

Conversion of Waste Water Hyacinth into High-Value Chemicals by Iron (III) Chloride under Mild Conditions

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This study examined a novel approach for converting waste water hyacinths into high-value chemicals under low temperature and low atmospheric pressure by using iron (III) chloride (FeCl_3), an oxidant that has the unique properties of nontoxicity, low-cost, and abundance. The conversion process and transformation products of water hyacinths under different conditions were investigated and characterized. The results showed that the content of lignocellulose gradually decreased in the reaction solution. The chemical structure of lignocellulose in the water hyacinths was changed, and the glycosidic bonds of the water hyacinths were cleaved. The surface structure and crystalline regions of the water hyacinths were also damaged during the reaction. Furthermore, the hemicellulose and cellulose in the water hyacinths were dissolved and hydrolyzed to reducing sugars in the reaction solution, and then the reducing sugars were further dehydrated to hydroxymethylfurfural (HMF) and furfural. Lignin in the water hyacinths was depolymerized into aromatic and hydrocarbon compounds. The process presented in this study effectively alleviates environmental pollution by efficient utilization of aquatic wastes, and it produces high-value chemicals from biomass waste.

Keywords: Biomass waste; Water hyacinth; Iron (III) chloride; Conversion; High-value chemical

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INTRODUCTION

Lignocellulosic biomasses, the world's most abundant renewable resources, have attracted considerable interest in recent years (Lan *et al.* 2015; Ji *et al.* 2017; Liu *et al.* 2017). Aquatic plants, such as water hyacinths, are an excellent biomass for further converting into fuels, chemicals, biosorbents for environmental monitoring, and other materials because of its high percentage of lignocellulose (Ibrahim *et al.* 2009; Ibrahim *et al.* 2012; Ammar *et al.* 2014; Singh *et al.* 2015). In most countries, water hyacinths are recognized as harmful plants because of their rapid propagation and robust nature (Barua and Kalamdhad 2017). Many rivers, reservoirs, and channels have been polluted and clogged by these plants, and they seriously affect the development of transport, tourism, and aquaculture. Therefore, a large amount of money and labor is spent annually on controlling water hyacinths (Girisuta *et al.* 2008; Gao *et al.* 2013b), but these aquatic plants cannot be completely eliminated. Thus, it is necessary to find a suitable way to utilize the water hyacinths that are mechanically removed from waterways.

New technologies have been developed to generate renewable fuels and chemicals from water hyacinths, including bioconversion, pretreatment, and ionic liquid catalysis

(Ma *et al.* 2010). Das *et al.* (2016) reported a method to obtain fuel ethanol from water hyacinths by pretreating the water hyacinths with dilute sulfuric acid and reacting at high temperature and high pressure. Gao *et al.* (2013a) reported that the yield of biogas produced by water hyacinths can be improved by destroying the lignocellulosic structure with ionic liquid. However, these methods have significant disadvantages, including high energy demands, unrecyclable reagents, high cost, and complicated operation. At present, the conversion of biomass into chemicals by using metal-salts as catalyst or oxidant has received much attention due to the unique properties of nontoxicity, low-cost, and high selectivity (Yoo *et al.* 2017). Yu *et al.* (2017) fabricated the hydroxymethylfurfural (HMF) in a microwave reactor from food waste by using metal-salts as catalyst, such as aluminum chloride (AlCl_3), chromium(III) chloride (CrCl_3), FeCl_3 , and tin(IV) chloride (SnCl_4). Amarasekara and Wiredu (2016) reported that the cellobiose can be hydrolyzed to glucose by using manganese(II) chloride (MnCl_2) as a co-catalyst in sulfuric acid and acidic ionic liquid mediums. However, the conversion of water hyacinths into high-value chemicals by use of a low-cost and nontoxic oxidant with low temperature and low atmospheric pressure has not been reported.

Herein, a simple and low-cost approach was developed for converting water hyacinths into high-value chemicals by using FeCl_3 as an oxidant. The water hyacinths do not require any pretreatment with chemical reagents, and the reaction was carried out at low temperature and low atmospheric pressure. The solid residues and liquid products at different conditions were characterized by different methods, and the reaction mechanism was discussed. This work proposes a green and effective approach for the utilization of biomass and the control of water hyacinth pollution.

EXPERIMENTAL

Materials

Water hyacinths were obtained from a local lake (Shenzhen, Guangdong, China). Iron(III) chloride was purchased from Aladdin (Shanghai, China). Hydrochloric acid (HCl) and ether were purchased from Guangzhou Chemical Reagent (Guangzhou, China). Hydroxymethylfurfural (HMF, > 99%) and furfural (> 99%) as standard samples were purchased from Aladdin.

Conversion of Water Hyacinths with FeCl_3 as Oxidant

The water hyacinths were washed to remove dirt, cut into small pieces, and dried at 60 °C for 48 h to a constant weight. The dried water hyacinths were ground into powder. The calculated FeCl_3 was dissolved in 0.85 M HCl solution. The prepared water hyacinths and FeCl_3 acid solution were added into a 250 mL glass flask. The mixture was stirred and heated under atmospheric pressure at a certain temperature for several hours. And the reactions at the temperature of 90 °C, 100 °C, 105 °C and 110 °C were investigated, respectively. Finally, the degradation solution was filtered to obtain the solid residuals and liquid products for further analysis. The schematic illustration of the conversion of water hyacinth is shown in Fig. 1.

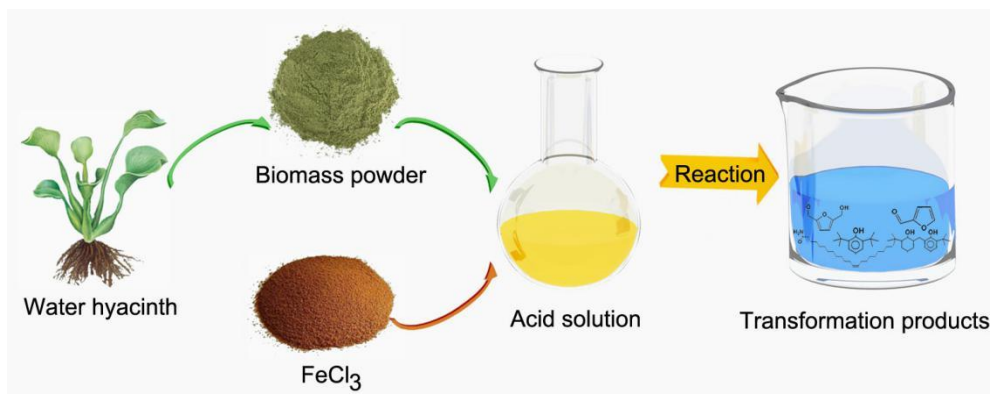


Fig. 1. Schematic illustration of the conversion process for water hyacinths

Characterization

The lignocellulosic compositions of the water hyacinths and their solid residues after reaction were analyzed by the Van Soest *et al.* (1991) method. The concentration of the total reducing sugars (TRS) was tested by the dinitrosalicylic acid (DNS) method (Miller 1959), and the absorbance of samples were measured using a UV-Vis spectrophotometer (TU-19, Persee, Beijing, China) at 540 nm. The structures of the water hyacinth and the solid residues were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet-6700, Thermo Fisher, Minneapolis, MN, USA) at a range of 4000 to 400 cm^{-1} with potassium bromide disc containing 1% samples. The micrographs of the water hyacinths and the solid residues were observed using a scanning electron microscope (SEM, JSM-7001F, JEOL, Tokyo, Japan) at 15 kV voltage. Crystallographic structural analysis was analyzed by X-ray diffraction (XRD, PW3040/60, PANalytical, Amsterdam, Netherlands). Diffraction patterns were recorded by using Cu-K α radiation at 40 kV, and the 2θ range was from 10° to 50° at a scanning speed of 2 °/min. The crystallinity index (CrI) was calculated by using the following equation: $\text{CrI} (\%) = [(I_{002} - I_{\text{am}}) / I_{002}] \times 100$, where I_{002} is the intensity for the crystalline portion of biomass (*i.e.*, cellulose) at 22 to 23°, I_{am} is the amorphous portion (*i.e.*, cellulose, hemicellulose, lignin) at 18° (Segal *et al.* 1959). The liquid products were analyzed by high performance liquid chromatography (HPLC, LC-20AT, Shimadzu, Kyoto, Japan) with a UV detector. The column (Luna 5u C18) and mobile phase (85% water and 15% acetonitrile) were used for the analyses with an injection volume of 30 μL . Gas chromatography-mass spectrometry (GC/MS, 7890A/5975C, Agilent, California, America) measurements were taken on an Agilent DB-5 capillary column coupled with a mass spectrometer. The column temperature was initially held at 35 °C for 1 min, then gradually increased to 300 °C at the rate of 15 °C/min and held for 6 min.

RESULTS AND DISCUSSION

Structures and Compositions of the Raw Water Hyacinths and their Solid Residues

The dissolutions of the water hyacinths with different reaction times are shown in Fig. 2a. In the reaction process, the water hyacinths were gradually dissolved, and the color of the solution changed from orange to brown when the reaction time was about 5 h. The

structural changes of the raw water hyacinths and the solid residues were analyzed by FTIR spectroscopy, as shown in Fig. 2b. The absorption peak located at 2926 cm^{-1} corresponded to the $-\text{CH}_2$ bond, which was obviously weakened after reaction. This result demonstrated that the crystal region of cellulose in water hyacinth was strongly destroyed during the reaction. The peak around 1046 cm^{-1} was attributed to C-O-C stretching vibration of glycosidic linkages between the sugar units in hemicellulose and cellulose, and it was weakened sharply after the reaction. This result indicated that the C-O-C bond was destroyed (Hao *et al.* 2016). The enhancement of the sharp peaks at 1609 and 1697 cm^{-1} were assigned to the absorbance of C=O, suggesting the oxidation of lignocellulose in water hyacinth. The peak near 3395 cm^{-1} was assigned to $-\text{OH}$ absorption peak and it was also changed a little. Additionally, the unsaturation bond of C-H at 3259 cm^{-1} and the peak of $\text{C}\equiv\text{C}$ at 2182 cm^{-1} were observed. These results demonstrated that the chemical structures of water hyacinths had been changed greatly due to the oxidation reaction between water hyacinths and FeCl_3 .

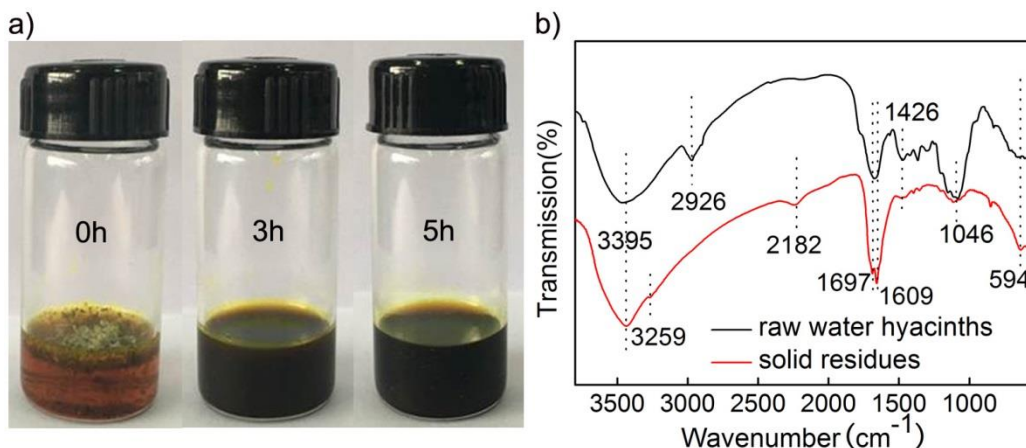


Fig. 2. a) Dissolutions of the water hyacinths with different reaction times; b) FTIR spectra of the raw water hyacinths and their solid residues after reaction.

The surface morphology of the water hyacinths and their solid residues at different times are shown in Figs. 3a, b, and c. The surface of the raw water hyacinths was tight and smooth. After the reaction of 6 h, the surface of the solid residues became loosened and cracked and there were many trenches on the surface of the solid residues. When the reaction time was 12 h, the water hyacinths had been cracked significantly, and many particles with different sizes were observed. The morphology changes revealed that the internal structure in the water hyacinths had greatly changed, and the water hyacinths were decomposed in a great extent after the oxidation by FeCl_3 . Figure 3d shows the XRD patterns of the raw water hyacinths and their solid residues after decomposition. It was found that the peaks at 15° and 22° were the (101) and (002) diffraction of cellulose, respectively. And the intensity of (002) diffraction at 22° represented the main crystalline structure of cellulose in the water hyacinths (Lü and Zhou 2011; Lin *et al.* 2015). The CrI of the raw water hyacinths was 19.90%, and it increased to 22.01% after reacting 6 h. However, it clearly decreased to 6.20% when the reaction time reached 12 h. The results indicated that the crystallographic structures in the raw water hyacinths were greatly destroyed after oxidizing by FeCl_3 (Onda *et al.* 2008).

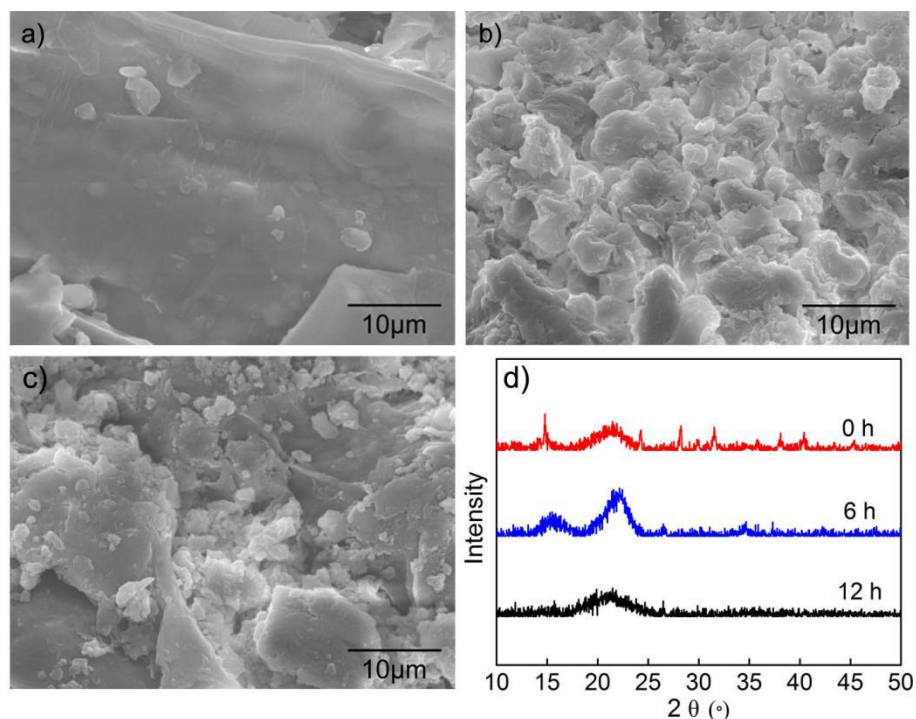


Fig. 3. a) SEM image of the raw water hyacinths; b) SEM image of the solid residues after reacting 6h; c) SEM image of the solid residues after reacting 12h; d) XRD pattern of the raw water hyacinths and their solid residues at different times

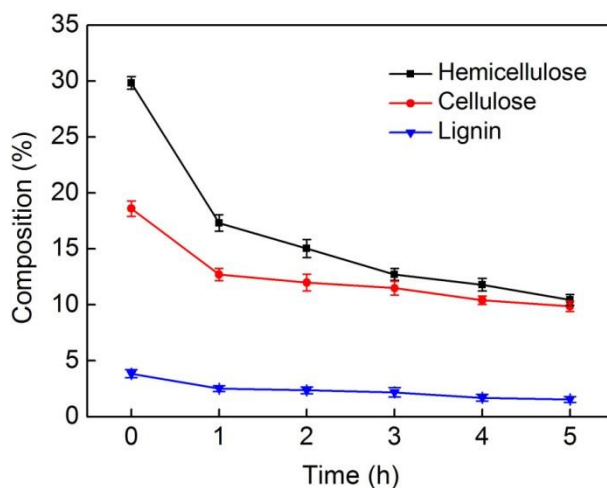


Fig. 4. The lignocellulosic compositions of the raw water hyacinths and its solid residues

As shown in Fig. 4, the initial compositions of the water hyacinths included 29.84 ± 0.57 % hemicellulose, 18.61 ± 0.68 % cellulose, and 3.84 ± 0.36 % lignin. The content of hemicellulose and cellulose decreased rapidly during the first hour. When the reaction time was 5 h, the content of hemicellulose, cellulose, and lignin decreased to 10.43%, 9.86%, and 1.54%, respectively. In other words, after reacting 5 h, the reduced percentages of hemicellulose, cellulose, and lignin were about 65%, 47%, and 60%, respectively. These results indicated that the lignocelluloses in the water hyacinths were degraded rapidly in the reaction solution and that the degradation of hemicellulose was easier than that of

cellulose and lignin. These results further indicated that the water hyacinths were oxidized by FeCl_3 successfully and their main composition may be depolymerized into sugar units (Climent *et al.* 2014).

Effect of Different Conditions on Conversion of the Water Hyacinths

To study the conversion process of water hyacinths, the TRS generated in the reaction, such as glucose, xylose, mannose, *etc.*, were measured by DNS method which used 3,5-dinitrosalicylic acid as chromogenic reagent. The concentration of TRS increased with the enhancement of the reaction temperature as shown in Fig. 5a. When the temperature was 90 °C, the generation of TRS was approximately linear with the extension of reaction time. When the temperature was lower than 105 °C, the TRS concentration increased with the extension of reaction time and the TRS concentration reached 38.5 mg/mL. But when the temperature was 110 °C, the concentration of TRS initially increased and then sharply decreased after reacting 10 h. It has been speculated that the reducing sugars generated in the reaction further decomposed to other chemicals (Tian *et al.* 2010). Therefore, the enhancement of temperature and the extension of reaction time can improve the decomposition speed of water hyacinths for generating TRS.

The influence of FeCl_3 concentration on the conversion of the water hyacinths was investigated as shown in Fig. 5b. With the enhancement of FeCl_3 concentration from 0.5 M to 1.0 M, the concentration of TRS increased linearly. When the FeCl_3 concentration was higher than 1.5 M, the TRS concentration increased during the first 10 h, and then decreased rapidly. The maximum TRS concentration was 56.2 mg/mL after reacting 10 h when the initial concentration of FeCl_3 was 2.0 M. Therefore, the conversion of water hyacinths into reducing sugars could be improved by increasing the concentration of FeCl_3 . FeCl_3 reacts with the hydroxyl groups of lignocelluloses, which disrupts inter- and intra-molecular hydrogen bonds in lignocellulose (Guo *et al.* 2012). The concentration of TRS increased with the amount of water hyacinths increasing as shown in Fig. 5c. If the amount of water hyacinths was too high (above 3.0 g in 65 mL solution), the water hyacinths were charred easily.

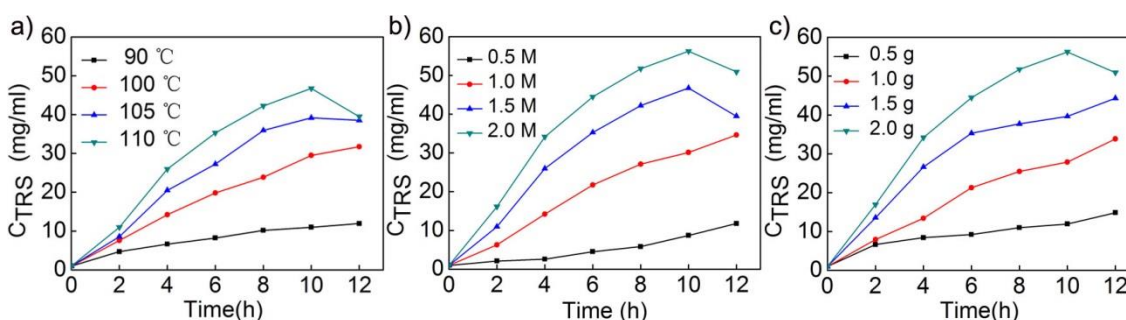


Fig. 5. TRS concentration in the reaction solution under different conditions. a) different temperatures with 2.0 g water hyacinths in 1.5 M FeCl_3 acid solution, b) different concentrations of FeCl_3 in acid solution with 2.0 g water hyacinth at 110 °C, c) different amounts of water hyacinths in 2.0 M FeCl_3 acid solution at 110 °C

Generation of High-Value Chemicals in the Liquid Products

High-value chemicals in the liquid products were measured by HPLC as shown in Fig. 6. In order to confirm the composition of the liquid products, the standard samples of HMF and furfural (FF) were tested first. The reaction time of HMF was 4.580 min (Fig.

6a), and the reaction time of furfural was 6.175 min (Fig. 6b). Figure 6c shows the chromatographic peaks of the liquid products measured under the same condition of the HMF and furfural standard samples. There were two peaks at 4.581 min and 6.121 min, which were identical to the peaks of the HMF and furfural standard samples. Thus, HMF and furfural, which are high-value chemicals, were obtained with the conversion of water hyacinths.

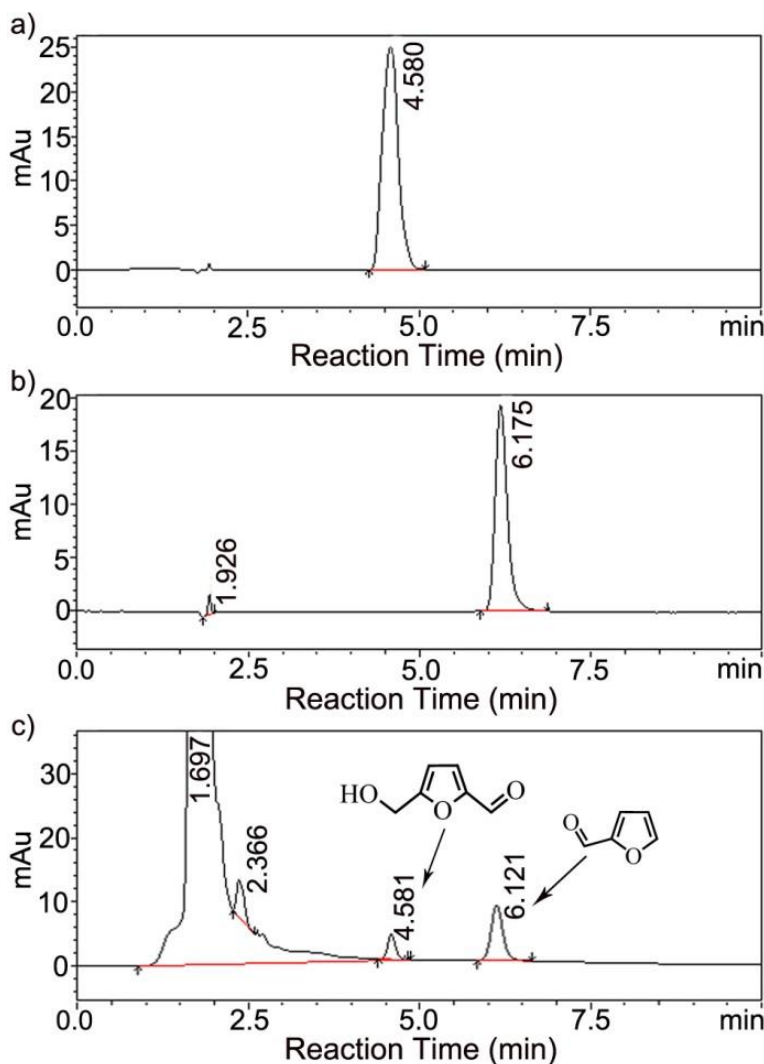


Fig. 6. a) HPLC analysis of the HMF standard sample (2 mg/ml); b) HPLC analysis of the furfural standard sample (1 mg/ml); c) HPLC analysis of the liquid products when the water hyacinths were degraded 12 h.

Figure 7 shows the GC/MS analysis of the liquid products. There were three strong peaks that represented butylated hydroxytoluene (BHT), 2,2'-Methylenebis(6-tert-butyl-4-methylphenol), and 13-Docosenamide. Moreover, as shown in Table 1, the content of 2,2'-Methylenebis(6-tert-butyl-4-methylphenol) and 13-Docosenamide was as high as 15.6% and 16.26%, respectively. Lignin is an amorphous heteropolymer consisting of three different phenylpropane units (Du *et al.* 2017). Hence, these results implied that the majority of the products were obtained by the depolymerization of lignin after 12 h.

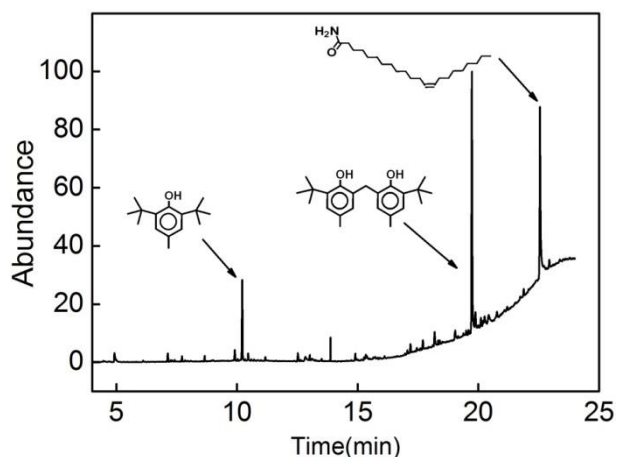


Fig. 7. GC/MS analysis of the liquid products when the water hyacinths were degraded 12 h.

Table 1. Relative Ratios of the Main Production in the Water Hyacinth

Peak Time (min)	Compound	Area (%)
10.223	butylated hydroxytoluene	2.99
19.736	2, 2'- Methylenebis(6-tert-butyl-4-methylphenol)	15.6
22.551	13-Docosenamide	16.26

Conversion Pathways of the Water Hyacinths with FeCl_3 as Oxidant

Based on the above analysis and discussion, the possible pathways for conversion of water hyacinths with FeCl_3 as oxidant are presented in Fig. 8.

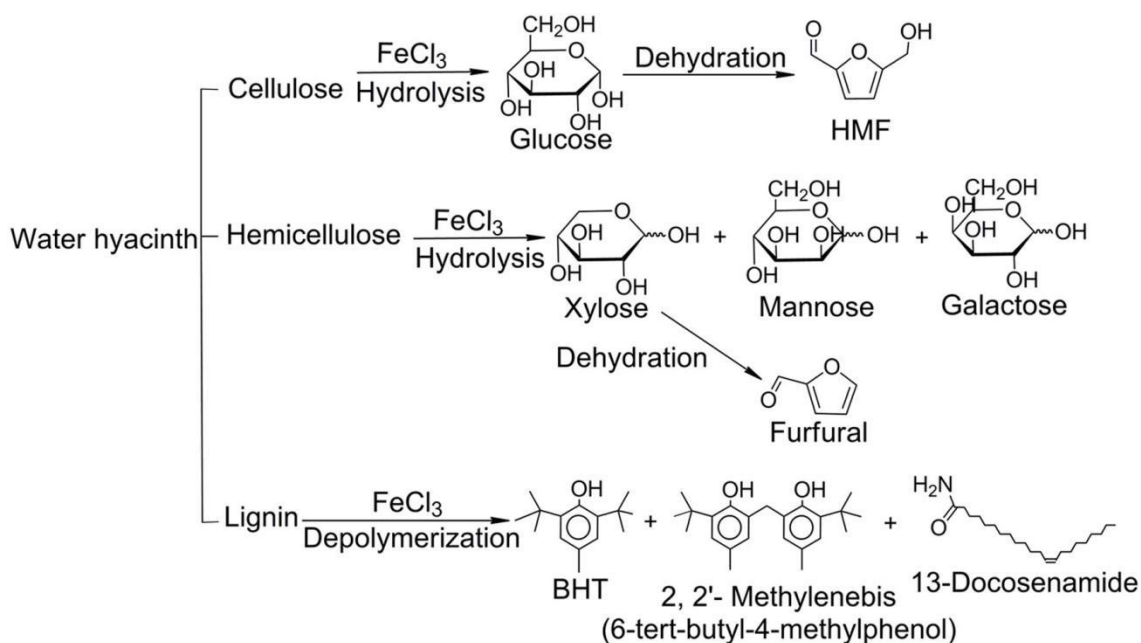


Fig. 8. The speculated conversion pathways of the water hyacinths in FeCl_3 acid solution

During the conversion, cellulose, hemicellulose, and lignin in the water hyacinths were gradually decomposed with the extension of reaction time. Meanwhile, the crystal regions of cellulose in water hyacinths were greatly destroyed, and the glycosidic linkages

between the sugar units in hemicellulose and cellulose were also destroyed after the reaction. Therefore, the sugar units, such as glucose, xylose, mannose and galactose, could be generated by hydrolysis of cellulose and hemicellulose during the conversion process (Zhang *et al.* 2016). Moreover, high-value chemicals, such as HMF and furfural, could be obtained from reducing sugars by dehydrogenation (Yoo *et al.* 2017). Lignin can be depolymerized to prepare aromatic and hydrocarbon chemicals, such as butylated hydroxytoluene, 2,2'-Methylenebis(6-tert-butyl-4-methylphenol), and 13-Docosenamide (Constant *et al.* 2015).

CONCLUSIONS

1. The conversion of water hyacinths can be effectively promoted at temperatures lower than 110 °C under atmospheric pressure by using FeCl₃ as an oxidant. High-value products were obtained, including HMF, furfural, and aromatic and hydrocarbon compounds. The proper conditions for the conversion reaction were 2.0 g of water hyacinths, 2.0 M FeCl₃, 110 °C, and 12 h of reaction time.
2. The FTIR, SEM, and XRD analyses showed that the structures and morphology of the water hyacinths were destroyed to a great extent by FeCl₃. The cellulose and hemicellulose in the water hyacinths were hydrolyzed to first form the reducing sugars, and then further decomposed into HMF and furfural based on the results of DNS and HPLC. The lignin in the water hyacinths was converted into aromatic and hydrocarbon compounds by depolymerization based on the GC/MS results.

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