INFLUENCE OF PH AND CONTACT TIME ON CADMIUM REMOVAL FROM WATER BY ADSORPTION IN ACACIA SHELL-DERIVED BIOCHAR

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ABSTRACT

This paper focuses on studying Cd adsorption capacity by acacia shell-biochar in the aqueous phase. The results show that pH value and contact time have an effect on the Cd adsorption capacity of acacia shell biochar which is calcined at different temperatures. The Cd adsorption capacity increased dramatically when the pH of the solution is increased from 5 to 6. When the pH is increased from 6 to 8, the Cd adsorption capacity is almost unchanged. And in the experimental period from 5 minutes to 60 minutes, the longer the sample shaking time, the higher the Cd adsorption capacity. The maximum adsorption capacities for Cd(II) on AS300, AS400 and AS500 were achieved at point of 60 minutes, and the values were 26.53, 25.39 and 28.09 mg/g, respectively. Furthermore, acacia shell-derived biochar show promise as an adsorbent for removal of Cd in wastewater.

Keywords: *Acacia shell, Biochar, Adsorption, Cd, pH, Contact time*

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1. INTRODUCTION

Biochar is a carbon-rich solid formed from the organic residue by pyrolysis organic materials such as wood, manure, leaves, agricultural by-products (straw) at a temperature (<700 ^{0}C) in the absence and lack of oxygen conditions (Lehmann and Joseph, 2009). Biochar has been proven as an effective adsorbent for various contaminants, organic and inorganic matter because of their large surface area and special structure (Jiang et al., 2012). Biochar has been widely recognized as a potential candidate for water and soil treatment due to its unique and flexible features, especially for the removal of cationic ions (Cu, Pb, Cd, etc.) in water and soil environments (Jiang et al., 2012; Qi et al., 2022; Wu et al., 2019).

Activated carbon is the most common adsorbent for heavy metal ion removal in wastewater due to its microvariable structure and easy surface functionalization. However, the separation of activated carbon from wastewater solution surface was limited to use because it's been faced a variety of challenges and high cost. Recently, an appearance of various new materials also shows their competitive ability in heavy metal ion removal. These promising new materials showing some excellent properties, such as large surface areas, great mechanical strength, and high chemical resistance. In recent years, researchers have carried out studies on the development of new adsorbents, especially nanostructured materials such as carbon nanotubes, graphene, fullerenes, MXenes and others (Chai et al., 2021).

The pollution of heavy metals (Cd) in water is currently one of the serious environmental problems that can affect the quality of the environment and human health due to the bioaccumulation of heavy metals, especially in the mining areas. Therefore, finding methods to treat heavy metal pollution is very important. Currently, there are a variety of the methods applied to treat heavy metal pollution such as chemical precipitation, adsorption, photocatalysis, biological treatment, ion exchange and membrane filtration. Among these methods, the adsorption method shows their easy operation and high removal efficiency, is one of the most promising for advanced treatment processes (Huang et al., 2015).

Acacia shell, a by-product of woodworking, is discarded tens millions tons each year. Most of acacia shell is used as cheap materials or neglected, piled up to decompose, make environmental pollution, and waste of resources. Using acacia shell as an adsorbent for pollutant removal will have great environmental significance in dealing with waste by waste.

Hence, new searches are necessary to find out a green sorbent that recycling waste, low-cost, and has high heavy metals adsorption capacity. The acacia shell-derived biochar is used for the removal of cadmium. The effects of contact time and pH value were evaluated in batch experiments. Data obtained, batch experiments were to analyze the sorption behavior of Cd^{2+} onto the acacia shell-derived biochar.

2. MATERIALS AND METHODS

2.1. Feedstock and Chemical

Acacia shell (AS) was collected from a local area at Vo Nhai district, Thai Nguyen province, Vietnam. Upon collection, AS was washed with tap water and deionized water (DI-water) to remove any water-soluble impurities and adhering dirt. After washing, AS was dried at 80 ^oC for 48 h and crushed to 0.074–0.105 mm particles using an electric grinder. All chemicals are analytical grade with the purity more than 95%.

2.2. Preparation of Acacia shell – derived biochar

The dried samples were placed in the oven at diffferent temperture (300 °C, 400 °C , and 500 °C) for 1 h to conclude the process of activation. The products were allowed to cool to room temperature and then were washed with deionized distilled water until their pH values were approximately 7.0. The products were dried in an oven overnight at 50 °C, and the AS-biochar samples were thus synthesized. Hereinafter, biochar derived from AS at different temperature (300°C, 400°C, 500°C) were designated as AS300, AS400, and AS500 respectively.

2.3. Sorption Experiment and Data Analysis

- Experiment 1: Studying the effect of pH into Cd removal in water by acacia shell-derived biochar. 4 experimental formulas: pH = 5, 6, 7, 8 were noted as CT1, CT2, CT3, and CT4 respectively. The experiment was arranged in a completely randomized and 3 times repeated.

- Experiment 2: Studying the effect of contact time into Cd adsorption capacity in water by biochar produced from acacia shell. 4 experimental formulas: t = 5, 10, 20, 40, and 60 minutes were designated as CT5, CT6, CT7, CT8, and CT9 respectively. The experiment was arranged in a completely randomized and 3 times repeated.

- To avoid adsorption interference, each adsorption experiment was conducted using a single adsorbate. Stock solutions of 1000 mg Cd/L (using $Cd(NO_3)2.4\ H_2O$) were prepared in distilled water. Approximately 0.1 g of the adsorbate was added to a Teflon centrifuge tube containing 50 mL of a solution with the fixed Cd concentration. The centrifuge tubes were placed in a reciprocating shaker at 150 rpm and 25 °C and equilibrated for 24 h. After the process, the solution was filtered with a 0.45 µm filter.

- Next cadmium were analyzed using ICP machine at the laboratory of University of Science, Thai Nguyen University.

- The adsorbed amount of Cd in equilibrium, q_e (mg/g), was calculated by the mas-balance equation.

$$q_e = (C_0 - C_e)\ V / m \qquad \text{(Eq.1)}$$

Where: C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium Cd concentrations, respectively; m (g) is the mass of the adsorbents, and V (L) is the volume of Cd solution.

- Using SAS software to calculate the mean, standard deviation from the raw data obtained from the results of the experiments, then calculate the adsorption capacity.

3. RESULTS AND DISCUSSION

3.1. The effect of pH into Cd adsorption in water of biochar produced from acacia shell

To investigate The effect of pH into Cd adsorption by biochar produced from acacia shell, the research conducted experiments with 4 formulas (pH = 5, 6, 7, 8), 3 times repeated with biochar which is calcined at different temperatures, the experiment was carried out with an initial Cd concentration of 100 mg/l, shaking time was 60 minutes, the experimental results are shown in Table 1 below.

Table 1. The effect of pH into Cd adsorption in water of biochar produced from acacia shell

Formula/Samples	AS300	AS400	AS500
Cd concentration in water after treated with acacia shell-derived biochar (mg/l)			
CT1	62,45 ± 0,34^{a}	63,26 ± 0,29^{a}	61,64 ± 0,70^{a}
CT2	55,74 ± 0,78^{b}	56,92 ± 0,81^{b}	53,48 ± 0,44^{b}
CT3	55,97 ± 0,59^{b}	56,72 ± 0,38^{b}	53,29 ± 0,66^{b}
CT4	55,56 ± 0,13^{b}	56,47 ± 0,16^{b}	52,74 ± 0,66^{b}
Cd adsorption capacity of acacia shell-derived biochar (mg/g)			
CT1	22,53	22,04	23,02
CT2	26,55	25,85	27,91
CT3	26,42	25,97	28,03
CT4	26,66	26,12	28,36

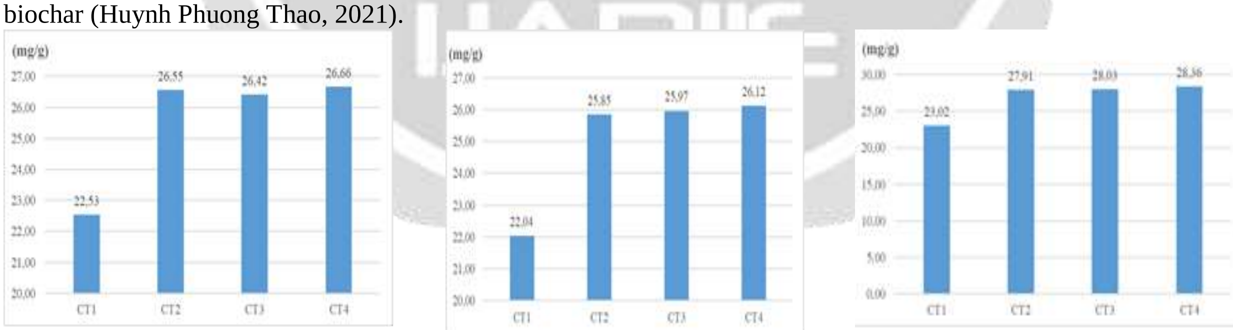
Table 1 displays that the Cd concentration in water decreased dramatically in all experimental formulas, all biochars were calcined at different temperatures (AS300, AS400 and AS500).

With acacia shell biochar which is calcined at 300^0C, Cd concentration decreased to 62,45 ± 0,34 mg/l (pH = 5); 55,74 ± 0,78 mg/l (pH = 6); 55,97 ± 0,59 mg/l (pH = 7); 55,56 ± 0,13 mg/l (pH = 8).

With acacia shell biochar which is calcined at 400^0C, Cd concentration decreased to 63,26 ± 0,29 mg/l (pH = 5); 56,92 ± 0,81 mg/l (pH = 6); 56,72 ± 0,38 mg/l (pH = 7); 56,47 ± 0,16 mg/l (pH = 8). Compared with acacia shell biochar which is calcined at 300^0C, Cd concentration in the following experiments tended to be higher, which means the treatment level was lower.

With acacia shell biochar which is calcined at 400^0C, Cd concentration decreased to 61,64 ± 0,70 mg/l (pH = 5); 53,48 ± 0,44 mg/l (pH = 6); 53,29 ± 0,66 mg/l (pH = 7); 52,74 ± 0,66 mg/l (pH = 8). Compared with acacia shell biochar which is calcined at 300^0C and 400^0C, Cd concentration in the experiment has the lowest tended, giving the highest treatment efficiency.

The adsorptive amounts of the three adsorbates, when pH = 5 gave the lowest Cd adsorption capacity and Cd adsorption capacity increased sharply when pH increased to 6. Then at pH = 7, 8 the Cd adsorption capacity in solution is not significant increase. Thereby, we can see that pH = 6 is the optimal pH for the Cd adsorption of three biochar. The Cd adsorption capacity of acacia shell-derived biochar corresponding to different pH levels ranged from 22.04 mg/g - 28.36 mg/g. This result is similar with the reasearch on Cd adsorption capacity of pine needle biochar (Huynh Phuong Thao, 2021).



a. AS300 b. *AS400* c. *AS4500*

Figure 1. The effect of pH into Cd adsorption in water of biochar produced from acacia shell

According to Table 1 and Figure 1, the results show that:

As for AS300, the amount of Cd adsorption capacity when pH = 5 reaches 22,53 mg/g; pH = 6 reaches 26,55 mg/g; pH = 7 reaches 26,42 mg/g and pH = 8 reaches 26,66 mg/g. Cd adsorption of biochar produced from acacia shell which is calcined at 300^0C increased dramatically when pH of the solution changed from 5 to 6. At pH values of 6, 7, 8, the adsorption capacity was almost unchanged. The optimal pH for the Cd adsorption of AS300 is pH = 6, similar with the reasearch on Cd adsorption capacity of pine needle biochar (Huynh Phuong Thao, 2021).

With AS400, the amount of Cd adsorption capacity when pH = 5 reaches 22,04 mg/g; pH = 6 reaches 25,85 mg/g; pH = 7 reaches 25,97 mg/g và pH = 8 reaches t 26,12 mg/g. Compared with AS300, the Cd adsorption capacity of AS400 tended to decrease. Cd adsorption of biochar produced from acacia shell which is calcined at 400^0C increased dramatically when pH of the solution changed from 5 to 6. At pH values of 6, 7, 8, the adsorption capacity was almost unchanged as similar results for AS300

At pH = 5, the maximum adsorption capacities for Cd by AS500 reaches 23,02 mg/g; pH = 6 reaches 27,91 mg/g; pH = 7 reaches 28,03 mg/g and pH = 8 reaches 28,36 mg/g. Compared with AS300 and AS400, the adsorptive amounts of Cd is highest with AS500. Cd adsorption of biochar produced from acacia shell which is calcined at 500^0C increased dramatically when pH of the solution changed from 5 to 6. At the same direction of AS300 and AS400, when pH values of 6, 7, 8, the Cd adsorption capacity of AS500 was almost unchanged.

3.2. The effect of contact time into Cd adsorption capacity in water of acacia shell-derived biochar

To investigate the effect of contact time into Cd adsorption capacity of biochar produced from acacia shell, the research conducted experiments with 5 formulas (shaking time = 5, 10, 20, 40 and 60 minutes), 3 times repeated with biochar which is calcined at different temperatures, the experiment was carried out with an initial Cd concentration of 100 mg/l, the experimental results are shown in Table 2.

Table 2. The effect of contact time into Cd adsorption capacity in water of acacia shell-derived biochar

Formula/Samples	AS300	AS400	AS500
Cd concentration in water after treated with acacia shell-derived biochar (mg/l)			
CT5	93,22 ± 0,29[a]	93,45 ± 0,40[a]	92,55 ± 0,45[a]
CT6	83,52 ± 0,65[b]	84,85 ± 0,08[b]	82,85 ± 0,08[b]
CT7	74,56 ± 0,47[c]	73,23 ± 0,48[c]	72,56 ± 0,47[c]
CT8	65,80 ± 0,90[d]	64,80 ± 0,90[d]	63,13 ± 0,61[d]
CT9	55,78 ± 0,64[e]	57,68 ± 0,39[e]	53,18 ± 0,42[e]
Cd adsorption capacity of acacia shell-derived biochar (mg/g)			
CT5	4,07	3,93	4,47
CT6	9,89	9,09	10,29
CT7	15,26	16,06	16,46
CT8	20,52	21,12	22,12
CT9	26,53	25,39	28,09

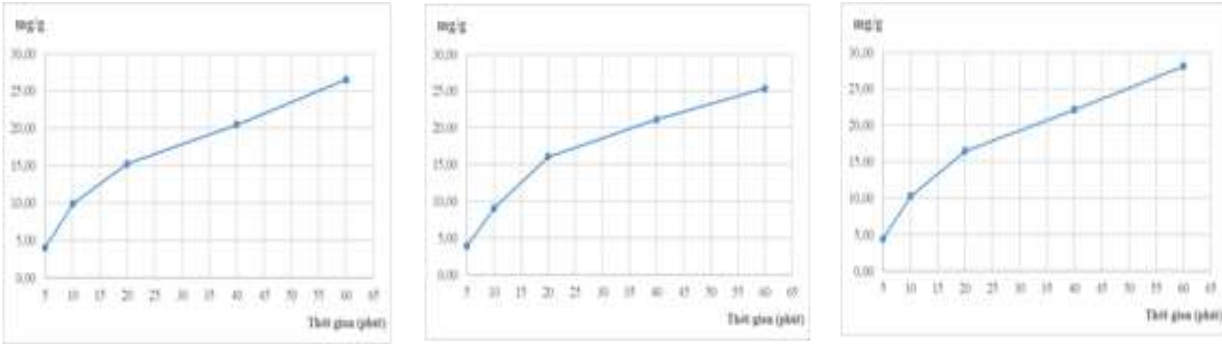
In general, Talbe 2 illutrated that the contact time effecting to the adsoptive amount of Cd in water by three kind of acacia shell-derived biochar**.** Cd concentration in water decreased sharply in all experimentals, all biochars were calcined at different temperatures. In the scope of the research, shaking time from 5 minutes to 60 minutes, we can see that the longer the shaking time, the lower the Cd concentration remaining in the water.

Cd adsorption of biochar produced from acacia shell which is calcined at 300^0C (AS300), Cd concentration decreased to 93.22 ± 0.29 mg/l (after 5 minutes of sample shaking); 83.52 ± 0.65 mg/l (after 10 minutes of sample shaking); 74.56 ± 0.47 mg/l (after 20 minutes of sample shaking); 65.80 ± 0.90 mg/l (after 40 minutes of sample shaking) and 55.78 ± 0.64 mg/l (after 60 minutes of sample shaking).

Cd adsorption of biochar produced from acacia shell which is calcined at 400^0C (AS400), Cd concentration decreased to 93.45 ± 0.40 mg/l (after 5 minutes of sample shaking); 84.85 ± 0.08 mg/l (after 10 minutes of sample shaking); 73.23 ± 0.48 mg/l (after 20 minutes of sample shaking); 64.80 ± 0.90 mg/l (after 40 minutes of sample shaking) and 57.68 ± 0.39 mg/l (after 60 minutes of sample shaking).

Cd adsorption of biochar produced from acacia shell which is calcined at 500^0C (AS500), Cd concentration decreased to 92.55 ± 0.45 mg/l (after 5 minutes of sample shaking); 82.85 ± 0.08 mg/l (after 10 minutes of sample shaking); 72.56 ± 0.47 mg/l (after 20 minutes of sample shaking); 63.13 ± 0.61 mg/l (after 40 minutes of shaking the sample) and 53.18 ± 0.42 mg/l (after 60 minutes of shaking the sample). Compared with AS300 an AS400, Cd adsorption in the experimental formulas tended to be the lowest, giving the highest treatment efficiency.

As for AS300, the adsorptive amount of Cd increased from 4.07 mg/g to 26.53 mg/g when shaking time increased from 5 minutes to 60 minutes. While, AS400 the Cd adsorption capacity increased from 3,93 mg/g to 25,39 mg/g when shaking time increased from 5 minutes to 60 minutes. And, AS500, the amount of Cd adsorption capacity increased from 4,47 mg/g to 28,09 mg/g when shaking time increased from 5 minutes to 60 minutes. The Cd adsorption capacity of biochar produced from acacia shell corresponding to different times are different. This result is similar to the results of Huynh Phuong Thao (2021); Deng et al (2017).



a.AS300 *b.AS400* *c.AS500*

Figure -2. The effect of contact time into Cd adsorption capacity of AS300, AS400 and AS500

When these biochar were used as sorbents for Cd adsorption, the Cd adsorption capacity at point of 5, 10, 20,40 and 60 minutes followed by the order of AS500 > AS400 > AS300. Especially, the maximum Cd adsorption capacity of biochar produced from acacia shell which is calcined at 500 ^{0}C (AS500) after shaking the sample for 5 minutes reached 4,47 mg/g; after 10 minutes reached 10.29 mg/g; after 20 minutes reached 16.46 mg/g; after 40 minutes reached 22.12 mg/g and after 60 minutes reached 28.09 mg/g. Hence, the Cd adsorption capacity of biochar acacia shell which is calcined at 300^{0}C, 400^{0}C and 500^{0}C also increased dramatically when shaking time increased.

4. CONCLUSION

The objective of this study was to investigate the influence of pH and contact time to Cd on acacia shell-derived biochar adsorbents. The following conclusion can be drawn from this study:

The pH value has an effect on the Cd adsorption capacity of acacia shell biochar which is calcined at different temperatures. The amount of Cd adsorption capacity increased dramatically when the pH of the solution is increased from 5 to 6. When the pH is increased from 6 to 8, the Cd adsorption capacity is remaining unchanged.

Cd adsorption capacity of acacia shell biochar which is calcined at different temperatures increase when the adsorption time increased from 5 minutes to 60 minutes.

Acacia shell-derived biochar show promise as an adsorbent for removal of Cd in wastewater.

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