



Rice hull/MnFe₂O₄ composite: Preparation, characterization and its rapid microwave-assisted COD removal for organic wastewater

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ABSTRACT

Adsorbent/ferrite composites can adsorb and degrade organics in the organic wastewater treatment. In this study, a rice hull/MnFe₂O₄ composite (RHM) was prepared via calcination under nitrogen atmosphere and was used to treat organic wastewater with the assistance of microwave radiation. Rice hull was pyrolysed to a porous substrate that consisted of silica and activated carbon under high temperature. Monodisperse spinel MnFe₂O₄ nanoparticles whose mean diameter is around 59 nm are distributed on the substrate. With the assistance of microwave radiation, RHM was motivated to a hotspot of adsorption and catalysis which could remove more than 70% COD of wastewater within 6 min. The maximum COD removal was 73.5% when the concentration of RHM was 15 mg mL⁻¹ and the irradiation time of microwave radiation was 6 min. Although the BET surface area and iodine value of RHM are half of rice hull ash (RHA), the COD removal of RHM is 7–20% higher than that of RHA. It is attributed to the presence of MnFe₂O₄, which enhances the catalytic activity of RHM. RHM can be regenerated via water washing. However, the surface area and the maximum COD removal of RHM decrease for each regeneration cycle. With the advantages of low cost and rapid processing, this novel rice hull/MnFe₂O₄ composite could gain promising application in wastewater treating-agent.

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1. Introduction

Chemical oxygen demand (COD) is a main parameter widely used to estimate the organic content of wastewater; high COD values suggest high organic pollutions in aqueous systems [1]. Developer wastewaters produced from printed circuit board (PCB) industry are rich in organic matter and thus have high COD values of 1000–20,000 mg L⁻¹. They are difficult to treat and toxic to aquatic life and humans [2,3]. Conventional treatments for these organic wastewaters include biodegradation [4,5], acidification [6], electrochemical technologies [7], chemical precipitation [8,9], adsorption by activated carbon [10,11], ozonation and oxidation [12–14] and so on. Nevertheless, these technologies are limited by high operating costs, low treatment efficiencies, or sensitive operating conditions.

Due to its porous structure and special surface reactivity, activated carbon is well used as adsorbent in air and water purification and catalyst in the chemical and petrochemical industries [15]. It has advantages of chemical stability and facile usage [16]. Many carbonaceous materials, such as petroleum coke, sawdust, lignite,

coal, peat, wood, charcoal, nutshell, and fruit pits, can be used for the manufacture of activated carbon. Rice hull, in particular, is the milling byproduct of rice and is a major waste material of the agricultural industry [17]. Dry rice hull contains 70–85% of organic matter and the remainder consists of silica. The abundance and low cost make rice hull as good precursor candidate for activated carbon. For instance, rice hull will transform to rice hull ash that consisted of silica and activated carbon when pyrolysed under inert atmosphere [18,19]. Moreover, the silica can be removed from rice hull via acidification or alkali treatment, resulted in pure activated carbon. Both rice hull ash and activated carbon can effectively adsorb heavy metals and organics in wastewater treatment and can economically yield high quality water [20–22]. However, the disadvantages of limited treatment capacity and long processing period restrict the applications of activated carbon.

Microwave is a form of electromagnetic energy with associated electric and magnetic fields. Since World War II, there have been major developments in the use of microwaves for heating selective materials. Compared with conventional heating techniques, microwave heating has advantages of rapid heating, ease of control, enhanced chemical reactivity, reduced equipment size and waste, and so on [23,24]. The spinel ferrites, MFe₂O₄ (where M = Co, Ni, Mn, Mg, etc.), is a well-known microwave ferrite material with a partial inverse spinel structure. When the microwaves are applied to spinel

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Table 1
Characteristics of COD-rich wastewater.

	Initial	After neutralization	
pH	0.28	9.33	11.33
COD value	2088 ± 20 mg L ⁻¹	2050 ± 25 mg L ⁻¹	2052 ± 18 mg L ⁻¹
Acrylic acid epoxy resin	562 ± 12 mg L ⁻¹	560 ± 10 mg L ⁻¹	563 ± 10 mg L ⁻¹
Trimethylolpropane triacrylate	307 ± 7.5 mg L ⁻¹	310 ± 9 mg L ⁻¹	308 ± 6 mg L ⁻¹
N-vinyl pyrrolidone	150 ± 5 mg L ⁻¹	150 ± 6 mg L ⁻¹	153 ± 10 mg L ⁻¹
Polyether	2.9 ± 0.2 mg L ⁻¹	3.0 ± 0.3 mg L ⁻¹	2.9 ± 0.2 mg L ⁻¹
EDTA-4Na	270 ± 12 mg L ⁻¹	272 ± 8 mg L ⁻¹	276 ± 15 mg L ⁻¹

ferrites, the dipoles align and flip around since the applied field is alternating. Subsequently, the ferrites are selected heated rapidly. On the other hand, spinel ferrites have excellent structural stability and catalytic ability because the ferrite can be reduced to a cation-excess composite $\text{AFe}_2\text{O}_{4-\delta}$ ($\delta < 1$) and re-oxidized to initial while keeping its spinel structure [25,26]. Ferrite catalysts have been employed in various reactions such as organic dehydrogenation, catalytic oxidation, fenton reaction, and CO_2 reduction [27–30]. Therefore, ferrite will be selectively heated and show excellent catalytic ability when heated by microwave radiation.

In the past years, many researches have focused on the adsorbent/ferrite composites to obtain wastewater treating-agents with both adsorption and catalytic abilities. For example, Suzuki and co-workers synthesized an active carbon-supported lithium ferrite via high temperature treatment and applied it as catalyst in oxidative dehydrogenation of ethylbenzene [31]. Ikenaga et al. prepared an activated carbon-supported zinc ferrite for hot-gas cleaning [32,33]. Furthermore, CuFe_2O_4 /activated carbon has been prepared and can adsorb and catalytic degrade acid orange II in the wastewater treatment [34].

In this study, we reported a novel rice hull/ MnFe_2O_4 composite (RHM) which composed of activated carbon, silica, and spinel manganese ferrite. Under the assistance of microwave radiation, RHM will be selectively heated to be hotspots of adsorption and catalytic degradation for organics. As a result, more than 70% COD of wastewater will be removed within 6 min.

2. Materials and methods

2.1. Materials

Ethanol ($\text{C}_2\text{H}_5\text{OH}$, CAS number 64-17-5, AR), manganese nitrate 50% solution ($\text{Mn}(\text{NO}_3)_2$, CAS number 10377-66-9, AR) and ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, CAS number 7782-61-8, AR) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and were used without further treatment. Rice hull was obtained from Quzhou, Zhejiang province and was washed thoroughly to remove impurities before usage. The organic wastewater was supplied by YanTat Printed Circuit Co., Ltd. (ShenZhen, China). It was a photoresist developer wastewater produced from printed circuit board (PCB) industry, with initial COD concentration of 2088 mg L⁻¹ and acid concentration of 0.52 mol L⁻¹ (pH 0.28). The main organic components of this wastewater are photosensitive resin and EDTA-4Na. The wastewater was neutralized by calcium hydroxide ($\text{Ca}(\text{OH})_2$) before using. The pH value was greater than 7 and the COD value and compositions of wastewater were kept invariant after the neutralization (Table 1).

2.2. Preparation of RHM and RHA

In a typical procedure, 11.8 mL $\text{Mn}(\text{NO}_3)_2$ 50% solution (0.05 mol) and 40.4 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 mol) were dissolved in 200 mL ethanol under continuous stirring. The mixture was poured onto 50 g rice hull and vigorously stirred for 15 min. Then the product was dried at 70 °C in a temperature-controlled oven

and calcined at 950 °C for 2 h under a nitrogen atmosphere with a heating rate of 30 °C min⁻¹. After cooled to room temperature, rice hull/ MnFe_2O_4 composite (RHM) was obtained. For comparison, rice hull was directly calcined at 950 °C for 2 h under a nitrogen atmosphere with a heating rate of 30 °C min⁻¹. The product was named rice hull ash (RHA).

2.3. Treatment of organic wastewater

We used RHM and RHA to treat organic wastewater, and investigated the effects of sample dosage and microwave heating on the COD of wastewater. The detailed processes are described as follows.

Sample dosage: a certain amount of RHM or RHA was added into 100 mL wastewater. The wastewater was heated by a WP700(21) domestic microwave oven (Galanz, China) with microwave frequency of 2450 MHz and output power of 700 W for 6 min without other treatments. The dosage of samples varied from 5 mg mL⁻¹ to 30 mg mL⁻¹. The experiment was repeated for three times. The COD value of wastewater was measured after each treatment.

Microwave treatment: 2 g RHM or RHA was added into 100 mL wastewater. The wastewater was heated by 700 W microwave radiation for 1–12 min. For comparison, 100 mL wastewater was treated by 2 g RHM or RHA for 3 min under room temperature without microwave radiation, and another 100 mL wastewater was heated by microwave radiation for 1–12 min without RHM or RHA added. By adjusting the microwave power from 120 W to 700 W, the influence of microwave power on the COD of wastewater was investigated by heating 100 mL wastewater for 6 min with 2 g RHM added. Each treatment was repeated for three times. The COD value of wastewater was measured subsequently.

2.4. Regeneration

For regeneration, RHM was washed by tap water for three times and dried at 60 °C for 5 h in a temperature-controlled oven.

2.5. Characterization of samples

The phase purity and crystal structure of the samples were determined by a D/max 2550 X-ray diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) at a scan rate of 0.02° s⁻¹. The operation voltage and current were maintained at 40 kV and 34 mA, respectively. The surface morphologies of the samples were studied by an S-4800 scanning electron microscope (Hitachi, Japan) at an accelerating voltage of 5.0 kV. Surface areas of the samples were measured by nitrogen adsorption at 77 K using a Coulter OMNISORP surface area and pore analyzer. Bulk density was determined using the following method: a 50 mL cylinder was filled to a specified volume with the samples that had been dried in a temperature-controlled oven at 80 °C overnight. The cylinder was tapped for at least 1–2 min to compact the samples, and then weighed. The bulk density was calculated as:

$$\text{bulk density (g cm}^{-3}\text{)} = \frac{\text{weight of dry sample (g)}}{\text{volume of packed dry sample (cm}^3\text{)}}$$

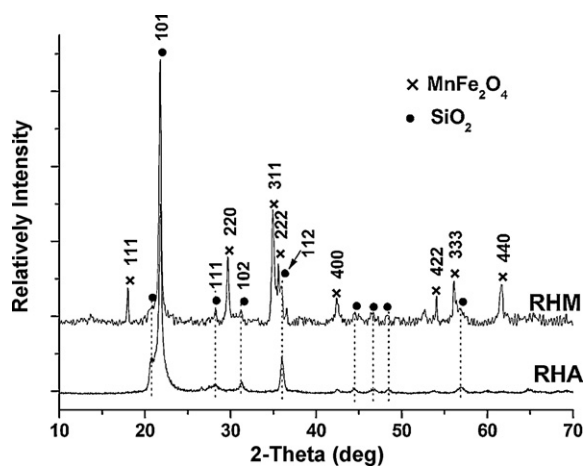


Fig. 1. XRD patterns of rice hull ash (RHA) and rice hull/ MnFe_2O_4 composite (RHM).

The particle size and iodine value of RHM and RHA were determined according to the China National Standard GB/T7702-1997. The COD of the wastewater was determined according to the China National Standard GB11914-89 – “Water quality – Determination of the chemical oxygen demand – Dichromate method.”

3. Results and discussion

3.1. Characterization of as-synthesized samples

To identify the crystalline structure and compositions of the samples, XRD analysis is performed on RHM and RHA (Fig. 1). As seen in Fig. 1, Bragg reflections for RHA can be indexed to a pure cristobalite phase (SiO_2 , JCPDF# 82-0512). No other phases including carbon can be found in the XRD pattern of RHA, suggesting that the organics of rice hull has been carbonized to amorphous carbon that cannot be detected by X-ray diffraction. Compared with

RHA, RHM yield an XRD pattern that contains additional diffraction peaks at $2\theta = 17.9^\circ, 29.6^\circ, 34.9^\circ$, and so on, which can be steadily indexed to jacobsite (MnFe_2O_4 , JCPDF# 74-2403). Calculated from the manganese ferrite (3 1 1) peak corresponding to $2\theta = 34.936^\circ$, the Scherrer analysis [35] indicates that the average grain size of MnFe_2O_4 particles is ~ 22 nm.

Fig. 2A–C shows the SEM images of RHM and RHA. Many pores pervade the surface and inner part of RHA, varying from $0.3 \mu\text{m}$ to $30 \mu\text{m}$ in diameter and slit-like to ellipsoidal in shapes (Fig. 2A). These pores are formed by the decomposition and carbonization of organics under high temperature treatment with nitrogen atmosphere. Because the preparation conditions of RHA and RHM are identical, the surface morphology of rice hull-based substrate in RHM should be similar with RHA. However, the appearance of RHM is largely different from RHA (Fig. 2B). The surface of RHM is smooth and merely shows several holes with $\sim 5 \mu\text{m}$ in diameter. It is attributed to the fact that the pores that generated from the decomposition and carbonization of rice hull were filled by the simultaneously formed MnFe_2O_4 . MnFe_2O_4 nanoparticles with various diameters are densely distributed on the surface of rice hull-based substrate (Fig. 2C). The size distribution pattern of these particles (Fig. 2, right bottom) indicates that 73% particles are less than 100 nm in diameter. The maximum, minimum, and mean diameters are 904 nm, 17 nm, and 59 nm, respectively. These nano-scale MnFe_2O_4 particles will enhance the chemical activity and catalytic ability of RHM due to the surface effect of nanomaterials.

Table 2 shows the physical characteristics of RHA and RHM. The relatively high surface area ($433.90 \text{ m}^2 \text{ g}^{-1}$) and iodine value (325 mg g^{-1}), and low bulk density (0.19 g cm^{-3}) of RHA indicate that RHA is a porous material with good adsorption capacity, coinciding with the SEM observations. The surface area and iodine value of RHM are half of RHA. However, the bulk density of RHM is twice than RHA, and the particle size of RHM is higher than that of RHA. These results indicate that the presence of MnFe_2O_4 will help to retain the initial morphology of rice hull and increase the density of products. More importantly, the presence of MnFe_2O_4 will decrease

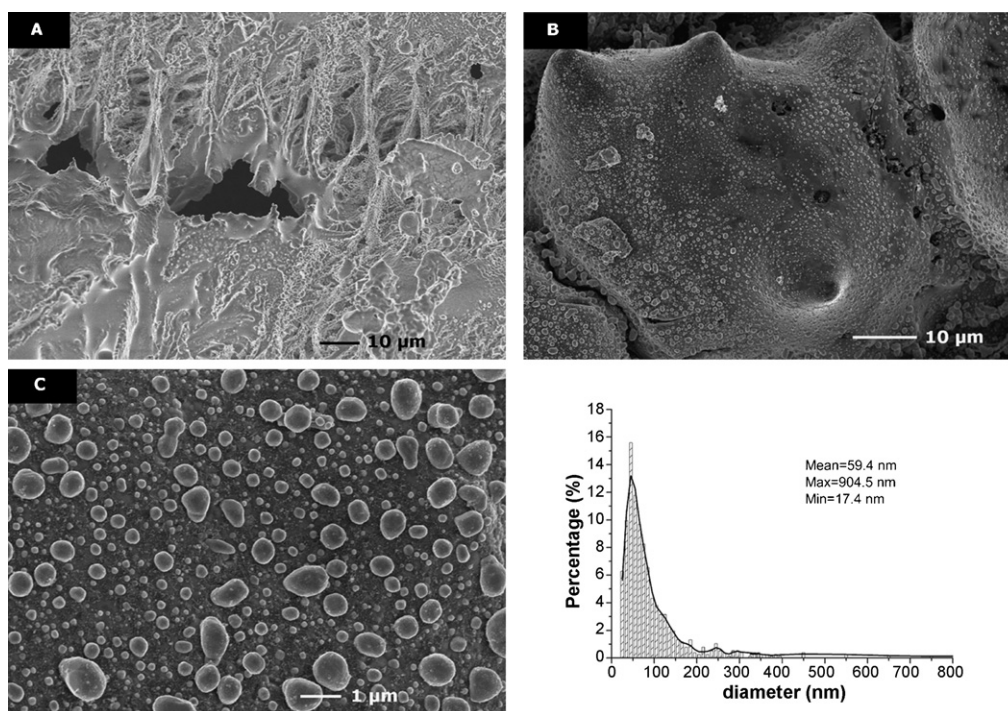


Fig. 2. SEM patterns of (A) rice hull ash (RHA) and (B and C) rice hull/ MnFe_2O_4 composite (RHM). The right bottom pattern is the size distribution of MnFe_2O_4 particles that calculated from (C).

Table 2
Physical characteristics of RHM and RHA.

Samples	Bulk density (g cm^{-3})	Particle size (mm)	Iodine value (mg g^{-1})	BET surface area ($\text{m}^2 \text{g}^{-1}$)
RHA	0.19 ± 0.01	0.24 ± 0.01	325 ± 3	433.90 ± 9.17
RHM	0.39 ± 0.01	0.31 ± 0.01	151 ± 4	214.54 ± 5.20

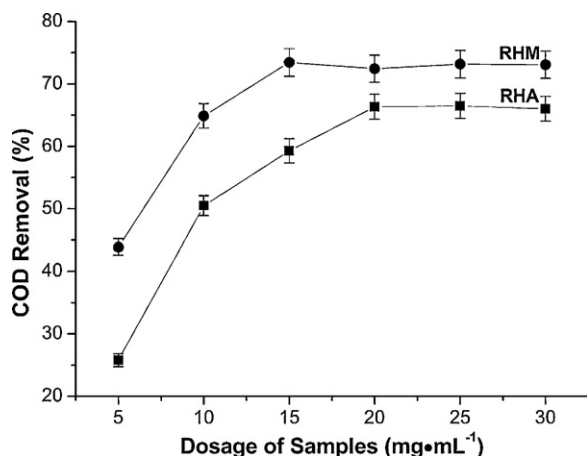


Fig. 3. Variations of the COD removal of wastewater as a function of sample dosage. The wastewater was treated by RHM or RHA with microwave radiation for 6 min. The initial COD of wastewater was 2050 mg mL^{-1} .

the adsorption ability of RHM because of the decreased BET surface area and iodine value.

3.2. Effect of sample dosage on the COD of wastewater

Fig. 3 shows the effect of sample dosage ranging from 5 mg mL^{-1} to 30 mg mL^{-1} on the COD removal of wastewater. The COD removal increases significantly with the dosage of RHM or RHA when the dosage was less than 20 mg mL^{-1} . Thereafter, its removal changes slightly and maintains at 73% (RHM) or 66% (RHA). Compared with RHA, the COD removal of RHM is higher at identical dosages. For instance, the COD removal of RHM is around 18% higher than that of RHA when the sample dosage is 5 mg mL^{-1} . The maximum COD removal of RHM (73.5%, at dosage of 15 mg mL^{-1}) is around 7% higher than that of RHA (66.5%, at dosage of 25 mg mL^{-1}). In addition, we investigated the adsorption abilities of RHM and RHA to the COD removal for wastewater by impregnating 2 g RHM or RHA into the organic wastewater without microwave-assisted. The results show that after impregnated for 2.5 h, both RHM and RHA will reach their maximum COD removals by adsorption, which is 46.5% for RHM and 64.2% for RHA. This result coincides with the surface area and iodine value of RHA ($433.90 \text{ m}^2 \text{ g}^{-1}$) and RHM ($214.54 \text{ m}^2 \text{ g}^{-1}$), indicating that RHA present stronger adsorption ability than that of RHM. Therefore, the catalytic ability of RHM is much stronger than that of RHA, attributed to the presence of MnFe_2O_4 . Organics were adsorbed to the surface of RHM and then catalytic degraded by the ferrite nanoparticles during the wastewater treatment, which is consistent with former researches [31,34].

3.3. Effect of microwave treatment on the COD of wastewater

Fig. 4 shows the variations of the COD of wastewater as a function of microwave heating time. When the wastewater was treated by 20 mg mL^{-1} RHM or RHA without microwave heating, the COD removal is less than 7%, which is attributed to the inadequate contact between RHM and organics. When the microwave radiation was added, the COD removal increases considerably in the first 3 min, from 41% to 72% for RHM and 19% to 60% for RHA. Thereafter, it changes little and maintains at around 73% for RHM and around

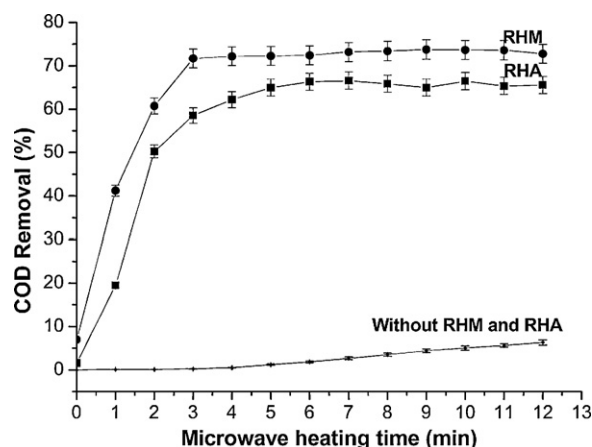


Fig. 4. Variations of the COD removal of wastewater as a function of microwave heating times. The wastewater was treated by 20 mg mL^{-1} RHM or RHA. The initial COD of wastewater is 2050 mg mL^{-1} . “0 min” represents for wastewater treatment by 20 mg mL^{-1} RHM or RHA for 3 min at room temperature without microwave heating, while other conditions were kept invariant. The bottom line represents the COD removal of wastewater that without RHM or RHA added.

65% for RHA. On the other hand, extremely low COD removals were obtained when the wastewater was heated by microwave radiation without RHM or RHA added. The COD removal is below 1% in the first 4 min. Thereafter, because the wastewater was heated and started to boil, the COD removal starts to increase and reaches 6.3% after 12 min.

As described in the above section, both RHM and RHA will reach their maximum COD removal by adsorption after impregnated for 2.5 h without microwave-assisted. However, as observed in the microwave treatment, RHM and RHA will reach their maximum COD removal within 6 min under the assist of microwave radiation, and the resulting COD removals (73.7% for RHM and 66.5% for RHA) are much higher than that of by impregnating for 2.5 h (46.5% for RHM and 64.2% for RHA). It is contributed to two reasons. First, microwave radiation will selectively heat and motivate some special materials such as active carbon and magnetic materials to be hotspots [36], which will adsorb and catalytic degrade the organics of wastewater rapidly. Second, the quantum energy of microwave can motivate the rotation of molecules and decrease the activation energy of reactions, which facilitates the breaking of chemical bonds and the adsorption of RHM or RHA for organics [37,38]. The microwave power affect significantly on the adsorption and catalysis efficiency of RHM. As shown in Fig. 5, the maximum COD removal increases almost linearly with the microwave power, suggesting that microwave provides the energy to enhance the adsorption and catalytic abilities of RHM and increase the contact between RHM and organics. Note that RHM reaches its maximum COD removal earlier than RHA does and the COD removal of RHM is higher than that of RHA at all periods, indicating that RHM is easier to be heated by the microwave radiation. It is still attributed to the presence of MnFe_2O_4 .

3.4. Regeneration of RHM

Regeneration of RHM is necessary so that it can be reused for repeated COD removal. In this study, we regenerated RHM via wash-

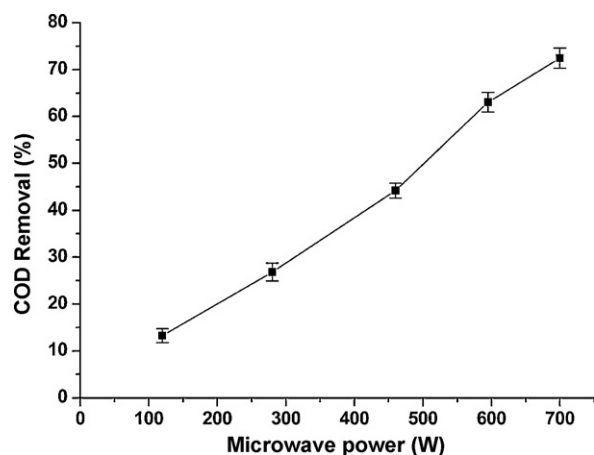


Fig. 5. Effect of microwave power on the COD removal of wastewater when microwave heated for 6 min with 20 mg mL⁻¹ RHM added.

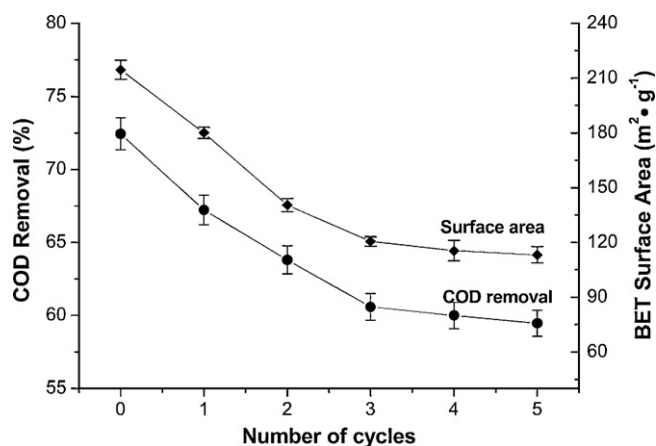


Fig. 6. Variations of the COD removal and BET surface area of RHM as a function of regeneration cycles.

ing, and investigated the variations of COD removal and BET surface area of RHM as a function of regeneration cycles (Fig. 6). The BET surface area of RHM decreases as the number of regeneration cycle increases. The extent of this decrease is greatly for the first three regeneration cycles, from 214 m² g⁻¹ to 120 m² g⁻¹. Thereafter, the surface area changes slightly and maintains at around 115 m² g⁻¹ after regenerated for five times. The COD removal of RHM varies with its surface area. The COD removal decreases greatly from 72.4% to 60.6% for the first three times, and maintains at around 60% afterwards. Because active carbon is difficult to regenerate and the regeneration conditions are commonly severe, water washing should be the most economical method to regenerate RHM.

4. Conclusions

In conclusion, we prepared a rice hull/MnFe₂O₄ composite (RHM) which composed of activated carbon and ferrite. The substrate of RHM is pyrolytic rice hull, where monodisperse MnFe₂O₄ nanoparticles distributed. This novel composite can remove more than 70% COD of wastewater within 6 min under the assistance of microwave radiation, and it can be used repeatedly. Because the resources of RHM including rice hull, manganese nitrate, and ferric nitrate are extensive, and their costs are low, RHM is a feasible wastewater treating-agent with advantages of low production cost and facile usage. Nevertheless, there are still some limitations. For instance, the treating efficiency of RHM is limited with maximum COD removal of 73.5%, and the COD removal mechanism of RHM has

not been proved. In the following studies, researches on the preparation conditions of RHM, wastewater treatment of RHM assisted by such as UV/O₃ oxidation, biodegradation and electrochemical methods will be preferred. It is hoped that RHM will be an economical and effective wastewater treating-agent after resolved these problems.

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