Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment

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ABSTRACT

Two types of pinewood chars, hydrothermal char (H300) and pyrolytic char (P700) from biomass-to-energy conversion were characterized and used as adsorbent for the copper removal from aqueous solution. The result showed that the pinewood underwent a deeper carbonization during pyrolysis process and more activated sites available and stable carbon-oxygen complex existed after hydrothermal treatment. Comparing with raw pinewood, hydrothermal treatment increased 95% total oxygen-containing groups (carboxylic, lactone and phenolic group) while 56% oxygen-containing groups decreased after pyrolysis process. SEM analysis indicated that both hydrothermal and pyrolytic processes developed rough surface with new cavities on the chars, and the BET surface area were 21 and 29 m²/g for H300 and P700, respectively. Although H300 had lower surface area, its adsorption capacity for copper was much higher than P700 since ion-exchange reaction was the predominant removal mechanism by H300, while physical adsorption dominated by P700. The adsorption data could be well described by Langmuir isotherm model for copper onto both H300 and P700.

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1. Introduction

There is a growing tendency nowadays for biofuel production using waste biomass because of the shortage of crude oil and environmental concern. The conversion from biomass to biofuel can be achieved through thermal and biological processes, and hydrothermal treatment and high-temperature pyrolysis are two major focuses in the thermal conversion [1–3]. Both thermal processes produce char as one of major products and with increasing importance on the biomass conversion, large amounts of chars from biofuel production will be produced in the near future. Some papers have been published about the characterization of chars from different biomass pyrolysis [4,5]. The chars from tobacco and pectin were studied and it was found that the physical and chemical characteristics of the chars were more dependent on treatment conditions than on nature of the substrates [6,7]. Chars obtained from pyrolysis of two hardwoods were characterized and the results showed that morphological features were strongly influenced by the operating conditions, especially temperature [8]. In the field of biofuel research, most attention has been paid to the liquid product and syngas but the char, which is also an attractive byproduct, has received less

attention. Thus far, there is not other value-added utilization available for this solid residue besides direct combustion for heat production.

Currently, adsorption is commonly regarded as the most excellent method for wastewater treatment, but the widespread utilization of this method is usually limited by technical and economical factors [9,10]. This calls for a research effort to develop effective and cheaper adsorbents to meet the demand. Under this situation, various kinds of adsorbents generated from agricultural and forest byproducts have been tested in order to evaluate their efficiencies in the removal of toxic metal ions and to develop a low cost and efficient process [11–15]. The fast thermal decomposition of biomass matrix resulted in complex surface structure and almost no extractable organic compounds left in the char. Considering these special characteristics, it is potentially more feasible to use chars as adsorbent in wastewater treatment.

To our best knowledge, there is no information related to the characterization and utilization of char produced from biomass hydrothermal conversion and, only limited reports on the application of chars from high-temperature pyrolysis [16–19]. In this study, pinewood was selected as a representative of waste biomass and two types of chars from pinewood thermochemical conversion processes were characterized and applied as adsorbents for copper removal from aqueous solution. The purpose of this preliminary research is to evaluate the feasibility of chars as adsorbent and to develop a value-added utilization for these byproducts.

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2. Materials and methods

2.1. Char preparation

The hydrothermal char used in this study was prepared using a typical hydrothermal treatment process [2]. Briefly, 5 g pinewood and 30 ml deionized water were added into a 100 ml stainless autoclave, and nitrogen gas was used to purge the air inside the reactor. The autoclave was heated to 300 °C at a heating rate of 10 °C/min. The reaction was held at 300 °C for 20 min and then cooled down to room temperature. The solid product was extracted with acetone to produce bio-oil and char was recovered as solid residue (sample designed as H300).

For pyrolytic char preparation, a tubular reactor was employed. Typically, 5 g pinewood sample was heated from room temperature with a heating rate of 10 °C/min. The inner atmosphere was nitrogen gas with a flow rate of 10 cm³/min, and the sample was kept at 700 °C for 2 h. The char was obtained as solid residue after the pyrolysis process (sample designed as P700).

The chars were washed several times using double-distilled water followed by drying in an oven at 105 °C for 24 h. Thereafter, the dried char samples were then ground to less than 0.5 mm and kept in a desiccator for use.

2.2. Char characterization

Elemental analysis of the chars were performed using a flash EA1112 Elemental Analyzer (USA). The BET surface area of the chars were measured using nitrogen as an adsorbate at 77 K in an automatic apparatus ASAP 2000 Micromeritics (USA). The Dubinin–Radushkevich method was used to determined the micropores volume of the chars and meso- and macropores volume was obtained using the Barrett–Joyner–Halenda method. The surface morphology was studied by SEM on S-3000N (Japan). FT-IR spectra were determined in the range of 400–4000 cm^{−1} using potassium bromide pelletization method on a Nicolet Nexus 670 spectrophotometer (USA). The amount of char and potassium bromide used in IR analysis were kept constant so as to compare the relative intensities of functional groups in different biochars. Copper concentration was analyzed by inductively coupled plasma optical emission spectroscopy OPTIMA 2000 (USA). Oxygen-containing functional groups (carboxylic, lactone and phenolic) were determined by Boehm titration method with different alkali solutions (NaOH, Na₂CO₃ and NaHCO₃). Briefly, a given amount of char was added to the alkali solutions (1 M) and the mixture was agitated at agitating bed for 24 h. The supernatant was drawn and back titrated with 1 M HCl [20]. The pH measurements were made using a METTLER TOLEDO DELTA 320 pH meter (Switzerland).

2.3. Adsorption experiment

Stock copper solution (1000 mg/l) was prepared by dissolving Cu(NO₃)₂·3H₂O in 100 ml double-distilled water. Different concentration solutions were prepared by diluting appropriate volume of stock solution and the pH value was adjusted by concentrated HNO₃ or NaOH solutions. The amount of copper removal was

Table 2

Oxygen-containing functional groups in H300 and P700.

Sample	Acidic surface functional group (meq/g)			pH Value
	Carboxylic (–COOH)	Lactone (C=O)	Phenolic (–OH)	
Raw pinewood	0.10	0.16	0.17	
H300	0.18	0.41	0.25	3.80
P700	0.02	0.01	0.16	6.60

determined by concentration difference in solutions before and after adsorption experiments.

2.4. Quality assurance

The data of given in present study were the average value of three-repeated runs for reliability. Analytical grade reagents and double-distilled water were used for adsorption experiments.

3. Results and discussion

3.1. Chemical composition analysis

Chemical composition of H300, P700 and the raw pinewood are shown in Table 1. As expected, the content of ash and carbon in H300 and P700 was much higher and the content of hydrogen and oxygen was much lower than the raw pinewood. The higher content hydrogen and oxygen in H300 indicated that more activated sites available and stable carbon–oxygen complex existed on the H300 surface than P700 [21]. The higher value of C/O and C/H in P700 than H300 indicated that pyrolysis at 700 °C underwent a deeper carbonization process than hydrothermal treatment at 300 °C. In comparison with P700, the lower ash content of H300 ascribed to the fact that most inorganic compounds contained in the wood dissolved in the water under hydrothermal conditions.

Table 2 shows the Boehm titration results for H300 and P700. As can be seen, total oxygen-containing functional groups was 0.84 meq/g for H300 which consist of 0.18, 0.41 and 0.25 meq/g for carboxylic, lactone and phenolic group, respectively. Total oxygen-containing functional groups for P700 were 0.19 meq/g with 0.02, 0.01 and 0.16 meq/g for carboxylic, lactone and phenolic group, respectively. Significant difference was observed for the content of lactone group in H300 and P700 (0.41 meq/g for H300 to 0.01 meq/g for P700). The total content of oxygen-containing groups in P700 decreased 77.39% in comparison with H300, confirming a deeper carbonization process took place in P700. The pH values were 6.60 and 3.80 for P700 and H300, respectively. The lower pH value of H300 was consistent with the higher content of carboxylic group in H300.

Fig. 1 shows the infrared spectra of raw pinewood, H300 and P700. The FT-IR spectra of the two chars were different in shape and intensity, indicating that different thermal decomposition processes took place during hydrothermal treatment and pyrolysis. The significant absorption bands in the spectrum of H300 suggested that large amount of polar groups remained on the surface after hydrothermal treatment. Compared with the raw pinewood, the adsorption intensities of carboxylic group (bands at

Table 1

Ultimate and proximate analyzes of the raw pinewood and the chars.

Sample	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	Ash (wt.%)	Volatile (wt.%)	Fixed carbon (wt.%)
Pinewood	49.25	6.18	0.30	44.17	0.30	78.86	14.25
H300	61.60	3.42	0.16	34.82	10.90	42.98	43.26
P700	95.30	0.82	0.12	3.76	38.83	3.20	57.05

Fig. 1. FT-IR spectra of raw pinewood and chars.

1600 cm^{-1} and 1460 cm^{-1}) and carbonyl group (band at 1700 cm^{-1}) were increased after hydrothermal treatment. While the content of C–O bonds (bands between 1000 cm^{-1} and 1300 cm^{-1}) and hydroxyl group (adsorption at 3430 cm^{-1}) decreased. As for P700, the spectrum was quite flat indicating nearly all the polar functional groups including oxygen-containing groups have been decomposed during high-temperature pyrolysis. The above analysis was consistent with a previous reported that carboxylic and lactone groups decomposed in the range from 200 °C to 800 °C, phenol and ether group in the range from 500 °C to 1000 °C [22]. The low polar group density on the surface denoted significant hydrophobic character of P700.

3.2. Surface property analysis

The surface property is important for char reactivity and the SEM images of the raw pinewood, H300 and P700 are shown in Fig. 2. It was noted that macropores were formed on the surface of P700, and H300 had coarser and rougher surface than P700. The smooth surface observed for P700 was developed by the melting and fusion process of the lignin and other small molecules

Fig. 3. Adsorption isotherm for N₂ at 77 K for H300 and P700.

compounds in pinewood, such as pectin and inorganic compounds [16,23]. The vesicles on the smooth surface of P700 resulted from the release of volatile gas contained in the soft biomass matrix during the pyrolysis process [16]. The matrix became brittle and the collapses of part of vesicles were observed on the surface of P700. As for H300, the vesicles were formed through chemical bonds decomposition and fragmentation release from pinewood matrix taking into account the fact that hydrolysis reaction is predominant for biomass hydrothermal treatment.

The adsorption isotherms for N₂ at 77 K for H300 and P700 are plotted in Fig. 3. From the shape of the isotherm, it may be stated that both chars belong to the Type IV according to IUPAC classification. The hysteresis loop observed in the isotherms was associated with capillary condensation taking place in the mesopores of chars. The BET surface areas were 21 m^2/g for H300 and 29 m^2/g for P700, respectively (Table 3). It has been reported that char surface area greatly depended on treatment temperature during biomass pyrolysis [19]. Thus the relatively low surface area of P700 accorded with previous reports that high temperature was unfavorable for the porous structure of the char [7,8,21]. Due to the high temperature and long residence time, the porous structure cracked

Fig. 2. SEM photographs of raw pinewood, H300 and P700.

Table 3

Comparisons of surface structure of H300 and P700.

Sample	Surface area (m ² /g)	Average pore diameter (Å)	Micropore volume (cm ³ /g)	Meso- and macropore volume (cm ³ /g)
H300	21	8.6	0.09	0.05
P700	29	14.8	0.13	0.89

and the pores might be partially blocked as a result of the softening and melting of the pinewood constituents, which could lead to a low surface area [24].

3.3. Adsorption studies

The effects of pH on copper removal by H300 and P700 are shown in Fig. 4. Experiments were not carried out beyond pH 6.2 to avoid copper hydrolysis and precipitation. Generally, the removal rate of copper increased with increasing initial pH value ranging from 1.2 to 6.2. It was found that the pH value has much more influence on H300 than P700, and the removal rate for H300 exhibited considerable increase from pH 3.2 to 4.2. These phenomena could be attributed to the change of the degree of ionization of oxygen-containing group on the adsorbent surface. At lower pH, the surface oxygen linked to H⁺, making these inaccessible for copper. With increased pH, the deprotonation of negative oxygen-containing group provided the chance to co-ordinate with copper, resulting in higher removal rate. Hence, the influence of pH on copper removal was caused by the competitive co-ordination between H⁺ and Cu²⁺. Due to fewer amounts of oxygen-containing groups on P700 surface, less effect of pH on P700 was observed. The final pH value after adsorption was also measured and the result was shown in Fig. 5. It was observed that at pH < 3.2 the final pH value was almost equal to initial value while at pH ≥ 3.2, the initial pH were higher than final value and the deviation trend increased with the increasing initial pH value especially for H300. The deviation was caused by the release of H⁺ from the chars to the solution and this result was agreed with previous reports [22,25]. To obtain the maximum copper removal rate, all the following experiments were carried out at initial pH 6.2.

The equilibrium adsorption data were fitted to Langmuir (Eq. (1)) and Freundlich (Eq. (2)) isotherms, which are two common functions for describing adsorption.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (\text{Langmuir model}) \quad (1)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{Freundlich model}) \quad (2)$$

where q_e is the copper adsorbed per gram of char (mg/g) at equilibrium, C_e the copper concentration in solution (mg/l) at equilibrium.

Fig. 4. Effect of pH on copper adsorption on H300 and P700. **Fig. 5.** The plot of initial pH against final pH value (copper concentration 10 mg/g, adsorbent dose 2.5 g/l, temperature 25 °C).

Fig. 6 shows the plots of Langmuir and Freundlich adsorption isotherms of the copper on H300 and P700 and the adsorption coefficients are listed in Table 4. Based on the correlation coefficients, the adsorption of copper on H300 and P700 were well described by Langmuir isotherm rather than Freundlich isotherm (correlation coefficient: $R^2 > 0.97$ and $R^2 < 0.90$ for Langmuir and Freundlich model, respectively). The worse fitness of Freundlich model could be attributed to the fact that the supply of adsorbent site was not infinite on the adsorbent surface. The Langmuir isotherm parameter $q_{\max}$ (mg/g) indicated the maximum adsorption capacity of adsorbent and the value calculated from Langmuir equation was 4.46 mg/g for H300 and 2.75 mg/g for P700, respectively. Several studies have been conducted using various types of adsorbents for copper adsorption. Table 5 presents a comparison of the adsorption capacity of results. In spite of variety of parameters and conditions, direct comparison was impossible. However, as can be seen from the Table 5 that the adsorption capacity of copper onto the chars exceeded or was comparable to other adsorbents reported in literatures qualitatively, revealing that the chars was suitable for copper removal from aqueous solutions.

Due to different reactions took place in the pinewood hydrothermal and pyrolytic treatment, two kinds of chars were obtained. The chars were utilized in copper removal from aqueous solutions and the adsorption mechanisms for H300 and P700 were proposed based on adsorption analysis and related literatures [31,32]. The main mechanism for H300 was ion-exchange reaction (exchange equal amount of charge (H⁺ and/or metal ions) to and from the solution), and physical surface adsorption for P700. Although fewer oxygen-containing groups on P700 surface, the maximum

Fig. 6. Adsorption isotherms of copper by H300 and P700. Conditions: initial pH 6.2, temperature 25 °C, adsorbent dose of 2.5 g/l. (—) Lines represent experimental data fitted by Langmuir model isotherm and (---) lines represent the data fitted by Freundlich model isotherm.

Table 4

Parameters of adsorption isotherms for Langmuir and Freundlich models.

Isotherm model	Parameters	Adsorbent	
		H300	P700
Langmuir	K_L (l/mg)	0.46	1.00
	$q_{\max}$ (mg/g)	4.46	2.75
	R^2	0.97	0.97
Freundlich	K_F (mg/g)	2.00	1.38
	n	4.32	5.24
	R^2	0.88	0.85

Table 5

Comparison of adsorption capacities of copper on other adsorbents.

Adsorbent	Adsorption capacity (mg/g)	Temperature (°C)	References
H300	4.21	25	This study
P700	2.73	25	This study
Sawdust carbon	5.73	30	[26]
H ₃ PO ₄ -activated rubber wood sawdust	5.729	30	[26]
Rice hulls activated carbon	6.64	18	[27]
Turkish coal	1.62	20	[28]
Sawdust	0.005	30	[29]
Bagasse fly ash	2.26	30	[30]

adsorption capacity, 2.75 mg/g, can be obtained due to higher surface area for adsorption.

4. Conclusions

The preliminary study has shown that a thorough carbonization process take place in P700 and nearly all the oxygen-containing groups decompose during pyrolysis process. Contrary to the pyrolysis process, the hydrothermal treatment creates much more oxygen-containing groups on the char's surface. Both hydrothermal treatment and pyrolysis could develop rough surface and porous structure through different reactions. Copper removal from wastewater by H300 is mainly through ion-exchange mechanism while physical surface adsorption for P700. The adsorption data could be well described by Langmuir model and the maximum adsorption capacities are 4.46 and 2.75 mg/g onto H300 and P700, respectively. Through comparison with other adsorbent, these byproduct chars from biomass-to-energy conversion, especially hydrothermal char, can be used as effective adsorbent for copper removal from wastewater.

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