

Effect of spent liquor recycle during hydrothermal carbonization on the properties of hydrochar

Jie Xu

ABSTRACT

Hydrothermal carbonization is a feasible way to convert biomass into valuable hydrochar, the recycle of spent liquor during HTC is beneficial to reduce the output of spent liquor. The effects of spent liquor recycle on the properties of hydrochar and the biogas potential of spent liquor are investigated in this study. Part of the spent liquor (50% volume fraction) was recycled four times at 220 and 240 °C HTC, respectively. The results showed that the surface area of hydrochar was in the range of 7.2–8.6 m²/g after spent liquor recycle, and the peak of -OH, C=O and C-O became more intense. The Cd²⁺ adsorption capacity of hydrochar was around 1.3 mg/g and it decreased by 0.02–0.15 mg/g after spent liquor recycle. The biogas yield of spent liquor kept declining from 263 to 29 mL/g-COD with each cycle of spent liquor. Our results suggest that spent liquor recycle is a promising method to improve hydrothermal carbonization process.

Key words | Cd²⁺ adsorption, hydrochar, hydrothermal carbonization, recycle, spent liquor

Jie Xu
School of City and Architecture Engineering,
Zaozhuan University,
Zaozhuan 277160,
China
E-mail: jaxon23@126.com

HIGHLIGHTS

- 1 g hydrochar could remove around 1.3 mg Cd²⁺.
- The Cd²⁺ adsorption capacity of hydrochar decreased by 5–20% after spent liquor (SL) recycle.
- The hydrochar yield was improved by 0.3–0.6% after SL cycle.
- The functional groups of hydrochar could be reinforced after SL recycle.
- The biogas yield of SL declined from 263 to 29 mL/g-COD after SL recycle.

INTRODUCTION

Energy demand continues to increase because of growing population and rapid industrialization; with diminishing reserves and the environmental issues of conventional fossil fuels, it is important and inevitable to find alternative clean and sustainable energy substitutes (Curtin *et al.* 2019). Because biomass is cheap, renewable and environmentally-friendly, it is deemed as a viable energy source and is expected to meet 25% of worldwide energy needs. However, some organics in biomass are difficult to decompose and most biomass contain significant amounts of moisture. Biomass often needs to be dried and pretreated before further use, so a large amount of energy is required for drying biomass (Clausen 2017).

Owing to its conversion of biomass into valuable products and elimination of the drying step, hydrothermal

technology has become hotspot researches for biomass treatment (Zhan *et al.* 2020). Hydrothermal carbonization (HTC), normally with a temperature of 200–280 °C and a residence time of 2–6 h, has gained prominent attention in recent years (Wang *et al.* 2018), because hydrochar, the solid product of HTC, can be used to remove heavy metal from contaminated water and soil (Xia *et al.* 2019).

Water is an important solvent and water consumption is normally 1–10 times the biomass amount, depending on the type of biomass, during the hydrothermal process. Thus, a large amount of spent liquor (SL) containing insoluble matter is produced after the hydrothermal process. Many researchers pay great attention to safe disposal of SL, although the residual carbon, phosphorous and nitrogen of

SL could be utilized through anaerobic digestion and microalgae cultivation (Wirth *et al.* 2015; Shi *et al.* 2019), but some refractory materials of SL such as furan and phenols are toxic to microorganisms (Becker *et al.* 2014).

Distilled water is generally used as the solvent in HTC experiments, and some scholars suggest recycling SL during HTC, which can obviously reduce the postprocessing cost of wastewater (Stemann *et al.* 2013). The existing studies on SL recycle in HTC have mainly focused on the energy output of hydrochar and the composition of SL, such as the yield and the heat value of hydrochar (Catalkopru *et al.* 2017; Wang *et al.* 2019a), but the environmental remediation capacity of hydrochar and the biogas potential of SL are not well studied. This study aims to investigate the effects of SL recycle in HTC on the properties of hydrochar and the biogas potential of recycled SL.

MATERIALS AND METHODS

Experimental materials

The fresh granatum without drying (water content, 35.24%) was chosen as the material for hydrochar preparation, which was obtained from the pomegranate research center in Zaozhuang University. Granatum was smashed into a slurry by a blender (CPEL-23, China). The homogenized granatum was stored at -20°C for further use. All chemicals of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). The Cd^{2+} standard solution (1,000 $\mu\text{g}/\text{mL}$, in 1% HNO_3) was purchased from Guobiao Testing & Certification Co., Ltd (Beijing, China).

HTC experiments and recycle of SL

A 100-mL stainless-steel cylindrical reactor (MMJ-200, Japan) was used to perform the HTC experiments, which was heated by an electric oven (DHG-9023A, China). The HTC temperatures of 220°C and 240°C were chosen and the residence time was 4 h.

In the first run, the reactors containing 4 g granatum and 40 mL distilled water were conducted at the designed temperature. After cooling to the ambient temperature, the solid (hydrochar) and the liquid (SL) were separated by vacuum filtration. The hydrochar was washed with distilled water and then dried at 105°C for 24 h. The dried hydrochar was stored in enclosed plastic bags for further use. For the collected liquid, 20 mL SL was recycled in the next set of

HTC experiments and 10 mL SL was used for testing biogas potential, the rest was used for further analysis.

In the SL recycle experiments, 4 g granatum and 40 mL liquid (20 mL SL and 20 mL distilled water) were used as substrate to perform the HTC. The recycle experiment was repeated four times at 220°C and 240°C , respectively. The hydrochar obtained from 220°C HTC in distilled water was labeled as H220, while those obtained from the first to fourth recycle HTC were defined as H220-R1 to H220-R4. The same naming rules were used for the abbreviations of SL220, SL220-R1 to SL220-R4. The hydrochar obtained from 240°C HTC was named by the same method.

The pH and chemical oxygen demand (COD) of SL were measured by a pH meter (PHS-3D, China) and a COD analysis meter (HACH), respectively. The volatile fatty acids (VFA) composition of SL was analyzed using gas chromatography (GC-2014, Shimadzu, Japan) equipped with a flame ionization detector (FID). Argon gas at a flow rate of 1.47 mL/min was used as a carrier gas. The temperatures of the injector and detector were set at 250°C and 280°C , respectively.

The pH of hydrochar was measured by a pH meter in deionized water at 1:10 ratio of hydrochar to water. The functional groups of hydrochar were determined by Fourier transform infrared (FTIR) spectroscopy (Nicolet IS50, USA) with KBr method. The Brunauer-Emmett-Teller (BET) surface area and pore diameter of the hydrochar were measured with an automatic nitrogen adsorption analyzer (JW-BK, China).

Anaerobic digestion of SL

The biogas production from the SL was carried out in batch in an anaerobic digestion system consisting of a 500-mL glass bottle, a 1-L glass bottle filled with a diluted hydrochloric acid solution ($\text{pH} < 3$) and a 500-mL plastic bottle, acting as the bioreactor, the biogas collection bottle and the liquid collection bottle, respectively. After loading with 10 mL SL and 70 g inoculum, the working volume of the bioreactor was 150 mL by adding deionized water and the top space was flushed with N_2 for 5 mins (Xu *et al.* 2017). The bioreactors were kept at $35 \pm 1^{\circ}\text{C}$ in a water bath and were shaken manually for 1 min twice daily.

Adsorption experiments

Batch adsorption experiments were performed on a shaking table with constant stirring of 150 rpm at 25°C for 4 h, using 50-mL conical flasks with the addition of 0.1 g hydrochar and 10 mL of Cd^{2+} adsorption solution (0.1 mg/mL). The

adsorption solution was prepared with 1 mL of Cd^{2+} standard solution (1 mg/mL) and 9 mL of HNO_3 solution (1 mol/L). Each group of adsorption experiments was repeated in triplicate. After that, the mixtures were filtered and the equilibrium concentration of Cd^{2+} (C_e , mg/mL) in aqueous solutions was determined by atomic adsorption spectrometry (Z-2000, Japan). The adsorption capacity of hydrochar (Q_e , mg/g) was calculated as follows:

$$Q_e = (C_0 - C_e) \times V/M \quad (1)$$

where C_0 (mg/mL) and C_e (mg/mL) stand for the initial solution concentration and equilibrium solution concentration, V (mL) stands for the volume of adsorption solution, M (g) stands for the content of hydrochar.

RESULTS AND DISCUSSION

Effect of SL recycle on the characteristics of SL after HTC

The COD, VFA, pH value and biogas yield of SL from different HTC conditions are displayed in Table 1. After HTC in distilled water at 220 and 240 °C, the COD concentration of SL were 13.66 g/L and 12.70 g/L, respectively. The decrease of COD was due to more organics in the biomass being transformed into gas at higher temperature (Zhang *et al.* 2019). Among the organics in liquid phase, the VFA amount, mainly consisting of acetic acid (78%) and formic acid (18%), were 3.26 g/L after 220 °C HTC and 2.81 g/L

after 240 °C HTC. The acidic pH of SL (4.0–4.1) was determined by the organic acids in SL.

The organics in the biomass were decomposed and transformed into the liquid during HTC, and the amounts of organics in SL were determined by the HTC temperature. The COD values of SL kept increasing with each cycle of SL, it is due to the contribution of organics from the added SL; however, the increment was gradually descending with the increasing cycle times and not as much as expected. For example, the COD of SL was 19.56 g/L after 4 cycles at 220 °C HTC, which was only 43.2% increase. The trend is consistent with the findings from others (Chen *et al.* 2018; Wang *et al.* 2019a), because more organics were either deposited on the hydrochar surfaces or degraded into gas. Chen *et al.* (2018) observed that both hydrochar yield and CO_2 emission increased with each cycle of SL. The VFA were also slightly accumulated with SL recycle, resulting in a drop of 0.01–0.03 on pH after each cycle of SL. The same course of COD, VFA and pH was observed at 240 °C HTC after SL recycle.

After HTC with distilled water at 220 and 240 °C, the biogas yield of SL was achieved to 263.1 and 245.2 mL/g-COD, respectively. The biogas yield of SL kept declining after each cycle of SL, although the amount of COD and VFA was increasing. For example, only 29 mL/g-COD of biogas yield was obtained after four times SL recycle. This indicated that some toxicants for digestion were accumulated in SL after each cycle of SL. For example, furfural compounds have been reported as a major component of SL, which were found to be inhibitory to methanogenesis (Becker *et al.* 2014).

Table 1 | The characteristic of SL after different HTC conditions

	pH	AA (g/L)	FA (g/L)	VFA (g/L)	COD (g/L)	Biogas yield (mL/g-COD)
SL220	4.02 ± 0.01	2.56 ± 0.04	0.57 ± 0.04	3.26 ± 0.04	13.66 ± 0.11	263.1 ± 14.55
SL220-R1	3.99 ± 0.01	3.14 ± 0.06	0.85 ± 0.05	4.08 ± 0.06	16.12 ± 0.13	240.9 ± 10.25
SL220-R2	3.97 ± 0.01	3.72 ± 0.09	0.96 ± 0.05	4.75 ± 0.09	18.28 ± 0.15	168.4 ± 7.04
SL220-R3	3.96 ± 0.01	3.98 ± 0.1	1.02 ± 0.06	5.06 ± 0.1	19.14 ± 0.17	70.3 ± 6.09
SL220-R4	3.96 ± 0.01	4.06 ± 0.1	1.06 ± 0.07	5.15 ± 0.1	19.56 ± 0.18	29.2 ± 4.88
SL240	4.09 ± 0.01	2.23 ± 0.04	0.49 ± 0.04	2.81 ± 0.04	12.70 ± 0.12	245.2 ± 13.72
SL240-R1	4.07 ± 0.01	2.64 ± 0.05	0.64 ± 0.05	3.35 ± 0.05	14.06 ± 0.13	228.3 ± 10.14
SL240-R2	4.04 ± 0.01	2.82 ± 0.06	0.71 ± 0.05	3.57 ± 0.06	14.72 ± 0.13	155.6 ± 8.23
SL240-R3	4.03 ± 0.01	2.89 ± 0.08	0.78 ± 0.05	3.7 ± 0.08	15.21 ± 0.14	54.1 ± 6.15
SL240-R4	4.03 ± 0.01	2.91 ± 0.08	0.81 ± 0.06	3.72 ± 0.08	15.57 ± 0.14	28.4 ± 3.96

Note: AA, acetic acid; FA, formic acid.

Effect of SL recycle on the properties of hydrochar

The BET surface area and the yield of hydrochar

The BET surface area, pore property and the yield of hydrochar from different conditions are listed in Table 2. After HTC in distilled water at 220 and 240 °C, the surface area of hydrochar was 7.99 m²/g and 8.45 m²/g, respectively. The surface area of hydrochar fluctuated in the range of 7.28–8.60 m²/g after SL recycle, and did not keep falling with increasing number of SL recycles. Some researchers also reported that the surface area of hydrochar was free from influence of HTC conditions, because HTC was a mild and inadequate reaction (Kabakc & Bara 2019).

The hydrochar yield was above 22% and was improved by 1.3–3% after SL cycle, but the increment of hydrochar yield was descending with the increasing cycle times. The trend can be explained by some substances in recycled SL being transformed into additional hydrochar, and the substances were gradually consumed after each cycle of SL (Chen *et al.* 2018).

FTIR analysis

The FTIR spectra in Figure 1 provide information about functional groups of the hydrochar. Various functional groups were found on the surface of the hydrochar, strong peaks were obtained in the band of 3,440, 1,600, 1,360 and 1,050 cm⁻¹, corresponding to –OH, C = O, C–O and C–H absorption peaks, respectively; whereas weak peaks were obtained in the groups of C–H stretching vibration (2,830–2,970 cm⁻¹), C–H absorption peak (890 cm⁻¹) and C–C (775 cm⁻¹) (Kambo & Dutta 2015). The peaks of

–OH and C = O showed stronger intensity than other functional groups, it due to dehydration and decarboxylation being the main aromatization reactions during HTC (Volpe *et al.* 2018).

The peak of –OH, C = O and C–O became more intense after SL recycle, suggesting that the intensities of the functional groups were reinforced. Chen *et al.* (2018) also found that the peak of C = C and C–H was enhanced after SL recycle during 220 °C HTC of sweet potato waste, which was attributed to the formation of more aromatic compounds from the added SL. However, it was reported that the intensity of functional groups exhibited almost no change after SL recycle during 260 °C HTC of sewage sludge (Xu *et al.* 2020). The difference in the changes of functional groups maybe depended on the biomass composition and HTC conditions.

The Cd²⁺ adsorption capacity of hydrochar

Figure 2 shows the Cd²⁺ adsorption capacity (Q_e) of different hydrochars, which was 1.31 mg/g and 1.33 mg/g after HTC in distilled water at 220 and 240 °C, respectively. The adsorption capacity of hydrochar showed a downward trend by increasing time of SL recycle, it decreased by 8% after two times of SL recycle and decreased by 20% after 4 times of SL recycle. The removal of hydrochar for heavy metal was mainly performed by the physical adsorption of pore structure and the complexation of functional groups (Wang *et al.* 2019b). The intensities of functional groups were reinforced after SL recycle, and the change of surface area was less than 0.7 m²/g, indicating that another reason was responsible for the decline in heavy metal removal, probably because some substances in the recycled SL were

Table 2 | The pore properties of hydrochar after SL recycle

	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)(nm)	Hydrochar yield (%)
H220	7.99 ± 0.07	0.019 ± 0.001	27.23 ± 0.37	24.1 ± 0.38
H220-R1	7.82 ± 0.14	0.018 ± 0.001	27.83 ± 0.21	25.4 ± 0.57
H220-R2	8.20 ± 0.12	0.020 ± 0.001	27.09 ± 0.22	26.1 ± 0.43
H220-R3	7.42 ± 0.09	0.017 ± 0.001	28.16 ± 0.17	26.5 ± 0.6
H220-R4	7.28 ± 0.09	0.016 ± 0.001	28.61 ± 0.17	26.8 ± 0.73
H240	8.45 ± 0.13	0.022 ± 0.001	27.84 ± 0.28	22.0 ± 0.39
H240-R1	8.60 ± 0.07	0.024 ± 0.001	27.03 ± 0.35	23.6 ± 0.44
H240-R2	8.38 ± 0.11	0.022 ± 0.001	27.98 ± 0.16	24.1 ± 0.48
H240-R3	8.03 ± 0.09	0.021 ± 0.001	28.22 ± 0.22	24.5 ± 0.67
H240-R4	8.15 ± 0.09	0.022 ± 0.001	28.08 ± 0.22	25.0 ± 0.65

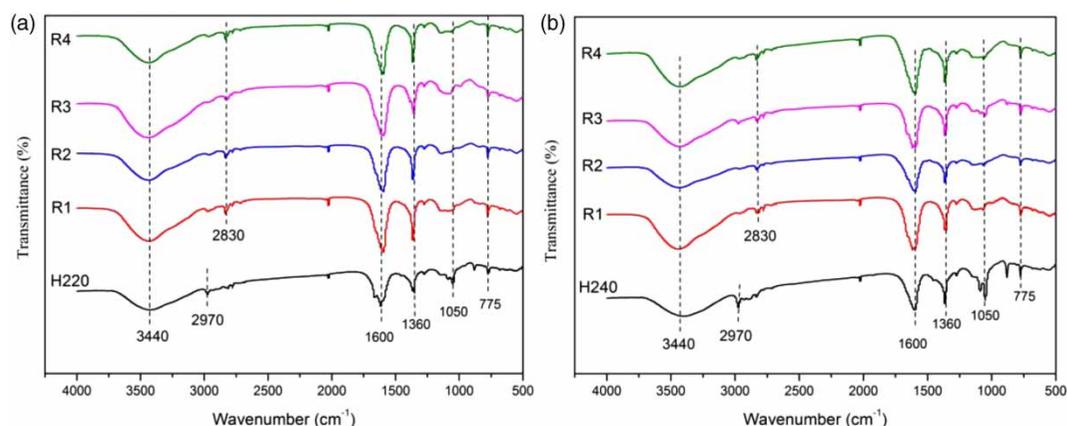


Figure 1 | The function groups of hydrochar from different temperature HTC (a) 220 °C (b) 240 °C.

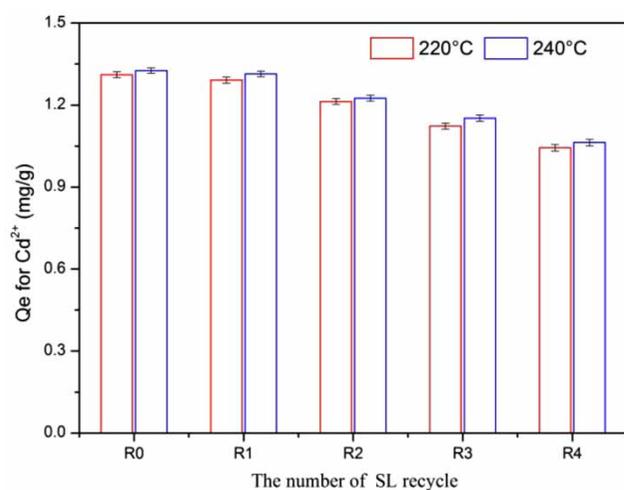


Figure 2 | The Cd^{2+} adsorption capacity of different hydrochars.

gradually deposited on the surface of the hydrochar and interfered with the removal of heavy metals by the pore structure and functional groups.

CONCLUSIONS

The SL after HTC is rich in acetic acid, formic acid, and other organics. The COD amount of SL increased after each cycle of SL, but the biodegradability of organics in SL showed a downward trend. The functional groups of hydrochar are strengthened and the hydrochar yield is increased after SL recycle. Although the capacity to remove heavy metal by hydrochar was decreased by SL recycle, the removal efficiency was still above 90% after two cycles of SL. SL recycle in HTC is a promising strategy to reduce the amount of SL.

ACKNOWLEDGEMENTS

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Becker, R., Dorgerloh, U., Paulke, E., Mumme, J. & Nehls, I. 2014 Hydrothermal carbonization of biomass: major organic components of the aqueous phase. *Chemical Engineering Technology* **37**, 511–518.
- Catalkopru, A. K., Kantarli, I. C. & Yanik, J. 2017 Effects of spent liquor recirculation in hydrothermal carbonization. *Bioresource Technology* **226**, 89–95.
- Chen, X. F., Ma, X. Q., Peng, X. W., Lin, Y. S., Wang, J. J. & Zheng, C. P. 2018 Effects of aqueous phase recirculation in hydrothermal carbonization of sweet potato waste. *Bioresource Technology* **267**, 167–174.
- Clausen, L. R. 2017 Energy efficient thermochemical conversion of very wet biomass to biofuels by integration of steam drying, steam electrolysis and gasification. *Energy* **125**, 327–336.
- Curtin, J., McInerney, C., Gallachóir, B. Ó., Hickey, C., Deane, P. & Deeney, P. 2019 Quantifying stranding risk for fossil fuel assets and implications for renewable energy investment: a review of the literature. *Renewable and Sustainable Energy Reviews* **116**, 109402.
- Kabakc, S. B. & Bara, S. S. 2019 Hydrothermal carbonization of various lignocellulosics fuel characteristics of hydrochars

- and surface characteristics of activated hydrochars. *Waste Management* **100**, 259–268.
- Kambo, H. S. & Dutta, A. 2015 A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renewable and Sustainable Energy Reviews* **45**, 359–378.
- Shi, Y., Luo, G., Rao, Y., Chen, H. H. & Zhang, S. C. 2019 Hydrothermal conversion of dewatered sewage sludge: focusing on the transformation mechanism and recovery of phosphorus. *Chemosphere*. **228**, 619–628.
- Stemann, J., Putschew, A. & Ziegler, F. 2013 Hydrothermal carbonization: process water characterization and effects of water recirculation. *Bioresource Technology* **143**, 139–146.
- Volpe, M., Goldfarb, J. L. & Fiori, L. 2018 Hydrothermal carbonization of *Opuntia ficus-indica* cladodes: role of process parameters on hydrochar properties. *Bioresource Technology* **247**, 310–318.
- Wang, T. F., Zhai, Y. B., Zhu, Y., Li, C. T. & Zeng, G. M. 2018 A review of the hydrothermal carbonization of biomass waste for hydrochar formation: process conditions, fundamentals, and physicochemical properties. *Renewable and Sustainable Energy Reviews* **90**, 223–247.
- Wang, F. B., Wang, J., Gu, C., Han, Y., Zan, S. J. & Wu, S. 2019a Effects of process water recirculation on solid and liquid products from hydrothermal carbonization of *Laminaria*. *Bioresource Technology* **292**, 121996.
- Wang, L., Wang, Y. J., Ma, F., Tankpa, V., Bai, S. S., Guo, X. M. & Wang, X. 2019b Mechanisms and reutilization of modified biochar used for removal of heavy metals from wastewater: a review. *Science of The Total Environment* **668**, 1298–1309.
- Wirth, B., Reza, T. & Mumme, J. 2015 Influence of digestion temperature and organic loading rate on the continuous anaerobic treatment of process liquor from hydrothermal carbonization of sewage sludge. *Bioresource Technology* **198**, 215–222.
- Xia, Y., Liu, H. J., Guo, Y. H., Liu, Z. G. & Jiao, W. T. 2019 Immobilization of heavy metals in contaminated soils by modified hydrochar: efficiency, risk assessment and potential mechanisms. *Science of The Total Environment* **6851**, 1201–1208.
- Xu, J., Mustafa, A. M. & Sheng, K. C. 2017 Effects of inoculum to substrate ratio and co-digestion with bagasse on biogas production of fish waste. *Environmental Technology* **38**, 2517–2522.
- Xu, Z. X., Song, H., Li, P. J., He, Z. X., Wang, Q., Wang, K. & Duan, P. G. 2020 Hydrothermal carbonization of sewage sludge: effect of aqueous phase recycling. *Chemical Engineering Journal* **387**, 123410.
- Zhan, L., Jiang, L., Zhang, Y. L., Gao, B. & Xu, Z. M. 2020 Reduction, detoxification and recycling of solid waste by hydrothermal technology: a review. *Chemical Engineering Journal* **390**, 124651.
- Zhang, Y., Jiang, Q., Xie, W. L., Wang, Y. F. & Kang, J. M. 2019 Effects of temperature, time and acidity of hydrothermal carbonization on the hydrochar properties and nitrogen recovery from corn stover. *Biomass and Bioenergy* **122**, 175–182.

First received 20 September 2020; accepted in revised form 2 November 2020. Available online 12 November 2020