Preparation of Sodium Pyrophosphate Modified Municipal Sludge Biochar for the Cu Adsorption in Aqueous Solution

Liangqian Fan¹, Qin Liu¹, Xianda Wang¹, Jie Cai², Jiaxin Miao¹ and Yan Wan¹
¹ College of Civil Engineering, Sichuan Agricultural University, Dujiangyan 611830, China
² Department of Physical and Chemical Analysis, Dujiangyan Center for Disease Control and Prevention, Dujiangyan, 611830, China
Email: flqjacky@163.com

Abstract. In this work, sodium pyrophosphate (SP) was used as a modifier to prepare the sodium pyrophosphate modified municipal sludge biochar (SP-MSB) for effectively adsorbing Cu in aqueous solution. Four modification factors, i.e., SP concentration factor, impregnation time factor, impregnation solid-liquid ratio factor, and impregnation temperature factor, were investigated to explore the suitable modification condition for the preparation of SP-MSB. In addition, the Cu adsorption efficiencies of the SP-MSB under the suitable modification condition and the unmodified municipal sludge biochar (MSB) were preliminarily evaluated. The results showed that the suitable modification condition for the preparation of SP-MSB was SP concentration of 60 g/L, impregnation time of 10 h, impregnation solid-liquid ratio of 1:30, and impregnation temperature of 25 °C. The Cu adsorption capability of the SP-MSB was 6.37 times than that of MSB, indicating that the SP-MSB can be used as an alternative adsorbent to adsorb Cu in aqueous solution.

1. Introduction
The Cu-containing wastewater is mainly originated from different industry activities such as Cu mining and smelting, electroplating, and printed circuit board [1,2]. The Cu concentration in these wastewaters was varied from less than 0.01 mM to hundreds mM [3]. Cu is one of toxic heavy metals, which can cause environmental pollution and harm to human health after accumulation [4]. At present, the Cu permissible emission limit of industrial effluents in China is 0.5 mg/L [5]. Thus, the excessive Cu needs to be removed from the Cu-containing wastewater before discharging it.

There are various techniques employed for removing Cu from wastewater, such as chemical precipitation, ion exchange, membrane separation, electrocoagulation, and adsorption [6,7]. Among these techniques, adsorption is an usually used method because of its easy operation, low cost and high efficiency [8]. For adsorption, removal efficiency mainly depends on absorbent [9]. In recent years, commercial activated carbon is usually used as absorbent to absorb Cu in aqueous solution, but its application is hindered due to its high cost and limited adsorption capacity [10,11]. At present, developing high adsorption-efficiency, low-cost, and sustainable adsorbents for Cu attracts much attention.

Municipal sludge is a kind of biomass byproduct produced from municipal wastewater treatment. It contains heavy metals, bacteria and pathogens, which can caused the second pollution without the proper treatment. In China, more than 30 million tons municipal sludge were generated every year [12]. Municipal sludge treatment is a focus of Chinese government. In recent years, Shen et al. and Zhou et al. used the biochar prepared from municipal sludge to adsorb Cu [13,14]. However, the Cu
adsorption efficiency of the pristine biochar was low. At present, some researchers adopted various modifiers, such as phosphoric acid [15], NaOH [16], and animo [17] to prepare modified biochars. In these studies, the modified biochars showed a higher adsorption efficiency for Cu compared with the pristine biochars. In general, modification is an effective way to enhance the Cu adsorption efficiency of biochar.

In this study, SP was used as a modifier to prepare the sodium pyrophosphate modified municipal sludge biochar (SP-MSB) for effectively adsorbing Cu in aqueous solution. To explore the suitable modification condition for the preparation of SP-MSB, four modification factors including SP concentration factor, impregnation time factor, impregnation solid-liquid ratio factor, and impregnation temperature factor were investigated. In addition, the Cu adsorption efficiencies of the SP-MSB under the suitable modification condition and MSB were compared. The aims of this study is to determine the suitable modification condition for the preparation of SP-MSB.

2. Materials and Methods

2.1. Raw Materials
Municipal sludge was collected from a sewage treatment plant in Chengdu, Sichuan Province, China. The municipal sludge was first air-dried to constant weight at room temperature. Then the dried municipal sludge was ground to pass a 10-mesh screen. So far, the municipal sludge used in following experiments was acquired.

2.2. Preparation of SP-MSB and MSB
Four modification factors including the SP concentration factor, impregnation time factor, impregnation solid-liquid ratio factor, and impregnation temperature factor were inspected to determine the suitable modification condition for the preparation of SP-MSB. For investigating a factor, a series of values of the factor were designed and the values of other three factors were fixed. The specific designed values of a factor and the fixed values of the other three factors are listed in Table 1. For each factor, the combination of a designed value and the fixed values of the other three factors was set as a modification condition for the preparation of SP-MSB. Under a modification condition, a sample of SP-MSB can be prepared.

Table 1. The designed values of a factor and the fixed values of the other three factors for the preparation of SP-MSB.

| The factors of modification | The setting value |
|-----------------------------|------------------|
| SP concentration (g/L)      | 1, 5, 10, 20, 30, 40, 60 |
| Impregnation time (h)       | 24, 1:25 |
| Impregnation solid-liquid ratio (mg/L) | 1:25 |
| Impregnation temperature (°C) | 25 |
| SP concentration            | 60 |
| Impregnation time (h)       | 1, 2, 4, 6, 10, 12 |
| Impregnation solid-liquid ratio (mg/L) | 1:25, 1:5, 1:10, 1:15, 1:20, 1:25, 1:30 |
| Impregnation temperature (°C) | 25, 35, 45, 45, 55, 65, 75 |
| Impregnation solid-liquid ratio (mg/L) | 1:30 |

For the preparation process of SP-MSB, a certain amount of municipal sludge was soaked into SP solution according to a specific modification condition (see Table 1). When the soaking was done, the soaked municipal sludge was filtered and then dried to constant weight to acquire the raw material for pyrolysis. Then, the raw material was put into a ceramic crucible with cover, and the crucible was put into a muffle furnace (SX2-4-10, Shenyang Energy Saving Electric Furnace Factory, Shenyang, China) for pyrolysis at 400°C for 2 h. After the pyrolysis finished, the pyrolyzed product was naturally cooled to room temperature, and then it was washed with hot deionized water several times. After that, the
washed product was dried at 80°C, and then ground to pass a 60-mesh sieve. So far, a sample of SP-MSB was prepared.

For MSB, the preparation process was as the same as that of SP-MSB except for the soaking and washing processes.

2.3. Suitable Modification Condition for Preparing SP-MSB

For each modification factor, the acquired different SP-MSB was used as adsorbent to adsorb Cu in aqueous solution, and the suitable designed value was selected according to the results of Cu adsorption rate. For the Cu adsorption experiment, it was conducted as follows. 0.1 g SP-MSB was added to 50 mL Cu solution with concentration of 50 mg/L. Then the initial pH of the mixed solution was adjusted to about 5.0, and the mixed solution were oscillated with a speed of 130 r/min at room temperature for 4 h. When time was out, the mixed solution was filtered and the filtrate was collected. The residual concentration of Cu in the filtrate was determined by using a flame atomic absorption spectrometer (900T, Perkin-Elmer Crop., Waltham, Massachusetts, USA). The Cu adsorption rate of SP-MSB was calculated by the following equation (1).

\[
R = \left( \frac{C_0 - C_i}{C_0} \right) \times 100\% \tag{1}
\]

Where \(C_0\) (mg/L) and \(C_i\) (mg/L) refers to the initial and residual Cu concentration, respectively. \(R\) (%) denotes the adsorption rate of Cu.

The combination of the suitable designed value of each factor was taken as the suitable modification condition for the preparation of SP-MSB.

2.4. Comparation of Cu Adsorption Efficiencies between SP-MSB and MSB

SP-MSB prepared under the suitable condition and MSB were used to absorb Cu in aqueous solution. The steps of adsorption experiment were the same as that in Section 2.2. The Cu adsorption rates of SP-MSB and MSB were also calculated according to equation (1).

3. Result and Discussion

3.1. SP Concentration Factor

Figure 1 shows the influence of SP concentration factor on the Cu adsorption rate of SP-MSB. It can be found that the different SP concentrations significantly influenced the adsorption of Cu of SP-MSB (p<0.05). In Figure 1, there was a positive correlation between adsorption rate of Cu and SP concentration. The maximum adsorption rate was 78.11 % at 60 g/L. The increment of Cu adsorption rate might be explained that there were more \(P_2O_7^{4-}\) ions loaded on the surface of municipal sludge biomass with increasing of SP concentration, which provided more active sites for the Cu adsorption. According to Figure 1, the suitable concentration of SP was selected as 60 g/L for the preparation of SP-MSB.

![Figure 1. The change of Cu adsorption rate of SP-MSB with the variation of SP concentration factor.](image-url)
3.2. Impregnation Time Factor
Figure 2 shows the effect of impregnation time factor on the Cu adsorption rate of SP-MSB. It was found that adsorption rate increased from 48.12 % to 85.35 % when impregnation time increased from 1 h to 12 h. With the prolong of impregnation time, $P_2O_7^{4-}$ ions were in sufficient contact with the surface of municipal sludge biomass, resulting in more $P_2O_7^{4-}$ ions loaded on the surface of municipal sludge biomass. Therefore, SP-MSB prepared from 1 h to 12 h of impregnation time had a mounting Cu adsorption rate. However, Cu adsorption rate of 10 h and 12 h (84.51% and 85.35%, respectively) had no significant difference ($p>0.05$), so 10 h was considered as the suitable impregnation time for the preparation of SP-MSB.

![Figure 2](image)

Figure 2. The change of Cu adsorption rate of SP-MSB with the variation of impregnation time factor.

3.3. Impregnation Solid-liquid Ratio Factor
The effect of impregnation solid-liquid ratio factor on the Cu adsorption rate of SP-MSB is shown in Figure 3. It was found that adsorption rate of Cu increased with an increase in impregnation solid-liquid ratio. When impregnation solid-liquid ratio increased to 1:30, adsorption rate reached the maximum ($p<0.05$). According to the results, the suitable impregnation solid-liquid ratio was 1:30 for the preparation of SP-MSB.

![Figure 3](image)

Figure 3. The change of Cu adsorption rate of SP-MSB with the variation of impregnation solid-liquid ratio factor.

3.4. Impregnation Temperature Factor
Figure 4 shows the effect of impregnation temperature factor on the Cu adsorption rate of SP-MSB. It can be seen that the adsorption rate of Cu decreased with increasing impregnation temperature from 25°C to 75°C. The maximum adsorption rate was observed at 25°C. The reason for this trend might be that the introduction of SP on the surface of municipal sludge biomass was an exothermic reaction. According to Figure 4, the suitable impregnation temperature was 25°C for the preparation of SP-MSB.
3.5. Adsorption of Cu with MSB and SP-MSB

The Cu adsorption rates of MSB and SP-MSB prepared under the suitable modification condition (i.e., SP concentration of 60 g/L, impregnation time of 10 h, solid-liquid ratio of 1:30 and impregnation temperature of 25°C) are shown in Figure 5. The Cu adsorption rate of MSB and SP-MSB was 14.29 % and 90.96 %, respectively. The Cu adsorption rate of SP-MSB was 6.37 times than that of MSB. For SP-MSB, the Cu adsorption rate might be related to the introduction of P₂O₇³⁻ ions, which could complex with copper ions [18]. The results indicated that the modification is help for the adsorption of Cu. In summary, SP-MSB can be used as an efficient adsorbent for the Cu adsorption in aqueous solution.

4. Conclusions

In this study, four modification factors including SP concentration factor, impregnation time factor, impregnation solid-liquid ratio factor, and impregnation temperature factor were discussed to determine the appropriate modification condition for the preparation of SP-MSB. The results revealed that the appropriate modification condition of SP-MSB was SP concentration of 60 g/L, impregnation time of 10 h, solid-liquid ratio of 1:30 and impregnation temperature of 25 °C. Under the modification condition, the Cu adsorption rate with SP-MSB was 6.37 times than that of MSB. Overall, the SP-MSB prepared in this study can be used as an effective adsorbent for Cu in aqueous solution.

5. Acknowledgment

This work was supported by the National Undergraduate Innovation Training Program Funded Project of Sichuan Agricultural University (No. 201610626042).

6. References

[1] Kanapathy S and Mohamed N 2013 Sep. Purif. Technol. 118 279-84
[2] Hu HM, Li XW, Huang PW, Zhang QW and Yuan WY 2017 J. Environ. Manage. 203 1-7
[3] Tao HC, Liang M, Li W, Zhang LJ, Ni JR and Wu WM 2011 J. Hazard. Mater. 189 186-92
[4] White RL, White CM, Turgut H, Massoud, A and Tian, ZR 2018 J. Taiwan Inst. Chem. Eng. 85 18-28
[5] Dong Y, Liu JF, Sui MR, Qu, YP, Ambuchi, JJ, Wang, HM and Feng, YJ 2017 J. Hazard. Mater. 321 307-15
[6] Pellera FM, Giannis A, Kalderis D, Anastasiadou, K, Stegmann, R, Wang, JY and Gidarakos, E 2012 J. Environ. Manage. 96 35-42
[7] Al-Shannag M, Al-Qodah Z, Bani-Melhem K, Qtaishat, MR and Alkasrawi, M 2015 Chem. Eng. J. 260 749-56
[8] Jin HM, Hanif M U, Capareda S, Chang ZZ, Huang HY and Ai YC 2016 J. Environ. Chem. Eng. 4 365-72
[9] Tong XJ, Li JY, Yuan JH and Xu RK 2011 Chem. Eng. J. 172 828-34
[10] Aran, D, Antelo J, Fiol S and Macias, F 2016 Bioresour. Technol. 212 199-206
[11] Li M, Liu Q, Guo LJ, Zhang YP, Lou ZJ, Wang Y and Qian GG 2013 Bioresour. Technol. 141 83-8
[12] Awasthi MK, et al 2017 Waste Manage. 68 760-73
[13] Shen TT, Tang YY, Lu XY and Meng Z 2018 J. Clean Prod. 193 185-93
[14] Zhou D, Liu D, Gao FX, Li MK and Luo XP 2017 Int. J. Environ. Res. Public Health 14 681
[15] Peng HB, Gao P, Chu G, Pan B, Peng JH and Xing BS 2017 Environ. Pollut. 229 846-53
[16] Ding ZH, Hu X, Wan YS, Wang SS and Gao B 2016 J. Ind. Eng. Chem. 33 239-45
[17] Yang GX and Jiang H 2014 Water Res. 48 396-405
[18] Chen FY, Zhao X, Liu HJ and Qu JH 2014 Chem. Eng. J. 253 478-85