Efficient adsorption removal of Cd$^{2+}$ from aqueous solutions by HNO$_3$ modified bamboo-derived biochar

Wenxiao Tang$^{1*}$, Ningning Cai$^{1#}$, Hongxia Xie$^{1#}$, Yachun Liu$^{1}$, Zhifeng Wang$^{2}$, Youhong Liao$^{1}$, Taotao Wei$^{1}$, Chao Zhang$^{1}$, Zaihui Fu$^{1}$, and Dulin Yin$^{1}$

1 National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and advanced materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan, 410081, China

2 Hunan Kangshou Pharmaceutical Co., Ltd., Changsha, Hunan, 410200, China

$^{*}$Corresponding author’s e-mail: yacl315@163.com
$^{#}$These authors contributed equally to this work

Abstract. In this work porous biochar was prepared from bamboo powder by ZnCl$_2$ chemical activation. The effects of preparation, modification and adsorption conditions on its removal performance of Cd$^{2+}$ in simulated wastewater were investigated by static adsorption. The adsorption kinetics and isotherms of Cd$^{2+}$ were further studied. The results showed that the good adsorption property was obtained over the biochar prepared under optimized preparation and modification conditions. The biochar reached the highest removal efficiency of 95.53% under optimum adsorption conditions. The adsorption process of Cd$^{2+}$ was well in accordance with the pseudo-second adsorption kinetics equation, and the equilibrium adsorption capacity was up to 16.62 mg·g$^{-1}$. The Freundlich isothermal adsorption model better fitted compared with the Langmuir model for this adsorption system and the maximum adsorption capacity was as high as 44.54 mg·g$^{-1}$. After four adsorption-desorption recycling, the adsorption removal percentage decreased a little, indicating that biochar had good regeneration performance. In short, this inexpensive porous biochar has the potential to become a practical adsorbent of cadmium.

1. Introduction

With the continuous development of economy and society, the harm of heavy metal ions containing industrial wastewater to the ecological environment and human health is becoming an increasingly serious problem in many developing countries[1, 2]. For example, cadmium ions in industrial wastewater have mutagenic, carcinogenic, teratogenic effects and thus cause serious damage to the respiratory system, kidney and other organs[3-6]. At present, there are a lot of reports on the removal methods of cadmium ions in wastewater, such as chemical precipitation, ion exchange and adsorption[1-6]. Among these methods, the adsorption using commercial activated carbon as an sorbent is a popular and effective means due to its high surface area, well-developed internal microporosity, and plentiful surface functional groups[7-9].
Conventional activated carbon sorbents, however, is to a certain extent limited owing to the existing problems originated from the raw material source including non-renewable resources such as coal tar and petroleum coke pitch derived one-time fossil resources and renewable resources like wood. A large-scale consumption of these natural resources can cause great environmental pressures. On the other hand, bamboo is an abundant and renewable biomass with its advantages of fast growth, extensive planting and high yield\cite{10, 11}, and accordingly leading to the rapid development of the bamboo products industry and the simultaneous production of a large number of bamboo processing residues. The residues can be easily converted to bamboo-derived porous biochar. The material possesses a high specific surface area, a high micropore ratio and abundant surface acidic groups by chemical activation. This preparation method of activated carbon has emerged as a very attractive approach due to its low cost, an easy process and mild conditions as compared to physical activation\cite{12, 13}. In recent years, some biochars have been reported to adsorb organic and inorganic contaminants with the high adsorption capacity\cite{14, 15}. However, there are a few studies on the treatment of cadmium ions containing wastewater by bamboo-derived porous biochar\cite{5, 16} especially little those on the influences of preparation, modification of the biochar on its removal performance of Cd$^{2+}$ in simulated wastewater. Therefore, the systematical study of the effects of preparation and modification of the biochar on its adsorption removal performance, the adsorption kinetics and equilibrium of Cd$^{2+}$ is of very high significance in the treatment of Cd$^{2+}$ containing wastewater.

In this work, bamboo-derived porous biochar was used as the adsorbent for removing the Cd$^{2+}$ in the simulated wastewater. The optimum preparation conditions of biochar and the effects of pH, adsorption temperature, adsorption time and the amount of adsorbent on the removal of cadmium ions in simulated wastewater were in details examined. The adsorption kinetics and equilibrium were studied, and the regenerative adsorption performance was investigated. This work will provide the theoretical and practical basis for biochar in the treatment of cadmium in industrial wastewater.

2. Experimental

2.1. Reagents and raw materials

The cadmium chloride, concentrated hydrochloric acid, concentrated nitric acid, concentrated sulfuric acid, sodium hydroxide, zinc chloride and sodium bicarbonate were analytical grade reagents and purchased from Sinopharm Group Chemical Reagent Co. Ltd. Bamboo powder (40-60 mesh) was prepared from bamboo processing residues from a local bamboo products factory by drying, grinding, and sieving. Wood commercial activated carbon was purchased from a local supplier. The chemicals were all used as received.

2.2. Preparation and modification of materials

Weigh 20g of bamboo powder and 10g of zinc chloride, respectively. ZnCl$_2$ was dissolved with a certain volume of distilled water to form the solution clarified by adding proper volume of concentrated hydrochloric acid. The bamboo powder was impregnated with the solution by the incipient wetness method for 12h at room temperature and then placed in oven at 60°C for 12h. The dried precursor was placed into the tube furnace and activated at 500°C or 700°C in N$_2$ for 3h. The carbonized precursor was washed with hot distilled water containing a proper amount of concentrated hydrochloric acid, and then repeatedly washed with distilled water until the filtrate became neutral. Finally, the washed material was dried at 110°C for 12h to yield the bamboo-derived porous biochar (denoted as BC-50-500 or BC-50-700, respectively, where BC is the abbreviation of the bamboo-derived porous biochar, 50 represents the amount of ZnCl$_2$ and 500 or 700 is the activation temperature).

1.0 g of BC-50-500 or 1.0 g of BC-50-700 was added to a 25 mL round-bottomed flask. 10 mL of concentrated sulfuric acid was slowly dropped to the flask under strong stirring with a glass rod, and was then treated at 180°C in oil bath for 5h under magnetic stirring. Next the filtrate was repeatedly washed with distilled water until the pH value of the filtrate was neutral, followed by final drying in
the oven at 110 °C for 12 h to yield the modified material (designated as BC-50-500-S or BC-50-700-S, respectively, where S refers to the sulfonation modification by concentrated sulfuric acid).

1.5 g of BC-50-500 or BC-50-700 or AC was added to a 25 mL round-bottomed flask. 9 mL of 65% concentrated nitric acid was slowly added to the flask under strong stirring with a glass rod, and was then treated at different temperature (83°C or 100°C or 120°C) for 3 h under magnetic stirring. Next the filtrate was repeatedly washed with distilled water until the pH value of the filtrate was neutral, followed by final drying in the oven at 110°C for 12 h to yield the modified material (designated as BC-50-500-N-83 or BC-50-700-N-83 or BC-50-700-N-100 or BC-50-700-N-120 or AC-N-100, where N refers to the oxidation modification by concentrated nitric acid).

2.3. Static adsorption experiment
A simulated wastewater containing Cd^{2+} with mass concentration of (25-200 mg/L) was prepared by CdCl\textsubscript{2}\cdot2.5H\textsubscript{2}O dissolved in a certain volume of distilled water. 25mL of simulated Cd\textsuperscript{2+} wastewater and a certain amount of biochar (from 0.025g-0.25g) was placed in 50mL round bottom flask. The pH (range from 3-7) of the system was adjusted with 0.1mol/L NaOH solution or 0.1mol/L HCl solution. The system was placed in thermostatic water bath (temperature’s range from 25°C-75°C) under magnetic stirring in a certain period of time (30-120min). The Cd\textsuperscript{2+} concentration in the filtrate was determined by atomic absorption spectrophotometer [TAS-990 (Beijing analysis Instrument Co.,Ltd.)] and the removal percentage of Cd\textsuperscript{2+} was calculated according to (1) [17].

\[
\text{Removal percentage (\%)} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \%
\]  

Where \(C_0\) refers to the initial concentration of Cd\textsuperscript{2+} in the simulated wastewater, and \(C_e\) refers to the concentration of Cd\textsuperscript{2+} in the filtrate after saturated adsorption. Each experiment was conducted in triplicate, and the observed data deviation between three parallel experiments was lower than ca. 5%.

2.4. Recycling test
After centrifugal separation of the biochar with the solution, the concentration of Cd\textsuperscript{2+} in the supernatant was determined by AAS. The spent biochar and 20mL hydrochloric acid with 0.5mol/L concentration were added to a 50 mL round-bottomed flask, refluxed in a thermostatic water bath at 50°C for 30min, and then filtrated. The filter residue was repeated 3 times according to the preceding procedure, washed with distilled water to neutral, dried, and then reused for adsorption of Cd\textsuperscript{2+}.

3. Results and Discussion

3.1. Cd\textsuperscript{2+} adsorption properties of different porous carbon materials

| Sample | Adsorption capacity/(mg·g\textsuperscript{-1}) | Removal percentage (%) |
|--------|---------------------------------|------------------------|
| BC-50-500 | 10.78 | 43.10 |
| BC-50-700 | 9.42 | 37.66 |
| BC-50-500-S | 10.57 | 42.26 |
| BC-50-700-S | 6.35 | 25.41 |
| BC-50-500-N-83 | 11.93 | 47.70 |
| BC-50-700-N-83 | 13.59 | 54.34 |
| BC-50-700-N-100 | 17.29 | 69.16 |
| BC-50-700-N-120 | 13.25 | 53.01 |

\textsuperscript{a}Adsorption conditions: 25 mL of simulated cadmium-containing wastewater (100 mg/L), 0.1000 g of adsorbent dosage, adsorption time of 90 min and adsorption temperature of 35°C.

Table 1 lists the adsorption capacity and the removal percentage of cadmium ions in simulated wastewater over some representative samples. As shown in Table 1, Cd\textsuperscript{2+} adsorption capacity of BC-50-700 is slightly less than that of BC-50-500. It may be that BC-50-700 possesses less acid functional groups and slightly lower pore structure parameters due to its higher preparation temperature [9, 15].
The result implies that the surface acid groups and pore structure of biochar are the two main factors affecting the adsorption of cadmium ions. The Cd\(^{2+}\) adsorption properties of materials after HNO\(_3\) oxidation were improved to varying extent, which indicate that the increase of acid groups is beneficial to improve the Cd\(^{2+}\) adsorption performance of materials\[7-9, 15\]. However, the improved Cd\(^{2+}\) adsorption capacity of BC-50-700-N-83 was stronger than that of BC-50-500-N-83, which may be due to BC-50-700’s better structural stability as compared to BC-50-500 \[7-9, 15\]. Furthermore, BC-50-700-N-100 exhibited the best Cd\(^{2+}\) removal percentage for the simulated cadmium-containing wastewater. This result may be due to BC-50-700’s better structural stability leading its higher acidic functional groups via HNO\(_3\) oxidation modification \[7-9, 15\], which benefit to the adsorption of Cd\(^{2+}\). BC-50-700-N-120 had a lower adsorption capacity similar to that of BC-50-500-N-83, which may be due to a further increase in HNO\(_3\) oxidation temperature leading to the greater damage to its pore structure \[7-9, 15\]. The adsorption capacity of BC-50-500-S and BC-50-700-S were not enhanced, suggesting that sulfonation did not seem to improve its adsorption performance.

3.2. Effect of adsorption conditions on Cd\(^{2+}\) removal performance

3.2.1. Effect of pH on Cd\(^{2+}\) removal percentage

The effect of pH on Cd\(^{2+}\) removal percentage over BC-50-700-N-100 (the optimum bamboo-derived biochar obtained by HNO\(_3\) oxidation modification) is shown in Figure 1 under the same conditions of 25 mL of cadmium-containing simulated wastewater, 0.20 g of biochar, 90 min and 35\(^\circ\)C. It can be seen from Figure 1 that the removal percentage of Cd\(^{2+}\) was lower at pH 3. When pH was enhanced from 3 to 4, the removal percentage of Cd\(^{2+}\) was increased from 75.36% to 86.96%, and then the value increased gradually\[5\]. The lower removal efficiency in strongly acidic media is due to the competition over the available adsorption sites between Cd\(^{2+}\) and H\(^+\) with the high H\(^+\) concentration under the low pH value, and thus suppresses Cd\(^{2+}\) adsorption\[6, 18, 19\]. With the increase of the pH value, the adsorption capacity of H\(^+\) decreased, accordingly, Cd\(^{2+}\) adsorbed gradually increased\[5, 20, 21\]. When the pH is greater than 7, Cd\(^{2+}\) begins to precipitate\[6, 18\]. Therefore, pH 7.0 in the simulated wastewater is the reasonable value for Cd\(^{2+}\) adsorption.

3.2.2. Effect of temperature on Cd\(^{2+}\) removal percentage

The effect of temperature on Cd\(^{2+}\) removal percentage over BC-50-700-N-100 is shown in Figure 2 under the same other conditions. As shown in Figure 2, the temperature increased from 25\(^\circ\)C to 35\(^\circ\)C, the removal percentage was enhanced from 90.23% to 94.65%. With further increasing temperature, the value decreased gradually. The result is consistent with the result of adsorption versus temperature in the literature\[22\]. The increase in adsorption reflects chemical interactions between the ions and the biochar, indicating that the adsorption process is endothermic in nature, whereas the decrease in adsorption with the further increase of temperature may be due to the weakening of adsorptive forces between Cd\(^{2+}\) and adsorption sites of the adsorbent\[22\]. Thus the proper adsorption temperature is about 35\(^\circ\)C.

3.2.3. Effect of adsorbent amount on removal percentage of Cd\(^{2+}\)

The effect of the adsorbent amount on Cd\(^{2+}\) removal percentage over BC-50-700-N-100 is shown in Figure 3 under constant other conditions. It can be observed from Figure 3 that the Cd\(^{2+}\) removal percentage increased with increasing the biochar’s amount from 0.025 to 0.200 g. When the biochar dosage was more than 0.200 g, the removal percentage of Cd\(^{2+}\) remained basically unchanged. At the beginning of adsorption, the increased biochar’s dosage provided a large number of the unoccupied adsorption sites to Cd\(^{2+}\)\[17, 23\], accordingly, the Cd\(^{2+}\) removal percentage was rapidly increase\[19\]. At the later stage of adsorption, the mass concentration of Cd\(^{2+}\) decreased gradually and thus the adsorption driving force of Cd\(^{2+}\) to the surface of biochar weakened. Although the adsorption removal percentage of Cd\(^{2+}\) was enhanced, the unit adsorption capacity of biochar was reduced. As a result, the adsorbent amount of 0.2000 g / 25mL is appropriate.
3.2.4. Effect of contact Time
The effect of contact time on the Cd$^{2+}$ removal percentage over BC-50-700-N-100 is shown in Figure 4 under constant other conditions. As shown in Figure 4, the Cd$^{2+}$ removal percentage increased with prolonging the contact time. The value reached 95.37% when the time was 90 min. As the time went on, the Cd$^{2+}$ removal percentage remained essentially unchanged. At the initial stage, the high Cd$^{2+}$ concentration and adsorption sites contributed to the fast adsorption rate. With the progress of the adsorption, the Cd$^{2+}$ concentration and adsorption sites decreased and thus the adsorption rate slowed down until the adsorption equilibrium was reached[22-24]. Accordingly, the adsorption time of 90 min is suitable. In summary, when the Cd$^{2+}$ concentration is 100 mg/L, the optimum conditions for Cd$^{2+}$ adsorption are pH 7, adsorption temperature of 35°C, adsorbent dosage of 0.2000g/25mL and adsorption time of 90 min.

3.2.5. Effect of temperature on Cd$^{2+}$ removal percentage
The effect of temperature on Cd$^{2+}$ removal percentage is shown in Figure 4. As the temperature increased, the adsorption rate of Cd$^{2+}$ over BC-50-700-N-100 was increased sharply in the initial 45 min owing to biochar possessing a large number of the unoccupied adsorption sites.

3.3. Cd$^{2+}$ adsorption kinetics and isotherm

3.3.1. Adsorption kinetics
The kinetic parameters are usually measured by fitting the kinetic data based on the Lagergren quasi-second order kinetic equation, contributing to study the mechanism of the adsorption process [25]. It can be seen from Fig.4 that the adsorption rate of Cd$^{2+}$ over BC-50-700-N-100 was increased sharply in the initial 45 min owing to biochar possessing a large number of the unoccupied adsorption sites.
With the prolongation of adsorption time, the active sites for adsorbing Cd\(^{2+}\) were relatively reduced, and thus Cd\(^{2+}\)-adsorption rate became slow. After 90 min, the adsorption of Cd\(^{2+}\) achieves equilibrium, and the adsorption percentage reached the maximum. The fitting results based on the equation (2) was shown in Figure 5.

\[
t/q_s = 1/k_2 q_s^2 + t/q_e
\]  

(2)

where \(q_s\) is the amount of Cd\(^{2+}\) adsorbed by biochar at time \(t\) (mg·g\(^{-1}\)); \(q_e\) is equilibrium adsorption capacity (mg·g\(^{-1}\)); \(k_2\) is the rate constant in the pseudo-second order kinetic equation (g mg\(^{-1}\)·min\(^{-1}\)) [2, 26-30]. It can be calculated from Fig. 5 that \(q_e\) is 16.62 mg·g\(^{-1}\) and the linear correlation coefficient \(R^2=0.9999\), which indicates that the pseudo-second order kinetic model can well describe the adsorption kinetics of Cd\(^{2+}\).

### 3.3.2. Adsorption isotherm

The adsorption isotherm of Cd\(^{2+}\) on over BC-50-700-N-100 at 35°C is shown in Fig.6. With the increase of Cd\(^{2+}\) concentration, the equilibrium adsorption capacity of Cd\(^{2+}\) also increased. When the equilibrium concentration of Cd\(^{2+}\) reached 20mg/L, saturated adsorption was achieved. This result is due to the limited amount of adsorption sites in the case of the constant amount of biochar. For the low initial Cd\(^{2+}\) concentration, sufficient active sites can be provided for the adsorption, so that the equilibrium adsorption capacity of biochar increases gradually. When the initial Cd\(^{2+}\) concentration is high, the active sites are relatively insufficient, leading to rapid saturation of the adsorption sites.

Langmuir and Freundlich adsorption isotherm models are commonly used to describe the adsorption equilibrium of liquid-solid systems. The Langmuir model is based on this assumption that the adsorption of components is a monomolecular layer that occurs on a uniform surface, while the Freundlich model is built on the hypothesis that the adsorption of metal ions occurs on non-uniform surfaces. The corresponding mathematical expression is as follows, respectively[2, 24, 31-33]:

\[
1/q_e = (1/QK_1)\times(1/C_e) + 1/Q
\]  

(3)

\[
\log q_e = n\log C_e + \log K_2
\]  

(4)
where $q_e$ is the equilibrium adsorption capacity (mg·g⁻¹); $C_e$ is the adsorption equilibrium concentration of Cd²⁺ (mg·L⁻¹); $Q$ is the maximum adsorption capacity (mg·g⁻¹); $K_1$ is Langmuir adsorption equilibrium constant (L·mg⁻¹); $K_2$ and $n$ are Freundlich adsorption constants.

The adsorption experiments data were fitted with the Langmuir and Freundlich models, respectively. As shown in Fig.7, Langmuir equation was fitted to $1/q_e=4.3014/C_e+0.02245$. The maximum adsorption capacity of Cd²⁺ was calculated as 44.54 mg·g⁻¹, and the correlation coefficient $R^2$ was 0.9702, which indicated that the adsorption behavior of biochar to Cd²⁺ accorded with Langmuir adsorption isotherm. Meanwhile, the adsorption data of biochar was fitted by Freundlich adsorption isotherm (see Fig.8), and the equation was obtained as $\lg q_e = -0.449+0.823\lg C_e$ where the correlation coefficient $R^2$ is 0.9859, and $1/n=0.823$. The large value $1/n$ indicates that the adsorption capacity of the adsorbent is strong and that the biochar by HNO₃ oxidation modification is a highly adsorbable adsorbent to Cd²⁺[32]. The above results show that the Freundlich isothermal adsorption model fitted better than the Langmuir isothermal adsorption model for this adsorption system, indicating that the surface of the porous biochar is not uniform.

### 3.4. Regeneration and recycling performance

The regeneration of over BC-50-700-N-100 was carried out by reflux in dilute hydrochloric acid[25]. The adsorption performance after 4 runs regeneration is shown in Figure 9. It can be seen from Fig. 9 that the Cd²⁺ removal percentage of biochar was reduced from 95.53% to 90.36% after 3 runs regeneration. For the 4th run regeneration, the removal percentage is reduced to 86.88%, which indicates that the biochar exhibits good regeneration performance.
4. Conclusions

In summary, in this work a bamboo-derived porous biochar with a good adsorption removal capacity to cadmium ions in the simulated wastewater was prepared by 50% ZnCl₂ chemical activation of bamboo processing residues at 700°C and further modification with the concentrated HNO₃ oxidation at 100°C. At the Cd²⁺ concentration of 100mg/L, the biochar achieved the adsorption removal efficiency of 95.53% under the optimum adsorption conditions (at pH 7, at adsorption temperature of 35°C, at adsorbent dosage of 0.2000g/25mL and in adsorption time of 90min). The adsorption process of Cd²⁺ on biochar was in accordance with the pseudo-second-order adsorption kinetics equation. Meanwhile, the Freundlich isothermal adsorption model fitted better than Langmuir isothermal adsorption model for this Cd²⁺ adsorption system. After four adsorption-desorption recycling, the adsorption capacity of Cd²⁺ over biochar has no significant decline, which indicates that biochar has high adsorption capacity and good regeneration performance. Such cheap and readily available biochar may therefore become a promising adsorbent for removal of cadmium ions in the industrial wastewater.

Acknowledgments

We acknowledge the financial support for this work by the National Natural Science Foundation of China (21073057, 21676079), the Natural Science Foundation of Hunan Province (11JJ6008, 2018JJ3335), the Innovation Platform Open Foundation of Hunan College (14K059, 18K016), and Hunan Normal University graduates innovative experiment project (201610542074, 201810542141).

References

[1] Sud, D., Mahajan, G., Kaur, M. P. (2008) Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. Bioresource Technol., 99 (14): 6017–6027.

[2] Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y.-H., Indraswati, N., Ismadji, S. (2009) Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. J. Hazard. Mater., 162 (2): 616–645.

[3] Molino, A., Erto, A., Natale, F. D., Donatelli, A., Iovane, P., Musmarra, D. (2013) Gasification of Granulated Scrap Tires for the Production of Syngas and a Low-Cost Adsorbent for Cd(II) Removal from Wastewaters. Ind. Eng. Chem. Res., 52 : 12154–12160.

[4] Lo, S.-F., Wang, S.-Y., Tsai, M.-J., Lin, L.-D. (2012) Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons. Chem. Eng. Res. Des., 90 (9): 1397–1406.

[5] Aziz, H. A., Adlan, M. N., Ariffin, K. S. (2008) Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: Post treatment by high quality limestone. Bioresource Technol., 99 (6): 1578–1583.

[6] Argun, M. E., Dursun, S., Karatas, M., Güürü, M. (2008) Activation of pine cone using Fenton oxidation for Cd(II) and Pb(II) removal. Bioresource Technol., 99 (18): 8691–8698.

[7] Qiu, J., Wang, G., Bao, Y., Zeng, D., Chen, Y. (2015) Effect of oxidative modification of coal tar pitch-based mesoporous activated carbon on the adsorption of benzothiophene and dibenzothiophene. Fuel Process Technol., 129: 85–90.

[8] Zhou, A., Ma, X., Song, C. (2009) Effects of oxidative modification of carbon surface on the adsorption of sulfur compounds in diesel fuel. Appl. Catal. B: Environ., 87 (3): 190–199.

[9] Bhatnagar, A., Hogland, W., Marques, M., Sillanpää, M. An overview of the modification methods of activated carbon for its water treatment applications. Chem. Eng. J., 219: 499–511.

[10] Tan, Z., Qiu, J., Zeng, H., Liu, H., Xiang, J. (2011) Removal of elemental mercury by bamboo charcoal impregnated with H₂O₂. Fuel, 90 (4): 1471–1475.

[11] Yang, W., Wang, H., Zhang, M., Zhu, J., Zhou, J., Wu, S. (2016) Fuel properties and combustion kinetics of hydrochar prepared by hydrothermal carbonization of bamboo. Bioresource
[12] Liu, Q.-S., Zheng, T., Wang, P., Guo, L. (2010) Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation. Ind. Crop Prod., 31 (2): 233–238.

[13] Ahmad, A. A., Hameed, B. H. (2009) Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon. J. Hazard. Mater., 172 (2): 1538–1543.

[14] Mohan, D., Sarswat, A., Ok, Y. S., Pittman, C. U. (2014) Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. Bioresource Technol., 160: 191–202.

[15] Yang, E., Yao, C., Liu, Y., Zhang, C. Jia, L., Li, D., Fu, Z., Sun, D., Robert Kirk, S., Yin, D. (2018) Bamboo-derived porous biochar for efficient adsorption removal of dibenzothiophene from model fuel. Fuel, 211: 121–129.

[16] Lu, K., Yang, X., Shen, J., Robinson, B., Huang, H., Liu, D., Bolan, N., Pei, J., Wang, H. (2014) Effect of bamboo and rice straw biochars on the bioavailability of Cd, Cu, Pb and Zn to Sedum plumbizincicola. Agr. Ecosyst. Environ., 191: 124–132.

[17] Yong, S. K., Bolan, N., Lombi, E., Skinner, W. (2013) Synthesis and Characterization of Thiolated Chitosan Beads for Removal of Cu(II) and Cd(II) from Wastewater. Water Air Soil Poll., 224: 1720–1732.

[18] Zeng, G., Liu, Y., Tang, L., Yang, G., Pang, Y., Zhang, Y., Zhou, Y., Li, Z., Li, M., Lai, M., He, X., He, Y. (2015) Enhancement of Cd(II) adsorption by polyacrylic acid modified magnetic mesoporous carbon. Chem. Eng. J., 259: 153–160.

[19] Tan, I. A. W., Chan, J. C., Hameed, B. H., Lim, L. L. P. (2016) Adsorption behavior of cadmium ions onto phosphoric acid-impregnated microwave-induced mesoporous activated carbon. J. Water Process Eng., 14: 60–70.

[20] Zheng, W., Li, X.-m., Wang, F., Yang, Q., Deng, P., Zeng, G.-m. (2008) Adsorption removal of cadmium and copper from aqueous solution by areca—a food waste. J. Hazard. Mater., 157 (2): 490–495.

[21] Li, X., Wang, S., Liu, Y., Jiang, L., Song, B., Li, M., Zeng, G., Tan, X., Cai, X., Ding, Y. (2017) Adsorption of Cu(II), Pb(II), and Cd(II) Ions from Acidic Aqueous Solutions by Diethylenetriaminepentaacetic Acid-Modified Magnetic Graphene Oxide. J. Chem. Eng. Data, 62 (1): 407–416.

[22] Wang, K., Gu, J., Yin, N. (2017) Efficient Removal of Pb(II) and Cd(II) Using NH2-Functionalized Zr-MOFs via Rapid Microwave-Promoted Synthesis. Ind. Eng. Chem. Res., 56 (7): 1880–1887.

[23] Garg, U., Kaur, M. P., Jawa, G. K., Sud, D., Garg, V. K. (2008) Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass. J. Hazard. Mater., 154 (1): 1149–1157.

[24] Zhao, F., Repo, E., Yin, D., Sillanpää, M. E. T. (2013) Adsorption of Cd(II) and Pb(II) by a novel EGTA-modified chitosan material: Kinetics and isotherms. J. Colloid Interf. Sci., 409: 174–182.

[25] Debnath, S., Nandi, D., Ghosh, U. C. (2011) Adsorption–Desorption Behavior of Cadmium(II) and Copper(II) on the Surface of Nanoparticle Agglomerates of Hydrous Titanium(IV) Oxide. J. Chem. Eng. Data, 56 (7): 3021–3028.

[26] Yan, L., Zhao, Q., Jiang, T., Liu, X., Li, Y., Fang, W., Yin, H. (2015) Adsorption characteristics and behavior of a graphene oxide–Al13 composite for cadmium ion removal from aqueous solutions. RSC Adv., 5 (83): 67372–67379.

[27] Shin, E. W., Karthikeyan, K. G., Tshabalala, M. A. (2007) Adsorption mechanism of cadmium on juniper bark and wood. Bioresource Technol., 98 (3): 588–594.

[28] Wang, H., Zhao, Y., Ma, L., Fan, P., Xu, C., Jiao, Ch., Lin, A. (2016) Preparation of Composite Modified Expanded Graphite and Its Adsorption on Acid Brilliant Blue Dye. Chem. J.
[29] Zhao, F., Repo, E., Sillanpää, M., Meng, Y., Yin, D., Tang, W. Z. (2015) Green Synthesis of Magnetic EDTA- and/or DTPA-Cross-Linked Chitosan Adsorbents for Highly Efficient Removal of Metals. Ind. Eng. Chem. Res., 54 (4): 1271–1281.

[30] Iqbal, M., Iqbal, N., Bhatti, I. A., Ahmad, N., Zahid, M. (2016) Response surface methodology application in optimization of cadmium adsorption by shoe waste: A good option of waste mitigation by waste. Ecol. Eng., 88: 265–275.

[31] Chen, Y., Gao., L., He, M., Wei, Y. (2014) High-capacity Polyvinyltetrazole-grafted Chelating Resin for Adsorption of Heavy Metal Ions. Chem. J. Chinese U., 35, (7): 1596–1602.

[32] Fouladi Tajar, A., Kaghazchi, T., Soleimani, M. (2009) Adsorption of cadmium from aqueous solutions on sulfurized activated carbon prepared from nut shells. J. Hazard. Mater., 165 (1): 1159–1164.

[33] Zheng, W., Li, X.-m., Yang, Q., Zeng, G.-m., Shen, X.-x., Zhang, Y., Liu, J.-j. (2007) Adsorption of Cd(II) and Cu(II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste. J. Hazard. Mater., 147 (1): 534–539.