Adsorption Characteristics of Cadmium Ions from Aqueous Solution onto Pine Sawdust Biomass and Biochar

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The adsorption capacity of cadmium ions by pine sawdust biomass and biochar was evaluated in batch experiments. Pine sawdust biochars were pyrolyzed at 500 °C and 700 °C and obtained in the absence of oxygen. The adsorption capacity of biochar was higher than the raw biomass (3.47 mg/g). Biochars produced at 700 °C showed better adsorption efficiency (6.09 mg/g) than that produced at 500 °C (4.78 mg/g). Also, the adsorption kinetics and adsorption isotherms were studied. The adsorption behavior of cadmium by pine sawdust biomass and biochar fitted Langmuir isotherms and pseudo-second order kinetics. In addition, the desorption experiment by different solutions (neutral, acidic, and alkaline) were conducted. The desorption of cadmium ions in neutral and alkaline environments was not obvious, while the desorption in an acidic environment was. Pine sawdust biochar, pyrolyzed at 700 °C, is a potential adsorbent for cadmium removal in neutral and alkaline environments.

Keywords: Cadmium; Pine sawdust biomass; Pine sawdust biochar; Adsorption; Desorption

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INTRODUCTION

Cadmium can be produced in different ways such as smelting processes, plating facilities, mining operations, battery manufacturing processes, and glass production industries (Zhao *et al.* 2018). These processes release substantial amounts of potentially toxic cadmium into the atmosphere, aquatic environments, and terrestrial environments (Patar *et al.* 2016). Cadmium ions are not always biodegradable, and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals and humans (Liu *et al.* 2015, 2017). Cadmium is highly toxic even at low concentrations and contributes to many human diseases, such as nephrotoxic impacts, cell death, kidney damage, and bone damage (Ahmaruzzaman 2011; Cao *et al.* 2017; Saha *et al.* 2017). Thus, it is of great importance to remove cadmium from wastewater (Rao and Kashifuddin 2014).

There are many methods for cadmium ions removal from wastewater, such as chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange, and adsorption (Park *et al.* 2017). The most widely applied methods may be chemical and electrochemical precipitation, but the disposal of the precipitate may create some problems (Uddin 2017). As reported, ion-exchange treatment, membrane technology, and electrolytic reduction are not economical methods for cadmium pollution treatment (Al-Shannag *et al.* 2017; Crini *et al.* 2018). In contrast, adsorption has become a widely studied method for cadmium treatment from wastewater due to its high efficiency and economy (Tang *et al.* 2010). Many agricultural wastes have been used as adsorbents for heavy metal removal from wastewater (Afroze and Sen 2018). The adsorption capacity of sawdust is in a range of 3.80 to 5.37 mg/g according to others' research (Taty-Costodes *et al.* 2003; Bulut and Tez 2007). Biochars are carbon-rich materials obtained from biomass by the pyrolysis method and are more effective in heavy metal removal (Reddy *et al.* 2014). Various low-cost materials, including coconut husk, peanut shell, sawdust, and agricultural waste materials, have been converted into biochars by the pyrolysis method and used for the treatment of wastewater containing heavy metals (Ahmad *et al.* 2014). China is an agricultural country and has a large amount of forest waste, such as sawdust (Cuiping *et al.* 2004; Li *et al.* 2010). This provides the possibility to convert sawdust into useful biochar. There have been some reports that sawdust was converted into biochar and used to adsorb organic and inorganic pollutant, dyes 398.8 mg/g; Cr 8.3 mg/g; Cu 6.2 mg/g; ammonium ions 1.70 mg/g; for example (Özacar and Şengýl 2005; Gode *et al.* 2008; Wahab *et al.* 2010; Çakir *et al.* 2017). However, few studies have studied the adsorption characteristics of cadmium by sawdust biochar.

In this study, pine sawdust (PS) biomass was pyrolyzed at 500 °C and 700 °C to obtain pine sawdust biochars (PSBs). The characteristics of PS and PSBs were studied. The adsorption efficiency of cadmium ions from aqueous solution by PS and PSBs were investigated. Batch adsorption experiments were conducted to understand the influence of different adsorption parameters, such as adsorption time, temperature, pH value, amount of adsorbent, and initial concentration, on adsorption behavior. Adsorption isotherms and adsorption kinetics were obtained according to the adsorption results. Desorption experiments were conducted to evaluate the desorption potential of distilled water (pH = 6.5), HNO_3 solution (pH = 4), and NaOH solution (pH = 9) for cadmium.

EXPERIMENTAL

Adsorbents and Reagents

Pine sawdust was obtained from pine trees in Shanxi, China. The raw PS was washed and dried at 70 °C for 48 h. The dried PS was placed in a quartz tube and pyrolyzed in a tubular muffle furnace (OTF-1200X, MTI corporation, Berkeley, CA, USA) at 15 °C/min in the absence of oxygen The char yield was stabilized at charring temperatures greater than 700 °C (Keiluweit *et al.* 2010). Thus, peak temperatures of 500 °C and 700 °C were adapted to carbonize the raw PS material, and the peak temperature was kept for 2 h. Then, the materials were cooled to room temperature inside the furnace, and the PSBs were obtained. PS and PSB at 500 °C (PSB-500) and PSB at 700 °C (PSB-700°C) were pulverized and then sieved through #16 mesh and #20 mesh. The sieves were shaken for 10 min. The particles between 0.85 mm and 1.18 mm were stored in a bottle to be used for the study.

The pH was measured using a pH meter according to ASTM D3838-05 (2017). Ultimate analysis was performed using an elemental analyzer (Thermo Fisher Scientific, Berlin, Germany). Brunauer-Emmett-Teller (BET) surface area was measured by using a nitrogen adsorption analyzer (Micromeritics ASAP 2020, Norcross, GA, USA) according to ASTM D6556-17 (2017). Fourier-transform infrared spectroscopy (FTIR) analysis was conducted using an FTIR spectrometer (TENSOR27, Bruker, Karlsruhe, Germany). Ash content was determined according to ASTM E1755-01 (2015). Thermal stability analysis was performed by using a thermogravimetric analysis (TGA) (Pyris 1 TGA, PerkinElmer, Waltham, MA, USA). The moisture content, volatile content, and fixed carbon content were obtained from the TGA results. A field emission scanning electron microscope (FE-SEM) (JEOL Ltd, Tokyo, Japan) was used to understand the morphology characteristics of the PS and PSBs.

Analytical grade $CdCl_2 \cdot 2.5H_2O$ was used to prepare the reagent solutions in distilled water, with concentrations ranging from 5 mg/L to 400 mg/L.

Procedures

An orbital shaker experiment machine (orbital motion: 45 rpm and radius of 15 cm) was used for the batch adsorption experiments. The cadmium solutions after adsorption were filtered through 0.45 µm membrane filters (ToyoRoshi Kaisha, Ltd, Tokyo, Japan). The concentration of cadmium in filtrates was measured using an atomic absorption spectrophotometer (AAS) (Analytik jena G, DE/novAA 300, Jena, Germany). The heavy metal content in sawdust was measured using solid AAS (Analytik jena GmbH, Germany)

All of the working volumes of cadmium solutions were fixed at 35 mL in test glass vials. The mixing test glass vials were put into the round stirrer to conduct the adsorption process. When researching the effect of pH value, the pH values were set as 3, 4, 5, 6, 7, 8, 9, and 10. To study the effect of temperature, the temperatures were set as 5 °C, 15 °C, 25 °C, and 40 °C. To investigate the effect of adsorbent amount, the values were set as 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1 g. To investigate the adsorption kinetic process, the adsorption times were set as 10, 30, 60, 120, 180, 300, 720, and 1440 min. The cadmium concentrations in many contaminated sites exceed 5 mg/g. To investigate the adsorption isotherms, the initial concentration values were 5, 10, 20, 40, 60, 100, 200, and 400 mg/L. Each adsorption experiment was replicated three times, and the mean values were used in the analyses. The amount of cadmium ions adsorption by the adsorbent was calculated according to Eq. 1. The removal ratio of cadmium ions adsorption by the adsorbent was calculated according to Eq. 2,

$$Q_e = \frac{(C_0 - C_e)V}{M \times 1000} \tag{1}$$

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{2}$$

where C_0 is the initial concentration of cadmium (mg/L), C_e is the concentration of cadmium after adsorption (mg/L), V is the volume of cadmium solution (L), and M is the amount of adsorbent (g).

Successive desorption experiments were conducted to evaluate the desorption potential of distilled water (pH 6.5), HNO_3 solution (pH 4), and NaOH solution (pH 9) for cadmium. The adsorption processes were completed in 5 h and the cadmium solutions were fixed at 50 mL in vials. Other variables were similar with the batch adsorption experiment. After 5 h of adsorption, 20 mL of the clear supernatant solution was decanted from the vial, and the desorption solution, equal to the volume of liquid decanted, was added to the vial. The vials were rotated in the orbital shaker experiment machine for 24 h for the desorption. The desorption process was repeated three times, including decanting 20 mL of the supernatant after desorption and adding back an equal volume of desorption solution. All desorption tests were conducted with three replications. The amount of cadmium uptake onto the adsorbent after desorption is calculated by Eq. 3,

$$Q_{\mathrm{di}} = \frac{C_0 \times V_0 - C_{di} \times V - \sum (C_{dacant} \times V_{dacant})}{1000 \times \mathrm{M}} \tag{3}$$

where C_{di} is the cadmium solution concentration after desorption i times (mg/L), $\Sigma(C_{decant} \times V_{decant})$ is the total amount of cadmium decanted before the desorption process (mg), C_{decant} is the concentration of decant solution (mg/L), and V_{decant} is the volume of the decant solution (L).

Kinetics and Isotherm Studies

Two kinds of kinetic models (pseudo-first order and pseudo-second order) were used to evaluate the adsorption rate of cadmium by PS, PSB-500, and PSB-700. The equilibrium adsorption capacities were investigated using Freundlich and Langmuir isotherm models. The goodness of fit of the experimental results were verified by comparison of coefficients of determination R^2.

RESULTS AND DISCUSSION

Characteristics of PS and PSBs

The characteristics of adsorbents are shown in Table 1. The proximate analysis revealed a higher fixed carbon content in PSB with an increase in pyrolysis temperature. The volatile content of PSB was lower than that of PS. From the ultimate analysis, PSB has a much higher carbon content than PS, which is coincidental with the proximate analysis result and indicates that PS is a potential material for biochar production. With the pyrolysis temperature increasing, the pH value and surface area of PSB increased and the production yield decreased.

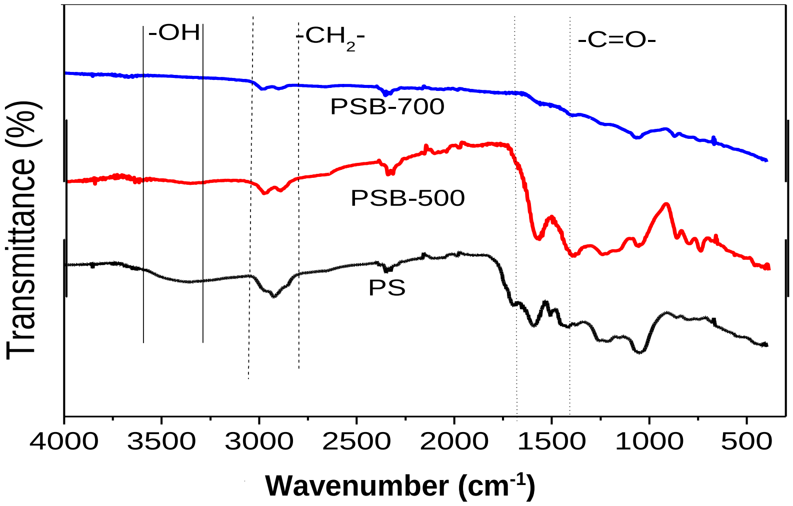
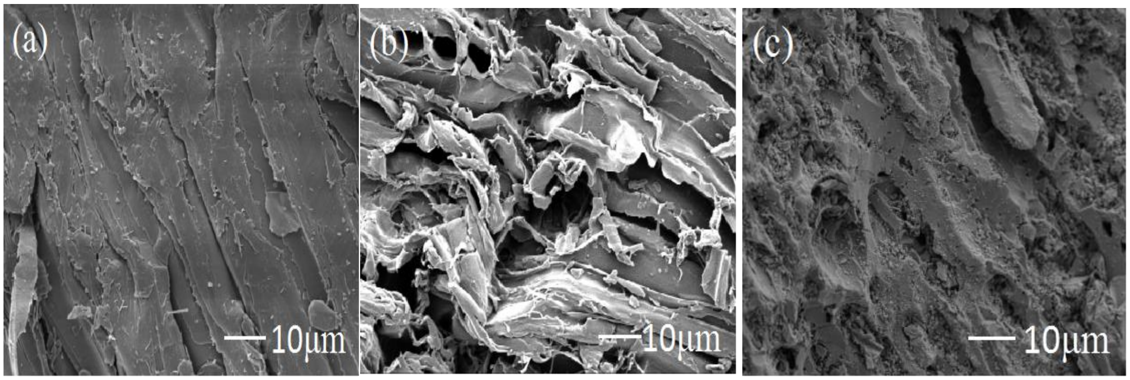


Fig. 1. FTIR Spectrometry of PS, PSB-500, and PSB-700

The pH value changed from 5.1 to 8.2 during the pyrolysis method. These results can be supported by the FTIR results in Fig. 1. The peak around 3400 cm^{-1} represents O-H stretching vibrations of phenol groups. This peak disappeared in PSBs. This indicates the dehydration of PS and the cleaving of phenolic groups in the pyrolysis process. The peak around 2900 cm^{-1} represents the $-CH_2-$ stretching vibrations of methylene groups and declined in PSBs (Li *et al.* 2007). The peak around 1700 cm^{-1} represents the vibration of C=O for lactone. This peak declined in PSBs. The peak between 1300 cm^{-1} and 1000 cm^{-1} can be attributed to C-O stretching vibrations of carboxylic groups. The carboxylic groups, lactone groups and phenol groups are some acid groups of PS (Farinella *et al.* 2007). Their disappearance or decline can change the pH value. In addition, PSB have higher ash content which could significantly change the solution pH. Thus, the pH of PSB is higher than PS (Shaaban *et al.* 2013).

Figure 2 presents the SEM images of the PS and the PSBs. Figure 2a shows that the surface structure of PS was smooth without any ridges or pores. However, after the pyrolysis process, there were many pores on the surface of PSB, which can be attributed to the volatilization of organic compounds. PSB-700 had much smaller pores than PSB-500. From the SEM images, it can be further inferred that the pyrolysis method can produce many adsorption sites on the PSB surface and enhance heavy metal removal efficiency. From SEM results, physical adsorption is expected to be an important reason for cadmium removal.



(a) (b) (c)

Fig. 2. SEM images of PS (a), and PSB-500 (b), and PSB-700 (c)

Table 1. Characteristics of PS, PSB-500, and PSB-700

Adsorbent	Proximate analysis (wt%)				Ultimate analysis (wt%)				Yield	pH	Surface area (m^2/g)
	Ash content	Fixed carbon	Volatile content	Moisture content	C	H	S	O			
PS	1.25	16.73	59.87	9.1	49.97	5.74	0.03	44.03		5.1	1.25
PSB-500	1.98	65.42	27.46	5.14	71.43	3.89	0.04	24.64	35.26	7.1	87
PSB-700	2.78	82.23	11.23	3.76	90.53	1.56	0	7.91	19.86	8.2	321

Effect of pH and Temperature on Adsorption Efficiency

The effect of pH on cadmium removal is illustrated in Fig. 3a. The cadmium removal ratios increased rapidly when the pH was increased from 3 to 5 and became stable between the pH levels of 5 and 7. This phenomenon can be explained with the help of pH_{pzc}.

In the acidic environment (low pH value), a large number of hydrogen ions in the solution competed with cadmium ions for the limited binding sites on the adsorbent surface, resulting in the reduction of cadmium ions adsorption. As the pH increased, the amount of hydrogen ions decreased and more binding sites became available for the adsorption of cadmium ions. Thus, the cadmium removal ratio increased. When pH is greater than 8, hydroxyl ions in solution can react with cadmium ions to bring about precipitation. Thus, the complete removal of cadmium ions in solution could be attributed to the precipitation (Argun *et al.* 2007). As shown in Fig. 3a, the precipitation ratio was almost one hundred percent when the pH was more than 8. Based on the results, the optimum pH for the adsorption of cadmium ions was between 5 and 7 for PS and PSBs. Therefore, the pH value of the batch adsorption experiments in this study was set at 6.5 (distilled water).

The effect of temperature on cadmium adsorption efficiency by PS and PSBs with other variables fixed is shown in Fig. 3b. It can be concluded that the amount of cadmium ions adsorbed increased with increasing temperature. There are three main reasons that can be used to explain this phenomenon. First, a higher temperature provides more energy for the adsorption process so that the cadmium ions can be better transferred from solution to the adsorption sites of the adsorbent. Second, increasing temperatures can stimulate the molecules of a material to move fast, thus enhancing the adsorption process. Third, temperature may in some cases improve the ion exchange capacities of PS and PSBs, which may be a possible reason for the adsorption of heavy metals (Tan *et al.* 2015).

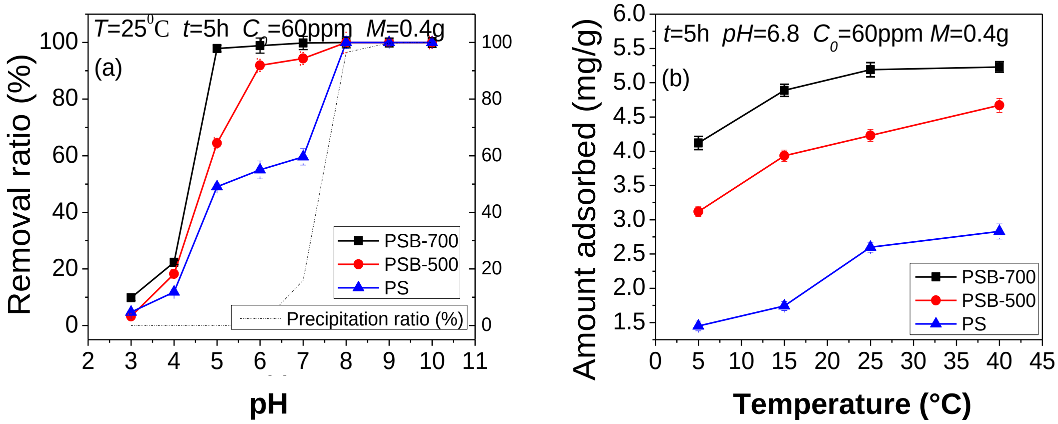


Fig. 3. Effect of pH and temperature on the amount of cadmium ions adsorption by PS, PSB-500 and PSB-700: (a) effect of pH value; and (b) effect of temperature

Effect of Adsorbent Amount

Effects of adsorbent amount on the adsorption capacity are shown in Fig. 4. With the adsorbent amount increasing, the removal ratio increased while the amount of cadmium ions adsorbed decreased. The increase in the amount of adsorbent caused an increase of adsorbent surface area in solution and thus, the adsorption sites of the adsorbent surface increased. Therefore, more cadmium ions could be removed. However, the removal ratio became constant afterwards, which can be attributed to the equilibrium limitation (Semerjian 2018). Because the total amount of cadmium ions in solution that can be adsorbed by the adsorbent was fixed, with the adsorbent amount increasing, the adsorption sites without attaching cadmium ions would increase. As a result, the adsorption of cadmium ions per unit mass of adsorbent showed a downward trend.

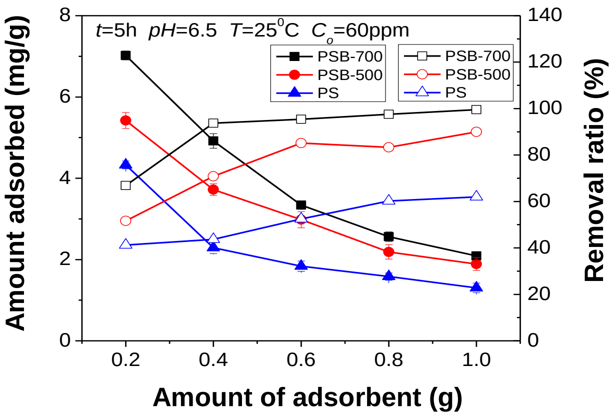


Fig. 4. Effect of adsorbent amount on the adsorption efficiency of cadmium ions by PS, PSB-500, and PSB-700

Adsorption Kinetics

Adsorption time is an important factor for investigating when the adsorption process reaches an equilibrium situation. Figure 5a shows the relationship between the amount of cadmium ions adsorption by the adsorbent and adsorption time at the initial concentration of 60 mg/L. The amount of cadmium ions adsorption increased remarkably at the initial stage and then remained stable in an equilibrium (maximum) adsorption capacity. It was confirmed that the equilibrium values were obtained within 300 min. PSB had greater adsorption efficiency (PSB-500: 4.23 mg/g and PSB-700: 5.19mg/g) than PS (2.65 mg/g), and the adsorption efficiency increased with the increase of the pyrolysis temperature (Lou *et al.* 2016).

The adsorption mechanism is not only related to the physical and chemical properties of adsorbents, but also in connection with the heavy metal ions' diffusion characteristics from liquid to solid. Adsorption kinetics can be investigated by kinetic models to better understand the adsorption mechanism and process (Tan *et al.* 2015). In this research, pseudo-first order and pseudo-second order kinetic models were introduced to study the adsorption behavior of cadmium ions by PS and PSB from an aqueous solution. The pseudo-first order kinetic model is expressed as Eq. 4 and the pseudo-second order kinetic model is presented as Eq. 5,

$$Log(Q_e - Q_t) = LogQ_e - K_1 t \tag{4}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 {Q_e}^2} + \frac{t}{Q_e} \tag{5}$$

where Q_e is the amount of adsorption by the adsorbent (mg/g), Q_t is the amount of adsorption by the adsorbent when the adsorption time is t (mg/g), K_1 is the rate constant of the pseudo-first order kinetic model (min^{-1}), and K_2 is the rate constant of the pseudo-second-order kinetic model (g/(mg·min)).

The fitting parameters of the linearized pseudo-first order and pseudo-second order kinetics are shown in Table 2. The R^2 values of the pseudo-second order model were all very close to 1 (0.999, 0.999, 0.999), which were higher than the corresponding values of the pseudo-first order model (0.811, 0.858, 0.995). This indicated that the adsorption behavior followed the rule of the pseudo-second order kinetic model very well. In addition, there was little difference between the experimental Q_e values and the calculated Q_e values in the pseudo-second order model. However, there was a wide gap between the experimental Q_e values and the calculated Q_e values in the pseudo-first order model. In conclusion, the adsorption process of cadmium ions by PS and PSBs can be expressed better by the pseudo-second order model than the pseudo-first order model. This indicates that the adsorption rate is related to the quantity of cadmium ions adsorption on the surface of the adsorbent at a certain adsorption time, and related to the quantity of adsorption at equilibrium (Ali *et al.* 2016). The fitting plot of the linear pseudo-second order kinetic model is shown in Fig. 5b. The absolute percentage error (MAPE) of the fitting results is shown in Fig. 5b. All the MAPE values were between 20% and -20%, which can indicate that the pseudo-second-order model can well express the adsorption process.

Table 2. Parameters of the Linearized Pseudo-First Order and Pseudo-Second Order Kinetic Models for Cadmium Adsorption by PS, PSB-500, and PSB-700 (pH = 6.5; T = 25 °C; C_0 = 6 ppm; M = 0.4 g)

Adsorbent materials	Q_e ,(mg/g) Experiment	Pseudo-first-order			Pseudo-second-order		
		k_1(min^{-1})	Q_e(mg/g)	R^2	k_2(g/(mg·min))	Q_e(mg/g)	R^2
PS	2.65	0.0021	0.629	0.811	0.0259	2.677	0.999
PSB-500	4.23	0.0076	4.278	0.858	0.0088	4.305	0.999
PSB-700	5.19	0.006	3.661	0.995	0.0104	5.269	0.999

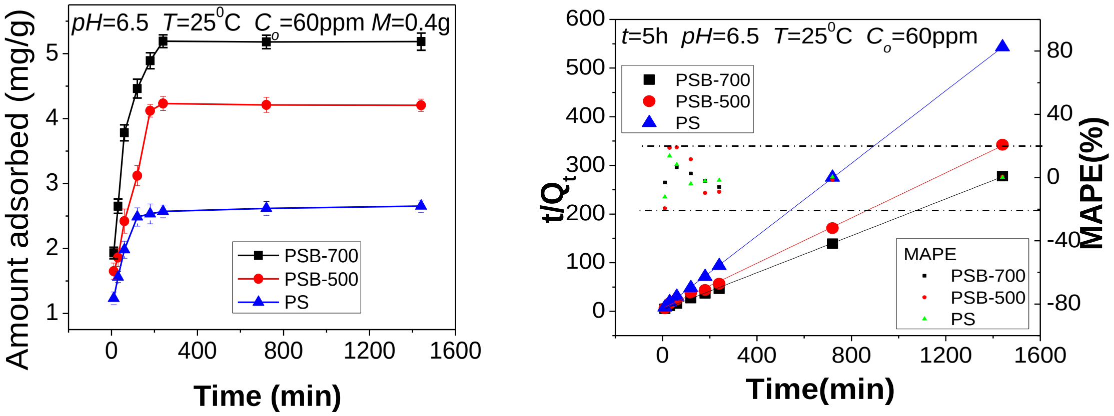


Fig. 5. Adsorption kinetic results: (a): effect of adsorption time on the amount of cadmium ions adsorption by PS, PSB-500, and PSB-700; and (b) linear pseudo-second order kinetic fitting

Adsorption Isotherms

Figure 6a shows the effect of the initial concentration on the adsorption efficiency of cadmium ions by PS and PSBs, as well as the cadmium ions adsorption and cadmium removal ratio. The results show that the amount of cadmium ions adsorption onto the adsorbent increased rapidly with the initial concentration increase at the initial stage and then remained constant. This phenomenon can be explained by two reasons: the driving force due to the concentration gradient and the saturation of the adsorption sites on the adsorbent surface. With the increase of initial concentration, the concentration gradient increased and the driving force also increased. Hence, the higher initial concentration enhanced the diffusion of cadmium ions from the solution to the adsorbent surface and increased the adsorption efficiency. However, for a given amount of adsorbent, the fixed adsorption sites could only adsorb a limited number of cadmium ions. Thus, with the increase in initial concentration, the amount of cadmium ions adsorption onto the adsorbent gradually increased before the adsorption sites of the adsorbent surface were saturated. Once all of the adsorption sites of the adsorbent surface were occupied by cadmium ions, the amount of cadmium ions adsorption by the adsorbent reached a plateau (Kırbıyık *et al.* 2016). The removal ratio of cadmium ions decreased as the initial concentration increased. This is because only a certain amount of cadmium ions can be adsorbed onto the adsorbent surface because the number of adsorption sites is finite. Thus, the greater initial concentration, the smaller percentage of cadmium ions can be removed for a given adsorbent mass (Komkiene and Baltrenaite 2016). PSB-700 has much higher surface area than PSB-500 (more than 3 times) yet their adsorption capacities were similar (6.09 mg/g vs. 4.78 mg/g). This is because that the presence of functional groups and ion exchange are more important than the surface area for cadmium adsorption.

Adsorption isotherms were used to investigate the adsorption behavior of cadmium ions by PS and PSB to understand how the cadmium ions transfer from aqueous solution to the adsorbent surface. The Langmuir isotherm and the Freundlich isotherm are two commonly used isotherm models to further study the relationship between the adsorption capacities and the initial concentration. The Langmuir isotherm is used to indicate the monolayer adsorption of heavy metal ions onto the adsorbent with a homogeneous surface, while the Freundlich isotherm is often used to fit adsorption that takes place on heterogeneous surfaces of the adsorbent (Ali *et al.* 2016). The linear form of the Langmuir isotherm model can be obtained from Eq. 6, and the Freundlich isotherm model can be explained from Eq. 7,

$$\frac{C_e}{Q_e} = \frac{1}{bk_l} + \frac{C_e}{b} \tag{6}$$

$$LgQ_e = Lgk_f + \frac{LgC_e}{n} \tag{7}$$

where C_e is the concentration of cadmium ions after adsorption (mg/L), Q_e is the amount of adsorption by the adsorbent (mg/g), b (mg/L) and k_l (L/mg) are the constants of the Langmuir isotherm model, and k_f (mg/g) and n are the constants of the Freundlich isotherm model.

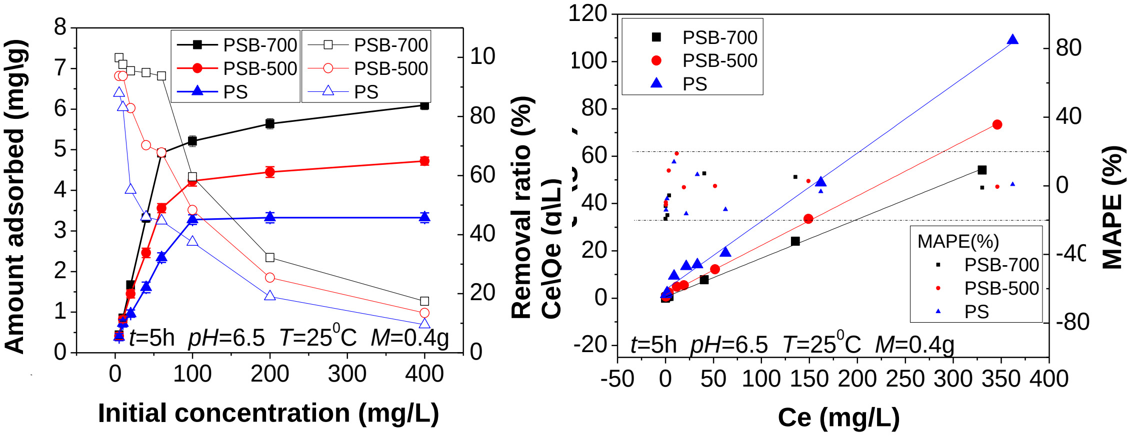


Fig. 6. Adsorption isotherm results: (a) effect of initial concentration on the adsorption of cadmium ions onto PS, PSB-500 and PSB-700; and (b) linear Langmuir isotherm fitting for cadmium

Table 3 shows the fitting results for the Langmuir and Freundlich models. The fitting degree values were 0.996 for PS, 0.999 for PSB-500, and 0.999 for PSB-700 when fitting with the Langmuir isotherm model. The values were closer to 1 than the corresponding R^2 values obtained by the Freundlich isotherm model (PS: 0.932; PSB-500: 0.915; and PSB-700: 0.874). This result indicated that the adsorption behavior of cadmium ions by PS and PSBs can be described by the Langmuir isotherm model quite well. The fitting plot of the linear Langmuir isotherm model is shown in Fig. 6b. The MAPE values were between 20% and -20%, and with the initial concentration increasing, the MAPE values become much smaller. Thus, it can be inferred that the Langmuir isotherm model is suitable for the adsorption behaviour. PS and PSBs in this adsorption experiment could be accurately represented as a homogeneous surface structure, where all adsorption sites were identical and energetically equivalent. The cadmium ions formed a monolayer on the surfaces of PS and PSB.

Table 3. Parameters of the Linearized Langmuir and Freundlich Isotherms for the Adsorption of Cadmium by PS, PSB-500 and PSB-700 (pH = 6.5; *T* = 25 °C; *t* = 5 h; *M* = 0.4 g)

Adsorbent Materials	Langmuir Isotherm			Freundlich Isotherm		
	b(mg/L)	k_l(L/mg)	R^2	k_f(mg/g)	*1/n*	R^2
PS	3.47	0.079	0.996	0.728	0.387	0.932
PSB-500	4.78	0.145	0.999	1.679	0.378	0.915
PSB-700	6.09	0.342	0.999	0.141	0.295	0.874

Desorption Analysis

To investigate the secondary pollution of cadmium in different environments after the adsorption process, three cycles of successive desorption experiments were conducted in distilled water (neutral), HNO_3 (acidic), and NaOH (alkali) environments after adsorption.

Figure 7 shows the adsorption and desorption results. Based on the results, the amount of cadmium ions adsorption by PS and PSBs was kept constant in the cycle desorption process when the desorption process was conducted using distilled water. This indicates that desorption of cadmium by distilled water can be ignored.

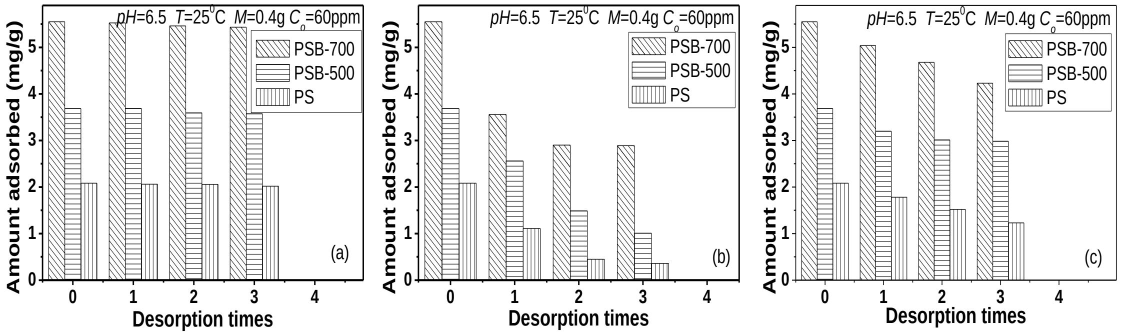


Fig. 7. Desorption of cadmium ions from PS, PSB-500 and PSB-700 in different environments: (a) neutral environment; (b) acid environment; and (c) alkali environment

In the alkali environment, precipitation could take place, although much more cadmium ions will be removed when the cadmium ions were desorbed by NaOH solution. The cadmium ions amount that was desorbed from sawdust increased with the increase in recycle time. When HNO_3 was selected as a desorption solution, the cadmium ions amount decreased with the recycle time increasing. In the acidic environment there is an abundance of hydrogen ions that can replace the cadmium ions and can be adsorbed onto the surface of the adsorbent. As a result, cadmium ions were desorbed from the adsorbent. Since there is no secondary pollution of cadmium after the adsorption process, it can be concluded that PS and PSBs can be used as adsorbent materials to remove cadmium ions from aqueous solution in neutral environments (Kołodyńska *et al.* 2017).

CONCLUSIONS

1. This paper investigated the adsorption process of cadmium ions from aqueous solution using pine sawdust (PS), biochar prepared at 500 °C (PSB-500), and biochar prepared at 700 °C (PSB-700). Based on the results, the removal efficiency increased with increases in pH value, temperature, and adsorption time. With the increase in adsorbent amount, the amount adsorbed per unit of adsorbent decreased while the removal ratio increased. With the increase in initial concentration, the amount adsorbed increased while the removal ratio decreased.
2. The adsorption behavior of cadmium ions by PS, PSB-500, and PSB-700 can be well described by the Langmuir isotherm model and the pseudo-second order model. The adsorption equilibrium time was 300 min. The adsorption capacity order of these three adsorbents was: PSB-700 (6.09 mg/g) >PSB-500 (4.78 mg/g) >PS (3.47 mg/g).
3. There was no desorption of cadmium by distilled water and NaOH solution, which indicated that PS and PSBs can be used for cadmium removal in neutral and alkali environments. There was obvious desorption in acid solution. Thus, elution of the biochar with acidic solution can be used to regenerate the biochar and allow it to be reused for adsorption of the cadmium ions.
4. As a potential adsorbent, the applicability of PSB-700 in remediation of cadmium-contaminated wastewater will be tested in further study.

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REFERENCES CITED

Ahmaruzzaman, M. (2011). “Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals,” *Advances in Colloid and Interface Science* 166(1-2), 36-59. DOI: 10.1016/j.cis.2011.04.005.

Al-Shannag, M., Al-Qodah, Z., Nawasreh, M., Al-Hamamreh, Z., Bani-Melhem, K., and Alkasrawi, M. (2017). “On the performance of *Ballota undulata* biomass for the removal of cadmium (II) ions from water,” *Desalination and Water Treatment* 67, 223-230. DOI: 10.5004/dwt.2017.20379.

Afroze, S., and Sen, T. K. (2018). “A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents,” *Water, Air, and Soil Pollution* 229(7), 225. DOI: 10.1007/s11270-018-3869-z.

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., and Ok, Y. S. (2014). “Biochar as a sorbent for contaminant management in soil and water: A review,” *Chemosphere* 99, 19-33. DOI: 10.1016/j.chemosphere.2013.10.071

Argun, M. E., Dursun, S., Ozdemir, C., and Karatas, M. (2007). “Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics,” *Journal of Hazardous Materials* 141(1), 77-85. DOI: 10.1016/j.jhazmat.2006.06.095.

Ali, R. M., Hamad, H. A., Hussein, M. M., and Malash, G. F. (2016). “Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis,” *Ecological Engineering* 91, 317-332. DOI: 10.1016/j.ecoleng.2016.03.015

ASTM D3838-05 (2017). “Standard test method for pH of activated carbon,” ASTM International, West Conshohocken, PA. DOI: 10.1520/D3838-05R17

ASTM D6556-17 (2017) “Standard test method for carbon black—Total and external surface area by nitrogen adsorption,” ASTM International, West Conshohocken, PA. DOI: 10.1520/D6556-17

ASTM E1755-01 (2015) “Standard test method for ash in biomass,” ASTM International, West Conshohocken, PA. DOI: 10.1520/E1755-01R15

Bulut, Y., and Tez, Z. (2007). “Removal of heavy metals from aqueous solution by sawdust adsorption,” *Journal of Environmental Sciences*, 19(2), 160-166. DOI: 10.1016/s1001-0742(07)60026-6

Cao, S., Duan, X., Ma, Y., Zhao, X., Qin, Y., Liu, Y., and Wei, F. (2017). “Health benefit from decreasing exposure to heavy metals and metalloid after strict pollution control measures near a typical river basin area in China,” *Chemosphere* 184, 866-878. DOI:10.1016/j.chemosphere.2017.06.052

Crini, G., Lichtfouse, E., Wilson, L. D., and Morin-Crini, N. (2018). “Conventional and non-conventional adsorbents for wastewater treatment,” *Environmental Chemistry Letters* 1-19. DOI: 10.1007/s10311-018-0786-8.

Cuiping, L., Chuangzhi, W., and Haitao, H. (2004). “Study on the distribution and quantity of biomass residues resource in China,” *Biomass and Bioenergy* 27(2), 111-117. DOI: 10.1016/j.biombioe.2003.10.009

Çakir, E., Tosunoğlu, V., Boncukcuoğlu, R., Korkmaz, M. and Fil, B.A. (2017). “Kinetic and fixed bed studies for copper removal from solutions by walnut tree sawdust (*Juglans regia* L.),” *Global NEST Journal* 19(2), 327-335

Farinella, N. V., Matos, G. D., and Arruda, M. A. Z. (2007). “Grape bagasse as a potential biosorbent of metals in effluent treatments,” *Bioresour. Technol*. 98, 1940-1946. DOI:10.1016/j.biortech.2006.07.043

Gode, F., Atalay, E. D., and Pehlivan, E. (2008). “Removal of Cr (VI) from aqueous solutions using modified red pine sawdust,” *Journal of Hazardous Materials* 152(3), 1201-1207. DOI: 10.1016/j.jhazmat.2007.07.104

Komkiene, J. and Baltrenaite, E. (2016). “Biochar as adsorbent for removal of heavy metal ions [cadmium (II), copper (II), lead (II), zinc (II)] from aqueous phase,” *International Journal of Environmental Science and Technology* 13(2), 471-482. DOI: 10.1007/s13762-015-0873-3

Kırbıyık, Ç., Pütün, A. E., and Pütün, E. (2016). “Comparative studies on adsorptive removal of heavy metal ions by biosorbent, bio-char and activated carbon obtained from low cost agro-residue,” *Water Science and Technology* 73(2), 423-436. DOI:10.2166/wst.2015.504

Kołodyńska, D., Krukowska, J., and Thomas, P. (2017). “Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon,” *Chemical Engineering Journal* 307, 353-363. DOI: 10.1016/j.cej.2016.08.088.

Keiluweit, M., Nico, P. S., Johnson, M. G., and Kleber, M. (2010). “Dynamic molecular structure of plant biomass-derived black carbon (biochar),” *Environmental Science & Technology* 44(4), 1247-1253. DOI: 10.1021/es9031419

Li, H., Dong, X., da Silva, E. B., de Oliveira, L. M., Chen, Y., and Ma, L. Q. (2017). “Mechanisms of metal sorption by biochars: Biochar characteristics and modifications,” *Chemosphere* 178, 466-478. DOI:10.1016/j.chemosphere.2017.03.072

Li, B., Zhou, F., Huang, K., Wang, Y., Mei, S., Zhou, Y., and Jing, T. (2017). “Environmentally friendly chitosan/PEI-grafted magnetic gelatin for the highly effective removal of heavy metals from drinking water,” *Scientific Reports* 7, 1-9. DOI: 10.1038/srep43082.

Li, K., Zhang, R., and Bi, J. (2010). “Experimental study on syngas production by co-gasification of coal and biomass in a fluidized bed,” *International Journal of Hydrogen Energy* 35(7), 2722-2726. DOI: 10.1016/j.ijhydene.2009.04.046

Li, F.T., Yang, H., Zhao, Y., Xu, R. (2007). “Novel modified pectin for heavy metal adsorption,” *Chin. Chem. Lett* 18, 325-328. DOI: 10.1016/j.cclet.2007.01.034

Liu, Y., Xiao, T., Baveye, P. C., Zhu, J., Ning, Z., and Li, H. (2015). “Potential health risk in areas with high naturally-occurring cadmium background in southwestern China,” *Ecotoxicology and Environmental Safety* 112, 122-131. DOI:10.1016/j.ecoenv.2014.10.022.

Lou, K., Rajapaksha, A. U., Ok, Y. S., and Chang, S. X. (2016). “Sorption of copper (II) from synthetic oil sands process-affected water (OSPW) by pine sawdust biochars: Effects of pyrolysis temperature and steam activation,” *Journal of Soils and Sediments* 16(8), 2081-2089. DOI: 10.1007/s11368-016-1382-9

Özacar, M. and Şengil, İ. A. (2005). “Adsorption of metal complex dyes from aqueous solutions by pine sawdust,” *Bioresource Technology* 96(7), 791-795. DOI:10.1016/j.biortech.2004.07.011

Park, C. M., Han, J., Chu, K. H., Al-Hamadani, Y. A., Her, N., Heo, J., and Yoon, Y. (2017). “Influence of solution pH, ionic strength, and humic acid on cadmium adsorption onto activated biochar: Experiment and modeling,” *Journal of Industrial and Engineering Chemistry* 48, 186-193. DOI: 10.1016/j.jiec.2016.12.038

Patar, A., Giri, A., Boro, F., Bhuyan, K., Singha, U., and Giri, S. (2016). “Cadmium pollution and amphibians–Studies in tadpoles of *Rana limnocharis, Chemosphere* 144, 1043-1049. DOI: 10.1016/j.chemosphere.2015.09.088

Rao, R. A. K., and Kashifuddin, M. (2014). "Kinetics and isotherm studies of Cd(II) adsorption from aqueous solution utilizing seeds of bottlebrush plant (*Callistemon chisholmii*)," *Applied Water Science* 4(4), 371-383. DOI:10.1007/s13201-014-0153-2

Reddy, K. R., Xie, T., and Dastgheibi, S. (2014). "Evaluation of biochar as a potential filter media for the removal of mixed contaminants from urban storm water runoff," *Journal of Environmental Engineering* 140(12), 04014043. DOI:10.1061/(ASCE)EE.1943-7870.0000872

Saha, N., Rahman, M. S., Ahmed, M. B., and Uddin, M. K. (2017). "A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade," *Chemical Engineering Journal* 308, 438-462. DOI: 10.1016/j.cej.2016.09.029

Semerjian, L. (2018). "Removal of heavy metals (Cu, Pb) from aqueous solutions using pine (*Pinus halepensis*) sawdust: Equilibrium, kinetic, and thermodynamic studies," *Environmental Technology and Innovation* 12, 91-103. DOI:10.1016/j.eti.2018.08.005

Shaaban, A., Se, S. M., Mitan, N. M. M., and Dimin, M. F. (2013). "Characterization of biochar derived from rubber wood sawdust through slow pyrolysis on surface porosities and functional groups," *Procedia Engineering* 68, 365-371. DOI:10.1016/j.proeng.2013.12.193

Tang, Q., Tang, X., Hu, M., Li, Z., Chen, Y., and Lou, P. (2010). "Removal of Cd (II) from aqueous solution with activated *Firmiana simplex* Leaf: Behaviors and affecting factors," *Journal of Hazardous Materials* 179(1-3), 95-103. DOI:10.1016/j.jhazmat.2010.02.062.

Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., and Yang, Z. (2015). "Application of biochar for the removal of pollutants from aqueous solutions," *Chemosphere* 125, 70-85. DOI: 10.1016/j.chemosphere.2014.12.058

Taty-Costodes, V. C., Fauduet, H., Porte, C., and Delacroix, A. (2003). "Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*," *Journal of Hazardous Materials*, 105(1-3), 121-142. DOI:10.1016/j.jhazmat.2003.07.009

Uddin, M. K. (2017). "A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade," *Chemical Engineering Journal* 308, 438-462. DOI:10.1016/j.cej.2016.09.029.

Wahab, M. A., Jellali, S., and Jedidi, N. (2010). "Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms modeling," *Bioresource Technology* 101(14), 5070-5075. DOI: 10.1016/j.biortech.2010.01.121

Zhao, X. M., Yao, L. A., Ma, Q. L., Zhou, G. J., Wang, L., Fang, Q. L., and Xu, Z. C. (2018). "Distribution and ecological risk assessment of cadmium in water and sediment in Longjiang River, China: Implication on water quality management after pollution accident," *Chemosphere* 194, 107-116. DOI:10.1016/j.chemosphere.2017.11.127

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