

Adsorption of Cd (II) from Aqueous Solutions by a Hydroxyapatite-Biochar Composite

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Abstract: Based on the rice husk biochar(BC), a creative hydroxyapatite(HA)-biochar composite (HAC) was fabricated in this study. SEM coupled with EDS, BET and XRD were employed to analyze the surface features and pore structures of BC, BC+HA (the mixture of BC and HA) and HAC. The effects of solution initial pH and the contact time between sorbents and Cd were also investigated. The results revealed that, on the surface of HAC, HA was well loaded. Though initial pH and contact time would significantly influence the adsorbing effects of Cd by all three sorbents, HAC showed a high efficient and capacity to adsorb Cd (II) in the aqueous solutions than simple biochar, and a low cost than adding nano-HA.

1 INTRODUCTION

Heavy metals are known as one type of the most severe contaminants in the environment because of their toxicity and threaten to the ecological system and human beings (Ahmad et al., 2014). Among numbers of heavy metals, Cadmium(Cd) receives the most concern because of its toxic, solubility, mobility and biological accumulation (Wang et al., 2015). The farmland and surrounding water bodies are vulnerable to threaten from Cd contamination, which is enhanced by industrial sludge, wastewater irrigation, atmospheric pollutant settlement, and utilization of organic fertilizer and pesticides (Lin et al., 2015). Numerous former researches have reported several methods to solve heavy metal contaminations from aqueous solutions, including ion exchange, sedimentation, adsorption, biological treatment, and electrokinetic remediation (Maatar and Boufi, 2015). Among these methods, adsorption has received more and more attentions due to their advantages in treating heavy metals in the environment, such as high efficiency, low cost, easy to use, selectivity and so on (Tapaswi et al., 2014).

Biochar, as a form of biomass-derived black carbon, is a type of adsorbent with high surface area and good cation exchange property. It is generally pyrolyzed under anaerobic condition by raw materials of waste biomass, including agriculture

and forest by-products (Xinde et al., 2009). The heavy metal adsorption mechanism of biochar includes surface adsorption, metal exchange with cations, electrostatic interactions and so on (Lu et al., 2012). However, the utilization of biochar is limited to its relatively low heavy metal adsorption capacity. Therefore, researchers have developed many modification methods for biochar, especially surface modifications by combining nanoparticles to prepare biochar-based nanocomposites (Ying et al., 2013). After modifications, biochar's removal ability of heavy metals will be remarkably improved (Zhang and Gao, 2013).

Hydroxyapatite (HA), naturally found in bones and teeth of animals, has been confirmed to have high adsorption capacity of divalent metal ions due to the existence of immobilizing metallic cations of P-OH groups and Ca on its surface (Saoiabi et al., 2016). However, nano-HA has the defect of tending to aggregate in clumps and encapsulated in aqueous solutions, which will influence its surface character and metal removal ability. Wang et al. reported that with a macroporous adsorbent as the carrier, the above disadvantages would be avoided (Wang et al., 2018). Biochar-based adsorbent composited with HA is produced to achieve desirable adsorption properties.

In this work, a rice-husk based hydroxyapatite-biochar composite (HAC) was fabricated to produce

a higher removing capacities of Cd(II) in aqueous solutions. The physical-chemical characteristics of HAC were analyzed and compared with these of biochar pyrolyzed from rice husk (BC) and the physical mixture of BC and hydroxyapatite (BC+HA). The effects of solution initial pH and contact time were also studied.

2 MATERIALS AND METHODS

All chemical reagents used were in analytical reagent grade and all the aqueous solutions were prepared with deionised water (DW). The nano-particle hydroxyapatite (HA) was purchased from the Macklin Biochemical (Shanghai, China). The rice husks were derived from farmlands of Ulanhot, Inner Mongolia, China.

2.1 Sorbent Preparation

Rice husk was applied as the raw material of biochar in this study. The biochar was prepared as the progress below. Rice husk was pyrolyzed in a programmable muffle furnace under an atmosphere of nitrogen ($100 \text{ cm}^3/\text{min}$). The furnace was programmed to heat to 500°C with a rate of $10^\circ\text{C}/\text{min}$ and keep for 3 hours. Biochar (BC) was obtained after the pyrolyzed rice husk was cooled to room temperature naturally.

After BC was prepared, the hydroxyapatite-biochar (HAC) composite was fabricated with the following process. The prepared BC (10.0 g) was first added to a H_3PO_4 (15 M) which was stirring vigorous to form the suspension solution A. Then a $\text{Ca}(\text{OH})_2$ (0.001 M) solution was prepared as the solution B. The pH levels of solutions A and B were both adjusted to about 10.0 with HCl or NaOH (0.1M). After that, solution A and B were mixed gradually. In the next 24 hours, the mixed solution was stirred occasionally and the pH of which was determined. After 24 h, the pH would achieve a constant. Then the solution was centrifuged to isolate the precipitate, which was washed three times with ethanol. Finally, the HAC composite was obtained after drying at the room temperature. The mixture of BC and hydroxyapatite (BC+HA) was obtained by a physical mixture and grind of BC and the nano-particle hydroxyapatite with a ratio of 2:1.

2.2 Sorbent Characterization

The sorbents of BC, BC+HA, and HAC were all characterized to compare similarities and differences.

Field emission scanning electron microscope (Hitachi, SU8010) was applied to perform SEM patterns of sorbents. The surface elemental composition analysis of the sorbents was conducted by energy-dispersive spectroscopy (EDS). Via a X'Pert PRO MPD X-ray diffractometer, the XRD patterns of sorbents were obtained. IR spectra from $4000\text{-}400 \text{ cm}^{-1}$ were measured on a Nicolet Nexus 470 FT-IR spectrometer. The specific surface area was measured by a BET analyzer of Micromeritics TriStar II 3flex.

2.3 Adsorption Experiments

In each adsorption kinetic experiment, 0.5 g sorbents were added to Cd (II) solutions (500 mL, 50 mg/L) and then stirred at 1000 rpm. Samples (0.5 mL) were collected at noted different adsorption time (from 10 to 1500 min), filtered through the filter of $0.45 \mu\text{m}$, and analyzed via Atomic Absorption Spectrophotometer (AAS). The impact of initial pH on adsorption efficiency was performed by varying the solution's initial pH between 2 and 7 using NaOH or HNO_3 .

All solutions in experiments were performed in 40 mL brown glass vials and shaken in a thermostatic oscillator with a speed of 150 r/min. Through calculating the difference Cd(II) concentrations between before and after the adsorption equilibrium, the adsorption capacities of adsorbents were valued. There were three replicates for all experiments in this study. Standard solutions were determined with every ten samples. The recovery percentages were 97.6-104.3%, and the relative standard deviations were below 2.45%.

3 RESULTS AND DISCUSSION

3.1 Characterization of Sorbents

The elemental contents of BC, BC+HA and HAC are shown in Table 1, indicating significant differences between three materials. BC+HA and HAC both showed significant decrease in surface carbon content and increase in surface oxygen content compared to BC. This result implied the existence of larger amounts of oxygen-containing functional groups and thus higher polarity in the sorbents of HAC and BC+HA than BC. The results of specific surface areas (S_{BET}), and average pore width of BC, BC+HA and HAC (Table 1) revealed that all materials showed mesoporous structures. The significant decrease of surface area of HAC suggested the occupation of pores of BC by HA,

which could also explained by the increase of average pore width.

Table 1: Selected physiochemical properties of BC, BC+HA and HAC.

Sorbents	BC	BC+HA	HAC
Surface atomic composition (%)			
C	66.8±1.08	18.1±0.44	16.1±0.61
O	29.1±1.39	38.9±0.67	37.9±0.77
P	-	11.6±0.18	3.79±0.15
Ca	-	22.5±0.29	16.0±0.29
S_{BET} (m ² /g)	204.8	193.7	68.64
Pore width (nm)	4.34	14.36	12.41

SEM images of BC, BC+HA and HAC showed the clear differences among three sorbents. BC showed a porous structure on its surface which indicating adsorption sites (Figure 1a). The surface of BC+HA and HAC both featured larger numbers of particles (Figure 1b&c), which could be thought as composing of hydroxyapatite deposited on the surface of biochar. This conclusion was supported by the fact of the increased percentages of Ca and P on the surface of BC+HA and HAC (Table 1).

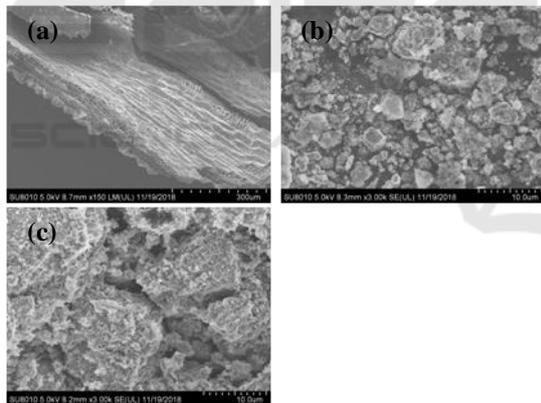


Figure 1: Electron microscopy of BC (a), BC+HA (b) and HAC (c).

The XRD results of BC, BC+HA and HAC were shown in Figure 2. The pattern of BC shows a broad hump peak at 23°, which indicates that the sample was amorphous. The XRD patterns of BC+HA and HAC were similar and significantly different from that of BC, indicating that HAP was loaded on the surface of the two biochars of BC+HA and HAC.

3.2 Effects of Initial pH

Figure 3 shows that initial pH is a very vital factor that affected the adsorption rates and processes of BC, BC+HA and HAC. The Cd (II) adsorption capacity increased when the initial pH ranged from 2 to 6, due to the electrostatic interactions were facilitated by affecting the electric charge density of the surface, resulting the increase of adsorption rate (Jefferson et al., 2015). However, when the initial pH was higher than 7, the metal-deposition reactions of Cd(II) led to the decrease of sorption rates.

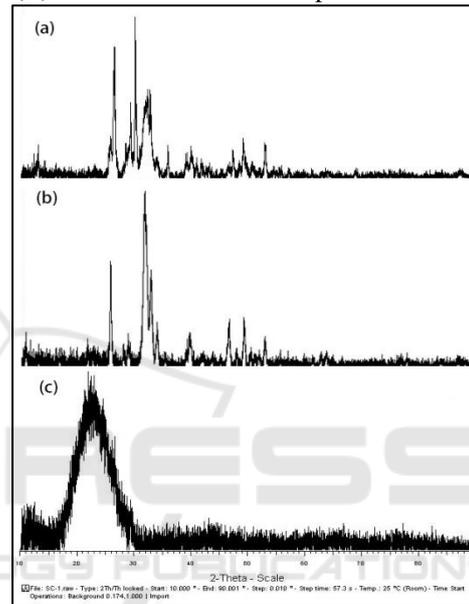


Figure 2: XRD patterns of BC (c), BC+HA (a) and HAC (b).

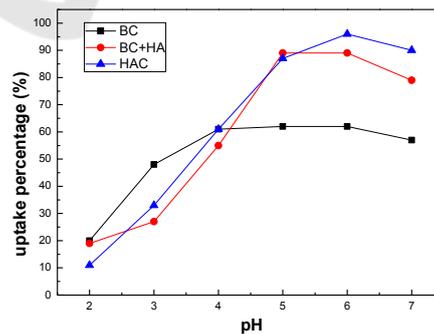


Figure 3: Effects of initial pH on the adsorptions of Cd.

3.3 Sorption Kinetics

Figure 4 revealed the Cd(II) sorption kinetics of three adsorbents in aqueous solutions. The adsorption rates increased quickly during the first

200 mins. Almost 90% of the ultimate sorption occurred in the first 300 mins for all three sorbents, and followed with a quick approach to the equilibrium. The Cd (II) removal percentages by BC, BC+HA and HAC at equilibrium were 41.1%, 80.5%, and 82.7%, respectively. To fit the experimental data, equations of pseudo first order and pseudo second order were both used. For HAC, the R^2 value of pseudo-second-order model (0.992) was relatively higher than that of pseudo-second-order model (0.982), indicating the chemisorption involved between Cd(II) and sorbents in the sorption process.

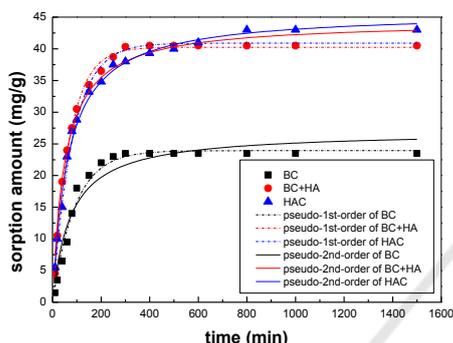


Figure 4: Cd(II) sorption kinetics of BC, BC+HA and HAC.

4 CONCLUSIONS

Based on the rice husk biochar and the hydroxyapatite, a hydroxyapatite-biochar composite was fabricated in this study. Through characteristics, effect of initial pH and kinetic analysis, HAC showed a better sorption performance than pure biochar and a lower cost than physical mixture of biochar and hydroxyapatite. The results revealed that HAC exhibited a potential application as an excellent sorbent for Cd (II) reduction from polluted waters.

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