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ENHANCED DURABILITY OF Mn-SUPPORTED Fe/DIATOMITE CATALYST FOR PHENOL OXIDATION

Pham Dinh Du[1] and Huynh Thanh Danh[2,3]*

[1]Thu Dau Mot University, Ho Chi Minh City, Vietnam

[2]Giong Rieng High School, An Giang Province, Vietnam

[3]University of Sciences, Hue University, Hue City, Vietnam

**Corresponding author, Email: Danhht.c3gr@gmail.com*

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Abstract

In this paper, the Fenton-type oxidation of phenol over Mn-Fe/diatomite catalyst was studied to evaluate the catalytic activity, durability and reusability of the catalyst material. The Mn-Fe/diatomite composite was synthesised by using a hydrothermal process (at 100–150℃) from a colloidal solution containing Mn(II), Fe(III), and diatomite. Under suitable synthesis conditions, the obtained Mn-Fe/diatomite contained 6.23% Fe and 0.10% Mn (by mass) with a specific surface area of 53.2 m^2/g. Phenol conversion can reach 99% after 240 minutes of reaction on the Mn-Fe/diatomite catalyst (under the following conditions: initial phenol concentration of 1 g/L, catalyst content of 1 g/L, initial H_2O_2 content of 6.5 g/L, initial pH ~7, and reaction temperature at 50°C). The bimetallic Mn-Fe/diatomite catalyst has lower oxidation activity than the monometallic Fe/diatomite catalyst but higher durability and reusability.

Keywords: *Durability, Fenton-type, Mn-Fe/diatomite, phenol oxidation, reusability.*

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TĂNG CƯỜNG ĐỘ BỀN CỦA XÚC TÁC Fe/DIATOMITE ĐƯỢC HỖ TRỢ BỞI Mn CHO PHẢN ỨNG OXI HÓA PHENOL

Phạm Đình Dũ[1] và Huỳnh Thanh Danh[2,3]*

[1]Trường Đại học Thủ Dầu Một, thành phố Hồ Chí Minh, Việt Nam

[2]Trường THPT Giồng Riềng, tỉnh An Giang, Việt Nam

[3]Trường Đại học Khoa học, Đại học Huế, thành phố Huế, Việt Nam

**Tác giả liên hệ, Email: Danhht.c3gr@gmail.com*

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Tóm tắt

Trong bài báo này, phản ứng oxi hóa phenol kiểu Fenton trên xúc tác Mn-Fe/diatomite đã được nghiên cứu để đánh giá hoạt tính xúc tác, độ bền và khả năng tái sử dụng của vật liệu xúc tác. Composite Mn-Fe/diatomite được tổng hợp bằng quá trình thủy nhiệt (ở 100–150℃) từ dung dịch keo của Mn(II)-Fe(III) và diatomite. Ở điều kiện tổng hợp thích hợp, Mn-Fe/diatomite thu được có chứa hàm lượng nguyên tố Fe và Mn tương ứng là 6,23% và 0,10% (về khối lượng), với diện tích bề mặt riêng là 53,2 m^2/g. Độ chuyển hóa phenol có thể đạt đến 99% sau 240 phút phản ứng trên xúc tác Mn-Fe/diatomite (ở điều kiện: nồng độ phenol ban đầu 1 g/L, hàm lượng chất xúc tác 1 g/L, hàm lượng H_2O_2 6,5 g/L, pH ban đầu ~7 và nhiệt độ phản ứng ở 50℃). Chất xúc tác lưỡng kim loại Mn-Fe/diatomite có hoạt tính oxi hóa thấp hơn so với chất xúc tác đơn kim loại Fe/diatomite, nhưng có độ bền và khả năng tái sử dụng cao hơn.

Từ khóa: *Độ bền, khả năng tái sử dụng, kiểu Fenton, Mn-Fe/diatomite, oxi hóa phenol.*

1. Introduction

Advanced oxidation processes (AOPs) are considered a promising method for the degradation of organic pollutants because of their increased removal efficiency and wide range of applications, such as dyes (Aneggi *et al.*, 2024), phenols (Salem-Gaballah *et al.*, 2024), and pharmaceuticals (Odabasi and Buyukgungor, 2024). Heterogeneous Fenton-based or Fenton-like catalysts activate H_2O_2 to generate hydroxyl radicals (•OH, the main reaction species for the degradation of organic pollutants) and exhibit numerous advantages, such as high reaction rate and cost saving (Li *et al.*, 2018). The heterogeneous Fenton reaction expands the pH application range, allowing the decomposition of organic wastewater under near-neutral or even alkaline conditions. Besides, the amount of iron ions in the solution after the reaction is small, and the catalyst has stable performance, easy separation, and good recycling (Zhang *et al.*, 2021).

However, monometallic Fe often suffers from metal leaching in acidic Fenton systems, which limits the activity and practical application of the materials. For solving these problems, low-cost, efficient, environmentally friendly, and recyclable multimetal-based materials have been developed. These materials can remove pollutants from aquatic environments, presenting great environmental significance. This is one of the most crucial rapidly growing research directions to improve the performance and increase the recycling value of monometallic materials through the concept of multimetallic synergistic catalysis. Compared with monometallic materials, bimetallic materials (e.g., Fe−Cu, Fe−Co, Fe−Mn, and Cu−Co) have been evidenced to have higher pollutant removal efficiency. In general, the introduction of a second metal to fabricate a bimetallic material has the following advantages: (i) The surface of the bimetallic material has numerous active sites and defects with and high metal dispersion, thus changing the surface properties and microstructure of the monometallic material; (ii) The difference in the standard redox potential of the bimetallic material can facilitate the valence cycling and electron transfer, thus enhancing the synergistic effect of the bimetallic material in water treatment; (iii) The metal ions of the bimetallic material can provide electron to each other to carry out the ion regeneration process, thus surpassing the catalytic efficiency and stability of the monometallic material (Dong *et al*., 2023).

Several authors have demonstrated that Fe-Mn/diatomite is an effective catalyst for the decomposition of phenol with hydroperoxide (Son *et al.*, 2017), and it is a Fenton-type catalyst for the decomposition of methylene blue (Li *et al.*, 2018), or photo-Fenton decomposition of rhodamine B in aqueous solutions (Dai *et al.*, 2020).

Son *et al.* (2017) studied the wet oxidation of phenol solution using Fe–Mn/diatomite catalyst. Diatomite was used as a substrate for modification with a mixture of two metals, Fe–Mn, via the redox reaction of $KMnO_4$ and $FeSO_4$. The results showed that Fe–Mn/diatomite is an effective catalyst capable of completely oxidizing phenol. The high catalytic efficiency of Fe–Mn/diatomite is attributed to the synergistic effect of iron oxide and manganese oxide present on the catalyst. The authors investigated the leaching experiment. The results confirmed that Fe–Mn/diatomite is a heterogeneous catalyst in the phenol decomposition reaction. Li *et al.* (2018) synthesized a magnetic core-shell composite material of MnO_2/Fe_3O_4/diatomite. This material exhibited significantly enhanced Fenton-type catalytic activity with peroxymonosulfate activation in methylene blue degradation assays. Furthermore, this synthesized nanomaterial showed excellent reusability with a recycling efficiency of 86.78% after five uses for methylene blue. Dai *et al.* (2020) evaluated the Fenton catalytic activity for the photocatalytic degradation of rhodamine B dye in aqueous solution on a granular Fe_2O_3/diatomite composite doped with Mn. Their

experimental results showed that the combination of Fe and Mn in the Fe–Mn bimetallic oxide was the most important factor in improving catalytic oxidation performance compared to diatomite with only an iron trioxide coating. The stability and reusability of the composite coating of the catalyst were also studied by comparing photocatalytic performance and Fe^{3+} ion loss. The results showed that the combination of components of the Fe–Mn bimetallic oxide coating enhanced the stability of Fe^{3+} ions, preventing the loss of Fe^{3+} ions. These reports indicate that the combination of manganese oxide and iron oxide not only increases catalytic performance but also enhances catalyst stability and reusability.

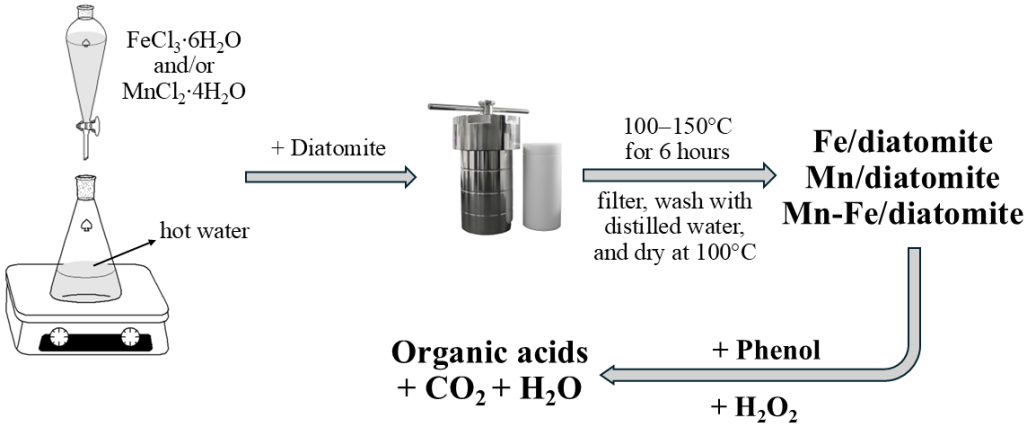
Phenolic compounds in wastewater are identified as a source of risk and danger to the environment as well as to humans. Phenol is widely known as a persistent toxicant that can increase the formation of free radicals and thus may lead to cancer or other serious health problems (Salem-Gaballah *et al.*, 2024). In this paper, a Mn-Fe/diatomite catalyst was synthesised via the hydrothermal method from a colloidal system of corresponding metals. Phenol is considered a model compound to evaluate the catalytic activity of the obtained materials in the Fenton-type reaction system. The effects of hydrothermal temperature and the Mn/Fe molar ratio in the synthesis mixture were investigated to determine the optimal synthesis conditions for producing Mn-Fe/diatomite with high catalytic activity. The catalytic activity, as well as the reusability, of monometallic (Fe/diatomite and Mn/diatomite) and bimetallic (Mn-Fe/diatomite) catalysts were also compared.

2. Experimental

2.1. Catalyst synthesis

The synthesis of Mn-Fe/diatomite was carried out as follows: (1) Slowly add 30 mL of a solution containing $FeCl_3 \cdot 6H_2O$ (Merck, India) and $MnCl_2 \cdot 4H_2O$ (Merck, Germany) into 150 mL of boiling distilled water to create a colloidal system of metals (the ratios Mn/Fe added to the reaction mixture is 1:5, 3:5, 5:5, 5:3 and 5:1 (in mmol)); (2) Take 1.0 g of diatomite (Tuy An, Phu Yen) and place it in a 200 mL steel-coated Teflon bottle and transfer the entire glue system above into the bottle; (3) Keep the bottle with the reaction mixture in a drying oven at a fixed temperature (100, 120, and 150°C) for 6 hours; (4) Cool the Teflon bottle, filter the solid product, wash several times with distilled water, and dry it at 100°C to obtain Mn-Fe/diatomite.

The Fe/diatomite and Mn/diatomite catalysts were synthesized in a similar manner, but the synthesized mixture contained only one metal, with the amount of metal added to the reaction mixture being 5.0 mmol. The synthesis process is described in Scheme 1.



Scheme 1. Synthesis process and investigation of the catalytic activity of the material

The content of elements in the samples was analysed by using energy-dispersive X-ray spectroscopy (EDX) on a JEOL (JED-2300 AnalysisStation) microscope; each sample was analysed at 3 different regions to determine the average content of the elements. The characteristic functional groups on the surface of the material were identified with FT-IR spectra recorded on a Jasco FT/IR-4600 spectrometer (Japan); the samples were dispersed on a KBr substrate. Scanning electron microscopy (SEM) images were obtained by using an S-4800 10.0 kV machine, and Transmission electron microscopy (TEM) images were obtained with an EMLab-NIHE machine at a voltage of 80 kV. X-ray diffractograms (XRD) were recorded on a Bruker D8 Advance powder diffractometer (Germany). The specific surface area was determined with the Brunauer-Emmett-Teller (BET) method from nitrogen adsorption-desorption isotherms data recorded at 77 K on a Tristar 3000 analyser; the samples were heat-treated with N_2 at 200°C for 5 h before measurement.

2.2. Phenol oxidation

0.1 g of catalyst was mixed with 100 mL of a phenol solution (Merck, Germany) at a concentration of 1.0 g/L and 2 mL of 30% (w/v) H_2O_2 (Fisher, Korea). The reaction vessel was placed on a heated magnetic stirrer at 50°C and a stirring speed of 500 rpm, with a reflux condenser. After each specified period, 5 mL of the solution was withdrawn and filtered on WHATMAN No. 42 slow quantitative filter paper (2.5 µm, Ø 110) to remove the catalyst. The concentration of the remaining phenol in the solution was determined with the HPLC (UFLC Shimadzu, Japan) method. The experimental conditions were as follows: a SPD-20A detector scanning at 254 nm, a Shim-pack GIST C18 column (particle size 5 µm, column size 4.6 × 250 mm, Shimadzu, Japan), an acetonitrile/methanol/water solvent system with a volume ratio of 1:1:8, a mobile phase speed of 1 mL/min, and a sample injection volume of 20 µL.

Phenol conversion was calculated according to formula (1).

$$\alpha(\%) = \frac{S_0 - S_t}{S_0} \times 100 \quad (1)$$

where S_0 and S_t are the phenol peak areas corresponding to the initial time and time t.

3. Results and discussion

3.1. Evaluation of catalytic activity of materials

3.1.1. Effect of metal composition

The Fe and Mn content of the catalyst samples determined by using EDX is presented in Table 1. The mass percentage of Fe in Fe/diatomite and Mn in Mn/diatomite is 22.25 and 0.31%, respectively. These values in Mn-Fe/diatomite were 5.28% for Fe and 0.19% for Mn (the samples were synthesised at 100°C and 5/5 mmol Mn/Fe). This content difference between Mn and Fe may relate to the hydrolysis constant, K_{sp}, of the metal ions in solution. The K_{sp} value of Fe(III) is more significant than that of Mn(II), in which the first hydrolysis constant $K_{sp}^{Mn(II)} = 10^{-10.58} << K_{sp}^{Fe(III)} = 10^{-2.20}$ (Brown and Ekberg, 2016). Therefore, Fe(III) ions hydrolyse substantially to form iron hydroxides and are capable of polymerizing to form FeOOH. They interacted with the hydroxyl groups (–OH) on the surface of the material in the form of adsorption to constitute composites. Therefore, the number of iron ions attached to diatomite was more substantial than that of the manganese ions.

Table 1. Elemental content of Fe and Mn of catalyst samples

Samples	General conditions		Content (wt.%)*	
	Temperature (°C)	Ratio Mn/Fe (mmol/mmol)	Fe	Mn
Fe/diatomite	100	0/5	22.25 ± 7.67	–
Mn/diatomite	100	5/0	–	0.31 ± 0.08
Mn-Fe/diatomite	100	5/5	5.28 ± 0.40	0.19 ± 0.07
	120	5/5	6.23 ± 2.12	0.10 ± 0.05
	150	5/5	18.54 ± 2.65	0.14 ± 0.06
Recovery Fe/diatomite**	100	0/5	7.12 ± 1.04	–
Recovery Mn-Fe/diatomite**	120	5/5	4.90 ± 0.94	0.07 ± 0.02

**Average of 3 EDX analysis regions; **Recovered after first use.*

The FT-IR spectra of the materials show similar characteristic absorption peaks (Fig. 1). The peaks at 1100, 797, and 470 cm^{-1} are characteristic of the vibrations of the Si–O–Si bond. The peaks in the 3700–3200 cm^{-1} region and at 1637 cm^{-1} represent the vibrations of the O–H bond, including Si–OH, Me–OH (Me is a metal), and freely adsorbed H_2O. The peak at 533 cm^{-1} is attributed to the deformation vibration of the Me–O bond (Dai *et al.*, 2021). It is noteworthy that the intensity of these absorption peaks in the modified diatomite was lower than that of the pristine diatomite, and Mn-Fe/diatomite had the lowest peak intensity. This decrease might result from the chemical interaction between the surface silanol groups and the metal oxides (Dai *et al.*, 2021).

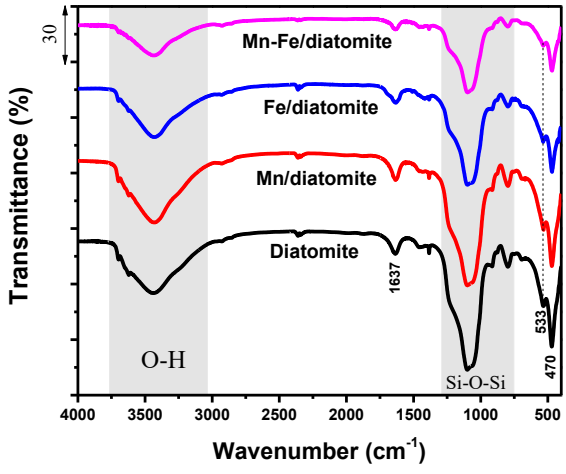


Fig. 1. FT-IR spectra of the material samples (Synthesis conditions: temperature and mmol of each metal added to the reaction mixture were 100°C and 5 mmol, respectively)

Fig. 2 compares the phenol conversion and the HPLC chromatograms of the products of phenol oxidation with H_2O_2 over different catalysts. As can be seen from Fig. 2a, the conversion increased rapidly on Fe/diatomite, reaching approximately 91% after 90 min and over 99% after 240 min of reaction. Meanwhile, with Mn/diatomite and Mn-Fe/diatomite, the reaction can be divided into two stages. The first stage (from the beginning to 120–150 min) experienced an insignificant change in the rate; the second stage (over 150 min) witnessed a rapid conversion (49% on Mn/diatomite and 74% on Mn-Fe/diatomite) until the end of the reaction.

Thus, Mn, Fe, or both on the diatomite acted as catalyst centres in the Fenton-type reaction and activated H_2O_2 to generate hydroxyl radicals (HO•) with strong oxidising capacity to decompose phenol. As Dũ *et al.* (2025) indicated, the phenol removal with H_2O_2 on unmodified diatomite only achieved about 8% conversion after 240 min of reaction under similar reaction conditions. The increased catalytic activity of Fe/diatomite is due to the high iron content in the material (22.25%); furthermore, iron is a highly active ion in the Fenton-type reaction system (Bokare and Choi, 2014).

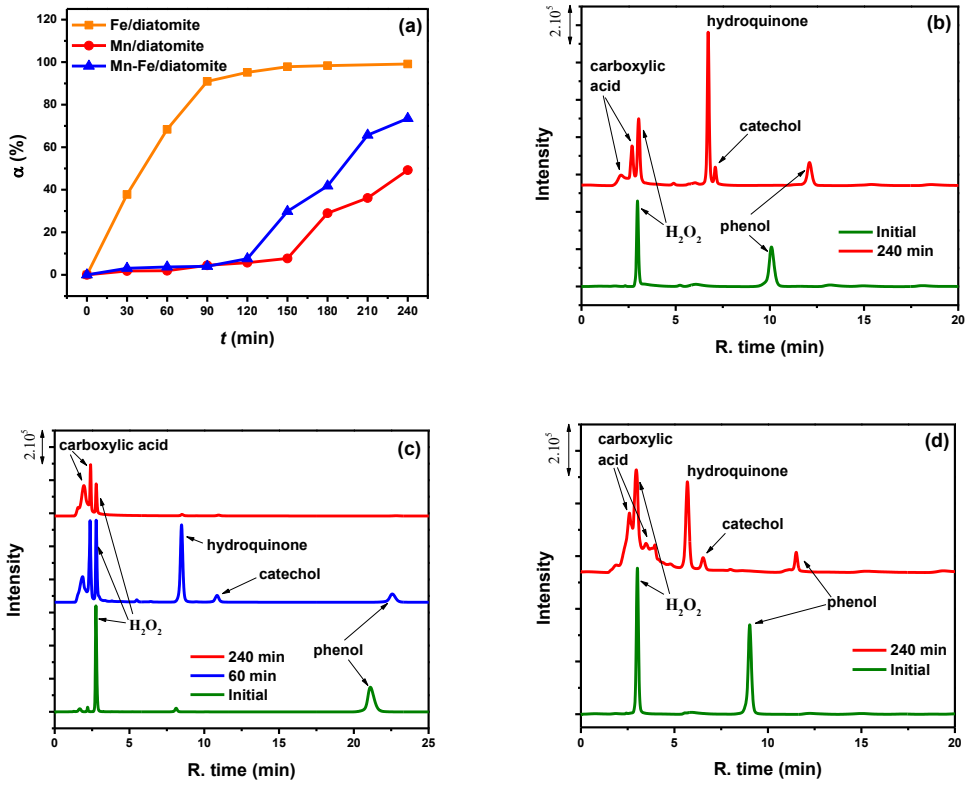


Fig. 2. a) Phenol conversion on different catalysts; HPLC chromatograms of phenol oxidation reaction solutions with H_2O_2: b) Fe/diatomite catalyst; c) Mn/diatomite catalyst; d) Mn-Fe/diatomite catalyst

Figs. 2b–d show that some intermediate products formed during the phenol oxidation process, such as hydroquinone, catechol, and carboxyl acids. It is obvious that the intensity of the characteristic peak for hydroquinone increases significantly compared with that of other products, indicating that the main intermediate product of phenol oxidation on the studied catalysts is hydroquinone. This product then opens its ring to form carboxyl acids with lower carbon numbers. On the chromatogram of the products formed on the

Fe/diatomite catalyst, the peaks of phenol, hydroquinone, and catechol are no longer observed after 240 minutes of reaction, indicating that these substances are completely decomposed. This shows that Fe/diatomite has enormous catalytic activity and can catalyse the complete decomposition of phenol to form simple carboxyl acids or completely mineralise phenol to CO_2 and H_2O. Mn/diatomite has the lowest activity among the three catalysts because the amount of Mn attached to the diatomite surface is negligible (0.31%) and also because of the low catalytic activity of Mn^{2+} form in the Fenton-type reaction (Hussain *et al.*, 2021). Mn-Fe/diatomite has an average catalytic activity. The reason for this decrease may be that the simultaneous modification of diatomite with Fe and Mn reduces the iron amount attached to the material (Table 1). Furthermore, the coexistence of Fe and Mn on the material surface may cause an antagonistic effect that limits the catalytic ability of Fe. According to Son *et al.* (2017), Fe-Mn/diatomite has a higher catalytic activity than Fe/diatomite or Mn/diatomite. These authors believed that the reason is the synergistic effect of iron oxides and manganese oxides present in the catalyst. This discrepancy may result from the different oxidation states of the Mn element in these two cases. According to our previous publication (Dũ *et al.*, 2025), diatomite modified with iron metal was unstable, and iron was easily washed into the reaction solution. Modifying diatomite with Mn and Fe does not increase the catalytic activity but improves the durability and reusability of the material. Therefore, the process of simultaneous modification of these two metals on diatomite is further investigated.

3.1.2. Effect of hydrothermal temperature and mmol Mn/Fe ratio on the catalytic activity of Mn-Fe/diatomite

Table 1 shows that the Fe content in Mn-Fe/diatomite increased significantly from 5.28 to 18.54% with hydrothermal temperature from 100 to 150°C, while the Mn content remained practically stable at around 0.1–0.2%. In general, increasing the temperature accelerated the rate of the hydrolysis reaction. Because Fe^{3+} is strongly hydrolyzed to form FeOOH precipitates, the Fe content in the obtained material increased significantly. Meanwhile, Mn^{2+} is poorly hydrolyzed in a neutral environment, so its content in the obtained material changed insignificantly (Brown and Ekberg, 2016). The phenol conversion on the Mn-Fe/diatomite synthesised at 120°C was more rapid than that on the sample synthesised at 100°C, and it is almost the same as that on the sample synthesised at 150°C (Fig. 3a). This indicates that a hydrothermal temperature of 120°C is suitable for preparing Mn-Fe/diatomite with high catalytic activity.

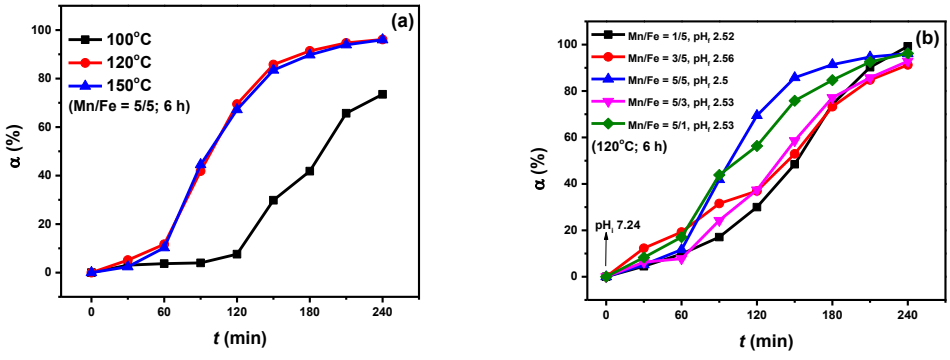


Fig. 3. Phenol conversion on Mn-Fe/diatomite samples synthesised under the following conditions: a) Different hydrothermal temperatures; b) Different mmol Mn/Fe ratios

The phenol conversion on Mn-Fe/diatomite prepared at different Mn/Fe ratios is shown in Fig. 3b. It can be seen that the catalytic activity of the catalysts remained similar. First, the conversion increased slightly over the first 60 minutes of reaction, then it rose faster and reached a high value of 91–99% after 240 minutes of reaction. The pH of the reaction solution decreased significantly from 7.24 at the beginning to about 2.5–2.56 when the reaction terminated after 240 min. This decrease was due to the formation of organic acids in the oxidation of phenol (Khieu *et al*, 2009).

In summary, the most suitable conditions for synthesising Mn-Fe/diatomite are as follows: a mmol Mn/Fe ratio of 5/5 per 1 g diatomite added to the synthesis mixture, a hydrothermal temperature of 120°C, and a time of 6 hours. Therefore, the Mn-Fe/diatomite synthesised under these conditions was selected to evaluate its durability and determine its characteristic properties.

Table 2 compares the phenol conversion in the decomposition reaction of phenol with H_2O_2 using different catalysts. Although the reaction conditions are different, it can be seen that the Mn-Fe/diatomite composite in this study is also an effective catalyst for the oxidation of phenol in aqueous solution.

3.2. Stability and characteristic properties of catalysts

The HPLC chromatograms of the products of phenol oxidation with H_2O_2 on pristine diatomite or catalyzed by the metal ions are presented in Fig. 4. As for pristine diatomite (Fig. 4a), it can be seen that the peaks representing phenol and H_2O_2 remain unchanged during the whole reaction. With the presence of the Mn(II) ion, the intensity of the characteristic peak for phenol decreased significantly right from the beginning of the reaction (compared with the case without the catalyst, only phenol and H_2O_2), and the characteristic peaks of intermediate products, such as hydroquinone and carboxylic acids, appeared. However, the peaks for phenol and hydroquinone were still visible after 120 minutes of reaction (Fig. 4b).

In the presence of Fe(III) ions or a mixture of Mn(II) and Fe(III), the peak for phenol disappears right at the beginning of the reaction, and the intensity of the carboxylic acids peaks decreased significantly after 120 minutes of reaction (Figs. 4c and 4d). This result shows that the reaction occurred rapidly, and phenol was completely decomposed, indicating that Fe(III) ions have powerful catalytic activity in homogeneous catalytic systems, which has been proven in numerous publications (Bokare and Choi, 2014). The Mn(II) ions in the H_2O_2/Fe(III)-Mn(II) homogeneous catalyst system has almost no effect on the reaction rate. However, the type of carboxylic acids formed may be different (because of the difference in the time these products remain in the two catalyst systems). These results also indicate that the catalytic activity of Mn(II) is significantly lower than that of Fe(III) in the homogeneous Fenton-type reaction system. The same situation also occurs in heterogeneous systems, and the phenol conversion on the Mn/diatomite catalyst is significantly lower than that on the Fe/diatomite catalyst. Notably, the presence of Mn in Mn-Fe/diatomite reduces the catalytic activity of iron (Fig. 2a).

The oxidation of phenol often produces carboxylic acids that substantially reduce the pH of the reaction solution (the pH after 240 minutes of reaction is 2.5, Fig. 3b). Therefore, the metal in the catalyst can leach into the solution; from this point, the reaction can also occur as in a homogeneous catalytic system. This is why the phenol conversion continues to increase rapidly even after the solid catalyst is removed. The experimental results of metal leaching on the Mn-Fe/diatomite catalyst are shown in Fig. 5a. After filtering the material just after 90 minutes of reaction, the conversion rate only increased slightly, meaning that the

reaction occurred significantly more slowly than in the presence of Mn-Fe/diatomite. The recovered Fe/diatomite and Mn-Fe/diatomite after the first use were also subjected to EDX measurement. The results show that the iron element content in the recovered Fe/diatomite sample was only 7.12% compared with the initial 22.25% (Table 1); in the recovered Mn-Fe/diatomite sample, the Fe and Mn element contents decreases to 4.90 and 0.07%, respectively, compared with the initial 6.23 and 0.10% (Table 1). This indicates that the metals in the Mn-Fe/diatomite material leached into the solution insignificantly, while the iron content in Fe/diatomite lost about 70% of its original value.

Table 2. Decomposition of phenol using H_2O_2 as an oxidizing agent on different catalysts

Catalysts	Phenol conversion (%)	pH	Experimental conditions	References
Mn-Fe/diatomite	99	No adjustments	Initial [phenol] = 1.0 g/L, [H_2O_2] = 0.192 mol/L, catalyst dosage = 1 g/L, reaction time = 4 h, temperature = 50°C	This work
$CuFe_2O_4$/NBR (Nitrile Butadiene Rubber)	85.4	4.208	Initial [phenol] = 300 mg/L, H_2O_2/catalyst (w/w) = 14.35, reaction time = 69.586 min (Response surface methodology)	Salem-Gaballah *et al.*, 2024
Iron-containing palygorskite clay	94 (the COD degradation efficiency of phenol)	3	Initial [phenol] = 100 mg/L, [H_2O_2] = 30 mmol/L, catalyst dosage = 0.5 g/L, reaction time = 15 min, temperature = 20°C	Xu *et al.*, 2021
Mn-Diatomite	0	4.7	Initial [phenol] = 1.0 g/L, [H_2O_2] = 6.6 g/L, catalyst dosage = 0.5 g/L, reaction time = 110 min, temperature = 90°C	Son *et al.*, 2017
Fe-Diatomite	100	4.7	Initial [phenol] = 1.0 g/L, [H_2O_2] = 6.6 g/L, catalyst dosage = 0.5 g/L, reaction time = 110 min, temperature = 90°C	Son *et al.*, 2017
FeMn-Diatomite	100	4.7	Initial [phenol] = 1.0 g/L, [H_2O_2] = 6.6 g/L, catalyst dosage = 0.5 g/L, reaction time = 50 min, temperature = 90°C	Son *et al.*, 2017
Fe-MCM-41(10,7)	95	No adjustments	Initial [phenol] = 2.5 g/L, [H_2O_2] = 0.558 mol/L, catalyst dosage = 0.01 g/L, reaction time = 30 min, temperature = 70°C	Khieu *et al*, 2009

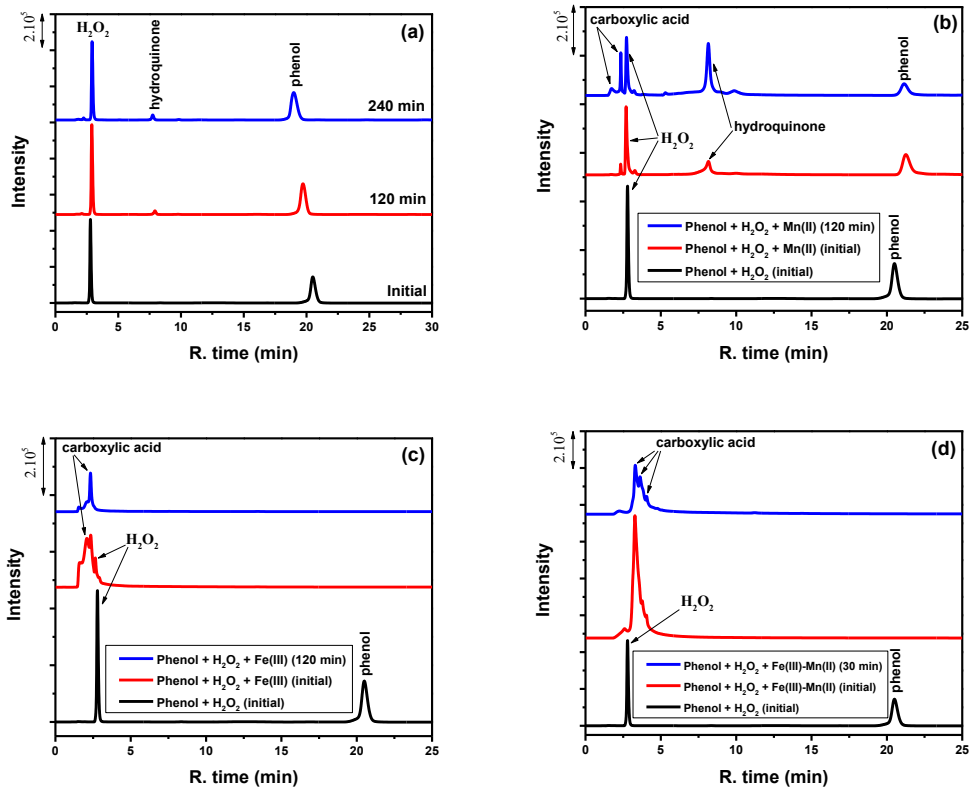


Fig. 4. HPLC chromatograms of phenol oxidation reaction solutions with H_2O_2: a) Diatomite catalyst; b) Mn(II) catalyst (5 mmol/L); c) Fe(III) catalyst (5 mmol/L); d) Mn(II) (5 mmol/L) and Fe(III) catalysts (5 mmol/L)

The catalyst after reaction was recovered and reused, and its reusability was evaluated. It can be seen that the phenol conversion on the Mn-Fe/diatomite catalyst still reached a high value in the third use (85%, Fig. 5b). Meanwhile, the phenol conversion decreased sharply on the Fe/diatomite catalyst in the second and third uses (only 22–12%) compared with the first use (99%), indicating that Mn-Fe/diatomite has very high durability and reusability.

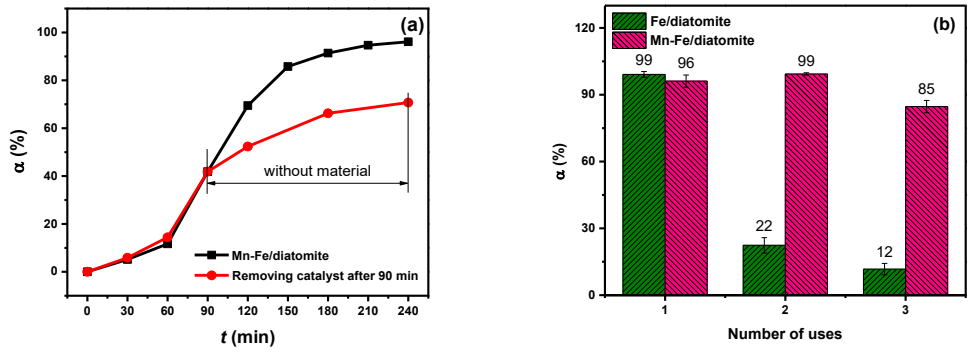


Fig. 5. Leaching (a) and reusing (b) experiments (Phenol conversion after 240 min of reaction, each experiment was repeated three times)

The SEM and TEM images of diatomite and Mn-Fe/diatomite are presented in Fig. 6. It can be seen that diatomite contains cylindrical and disc-shaped structures with about 50 nm diameter pores (Fig. 6a). For Mn-Fe/diatomite (Fig. 6b), there are dark black clusters on the diatomite background with a diameter of about 50-100 nm. This new morphology indicates the presence of the Mn and Fe elements. The mapping of the Mn and Fe elements also shows that manganese and iron are evenly distributed over the surface area of the material (Fig. 7).

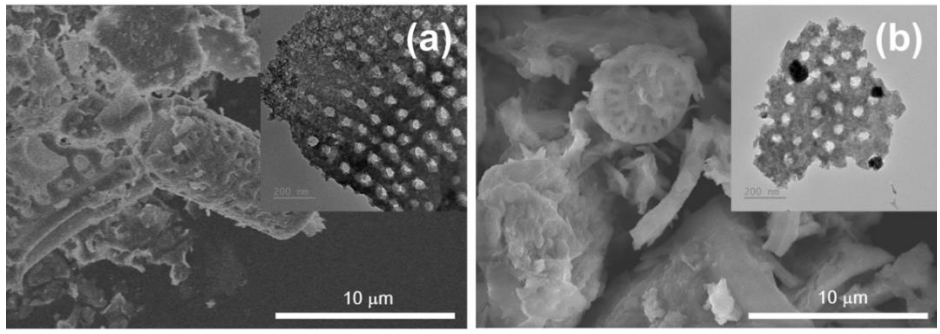


Fig. 6. SEM and TEM images (inset): a) Diatomite; b) Mn-Fe/diatomite (Synthesis conditions: mmol ratio Mn/Fe = 5/5, hydrothermal temperature and time are 120°C and 6 h)

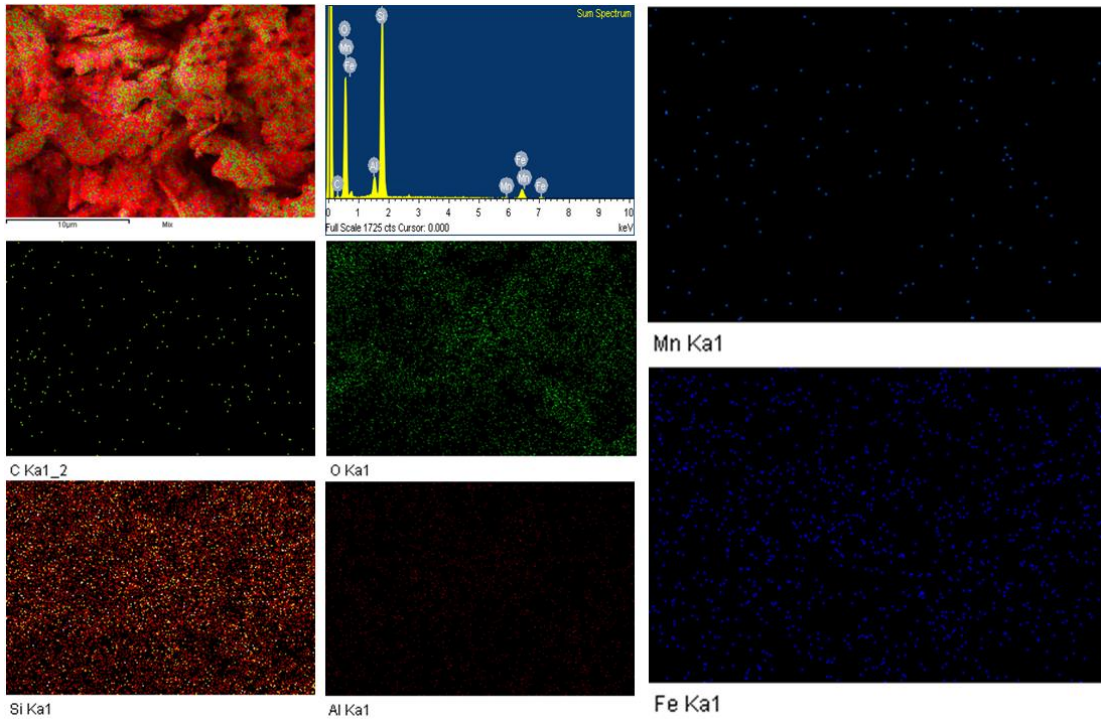


Fig. 7. EDX Spectrum and elemental distribution image of Mn-Fe/diatomite (Synthesis conditions: mmol ratio Mn/Fe = 5/5, hydrothermal temperature and time are 120°C and 6 h)

The XRD patterns and isotherms of diatomite and Mn-Fe/diatomite are displayed in Fig. 8. The diffractogram displays no characteristic peaks of metals. The absence of the peaks is probably due to tiny metal clusters formed with low crystallinity, or even they are amorphous. Similar XRD patterns are published in the literature (Dai *et al.*, 2021; Son *et al.*, 2017). Both diatomite and Mn-Fe/diatomite exhibited type II isotherms with large hysteresis loops of type H3, indicating the existence of large pores with irregular sizes and shapes. The pore-size distribution curve (Fig. 8c) indicates that diatomite has pores of about 4.3 nm in diameter, while the Mn-Fe/diatomite sample has smaller pores (3.9 nm). This decrease is caused by the layer of metal oxides coating the surface. The porous properties of diatomite and the Mn-Fe/diatomite sample are listed in Table 3. The specific surface area of diatomite and Mn-Fe/diatomite is 55.4 and 53.2 m^2/g, respectively. These similar values indicate that the modification process had little effect on the structure of the support. The metal oxides partially covered the pores but did not disrupt the microstructure of the substrate material.

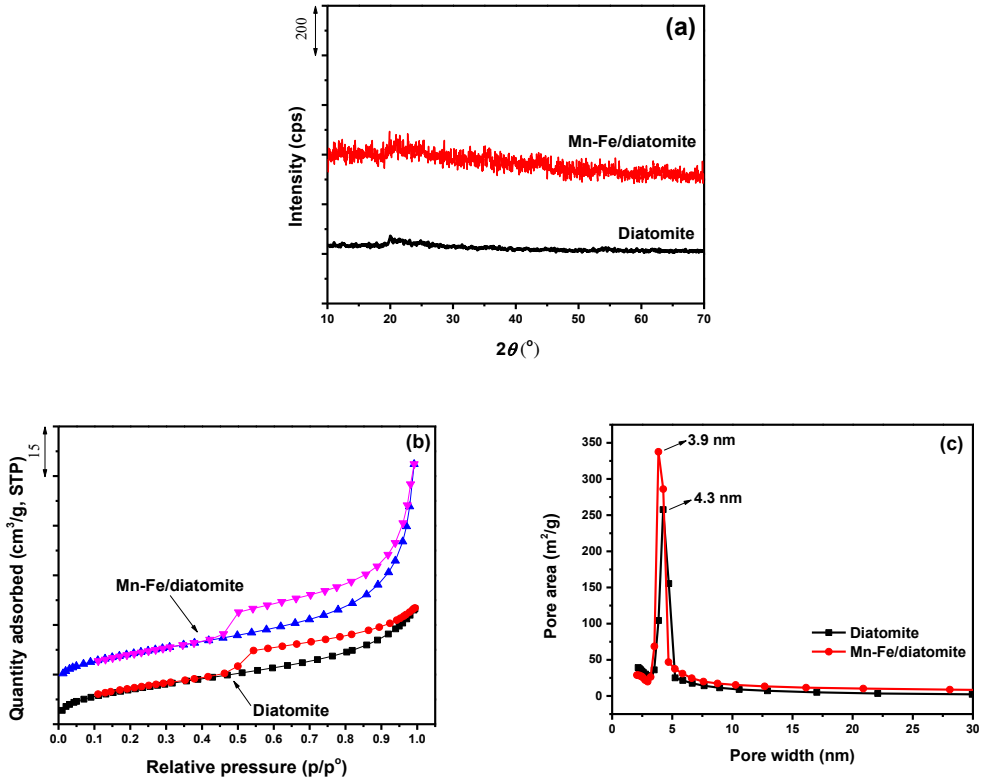


Fig. 8. XRD patterns (a), nitrogen adsorption-desorption isotherms (b), pore-size distributions (c) of diatomite and Mn-Fe/diatomite (Synthesis conditions: mmol ratio Mn/Fe = 5/5, hydrothermal temperature and time are 120°C and 6 h)

Table 3. Textural properties of catalyst samples

Sample	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	V_{mic} (cm^3/g)	V_{tot} (cm^3/g)
Diatomite	55.4	19.2	36.2	0.0088	0.0513
Mn-Fe/diatomite	53.2	16.7	36.5	0.0078	0.0996

4. Conclusion

In this paper, the Mn-Fe bimetallic composites on diatomite support were successfully synthesised from a colloidal system of Mn(II)-Fe(III) under the following conditions: a 5/5 mmol Mn/Fe ratio per 1 g of diatomite added to the initial synthesis mixture, a temperature of 120°C, and a time of 6 hours. The composites contained 6.23% Fe and 0.10% Mn (by mass), with a specific surface area of 53.2 m^2/g. The catalytic activity of Mn-Fe/diatomite composite lies between that of Fe/diatomite and Mn/diatomite. However, the presence of Mn in the Mn-Fe/diatomite composite reduced the leaching of metal into the reaction solution at low pH (2.5–2.56) and increased the reusability of the catalyst. After three cycles of reuse, the phenol conversion rate decreased sharply from 99% to 12% on the Fe/diatomite catalyst, while on the Mn-Fe/diatomite catalyst it only decreased from 96% to 85%. The Mn-Fe/diatomite composite exhibited high activity and long-term durability under Fenton-type conditions. This material can be applied as a catalyst in the phenol decomposition with H_2O_2 as an oxidising agent.

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