

Adsorption of Cd(II) and Cu(II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste

Wei Zheng, Xiao-ming Li*, Qi Yang, Guang-ming Zeng,
Xiang-xin Shen, Ying Zhang, Jing-jin Liu

College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China

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Abstract

Carbonate hydroxylapatite (CHAP) synthesized by using eggshell waste as raw material has been investigated as metal adsorption for Cd(II) and Cu(II) from aqueous solutions. The effect of various parameters on adsorption process such as contact time, solution pH, amount of CHAP and initial concentration of metal ions was studied at room temperature to optimize the conditions for maximum adsorption. The results showed that the removal efficiency of Cd(II) and Cu(II) by CHAP could reach 94 and 93.17%, respectively, when the initial Cd(II) concentration 80 mg/L and Cu(II) 60 mg/L and the liquid/solid ratio was 2.5 g/L. The equilibrium sorption data for single metal systems at room temperature could be described by the Langmuir and Freundlich isotherm models. The highest value of Langmuir maximum uptake, (*b*), was found for cadmium (111.1 mg/g) and copper (142.86 mg/g). Similar Freundlich empirical constants, *K*, were obtained for cadmium (2.224) and copper (7.925). Ion exchange and surface adsorption might be involved in the adsorption process of cadmium and copper. Desorption experiments showed that CaCl₂, NaCl, acetic acid and ultrasonic were not efficient enough to desorb substantial amount of metal ions from the CHAP. The results obtained show that CHAP has a high affinity to cadmium and copper.

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Keywords: Carbonate hydroxylapatite (CHAP); Heavy metals; Adsorption; Cadmium and copper removal; Adsorption isotherm

1. Introduction

The removal of toxic metals from wastewater is a matter of great interest in the field of water pollution, which is a serious cause of water degradation. Numerous metals such as chromium, mercury, lead, copper, cadmium, manganese, etc., are known to be significantly toxic.

Cadmium and copper, the metals considered in this study, are the widely used materials, where an intake of excessively large doses by man may lead to serious kidney failure and liver disease.

These facts have motivated many physicochemical methods for heavy metal removal from aqueous solution, including adsorption, chemical precipitation, solvent extraction, reverse

osmosis, ion exchange, chemical oxidation and reduction, filtration, and electrochemical treatment. Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness. At present, there is growing interest in using low cost, non-conventional alternative materials which used to be considered as waste, e.g. grape stalks [1], crop milling waste [2], olive stone [3] and sawdust [4] instead of traditional adsorbents for heavy metals removal from wastewater. Most cases have also confirmed that the use of large quantities of such kind of wastes for the treatment of polluted water is an attractive and promising option with a double benefit for the environment. Hydroxylapatite (HAP) as an efficient adsorbent, which has high stability in Pb immobilization has been reported [5–7]. Many researchers have assessed its dissolution [8], crystallizability [9], surface activity [9], and thermal stability. Previous works [10–14] also mentioned that the synthetic CHAP had higher efficiency in the removal of heavy metals (Pb(II), Cd(II), Cu(II), Hg(II)) than HAP, but, lacking of the details about its adsorption

Abbreviations: CHAP, carbonate hydroxylapatite [Ca₁₀{(PO₄)_{6-x}(CO₃·OH)_x}(OH)₂]; HAP, hydroxylapatite [Ca₁₀(PO₄)₆(OH)₂]; AAS, atomic absorption spectrophotometer; SEM, scanning electron microscopy

* Corresponding author. Tel.: +86 731 8823967; fax: +86 731 8822829.

E-mail address: xmli@hnu.cn (X.-m. Li).

characteristics to heavy metals, which might due to the high cost of the preparation of CHAP.

In this research, a new process for CHAP synthesized by using eggshell, which is considered as a kind of waste byproduct from the food products industry, was proposed. No related information about this process and its further adsorption characteristics to heavy metals could be available.

The objective of this study is to investigate the adsorption capacity of CHAP prepared by eggshell waste and its characteristics for the removal of cadmium and copper.

2. Materials and methods

2.1. Apparatus and instrumentation

- A Perkin-Elmer 700 atomic absorption spectrophotometer (AAS, School of Natural Resources) was used to analyze dissolved Cd and Cu. A calibration curve was established. Standard aqueous solutions of cadmium and copper were prepared to read the residual concentrations of metals.
- The solid sample was analyzed by scanning electron microscopy (SEM, School of Natural Resources).
- pH were determined according to a Multiline 330i phmeter which was standardized using buffer solutions of different pH values (4.01, 7.00, 10.00).
- The suspensions in all studies were filtered through 0.45 μm Nucleopore polycarbonate membrane filters. All experimental treatments in this study were prepared in triplicate and were conducted in acid-washed (2% HNO_3) polycarbonate labware.

2.2. Adsorbate solution

Simulated aqueous solutions containing cadmium and copper were prepared by dissolution of cadmium nitrate and cupric nitrate in deionized water. NaCl, $\text{Ca}(\text{OH})_2$, NaOH, HNO_3 , $\text{Cd}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, CaCl_2 , acetic acid and Ultrasonic were used. All chemicals used were of AR grade, and water for all solutions preparation had been treated by purification system beforehand.

2.3. Experimental procedure

2.3.1. Sample preparation

Carbonate hydroxylapatite samples were prepared as follows: the pretreated (washed and dried) eggshell waste was ground and sieved into powder (mesh size 30) at first. Then, the eggshell was added to industrial H_3PO_4 aqueous in molar ratio 1:1, kept at 303–313 K for 2–3 h, under pH 1–3. The reaction happened based on the equation:



Insoluble matter was separated and removed by filtration. Subsequently, $\text{Ca}(\text{OH})_2$ was added into the solution, kept at 323–333 K for 24 h, adjusting pH 9–12 by NaOH 0.1 M (1 M).

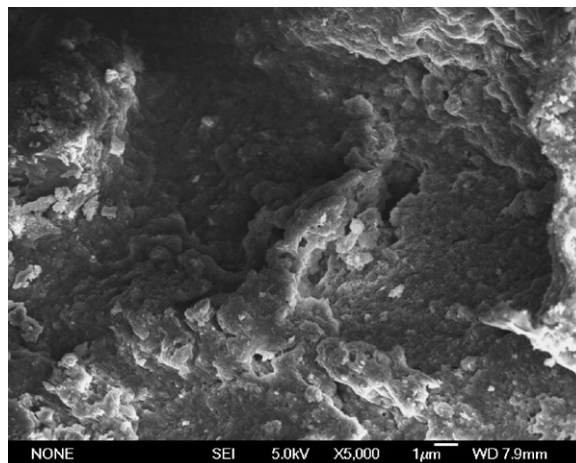
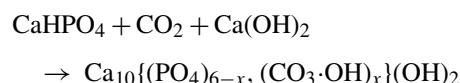


Fig. 1. SEM photomicrograph of CHAP.

The reaction processed following the equation:



At last, the suspension was dried and ground into powder manually (mesh size 30) to get the sample.

2.3.2. Scanning electron spectroscopy

SEM was carried out on a scanning electron microscope (SEM, JSM-6700F, Hitachi, Japan). The surface of CHAP was coated with gold, to be observed and photographed. Different pore sizes may be observed on the surface of CHAP as shown in Fig. 1.

2.3.3. Chemical composition of the CHAP

CHAP used in these experiments synthesized by using eggshell waste as raw material. Its chemical composition is presented in Table 1. Through the Chemical composition of the CHAP, we can simulated the molecular formula of CHAP as $\text{Ca}_{10}\{(\text{PO}_4)_4, (\text{CO}_3 \cdot \text{OH})_2\}(\text{OH})_2$.

2.3.4. Sorption experiments

Batch experiments were carried out at room temperature (293 ± 2 K) in beakers by agitating a different mass of CHAP (0.100, 0.200, 0.500, 1.000, 2.000 and 3.000 g), with 200 mL of metal solution at 350 rpm until equilibrium reached. The concentration of metal ions used for experiments was within a range of 60–200 mg/L.

After agitation, the solid was removed by filtration through a 0.45 μm Nucleopore polycarbonate membrane filters. The final

Table 1
Chemical composition of the CHAP

Constituent	Wt. %
Ca as Wollastonite	33.03
O as SiO_2	46.61
C as CaCO_3	10.30
P as GaP	10.06

metal concentration in the filtrates as well as in the initial solution was determined by AAS.

When the initial pH of metal solutions was adjusted to the desired value using 0.1 M NaOH and 0.1 M HNO₃, no efforts were made to maintain the solution pH while metal ions were being sorbed. The reaction time was kept at a room temperature and at a constant agitation rate of 350 rpm on a shaker for 180 min.

Each experiment was carried out in triplicate and the average results are presented in this study.

2.4. Adsorption isotherms

Several mathematical models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. The most widely used models are the Langmuir and Freundlich adsorption isotherm models.

The cadmium and copper adsorption capacities of the CHAP were calculated as the Eq. (1) below:

$$q = \frac{(C_0 - C)V}{m} \quad (1)$$

where q , adsorption capacity per unit mass of CHAP (mg/g); C_0 , initial concentration of metal ions in the aqueous solution (mg/L); C , equilibrium concentration of metal ions aqueous solution (mg/L); m , mass of CHAP (g); V , the volume of sample (L).

2.4.1. Langmuir isotherm

Langmuir is the most important model of monolayer adsorption, based on the assumption that there are a fixed number of adsorption sites, and each site can hold only one adsorbate molecule (the adsorbed layer is one molecule in thickness). All sites are equivalent and there is no interaction between adsorbed molecules.

The Langmuir equation can be expressed as follows:

$$\frac{1}{q_e} = \frac{1}{ab} \frac{1}{C_e} + \frac{1}{b} \quad (2)$$

where q_e , the amount of metal per unit of CHAP at equilibrium (mg/g); a , a constant related to the affinity of the binding sites (L/mg); b , the maximum amount of metal ion per unit of CHAP (mg/g); C_e , the residual metal concentration in solution at equilibrium (mg/L).

2.4.2. Freundlich isotherm

The Freundlich isotherm was also employed to explain the observed phenomena. The Freundlich isotherm is represented by the Eq. (3).

$$\lg q_e = \lg K + \frac{1}{n} \lg C_e \quad (3)$$

where q_e , the amount of adsorbed per unit weight (mg/g); K , Freundlich constants related to adsorption capacity; C_e , the equilibrium concentration (mg/L); n , Freundlich constants related to adsorption intensity.

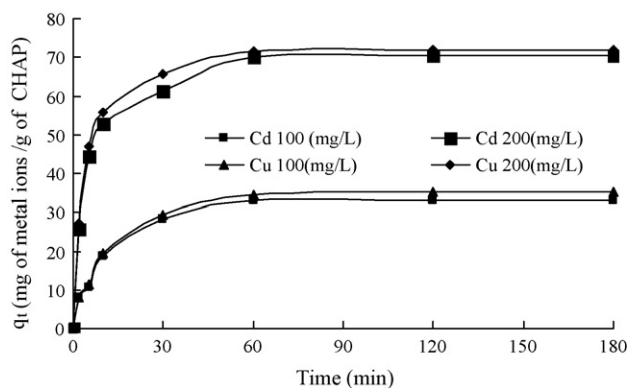


Fig. 2. Effect of the initial concentration on removal of cadmium and copper (amount of CHAP = 2.5 g/L, pH 5).

3. Results and discussion

3.1. Effect of initial concentration of metal ions

The heavy metal ions sorption capacities of the CHAP were given as a function of the initial concentrations of metal ions within the aqueous phase in Fig. 2. The solution concentration of cadmium and copper was varied in the range 100–200 mg/L and the solution pH was adjusted to 5.0. For all initial concentrations of cadmium and copper, the sorption capacity increases rapidly at an initial stage of sorption and no appreciable increase was observed beyond this time which shows saturation of the active sites (which are available for specific metal ions) in the CHAP. In addition, the results demonstrated that around 90% of the metal ions were removed in the first 60 min. It was observed that under the experimental conditions, no significant adsorption was seen after 120 min of stirring. For subsequent experiment, the contact time was thus maintained for 180 min to ensure that equilibrium could be achieved.

3.2. Effect of amount of CHAP

To study the effect of amount of CHAP on the retention of cadmium and copper, six different values were taken by varying the amount of CHAP while keeping the volume of the metal solution constant (200 mL) as shown in Fig. 3. It can be observed

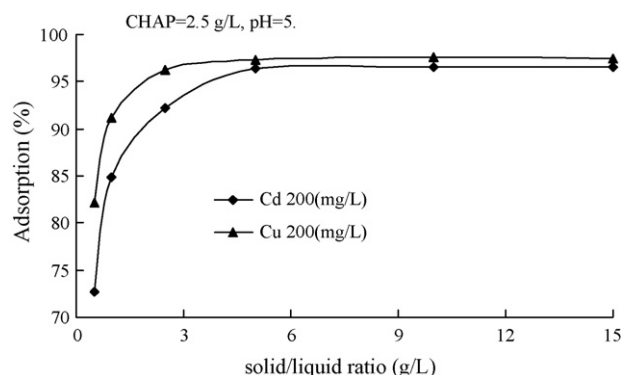


Fig. 3. Effect of amount of CHAP (pH 5, agitation time is 180 min).

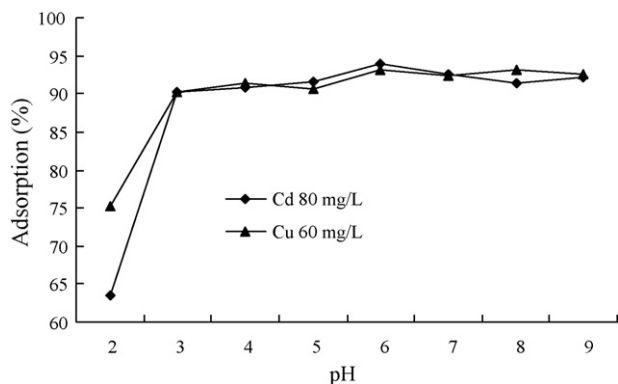


Fig. 4. Effect of initial pH value on removal of heavy metal ions by CHAP (amount of CHAP=2.5 g/L, agitation time is 180 min).

amount of metal ions removed increased with the solid/liquid ratio increasing firstly, due to more active sites or bigger surface area [15]. Then no obvious increasing was observed when the solid/liquid ratio reached 5 g/L. This possibly caused by the saturation of the active sites. So the determination of the weight of adsorbent is important when employing CHAP for Cd(II) and Cu(II) removal and in this study we chose 5 g/L as the optimum solid/liquid ratio.

3.3. Effect of initial pH value on removal of heavy metal ions by CHAP

The pH of the aqueous solution is one of the main variable parameters in the adsorption process [16]. The pH may affect the ionization degree of the sorbate and the surface property of the sorbent [17]. The optimum pH value for the uptake of metals was determined. Eight different pH tests were carried out and the results were shown in Fig. 4. The initial Cd(II) and Cu(II) concentration were 80 and 60 mg/L and the amount of CHAP was 0.5 g. As shown in Fig. 4, the removal efficiency of metal ions generally increased when the initial pH was increased. It is assumed from the results that the governing mechanism during the removal is probably due to the ion exchange. At low pH, the existence of relatively high concentration of H^+ may change the direction of reversible ion exchange equilibrium back to starting materials. When the pH passed over 6, the removal efficiency decreased slightly as pH increasing, possibly caused by the formation of soluble hydroxy complexes [18,19]. From Fig. 4, we can find that pH 6 is the optimum pH value for Cd(II) and Cu(II) sorption with CHAP in this study.

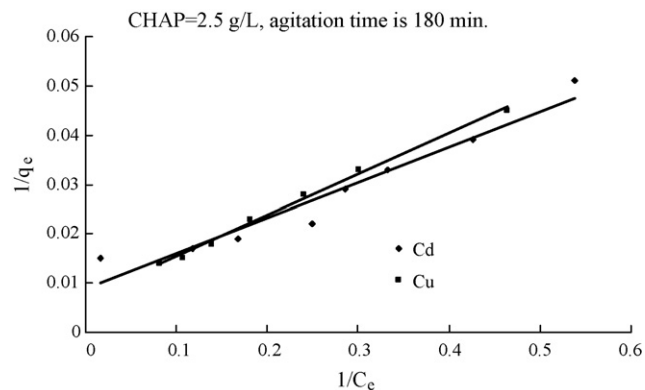


Fig. 5. Langmuir isotherm for the adsorption of copper and cadmium on CHAP.

3.4. Desorption experiments

Desorption experiments put into evidence that $CaCl_2$, NaCl, acetic acid and ultrasonic were not efficient to desorb metals from the CHAP. In general, all stripping solutions lead to similar desorption yield. The highest desorption percentage was obtained for Cd (14.6%) and Cu (12.4%) when the highest tested NaCl concentration (0.2 M) was used. In the same conditions, desorption percentage was all less than 10% for Cd(II) and Cu(II) when $CaCl_2$, acetic acid or Ultrasonic. The results of desorption suggest that CHAP has high affinity to metal ions.

3.5. Adsorption isotherms studies

A plot of $1/q_e$ versus $1/C_e$ gives a straight line of slope $1/ab$ and intercept $1/b$ shown in Fig. 5. The sorption data were analyzed according to the linear form of the equation. Results are shown in Table 2. The equilibrium adsorption of cadmium and copper on CHAP was found to follow the Langmuir Model. The experimental data were well correlated ($R_{Cd}^2 = 0.9404$; $R_{Cu}^2 = 0.9943$) to the Langmuir equation. The adsorption of cadmium and copper could be described by Eqs. (4) and (5), respectively.

$$q_e = \frac{111.1C_e}{7.49 + C_e} \quad (4)$$

$$q_e = \frac{142.86C_e}{11.9 + C_e} \quad (5)$$

Table 3 gives comparative equilibrium capacities (X_m) of metal ions on various adsorbents. The results in Table 3 indicate that CHAP was effective in attenuating cadmium and copper in aqueous solutions.

Table 2
Langmuir and Freundlich constants and correlation coefficients for the adsorption of Cd^{2+} and Cu^{2+} on CHAP

Type of ions	Adsorption isotherm	Linear regression equation	Correlation coefficient (R^2)	Adsorption constant
Cd	Langmuir	$y = 0.0716x + 0.09$	0.9404	$a = 0.126, b = 111.1, K = 2.224, 1/n = 2.1881$
	Freundlich	$y = 2.1881x + 0.3472$	0.9472	
Cu	Langmuir	$y = 0.0837x + 0.007$	0.9943	$a = 0.084, b = 142.86, K = 7.925, 1/n = 0.899$
	Freundlich	$y = 0.899x + 0.9573$	0.9221	

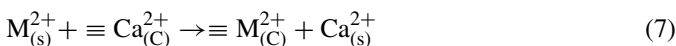
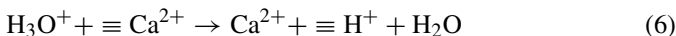
Table 3
Comparison of the equilibrium capacities of metal ions on various adsorbents

Adsorbent	X_m (mg/g)	Ion	Source
Sawdust	1.79	Cu ²⁺	Yu et al. [4]
Sawdust	3.19	Pb ²⁺	Yu et al. [4]
Olive stone waste	7.73	Cd ²⁺	Fiol et al. [3]
Olive stone waste	9.26	Pb ²⁺	Fiol et al. [3]
Olive stone waste	2.13	Ni ²⁺	Fiol et al. [3]
Olive stone waste	2.03	Cu ²⁺	Fiol et al. [3]
Grape stalk wastes	1.01	Cu ²⁺	Villaescosa et al. [1]
Grape stalk wastes	1.06	Ni ²⁺	Villaescosa et al. [1]
Crop milling waste	39.99	Cd ²⁺	Saeed et al. [2]
Crop milling waste	49.97	Pb ²⁺	Saeed et al. [2]
CHAP	111.1	Cd ²⁺	Present study
CHAP	142.86	Cu ²⁺	Present study

The linear plot of $\lg q_e$ versus $\lg C_e$ shows that the adsorption also obeys Freundlich isotherm (Fig. 6). The constants K and n are presented in Table 2. The parameter K is related to the distribution coefficient, and consequently to the degree of Cd or Cu affinity and mobility to the CHAP. Cu has a higher CHAP affinity than Cd ($K_{Cu} > K_{Cd}$).

3.6. Metal removal mechanism

The experimental results obtained are very important and are directly associated with the mechanism of the process. On one hand, the high pH values and the relatively high metal ions concentration result in the formation of hydroxide and their coagulation/precipitation on the surface of CHAP and in the space between the particles are prevailing. On the other, at lower pH the surface calcium is changed by the hydrogen ions and metal ions. These interactions can be presented as follows [20,21]:



where M is the heavy metal ion in aqueous solution and subscripts (s) and (C) denote solution and CHAP phase, respectively. The metal in the solution ($M_{(s)}^{2+}$) replaces a surface Ca ion of the sorbent ($\equiv Ca_{(C)}^{2+}$). Ion exchange may be the principal mechanism for the removal of heavy metal ions such as Cd(II) and Cu(II).

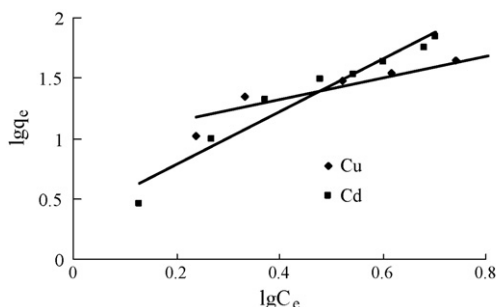


Fig. 6. Freundlich isotherm for the adsorption of copper and cadmium on CHAP.

Physical adsorption can be another mechanism for the heavy metals removal. As it is well known, heavy metals exist in acidic solution as cations. In this case, the main mechanism may be the ion exchange. At lower pH, the existing of relatively high concentration of H⁺ may change the direction of reversible ion exchange equilibrium back to start materials. With increasing pH the metal ions will be associated with hydroxide and become neutral at a certain pH range. Therefore, at this stage the adsorption mechanism can be the adsorption affinity. In a higher pH range, existing of counter ions might result in lower efficiency of adsorption and ion exchange as well. This trend is clearly shown in Fig. 4. In addition, metal ion may also be adsorbed over the $\equiv PO_4H^-$ surface group of CHAP, as described in the following equilibrium:



The extent of sorption will therefore, depend upon experimental parameters that could affect the surface charge. Subsequently, the apparent mechanisms of metal ions removal by CHAP are ion exchange/adsorption and precipitation.

4. Summary and conclusions

CHAP was prepared by eggshell waste was investigated for the removal of cadmium and copper from aqueous solution and the following conclusions can be drawn from the results of the present study:

- CHAP was effective in attenuating cadmium and copper in aqueous solutions. The adsorption processes were rapid, near completion in 60 min.
- The experimental results were well fitted with the Langmuir and Freundlich isotherms. The adsorption capacities of CHAP used in this study were 111.1 mg/g for cadmium and 142.86 mg/g for copper, respectively.
- From the results obtained, the mechanism of metal ions removal by CHAP includes ion exchange/adsorption and precipitation.

Acknowledgments

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