One-Step Preparation of Rice Husk-Based Magnetic Biochar and Its Catalytic Activity for p-Nitrophenol Degradation

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In this study, magnetic biochar was successfully synthesized via one-step pyrolysis of $FeCl_3$-loaded rice husk. Properties of the obtained magnetic biochar were determined by X-ray powder diffraction, SEM image, nitrogen adsorption isotherm, and vibrating sample magnetometer. The results revealed that magnetic Fe_3O_4 particles along with zero-valent iron particles were formed over biochar support at 600 °C in 2 h. The magnetic biochar samples were subsequently utilized as oxidation catalysts for p-nitrophenol degradation by H_2O_2. Parameters including pH value, H_2O_2 concentration, biochar catalysts with different Fe-loaded contents were investigated. At high pH 6, 540 ppm H_2O_2 and 0.1 g magnetic biochar with 20 wt% Fe-loaded content, 99.8% p-nitrophenol could be removed after 90 min treatment. In addition, magnetic biochar particles could be removed from the treated solution by magnets easily. Overall, eco-friendly magnetic biochar can potentially be an effective catalyst for p-nitrophenol treatment in wastewater.

1. Introduction

Rice husk has been well-known as a typical agricultural waste with annual world production of appropriately 150 million tons (Pode, 2016). This biomass is normally burned in landfills (Azat et al., 2019) and releases a huge amount of CO_2 greenhouse gas into the atmosphere (Thines et al., 2017). Therefore, pyrolysis of rice husk into biochar can result in advantages like energy production, sustainable waste recycling and carbon sequestration (Vakalis et al., 2018). The eco-friendly and cost-effective biochar can be utilized for various purposes such as a soil amendment, an adsorbent for removal of various wastewater contaminants (Thines et al., 2017), and a catalyst supporting material (Vuppala et al., 2018).

In recent years, Fe_3O_4 nanomaterials have been receiving increasing interest due to their magnetic properties and catalytic activities. The magnetic particles can be easily separated from mixture by an external magnetic field (Vuppala et al., 2018). On the other hand, Fe_3O_4 nanoparticles can be used as a heterogeneous catalyst for effective degradation of organic compounds in wastewater. To prevent magnetic nanoparticles from aggregating into larger species and recover biochar after adsorption treatment, much effort has been made to disperse magnetic particles on biochar (Shirinova et al., 2016). The obtained iron oxide/biochar composite is known as magnetic biochar (MBC).

Magnetic biochar is commonly prepared through chemical coprecipitation of available biochar. This method not only is a complex process, but also triggers negative impact on the porosity of MBC product. One-step pyrolysis of $FeCl_3$-loaded biomass is newly introduced for synthesis of MBC. The facile method can form magnetic iron oxide particles and activate carbon surface simultaneously during pyrolysis, as reported by Yang et al. (2016). As reviewed by (Thines et al., 2017), MBC was explored for different applications such as supercapacitor production, adsoprtion of arsenic, heavy metal ions, organic dyes, antibiotics, pesticides. Conversely, very few studies regarding catalytic activity of MBC were found in the literature. Recent research mainly focuses on the adsorption ability of carbon support and recoverability of magnetic particles and does not pay attention on the catalytic activities of Fe_3O_4 particles for complete oxidation of organic compounds. To valorize rice husk biomass, reduce CO_2 emission and expand MBC application, the objectives of the current research are successful one-step conversion of rice husk to MBC and its potential utilization as a heterogeneous Fenton catalyst for p-nitrophenol degradation.

2. Materials and methods

2.1 Material and reagents

p-Nitrophenol (99 wt%), $FeCl_3.6H_2O$ (99 wt%), H_2O_2 solution (30 wt%), $Na_2S_2O_3$ (98 wt%), NaOH (97 wt%) and H_2SO_4 (97 wt%) were purchased from Sigma-Aldrich. Raw rice husk used in this study was collected from My Nhon Village, Ba Tri District, Ben Tre Province, Vietnam. The biomass was washed with distilled water and dried in an oven at 100 °C within 18 h. The dried material was then crushed and sieved to obtain particle size between 0.25 and 0.50 mm.

2.2 Preparation of magnetic biochar

5.0 g dried rice husk was firstly added into 100 mL $FeCl_3$ solution with appropriate concentrations in a flask. Fe-load content was the weight ratio of the Fe element in $FeCl_3$ solution and the dried rice husk. The mixture was then stirred by a magnetic bar in 15 h, evaporated and dried at 100 °C in 18 h. To obtain MBC, 2.0 g of the dried $FeCl_3$-loaded rice husk was placed in a glass cylinder tube (diameter of 3 cm x length of 25 cm) under a continuous nitrogen flow of 200 mL/min. The material was heated to 500, 600 or 700 °C with a heating rate of 10 °C/min and the temperature was maintained constantly in 1, 2 or 4 h. After the pyrolysis finished, the tube was allowed to cool to room temperature. The weights of the tube containing the sample before and after pyrolysis were measured to determine MBC yield. The produced MBC was collected from the tube and then washed with distilled water until pH became neutral. MBC samples are denoted as MBC-X-Y-Z (X: Fe-loaded content (wt%), Y: pyrolysis temperature (°C), Z: pyrolysis time (h)).

2.3 p-Nitrophenol removal by magnetic biochar

p-Nitrophenol removal was performed in a flask 600 mL at room temperature (30 °C). 0.1 g MBC was added into 500 mL p-nitrophenol solution with its initial concentration of 100 ppm. Initial pH values of the mixture were adjusted by H_2SO_4 0.1 M and NaOH 0.1 M solutions. A magnetic stirrer was used to mix the suspension continuously. After 10 minutes adsorption, various H_2O_2 concentrations were rapidly poured into the mixture. At different time intervals, each 4 mL suspension was withdrawn from the mixture and added into a solution of $Na_2S_2O_3$ and NaOH to remove excess H_2O_2 and adjust pH value to around 11. Important parameters including pH value, H_2O_2 concentration, and MBC catalyst with different Fe-loaded content were investigated.

2.4 Analysis

X-ray powder diffraction (XRD) of MBC samples was performed using a Brucker AXS D8 diffractometer over the 2θ range of 10-90° and the scan rate was of 1°/min. Copper was used as the target (λ = 1.5418 Å). Scanning Electron Microscope (SEM) images were recorded with a FE-SEM S-4800. Nitrogen adsorption and desorption isotherms of MBC were conducted at 77 K on a NOVA 2200e Surface Area & Pore Size Analyzer. All samples were degassed at 150 °C in 3 h. Magnetic measurements of MBC were performed by a Vibrating Sample Magnetometer (VSM). To determine adsorption capacity and catalytic activity of MBC samples, p-nitrophenol concentration was measured by a UV-Vis Spectronic Genesys 2 PC at 400 nm.

3. Results and discussion

3.1 Effects of various parameters on characterization of magnetic biochar

Figure 1a shows the effect of pyrolysis temperature on XRD patterns for MBC samples. In general, all three patterns exhibited peaks at 2θ = 30.0, 35.3, 52.4, 56.8, 62.5, which correspond to (220), (311), (422), (511), (440) planes of crystal Fe_3O_4 (Li et al., 2019). Especially, a sharp peak at 2θ = 45.1 for body-centered cubic structure of crystal Fe (Liu et al., 2019) was observed clearly for MBC-10-600-2 and MBC-10-700-2 samples. When pyrolysis temperature increased from 500 to 700 °C, diffraction peak intensities of Fe_3O_4 decreased but those of Fe increased remarkably. These results indicated that increasing pyrolysis temperature enhanced the reduction of Fe_3O_4 to Fe over biochar support. Liu et al. (2019) prepared zero valent iron magnetic biochar in a similar manner, but the pyrolysis was conducted at 750 to 800 °C to convert iron oxides into iron. In fact, Zhang et al. (2018) proposed that ferric chloride could be converted into iron oxides over carbon support according to the reactions shown in Eq(1) to (6):

$$FeCl_3 + 2H_2O \rightarrow FeOCl.H_2O + 2HCl \tag{1}$$

$$FeOCl.H_2O \rightarrow FeO(OH) + HCl \tag{2}$$

$$2FeO(OH) \rightarrow \gamma\text{-}Fe_2O_3 + H_2O \tag{3}$$

$$3\ \gamma\text{-}Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \tag{4}$$

$$3\ \gamma\text{-}Fe_2O_3 + C \rightarrow 2Fe_3O_4 + CO \tag{5}$$

$$Fe_3O_4 + 4C \rightarrow 3Fe + 4CO \tag{6}$$

As presented in Table 1, pyrolysis temperature affected MBC yields from the $FeCl_3$-loaded rice husk. When the temperature increased from 500 to 700 °C, MBC yield decreased from 65 to 41 wt%. In addition to carbonization of rice husk, Eq(1-6) reveal that the decomposition of $FeCl_3$ and the reduction of iron oxides could lead to the decrease of MBC yield. Generally, these processes were accelerated with the increase of pyrolysis temperature.

Similar to pyrolysis temperature, pyrolysis time significantly affected the properties of MBC (Figure 1b). Diffraction peak intensities of Fe_3O_4 diminished, whereas those of Fe increased when pyrolysis time was prolonged. In fact, MBC yield decreased from 67 to 42 wt% when pyrolysis time increased from 1 h to 4 h. Nonetheless, there has a slight difference in MBC yield between 2 h (47 wt%) and 4 h pyrolysis (42 wt%). The results proved that the carbonization and decomposition processes nearly completed after 2 h at 600 °C.
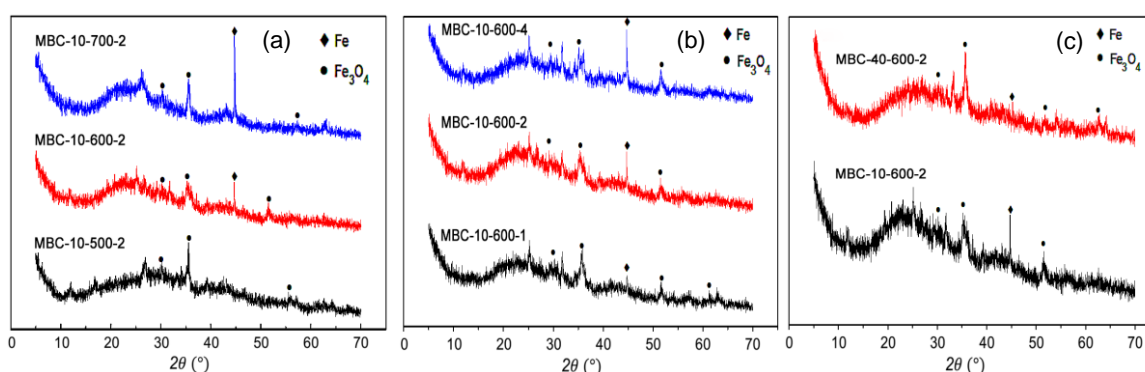

Figure 1: Effects of (a) pyrolysis temperature, (b) pyrolysis time and (c) Fe-loaded content on XRD patterns of MBC samples

Figure 1c shows that the peak intensity of Fe in MBC-40-600-2 is lower than that in MBC-10-600-2. Higher Fe-loaded content against lower carbon content might limit the reduction of iron oxide to iron. Furthermore, specific surface area of MBC was generally improved with increasing Fe-load content (Table 1). In particular, S_{BET} of MBC-40-600-2 (229 m^2/g) was much higher than that of MBC-20-600-2 (111 m^2/g). Liu et al. (2013) proved that the presence of Fe compounds can activate the formation of porous structures during biomass carbonization. Jenie et al. (2017) reported that the decomposition of $FeCl_3$ can emit volatile matters such as HCl, H_2O, CO and CO_2 during pyrolysis process, which might expand surface area and pore volume of MBC.

Table 1: Parameters for preparation of magnetic biochar samples from rice husk and their yields

Sample	Fe-loaded content* (wt%)	Pyrolysis temperature (°C)	Pyrolysis time (h)	MBC yield** (wt%)	S_{BET} (m^2/g)
MBC-10-500-2		500		65	-
MBC-10-600-2	10	600	2	47	-
MBC-10-700-2		700		41	-
MBC-10-600-1			1	67	-
MBC-10-600-2	10	600	2	47	-
MBC-10-600-4			4	42	-
MBC-10-600-2	10			47	15
MBC-15-600-2	15	600	2	47	15
MBC-20-600-2	20			50	111
MBC-40-600-2	40			60	229

* Fe-load content was the weight ratio of the Fe element in $FeCl_3$ solution and the dried rice husk
** MBC yield was the weight ratio of the obtained MBC and the $FeCl_3$-load rice husk

Figure 2a presents a SEM image of MCM-10-700-2 sample. It was strongly fragmented because of crushing, pyrolysis and activation processes. With regard to magnetic properties, all MBC samples can be attracted by a rare-earth magnet, as illustrated in Figure 2b. The magnetic hysteresis curve of MBC-10-700-2 sample showed superparamagnetic properties with the saturation magnetization of 6.42 emu/g. In addition to Fe_3O_4 particles, many reports indicated that and Fe particles were good magnetic materials (Liu et al., 2019). Thus, both Fe_3O_4 and Fe particles co-existed in MBC could contribute to magnetic properties, which play an important role in the convenient separation of MBC from certain suspension. In this study, MBC was used as oxidation catalyst and was recovered from the treated mixture by a rare-earth magnet.
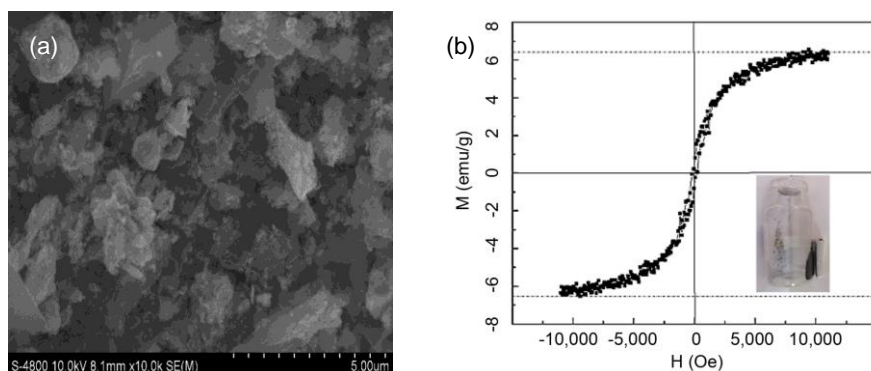

Figure 2: (a) SEM image and (b) magnetic hysteresis loop of MBC-10-700-2 sample

3.2 Catalytic activity of magnetic biochar

MBC-15-600-2 sample was selected as a catalyst for exploring the effects of pH and H_2O_2 concentration on p-nitrophenol removal. The experiments were divided into adsorption step and oxidation step. Figures 3a,b,c show that all adsorption processes reached equilibrium before 10 min. Adsorption capacity gradually decreased from 104 to 65 mg/g when pH decreased from 8 to 3, as detailed in Table 2. Dąbrowski et al. (2005) reported that the adsorption of weak organic electrolytes like p-nitrophenol on carbon surface depends on the electrostatic interaction potential of the ionized solute with the charged surface. When pH increased, p-nitrophenol molecules with pKa 7.15 could be gradually dissociated into anions and the net charge on the surface of MBC became negative. Electrostatic repulsions could then restrict the interactions between the carbon surface and the p-nitrophenol anions, and adsorbed anions could repel adjacent ones, as described by Tang et al. (2007).
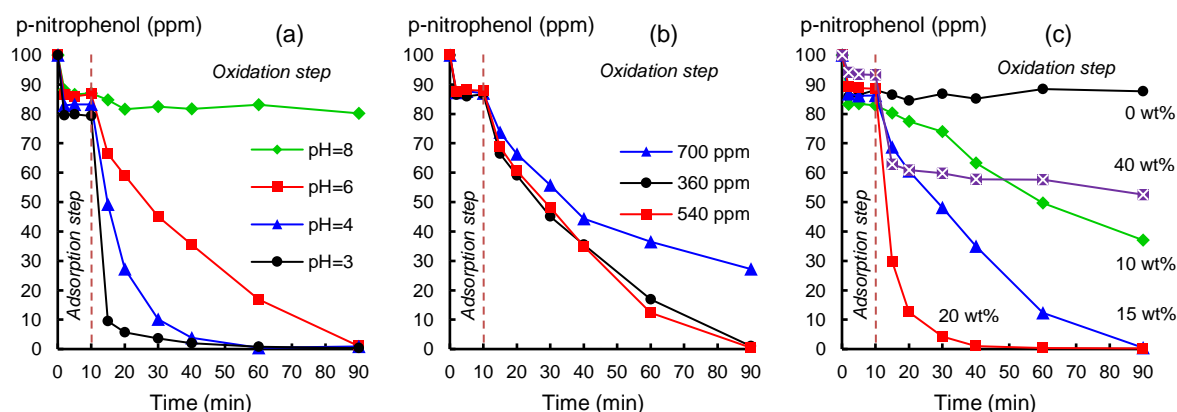

Figure 3: Effects of (a) pH value (MBC-15-600-2 catalyst), (b) H_2O_2 concentration (MBC-15-600-2 catalyst) and (c) Fe-loaded content (MBC-X-600-2 catalysts) on adsorption and oxidation of p-nitrophenol by MBC

After 10 minutes, p-nitrophenol degradation was commenced by adding H_2O_2 into the mixture. Figure 3a exposes that pH significantly affected p-nitrophenol mineralization by MBC. At low pH 3, 4 or 6, p-nitrophenol degradation occurred strongly and almost completed before 90 min. In particular, degradation rate gradually reduced with increasing the pH value from 3 to 6. Nonetheless, very little p-nitrophenol was degraded at alkaline pH 8 until 90 min. In Fenton mechanism, pH strongly affects the formation of hydroxyl radicals (•OH)

which directly oxidize p-nitrophenol (Zhang et al., 2012). High pH can lead to the decomposition of H_2O_2 to oxygen and water, rather than the formation of hydroxyl radicals. In addition, CO_2 released during p-nitrophenol oxidation could be converted to CO_3^{2-} and HCO_3^- under alkaline environment. These anions could react with •OH, causing the decline of p-nitrophenol mineralization. Thus, p-nitrophenol degradation by heterogeneous MBC catalyst could be practiced in a wide range of pH from 3 to 6, as compared with a narrow range of pH 2-3 by homogeneous Fenton reagents (Prochazka et al., 2019). To treat real wastewater containing p-nitrophenol, high pH 6 can reduce not only chemical uses for pH adjustment before and after treatment, but also leakage of Fe catalyst and corrosion of equipment caused by acid environment.

Table 2: Summary of adsorption capacities and catalytic activities of MBC samples with p-nitrophenol

MBC samples	pH	H_2O_2 concentration (ppm)	Adsorption (after 10 min)		Oxidation (after 90 min)	
			p-nitrophenol concentration (ppm)	Adsorption capacity (mg/g)	p-nitrophenol concentration (ppm)	p-nitrophenol removal (%)
MBC-15-600-2	3	360	79.28	104	0.33	99.7
	4		83.25	84	0.87	99.1
	6		86.68	67	0.98	99.0
	8		87.01	65	80.19	19.8
MBC-15-600-2	6	360	86.68	67	0.98	99.0
		540	87.87	61	0.44	99.6
		700	87.01	65	27.20	72.8
BC-0-600-2			88.13	59	87.72	12.3
MBC-10-600-2			82.93	85	37.03	63.0
MBC-15-600-2	6	540	86.26	69	0.44	99.6
MBC-20-600-2			88.51	57	0.22	99.8
MBC-40-600-2			93.23	34	52.55	47.5

Theoretically, the oxidation of 100 ppm p-nitrophenol requires 342 ppm H_2O_2 (Zhang et al., 2012). Different initial H_2O_2 concentrations of 360, 540 and 700 ppm was therefore examined for p-nitrophenol degradation (Figure 3b). Similar performances were observed for p-nitrophenol degradation using 360 and 540 ppm H_2O_2. In actual application, higher dosages of H_2O_2 like 540 ppm may be selected to yield higher mineralization efficiency. Nevertheless, 700 ppm H_2O_2 caused a significant decrease in degradation efficiency, as compared with 360 and 540 ppm ones. Zhao et al. (2010) proposed that an excess of H_2O_2 amount can react with strong oxidant •OH radicals to produce less reactive •OOH radicals.

MBC catalysts with different Fe-loaded contents (10, 15, 20, 40 wt%) were explored for p-nitrophenol degradation. A biochar sample without Fe element denoted as BC-0-600-2 was used as reference to determine the role of iron oxide catalyst and biochar support. In adsorption step, p-nitrophenol removal and adsorption capacity of MBC samples were presented in Figure 3c and Table 2. Adsorption capacity decreased from 85 to 34 mg/g with increasing Fe-load content from 10 to 40 wt%. p-Nitrophenol may accordingly have good interaction with carbon surface instead of iron oxide and iron particles.

As shown in Figure 3c, maintaining p-nitrophenol concentration during the oxidation step demonstrated that biochar support did not perform catalytic activity. Hence, iron constituents were the dominant catalytic sites of MBC. As reported by Rodriguez et al. (2019), Fe_3O_4 and/or Fe particles existing in MBC could become catalytic sites, according to Eq(7-8) provided below:

$$Fe(0) + H_2O_2 + 2H^+ \rightarrow Fe(II) + 2H_2O \tag{7}$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + •OH + OH^- \tag{8}$$

p-Nitrophenol degradation rate increased remarkably with increasing Fe-loaded content from 10 to 20 wt% (Figure 3c). High density of catalytic sites on MBC could be a mainly possible reason for the increase of degradation rate. On the contrary, MBC-40-600-2 catalyst removed promptly 30.4% p-nitrophenol in the first 5 min of oxidation step, then only 10.3% p-nitrophenol in next 75 min. Overall, only 47.5% p-nitrophenol was disappeared after 90 min treatment by both adsorption and degradation. These results revealed that high Fe-loaded content might inhibit the Fenton oxidation process.

4. Conclusions

To valorize abundant rice husk released from rice production, one-step preparation of magnetic biochar was studied. The results demonstrated that Fe_3O_4 crystals was formed from ferric chloride and then reduced to Fe

by carbon support. Interestingly, these reduction reactions actived biochar surface. MBC was accordingly utilized as oxidation catalysts for p-nitrophenol degradation by H_2O_2. The results demonstrated that MBC was not only a practical adsorbent but also an effective catalyst for p-nitrophenol removal. Maximum adsorption capacity (104 mg/g) was observed for MBC-15-600-2 sample at 30 °C and pH 3. For p-nitrophenol degradation, MBC samples showed fast p-nitrophenol degradation in a wide range of pH from 3 to 6. At high pH 6, 540 ppm H_2O_2 and 0.1 g MBC with 20 wt% Fe-loaded content, 99.8% p-nitrophenol was degraded after 90 min following by heterogeneous Fenton mechanism. Furthermore, MBC powders could be easily removed from the treated solutions by a magnet bar. Conclusively, eco-friendly, sustainable and cheap magnetic biochar can potentially be an effective catalyst for p-nitrophenol treatment in wastewater.

Acknowledgments

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