Lead Removal by Hydrochar from Hydrothermal Carbonization of Food Waste

Thi Hoang Tuyen Do¹, Thai-Hoang Le² and Thi Phuong Thuy Pham*¹

¹ Faculty of Biotechnology, Ho Chi Minh City University of Food Industry, Vietnam
² Department of Environmental Engineering, International University, Vietnam
E-mail: thuyppt@hufi.edu.vn

Abstract
Food waste recently emerged as a resource with a potential to be converted to hydrochar which could be utilized in various applications. In this study, we focused on investigation of the lead removal of hydrochar obtained from hydrothermal carbonization of food waste. Hydrochar was collected after hydrothermal liquefaction of food waste at 180°C for 2 h. The adsorption of hydrochar towards Pb²⁺ in aqueous solution was conducted in batch mode to investigate the sorption kinetics, isotherm and pH edge. The results showed that hydrochar derived from food waste exhibits high performance in adsorption of lead from aqueous solution, achieving 160.21 mg g⁻¹ removal capacity within the first 2 h of reaction. This indicated promising application as heavy metal sorbents of hydrochar from hydrothermal conversion of food waste.

1. Introduction
Recently, the municipal solid waste generation rate in Vietnam is reaching critical levels due to rapid urbanization, industrialization and growth in population. According to Schneider et al. (2017), the municipal solid waste composition is dominant by food waste with a high percentage of 65% [1]. Current waste management strategies mostly rely on landfilling, which raises significant environmental concerns. It was reported that food waste decomposition in landfill results in direct and indirect emission of methane, which is 23 times more potent than carbon dioxide as a greenhouse gas and contributes to climate change [2]. It is therefore important to manage food waste in a sustainable way to reduce environmental issues and minimize risk to human health.

Many researchers proved that food waste is a promising resource with great potential for generating energy [3-5]. There have been various technologies developed for efficient treatment of food waste, which help to recover valuable fuel and chemicals that are environmentally viable. Among these, hydrothermal carbonization (HTC) is gaining considerable attention in waste-to-energy conversion especially food waste because it is a wet process that converts waste streams with high moisture content to an energy-rich resource [6]. Aierzhati et al. (2019) obtained up to 79% of biocrude oil from food leftovers collected in a university campus dining hall using hydrothermal liquefaction at 280-380°C during 10-60 min [7]. In another study, cafeteria food residues were processed at 200°C for 6 h to gain hydrochar which could be used for co-combustion [8]. There are many functional groups presented on the surface of hydrochar such as hydroxyl, carboxylate and carbonyl, making it a potential adsorbent [9]. Liu and Zhang (2009) showed that hydrochar from rice husk was capable of removing Pb²⁺ with adsorption capacity of 2.4 mg/g after 5 h at 45°C and pH
which was similar to other published literatures. Metal ions on hydrochar surface are protonated at low pH, leading to reduction in their interaction with the hydrochar. The adsorption capacity of hydrochar ranged from 109.4 to 188.6 mg g⁻¹. It was also mentioned that some active functional groups on hydrochar surface are protonated at low pH, leading to reduction in their interaction with metal ions. The data in this study showed that pH optimal for highest adsorption capacity was 7.0, which was similar to other published literatures.

2. Materials and methods

2.1. Materials

Food waste was collected from canteen in the dormitory of Ho Chi Minh City University of Food Industry. The waste was then homogenized and stored at -20°C prior to further experiments. Production of hydrochar by hydrothermal carbonization Hydrothermal carbonization of food waste was carried out in a 100 mL Teflon®-lined high-pressure reactor vessel purchased from Latech Scientific Supply Pte. Ltd. The reactor was run with 25% of solid (as-received food waste) and kept in a heating oven at 180°C for 6 h. When the reaction completed, the reactor was cooled to room temperature and the hydrochar was obtained by filtration. The hydrochar product was then washed with deionized water, dried in air and stored in a sealed container.

2.2. Adsorption experiments

Adsorption of Pb²⁺ was investigated in batch tests with the hydrochar concentration fixed at 2 g L⁻¹. Kinetic tests were performed at 25°C and initial concentration of Pb²⁺ was 500 mg L⁻¹. Samples were regularly taken from 0.5 – 24 h. pH was adjusted to 7.0 using 0.1 N NaOH. The taken samples were filtered to remove some particles in suspension and injected to AAS for quantitative analysis of Pb²⁺. The estimated data points were fitted by pseudo-first-order and pseudo-second-order models to calculate the equilibrium characteristics of Pb²⁺ onto hydrochar. The pseudo-first-order model can be expressed as:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]

The pseudo-second-order model based on equilibrium can be expressed as:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]

where \( q_e \) and \( q_t \) are the amounts of Pb²⁺ adsorbed (mg g⁻¹) at equilibrium and time t (min), respectively, and \( k_1 \) (L min⁻¹) and \( k_2 \) (L min⁻¹) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

The adsorption isotherm tests were performed at 25°C and the concentrations of Pb²⁺ were ranged from 10 – 500 mg L⁻¹. The pH of Pb²⁺ solutions was adjusted at 7.0 as the kinetic tests were done. Samples were taken after 1 day and were filtered for AAS analysis. The pH edge tests were performed at a fixed concentration of Pb²⁺ and the pH of Pb²⁺ solution was adjusted to the desired pH from 2.0 to 7.0 using 0.1 N HCl or 0.1 N NaOH.

3. Results and discussion

3.1. Effect of pH on lead adsorption

The pH adsorption edge tests were performed to estimate the effect of pH on Pb²⁺ adsorption onto the foodwaste-derived hydrochar since molecular interaction potentials of Pb²⁺ and the functional groups of the adsorbent can be different at various pH levels. The effect of pH on lead adsorption was investigated with pH range between 2 and 7 as it was reported that Pb²⁺ is precipitated in the form of Pb(OH)₂ at higher pH values. Figure 1 showed that the Pb²⁺ removal efficiencies by hydrochar from food waste were affected by solution pH. The adsorption capacity was found to increase with an increase in pH and ranged from 109.4 to 188.6 mg g⁻¹. At low pH, there is competition between H⁺ and Pb²⁺ on the surface of hydrochar, thus lowered the adsorption uptake. It was also mentioned that some active functional groups on hydrochar surface are protonated at low pH, leading to reduction in their interaction with metal ions. The data in this study showed that pH optimal for highest adsorption capacity was 7.0, which was similar to other published literatures.
capacity of food waste hydrochar was 188.6 mg g⁻¹, which was comparable to removal efficiency of hydrochar from hickory hull (162.3 mg/g) [17].

**Figure 1.** Effect of pH on the Pb²⁺ adsorption capacity of food-waste hydrochar

3.2. Adsorption kinetic studies

Fig. 2 shows the effect of contact time on Pb²⁺ adsorption over food-waste derived hydrochar. Lead removal efficiencies at different time intervals ranging from 0.5 – 24 h are obtained. Results showed that adsorption equilibrium is achieved within approximately 2 h. Modeling results for Pb sorption using the pseudo-second-order equation showed correlation coefficient (R²) exceeds 0.999 (Table 1). This indicated the sorption mechanism is based on chemisorption rate-controlling mechanism [18].

**Figure 2.** Pb²⁺ adsorption kinetics of food-waste hydrochar
Table 1. Parameters of Pb\(^{2+}\) adsorption on food-waste hydrochar

| Models               | Parameters                        | Parameters       |
|----------------------|-----------------------------------|------------------|
| Pseudo-first order   | \(q_{e, \text{exp}}\) (mg g\(^{-1}\)) | 160.21           |
|                      | \(q_{e, \text{cal}}\) (mg g\(^{-1}\)) | 160.02           |
|                      | \(K_{1}\) (h\(^{-1}\))            | 4.1097           |
|                      | \(R^2\)                           | 0.8876           |
| Pseudo-second order  | \(q_{e, \text{exp}}\) (mg g\(^{-1}\)) | 160.21           |
|                      | \(q_{e, \text{cal}}\) (mg g\(^{-1}\)) | 163.93           |
|                      | \(K_{2}\) (g mg\(^{-1}\)h\(^{-1}\)) | 0.0532           |
|                      | \(R^2\)                           | 0.9999           |

3.3. Batch adsorption isotherm tests

The isotherm experiments were carried out to evaluate the adsorption capacities of hydrochar for Pb\(^{2+}\), and the experimental data points were fitted by Langmuir and Freundlich models to calculate maximum adsorption capacity \(q_m\) values. The Langmuir isotherm model is given below:

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]

where \(q_m\) and \(b\) are the maximum adsorption capacity (mg g\(^{-1}\)) and free energy of adsorption (L mg\(^{-1}\)), respectively. Here, \(b\) means the adsorption affinity between adsorbent and adsorbate. The Freundlich isotherm model can be expressed as:

\[ q_e = K_f C_e^{1/n} \]

Where \(q_e\) (mg g\(^{-1}\)) is the uptake of Pb\(^{2+}\), \(C_e\) (mg L\(^{-1}\)) is the liquid-phase sorbate concentration at equilibrium, \(K_f\) (mg g\(^{-1}\)) and \(n\) are Freundlich isotherm constants.

The maximum Pb adsorption capacity of food-waste hydrochar calculated from the Langmuir model (Table 2) is 263.16 mg g\(^{-1}\) which is comparable to the capacity of most reported adsorbents i.e. hydrochar from peanut hull [17], fungus biomass [19].

Table 2. Parameters of the Freundlich and Langmuir isotherms

|               | Freundlich | Langmuir |
|---------------|------------|----------|
| \(K_f\)      | 2.56       | 468.17   |
| \(n\)        | 1.27       | 0.92     |
| \(R^2\)      | 0.92       | 0.91     |
| \(q_m\) (mg g\(^{-1}\)) | 263.16     |          |
| \(b\) (L mg\(^{-1}\))  | 468.17     |          |
| \(R^2\)      | 0.91       |          |

Figure 3. Effect of initial Pb\(^{2+}\) concentration to the adsorption capacity of food-waste hydrochar

Results in Fig. 3 showed that Pb\(^{2+}\) from aqueous solutions could be strongly adsorbed by hydrochar and the adsorption capacities increased in correlation with the increase in initial Pb\(^{2+}\) concentration. This could be attributed to the driving force given by the difference in Pb\(^{2+}\) concentration in the aqueous and solid phases.
4. Conclusions
Hydrochar was synthesized through hydrothermal carbonization of food waste and it exhibits high \( \text{Pb}^{2+} \) removal capacity. The adsorption capacity was obtained to be 160.21 mg g\(^{-1}\) of \( \text{Pb}^{2+} \) in aqueous solutions and the adsorption equilibrium was achieved within approximately 2 h. The results of the present study suggest potential applications of food-waste derived hydrochar for the removal of toxic metal ions from wastewater streams.

5. References
[1] Schneider P, Anh LH, Wagner J, Reichenbach J and Hebner A 2017 Sustainability 9 286.
[2] Pham TPT, Kaushik R, Parshetti GK, Mahmod R and Balasubramanian R 2015 Waste Manage. 38 399.
[3] McKendry P 2002 Bioresour. Technol. 83 47.
[4] Matsakas L, Kekos D, Loizidou M and Christakopoulos P 2014 Biotechnol Biofuels 7 4.
[5] Ahmed II and Gupta AK 2010 Appl. Energy 87 101.
[6] Berge ND, Ro KS, Mao J, Flora JR, Chappell MA and Bae S 2011 Environ. Sci. Technol. 45 5696.
[7] Aierzhati A, Stablein MJ, Wu NE, Kuo C-T, Si B, Kang X and Zhang Y 2019 Bioresour. Technol. 284 139.
[8] Tradler SB, Mayr S, Himmelsbach M, Priefwasser R, Baumgartner W and Stadler AT 2018 Bioresour. Technol. Reports 2 77.
[9] Parshetti GK, Chowdhury S and Balasubramanian R 2014 Bioresour. Technol. 161 310.
[10] Liu ZG and Zhang FS 2009 J. Hazard. Mater. 167 933.
[11] Liu Z, Zhang F-S and Wu J 2010 Fuel 89 510.
[12] Hammud HH, Karnati RK, Shafee MA, Fawaz Y and Holail H 2019 Chem. Eng. Commun. DOI: 10.1080/00986445.2019.1702975.
[13] Tan X, Liu Y, Zeng G, Wang X, Hu X, Gu Y and Yang Z 2015 Chemosphere 125 70.
[14] Yan G, Viraraghavan T and Chen M 2001 Adsorpt. Sci. Technol. 19 25.
[15] Fazal A and Rafique U 2013 J. Environ. Eng (New York) 3 288.
[16] Horsfall M and Spiff AI 2014 Electron. J. Biotechnol. 7 310.
[17] Fang J, Gao B, Mosa A and Zhan L 2017 Chem. Speciat. Bioavailab. 29 197.
[18] Xue Y, Gao B, Yao Y, Inyang M, Zhang M, Zimmerman AR and Ro KS 2012 Chem. Eng. J. 200-202 673.
[19] Subbaiah MV, Yuvaraja G, Vijaya Y and Krishnaiah A 2011 J. Taiwan Inst. Chem. Eng. 42 965.

Acknowledgements
This study was supported by The Youth Incubator for Science and Technology Program managed by Youth Development Science and Technology Center – Ho Chi Minh Communist Youth Union and Department of Science and Technology of Ho Chi Minh City, the contract number is “05/2019/HDCNT-VU”.