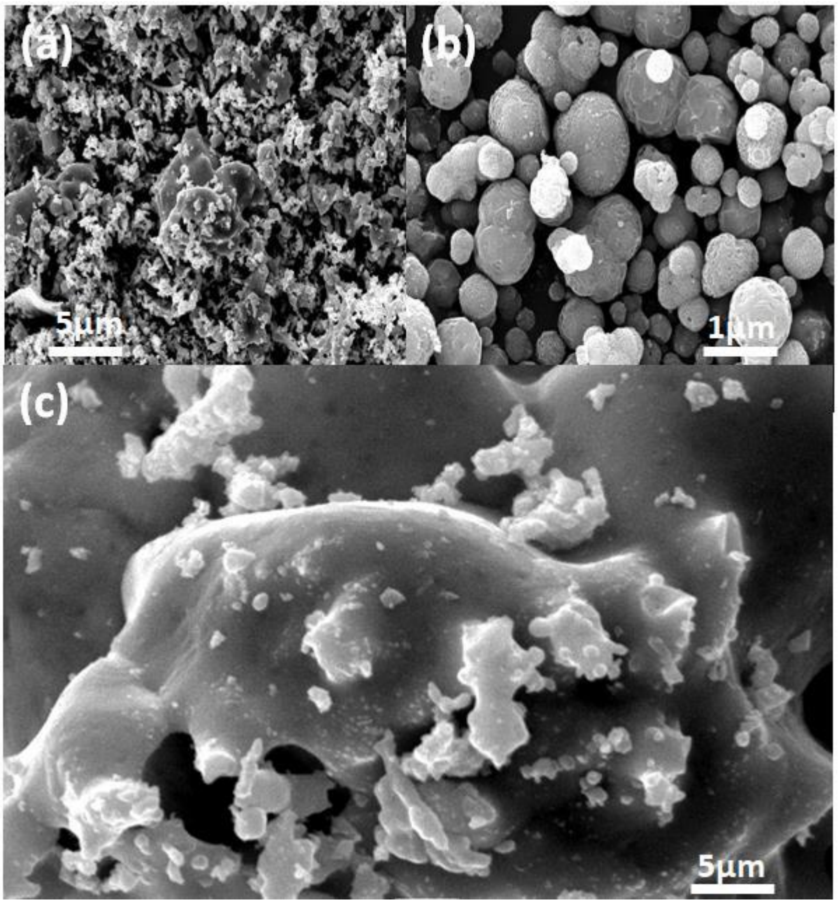

Fig. 2. SEM images of pure montmorillonite, pure Fe_3O_4 and MMT/Fe3O4 composite

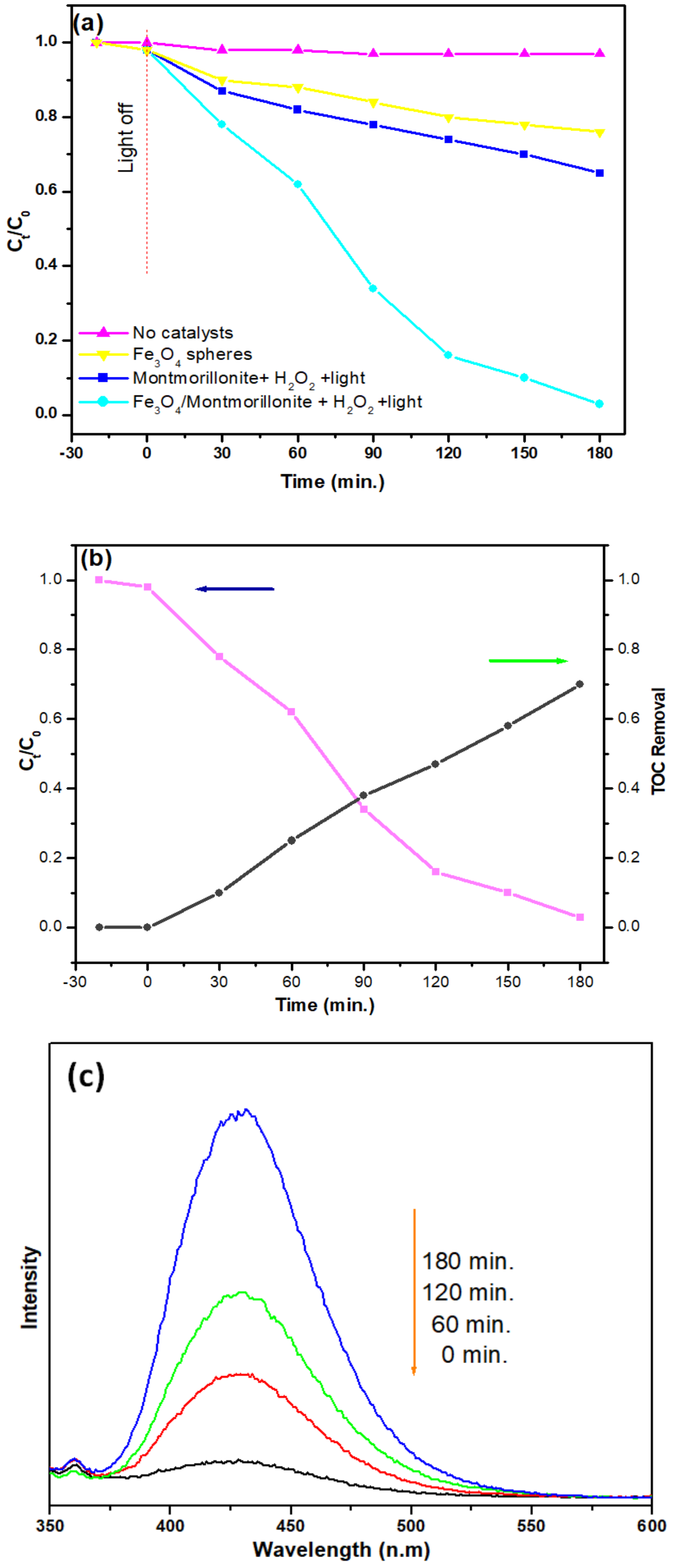

Fig. 3. (a) The photo-Fenton degradation of RhB under visible light irradiation; (b) The % TOC removal under MMT/ Fe/ H_2O_2 / light ; (c) UV-Vis absorption spectra of RhB aqueous solution in the presence of the photocatalysts.

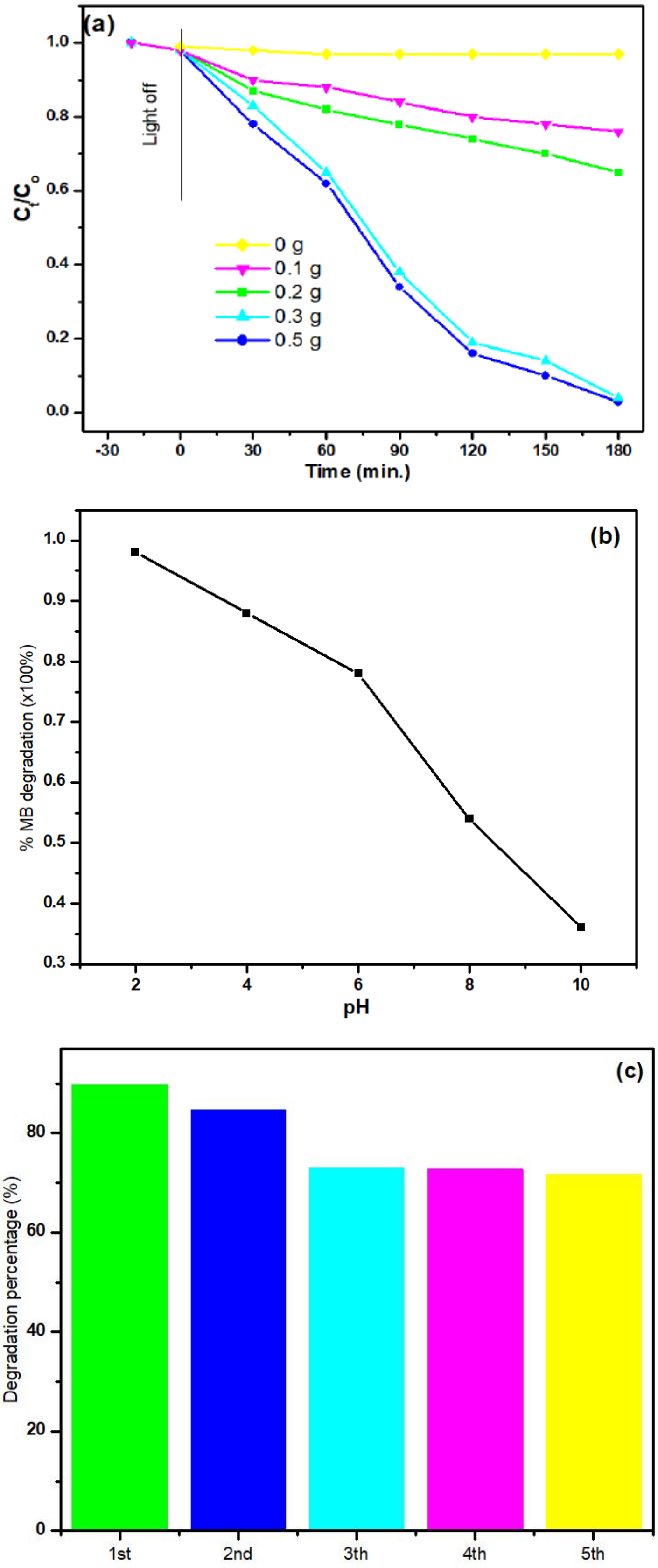

Fig. 4. (a) The effect of photocatalyst amount; (b) The effect of pH on RhB removal %; (d) Stability test of the MMT/Fe catalysts after 5 cycles.

The photocatalytic performance of as prepared MMT/Fe composites was evaluated by the photodegradation of RhB solution (10 mg/L, pH=5) under visible light irradiation. The efficiency of the photocatalytic degradation of cephalexin over different photocatalyst is mentioned in Fig. 3a. It can see that pure MMT or pure Fe_3O_4 showed low photocatalytic activity in the degradation of RhB under visible light irradiation. During 180 minutes irradiation, only 15% and 10% RhB was removed with pure Fe_3O_4 and pure montmorillonite, respectively . This can be assigned to the fast recombination of photogenerated electron/hole pair [12]. However, the as-prepared MMT/Fe composites exhibited enhanced efficiency for the photodegradation of RhB in comparison to that of pure montmorillonite and pure Fe_3O_4. From Fig. 3a, it can be observed that 93% RhB was degraded in the present of MMT/Fe 20% under the same time irradiation. This can be explained that with suitable content Fe_3O_4 introduced, the interfacial interaction can be created between montmorillonite and Fe_3O_4 which lead to the enhanced transfer and separation of photogenerated electron/hole pairs [13]. Whereas, increasing further content of montmorillonite in the composite will result in blocking the internal space void Fe_3O_4 hollowshere, which can make the active sites reduced [14]. The adsorption of RhB on the composites also plays a important role for enhancement the removal of RhB in photo-Fenton reaction. The mineralization of RhB was also investigated as depicted in Figure 3b. The results reveal that the TOC removal of RhB using MMT/Fe composites as catalysts gained about 73.5%. The results suggest that as-prepared MMT/Fe composites show the high capacity for the mineralization of contaminants. Fig. 3c displays the absorption spectra of the RhB solution show a characteristic peak at 554 nm. From figure 3c, it is seen that the intensity of the absorption peak at 554 nm decreased gradually following time reaction. At a reaction time of 180 minutes the absorption peak intensity is minimal, demonstrating that the RhB was removed.

Effect of catalyst amount and pH in the range of 2 to 10 on RhB degradation efficiency was also studied (as shown in Fig. 4a and 4b). The results show the degradation rate of RhB enhanced with an increase in catalyst amount as exposed in Fig. 4a. However at the catalyst dosage of 0.5 g, the dye removal percentage slightly decreased. Based on the experiment, 0.3 g MMT/Fe 20% wt composites are consistent for the RhB photo-Fenton removal. The experiment results on the effect of pH reveal that the optimum pH was 5.5 (Fig. 4b). With pH below 5.5, in high H^+ concentration, the formation of stable oxonium ion $[H_3O_2]^+$ makes hydrogen peroxide more stable and then decrease its activity with ferrous ions. Moreover, the formation of Fe(II) complexes and ferric oxyhydroxides precipitation at a pH above 5.5 are probably reasons for efficiency decreases in the photo-Fenton RhB removal processes [15].

In addition, the recycle tests were conducted to survey the stability of the as-obtained products in the photo-Fenton process. The results show that the catalyst was easily separated by an internal magnet. The cephalexin degradation effectively has no significant change after the five successive runs with only 5% loss, indicated high stability of the catalysts (Fig. 4c). These properties makes the as-prepared MMT/Fe composites unique for the water treatment application at industrial scale.

IV. CONCLUSIONS

A high activity of magnetic separable MMT/Fe composite was successfully synthesized by simple solvothermal route. The results showed MMT/Fe composite with added 20% Fe_3O_4 exhibited the high photocatalytic activity for RhB under visible light irradiation. The improved photocatalytic activity of MMT/Fe can be ascribed to the low combination rate of photoinduced electron/hole pairs. Specially, MMT/Fe can be recovered easily by using an external magnetic field and posse the high stability after five cycles. These properties of the MMT/Fe composites could be a promising photocatalyst for the dye contaminants degradation.

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