

COMPARISON OF CATALYTIC ACTIVITIES OF MAGNETIC IRON OXIDES IN PHENOL DEGRADATION

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ABSTRACT

Magnetic iron oxide-based materials have attracted great attention in catalysis due to their high activity, large availability, and easy catalyst collection and recycling. This work reports catalytic activities of magnetic iron oxides, which were synthesized via two different routes involving organic stabilizers, for the heterogeneous Fenton-like oxidation of phenol. Two kinds of catalysts, including crystalline Fe_3O_4 and amorphous nano-sized iron oxide particles, were formed according to the XRD and SEM data. Effects of reaction time, hydrogen peroxide amount, and solid catalyst on phenol degradation efficiency using the as-synthesized materials were investigated. The results showed that the synthesized crystalline Fe_3O_4 particles (1–5 μm) provided a higher overall phenol removal efficiency than the amorphous nano-sized iron oxide under similar reaction conditions. However, the initial oxidation rate was much faster by using the amorphous one. More than 98% phenol removal was obtained with the crystalline Fe_3O_4 after 60 min, while a similar efficiency was also achieved with the amorphous nano-sized iron oxide after 15 min but at significantly higher catalyst and H_2O_2 amounts.

Keywords: Fenton reaction, phenol degradation, iron oxides, magnetic.

1. INTRODUCTION

The great development of science and technology has a positive impact on the enhancement of human life quality these days; however, the world is also facing unexpected side effects of severe environmental pollution. Therefore, environmental protection and treatment have become a very urgent and important task for scientists and researchers worldwide. Phenols and phenol derivatives are very common pollutants discharged from various industrial processes such as petroleum refining, petrochemicals, production of pharmaceuticals, paper, plastics, coloring preparations, detergents, pesticides, and herbicides [1, 2]. To remove phenol compounds from wastewaters, a number of methods, including oxidation by oxygen in aqueous solution, electrochemical oxidation, adsorption, biodegradation, and Fenton (or Fenton-like) oxidation, have been studied and implemented [1, 3].

Recently, a heterogeneous Fenton-like process has emerged as a powerful solution for removing organic pollutants such as phenol and phenol derivatives. This process employed hydrogen peroxide and solid redox catalysts to degrade organic matters [4]. The catalytic decomposition of H_2O_2 results in the formation of hydroxyl ($\cdot\text{OH}$) and per hydroxyl radicals ($\cdot\text{HO}_2$), which are robust oxidants to mineralize organic matters into H_2O and CO_2 [3]. Iron oxide-based Fenton catalysts have always received great interest for both research and practical applications, especially in environmental treatment, owing to their effectiveness, large availability, and reasonable cost [5]. Moreover, the magnetic ferric oxides are more advantageous for accessible collection and recycling of the used materials. Zelmanov *et al.*

reported the high performance of iron oxide-based nanoparticles as catalysts for the degradation of ethylene glycol and phenol [6]. W. Wang *et al.* reported the synthesis and utilization of nano Fe_3O_4 materials, without using any surfactant or capping agent during the synthesis process, as a heterogeneous Fenton catalyst to remove phenol at a wide pH range [5]. In another work, Guohui Qi *et al.* studied phenol degradation in microbial fuel cells with a Fe_3O_4 -reduced graphene oxide cathodic catalyst [7].

Many forms of iron oxides (such as goethite, hematite, magnetite, and ferrihydrite) have been found to be capable of transforming H_2O_2 into reactive free radicals. According to literature, this capacity is governed by some important properties such as surface area, particle size, and crystallinity. These properties depend essentially on the synthesis approach [8]. In this study, two synthesis routes were adopted to fabricate magnetic iron oxide catalysts and their application in the Fenton-like oxidation of phenol. Oxalic acid and polyvinyl pyrrolidone (PVP) were employed as stabilizers in the synthesis process as these substances contain groups that have a strong coordination affinity to ferric ions and thus possibly prevent them from aggregating into large crystals [9, 10]. The resulting materials were characterized using XRD and SEM. In application for phenol degradation, effects of reaction conditions including reaction time, hydrogen peroxide concentration, and catalyst amount, are investigated in detail.

2. MATERIALS AND METHODS

2.1. Chemicals

Phenol (99%), oxalic acid (99,5%), hydrogen peroxide (30%), iron (II) sunfat heptahydrate. (99%), potassium ferricyanide (99,5%), 4-aminoantipyrine (99%), ammonia solution (25%), ammonium chloride (99,5%) and polyvinyl pyrrolidone (PVP) were purchased from Xilong Chemical Co.Ltd. (Shantou, China).

2.2. Synthesis of iron oxides

In the first method, iron oxide was fabricated by using NH_4OH as a precipitating agent and oxalic acid as an electrostatic stabilizer [9]. Firstly, a solution of 50 mL of H_2O containing 2.28 g $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was stirred, heated to 50 °C, and subsequently mixed with a solution of 50 mL H_2O containing 5.56 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Next, the ammonia solution was added drop-wise to the mixture. The received precipitates were washed several times with DI water until the pH reached the neutral value before being dried in an oven at 110 °C for 3 h. Finally, the powder was calcined at 300 °C for 2h and the resulting iron oxide was labeled S1.

In another method, iron oxide was synthesized following the procedure previously used to fabricate Fe_3O_4 nanoparticles by J. Liu *et al.* [10]. A solution of 0.02 M NaOH, 2.78 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and 1.5 g PVP was stirred and heated at 70 °C until the mixture was completely dissolved. Then, the solution was transferred to a thermostatic bath and stabilized at 70 °C for 2 h. The resulting suspension was centrifuged and collected precipitates were washed with ethanol and distilled water several times until pH reached the neutral value. Finally, the received powder was dried in the oven at 50 °C and the resulting iron oxide was labeled S2.

2.3. Evaluation of influencing factors

Experiments for phenol degradation were performed as follows. A determined mass of iron oxides and a determined volume of H_2O_2 solution were added together to a 40 mL aqueous solution of phenol in a conical flask. The mixture was shaken for a predetermined time (KS260, German) and then the catalyst was separated from the solution by centrifugation at 5000 rpm for 5 min (HERMLE Z206A, German). The supernatant was collected for phenol analysis

referred to the Vietnam Standard TCVN 6216:1996 (ISO 6439: 1990). The procedure for analyzing phenol content in the sample is described as follows. A determined amount of phenol solution, which depended on the dilution factor, was mixed with 0.25 mL of pH = 10 buffer, 0.1 mL of 4-amino antipyrine solution and 0.1 mL of potassium ferricyanide solution to form red-orange complex. The solution was diluted in a 25-mL volumetric flask, left in dark for 10 min and then subjected to analysis (UV-Vis JENWAY 6305, wavelength of 510 nm). The calibration curve was constructed in the range 0.5-7 ppm.

To examine the effect of time on catalyst performance, phenol treatment efficiency was measured at different times within 2h. The H_2O_2 volume was fixed at 35 μL . The catalyst mass was fixed at 0.05 g. Influence of H_2O_2 amount on treatment efficiency was examined in the H_2O_2 volume range 0–70 μL at the catalyst mass of 0.05 g and reaction time of 30 min. The influence of varying catalyst mass was examined at three points of 0.0250, 0.0500, and 0.075 g. The initial concentration of phenol solutions used for all experiments was fixed at 200 ppm ($V = 40 \text{ mL}$). Each experiment was performed 3 times to get mean values.

2.4. Characterization of materials

The scanning electron microscopy imaging was performed on a JSM IT-200 (Japan). X-ray diffraction analyses were performed with a D2 Phaser. Typical radiation conditions were 30 kV, 10 mA, Cu K_α radiation ($\lambda = 1.54\text{\AA}$) and 2 theta in range of 5 – 80°. These characterizations were conducted at Viet Duc Center- Ho Chi Minh City University of Food Industry.

3. RESULTS AND DISCUSSION

3.1. Characteristics of synthesized iron oxides

The iron oxide received from the fabrication route S1 has a dark-brown color and was strongly attracted by a magnet showing a good magnetic property (Figure 1). The fabrication route S2 provided the yellow-brown oxide powder, which is likely in hydrated form. S2 was not as active as S1 under the effect of a magnet. The SEM image of S1 shows the presence of discrete Fe_3O_4 particles of 1–5 μm , while S2 has much smaller grains at nano sizes and some zones indicate the formation of large aggregates (Figure 2).

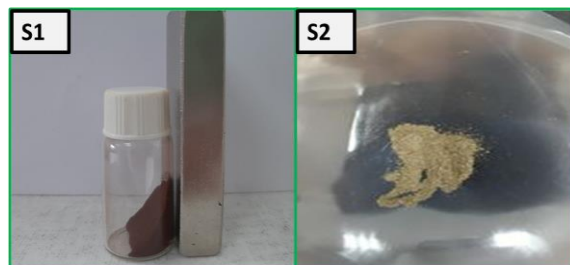


Figure 1. Iron oxides received from the fabrication route 1 and 2

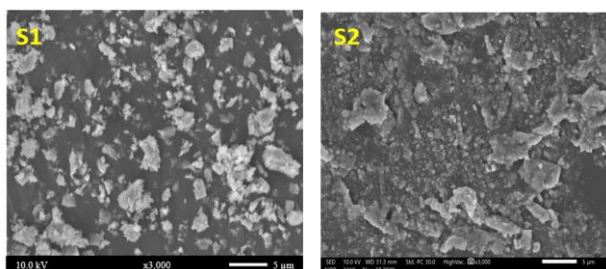


Figure 2. SEM images of S1 and S2

The XRD pattern of S1 (Figure 3a) shows typical diffraction peaks of magnetite (Fe_3O_4) at 30.15° ; 36.27° ; 43.32° ; 53.89° ; 57.13° and 62.29° corresponding to the (220), (311), (400), (422), (511) and (440) crystalline planes, respectively [11]. In addition, small shoulders around 32° and 49° were detected and could be assigned to the presence of hematite $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS card No. 33-0664, 19-0629, and 70-1522 for hematite and magnetite, respectively). The XRD results indicate that the majority phase of S1 is magnetite with a small presence of hematite. This further explains why the powder does not have the typical black color of the pure magnetite but has a dark-brown color. A small number of iron species was possibly transformed to separate hematite phases during the calcination process. The dark-brown color of the mixture of hematite (minor phase) and magnetite (major phase) was also previously reported by N. Mufti *et al.* [12]. On the other hand, the amorphous phase is the major phase of S2 and the only crystalline plane of iron oxides was detected at around 35.8° (Figure 3b).

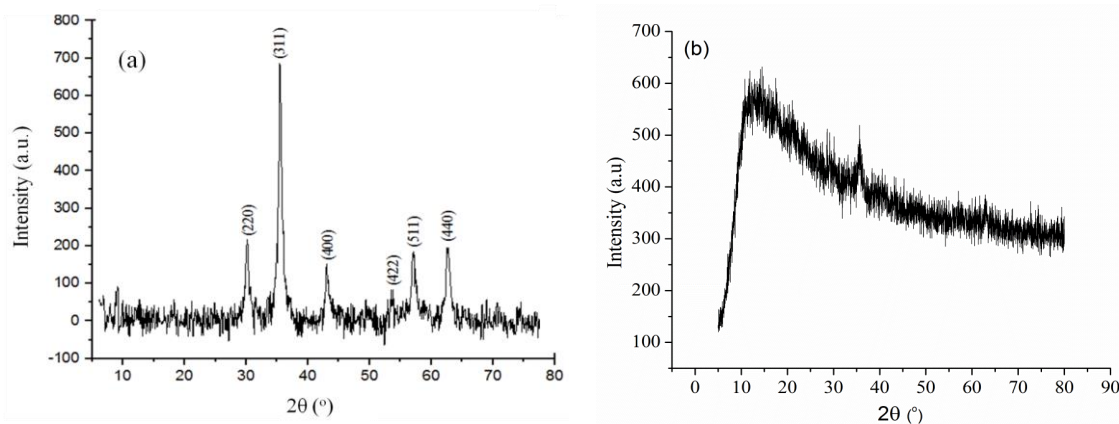


Figure 3. XRD patterns of S1 (a) and S2 (b)

3.2. Catalytic performance in phenol degradation

3.2.1. Effect of reaction time

For the Fenton-like reaction with S1 catalyst, the phenol degradation rate was fast in the first 15 min (from around zero level to 87%) and slowed down until remaining almost unchanged after 60 min (98.2%). Further increasing reaction time to 90 min did not considerably change the treatment efficiency (Figure 4). The degradation reaction with S2 occurred much stronger in the first 5 min and the efficiency fluctuated at about 69% from 15 min. S1 and S2 catalysts required 60 and 15 min to reach the highest degradation efficiency. Interestingly, although S2 had a more kinetic advantage at the beginning, S1 appeared more efficient in general as the final treatment efficiency reached about 93%, which is about 1.3 times higher than that obtained with S2. It can be explained that the smaller-sized grains of S2 (according to SEM image) contribute to the initial fast reaction rate but the majority of the crystalline phase (according to XRD pattern) allow for the higher overall catalytic performance of S1. This finding agrees well with the literature indicating the prevailing effect of crystallinity of iron oxide over the surface area on catalytic activity [8].

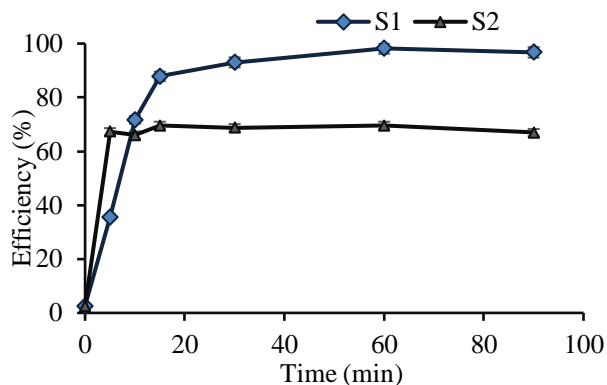
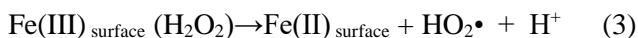
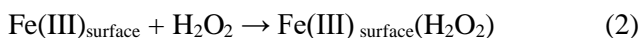


Figure 4. Effect of time on phenol degradation efficiency

3.2.2. Effect of H_2O_2 amount

The effect of increasing H_2O_2 volume from zero to 70 μL on phenol treatment efficiency is presented in Figure 5. In general, higher H_2O_2 content supports higher treatment efficiency for both catalysts. According to literature, higher content of H_2O_2 could promote more interaction between H_2O_2 and iron oxides, thereby generating more hydroxyl radicals active for phenol degradation via the following reactions [4]:



According to the obtained results, 35 μL H_2O_2 is at least required for the two catalysts to achieve significant phenol degradation under the tested reaction conditions. For S1, the efficiency increased significantly when increasing H_2O_2 volume to 35 μL and a further addition to 70 μL did not change the efficiency. For S2, the efficiency increased gradually until 70 μL but a much stronger effect of H_2O_2 amount was observed in the range 0–35 μL . Compared to the activity of S2, that of S1 was influenced more significantly in the H_2O_2 range 10–35 μL and reached a maximum level sooner. However, it should be noted that the excess H_2O_2 may also react with the hydroxyl radicals, thereby reducing the oxidizing capacity, when the H_2O_2 content is too high [13].

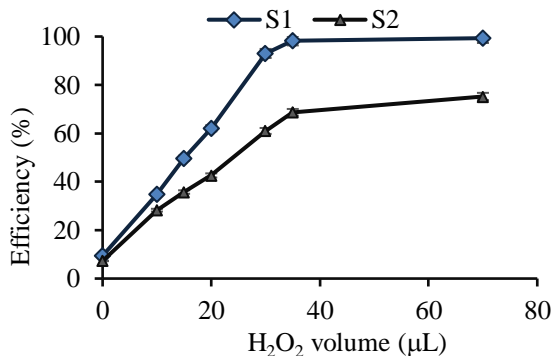


Figure 5. Effect of H_2O_2 amount on phenol degradation efficiency

3.2.3. Effect of catalyst amount

Effect of catalyst amount on phenol degradation efficiency was investigated at 0.025, 0.05 and 0.075 g (equivalent to 0.0625, 0.125 and 0.1875% (w/v)) with the results shown in Figure 6.

The degradation efficiency improved significantly as the mass of the two catalysts increased from 0.025 to 0.05 g as a result of the presence of more active sites for the degradation reaction. Increases in the efficiency by nearly 23% and 30% were recorded for S1 and S2, respectively, when the catalyst amount doubled from 0.025 to 0.05 g. Further increase of the catalyst amount to 0.075 g, however, offered just a slight enhancement in the performance. These results show that the catalyst mass of 0.05 g, or the solid to solution ratio of 0.125%, is sufficient for phenol degradation under tested reaction conditions.

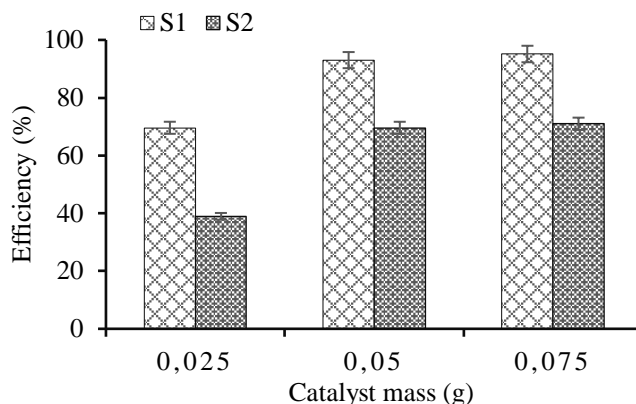


Figure 6. Effect of catalyst mass on phenol degradation efficiency

3.2.4. Reaction conditions for high removal efficiencies

The reaction conditions for phenol degradation using the two catalysts, including the catalyst mass/solution volume ratio, H_2O_2 /solution volume ratio, and required time to obtain more than 98% degradation efficiency (at phenol concentration of 200 ppm) are listed in Table 1. It can be seen that, in order to achieve nearly complete degradation of phenol, the crystalline Fe_3O_4 particles (S1) required much less H_2O_2 amount but a longer reaction time as compared to the amorphous nano-sized iron oxide (S2). Meanwhile, S2 is more advantageous in terms of shorter reaction time at the compensation of higher amounts of the catalyst or H_2O_2 .

Table 1. Comparison of the reaction conditions for two catalysts to achieve high phenol degradation activity

Material	Catalyst amount / solution volume ratio (% , w/v)	H_2O_2 ratio (% , v/v)	Reaction time (minimum required) (min)	Removal percentage (%)
Crystalline Fe_3O_4 particles (S1)	0.125	0.0875	60 min	98.29
Crystalline Fe_3O_4 particles (S1)	0.125	1.75	60 min	99.32
Amorphous nano-sized iron oxide (S2)	0.125	2.625	15 min	98.41
Amorphous nano-sized iron oxide (S2)	0.1875	2.625	15 min	99.05

4. CONCLUSION

This study reports the synthesis of iron oxide catalysts for efficient phenol degradation by using two different synthesis routes. Two kinds of materials, including the crystalline Fe_3O_4 particles and the amorphous nano-sized iron oxide, were produced according to SEM and XRD data. Both catalysts were found to exhibit remarkable performance in the Fenton-like oxidation of phenol. The crystalline Fe_3O_4 particles required much less H_2O_2 but longer reaction time compared to the amorphous nano-sized iron oxide to achieve nearly complete degradation of phenol. On the other hand, the amorphous nano-sized iron oxide was more advantageous in terms of shorter reaction time. For approximate 99% removal of phenol, reaction conditions with the crystalline Fe_3O_4 were found at the catalyst /solution ratio of 0.125% (w/v), H_2O_2 /solution volume ratio of 1.75%, and reaction time of 60 min. A similar efficiency was obtained with the amorphous nano-sized iron oxide at the catalyst/solution ratio of 0.1875% (w/v), H_2O_2 /solution volume ratio of 2.625%, and reaction time of 15 min.

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TÓM TẮT

SO SÁNH HOẠT TÍNH XÚC TÁC CỦA CÁC OXIT SẮT MANG TỪ TÍNH TRONG PHẢN ỨNG PHÂN HỦY PHENOL

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Các vật liệu mang từ tính trên nền oxit sắt luôn thu hút được sự chú ý lớn trong lĩnh vực xúc tác do chúng có độ hoạt động hóa học cao, nguồn cung cấp rộng, cũng như dễ thu hồi và tái sử dụng. Nội dung chính của nghiên cứu này là khảo sát hoạt tính xúc tác của các loại oxit sắt, được tổng hợp qua hai quy trình khác nhau, trong phản ứng dị thể kiểu Fenton để phân hủy phenol. Dữ liệu phân tích XRD và SEM cho thấy hai loại oxit sắt là Fe_3O_4 tinh thể và oxit sắt vô định hình kích thước nano đã được tạo thành. Ảnh hưởng của thời gian phản ứng, lượng hydrogen peroxide và lượng chất xúc tác rắn lên hiệu suất loại bỏ phenol đã được khảo sát chi tiết. Kết quả cho thấy vật liệu từ tính Fe_3O_4 tinh thể (1-5 μm) cho hiệu suất xử lý phenol cao hơn so với vật liệu oxit sắt vô định hình kích thước nano trong cùng điều kiện phản ứng. Tuy nhiên, tốc độ oxy hóa phenol ban đầu nhanh hơn nhiều khi dùng vật liệu xúc tác oxit sắt vô định hình. Hiệu suất loại bỏ phenol hơn 98% (nồng độ ban đầu 200 ppm) đã đạt được với xúc tác Fe_3O_4 tinh thể sau 60 phút. Vật liệu oxit sắt vô định hình cũng cho hiệu suất tương đồng chỉ sau 15 phút nhưng cần lượng chất xúc tác và lượng hydrogen peroxide cao hơn đáng kể so với xúc tác Fe_3O_4 tinh thể.

Từ khóa: Phản ứng Fenton, phân hủy phenol, oxit sắt, từ tính.