KKU ENGINEERING JOURNAL 2016;43(S2):275-278 Research Article

KKU Engineering Journal

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Adsorption of Cu(II) from synthetic wastewater employing chicken eggshell

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Received April 2016
Accepted June 2016

Abstract

Adsorption of Cu(II) on Hydroxyapatite (HAp) derived from chicken eggshell by chemical precipitation method with H_3PO_4 was studied. Effective determinants of equilibrium contact time, initial concentration, and thermodynamic parameters to understand the nature of adsorption were investigated. Equilibrium contact time was found to be 210 min at an initial Cu(II) concentration of 200 mg/L, yielding an adsorption capacity of 32.19 mg/g. Freundlich, Langmuir and Temkin isotherms were used to fit the experiment data and the adsorption was best explained by the Freundlich isotherm. The Pseudo-second order kinetics model performed at 25°C and pH 6 was found to be more suitable than that of the first order. Eggshell HAp pellet adsorption capacity was finally compared with eggshell HAp powder and other commercial HAps; the best adsorption capacity at 115.9 mg/g was derived from eggshell HAp powder. Eggshell HAp pellet hence needs be further investigated on how to improve its adsorption capacity because of its requirement for convenience operations.

Keywords: Hydroxyapatite, Adsorption isotherm, Kinetic, Eggshell, Pellet

1. Introduction

Copper compounds contaminating to environments resulted in population health which related to liver toxicity, lung cancer and dementia [1]. A Variety of treatment methods have been used for contaminated fluids such as filtration, flocculation, ion exchange and adsorption. Among these methods, adsorption is the most popular technique. Adsorption method is efficient but has some limitations and is costly [2]. To overcome this, low-cost alternative materials as adsorbents are of interest.

Hydroxyapatite (HAp) [$Ca_{10}(PO_4)_6(OH)_2$] is commonly used in dentistry and osteopathy [3] since it is a major biocompatible mineral constituent in teeth and bone. Chicken eggshell also has high porosity and can be raw material for hydroxyapatite which is suitable for removal of heavy metal from wastewater [1, 4-6].

The objective of this research focuses on synthetic hydroxyapatite (HAp) derived from chicken eggshell and its efficiency in the removal of Cu(II) from synthetic solution, both in the form of pellet and powder. Isotherms and kinetics including thermodynamic of adsorption were investigated.

2. Materials and methods

2.1 Materials

Eggshells were collected from eateries around the Prince of Songkla University, Hat Yai Songkhla, Thailand. Phosphoric acid (H_3PO_4) for the chemical precipitation method was purchased from Mallinckrodt Chemicals Ltd. Copper sulphate penta hydrate ($CuSO_4{\cdot}5H_2O$) for stock solution, and hydrochloric acid (HCl) for pH adjustment were of Baker Analyzed^{TM} A.C.S Reagents. Sodium hydroxide (NaOH) was obtained from QRëC, New Zealand.

2.2 Methods

2.2.1 Adsorbent preparation

Chicken eggshells were cleaned and boiled for 20 minutes, then placed in a *stainless steel* tray. A two-step thermal treatment was conducted. In the first step eggshells in the tray were heated up to 450 °C at a heating rate of 5 °C/min to eliminate all organic residues. In the second step these were further heated up to 900 °C at one-tenth of the former heating rate (0.5 °C/min). The sample was then ground with a ball mill at 350 rpm for 10 h. Calcium oxide (CaO) obtained from calcination of the eggshells was transformed by a chemical precipitation method employing H_3PO_4 into HAp [7].

2.2.2 Batch adsorption experiment

Adsorption isotherms and adsorption kinetics were studied on synthetic wastewater from metal salt of $CuSO_4{\cdot}5H_2O$. The 250 mL experiment solutions were prepared by diluting the stock solution to concentrations of 10, 20, 50, 100 and 200 mg/L.

Pellets of HAp from chicken eggshell were made by mixing the CaO powder from the calcination with polyvinyl alcohol (molecular weight 85,000-124,000, Aldrich USA).

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doi: 10.14456/kkuenj.2016.108

Ground sugar, as porogen, was added to the mix, and the blended mixture was processed into pellets. Pellets were thereafter shaken in distilled water to eliminate the sugar, leaving behind the pores created.

On the adsorption experiments, HCl or NaOH was first used to adjust pH of the initial solution to the optimum value of 6 [5]. A 1.4 g pellet was put into the solution in the flask and then vibrated at 250 rpm. Samples of the solution (2 mL each) were drawn at 15-min intervals, passed through a 0.45 µm syringe filter, then tested for the remaining Cu(II) concentration employing an AAS (Perkin Elmer Thermos Scientific S-series model(AAnalyst100)) apparatus until this value approached equilibrium. Normally 12-14 samples were adequate.

2.2.3 Adsorption isotherm

Cu(II) adsorption capacity on an adsorbent can be obtained using:

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \tag{2}$$

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{3}$$

$$q_e = B\ln A + B\ln C_e \tag{4}$$

Eq (1) where q is the adsorption capacity per unit mass of pellet (mg/g); C_0, the initial concentration of synthesized wastewater; C_e, the equilibrium concentration of the wastewater (mg/L); m, the mass of the pellet (g); V, the volume of the wastewater sample (L). *Langmuir Isotherm*, *Freundlich Isotherm* and *Temkin Isotherm* were listed accorded to Eq. (2), (3) and (4), respectively.

2.2.4 Adsorption isotherm [8]

Linearized forms of the pseudo-first-order, Eq (5), and the second-order, Eq (6):

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{6}$$

Where q_e, is the amount of heavy metal at equilibrium (mg/g); q_t, the amount of heavy metal adsorbed (mg/g) at time t; k_1, the pseudo-first-order reaction rate constant (m^{-1}); and k_2, the second-order reaction rate constant for adsorption (mg/g·min).

2.2.5 Thermodynamics study

Thermodynamic parameters of Cu(II) adsorption were studied at three set temperatures: 25°C, 45°C and 65°C. The Gibbs free energy change (ΔG^0) and K_D (=q_e/C_e) can be determined using Eq (7) and Eq (8).

$$\Delta G^0 = -RT\ln K_D \tag{7}$$

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

Where ΔS^0 is the standard entropy change (J/mol K), and ΔH^0 is the standard enthalpy change (kJ/mol).

3. Results and discussion

3.1 Characterization of CaO and HAp

Characteristic results obtained from the chicken eggshell two-step calcination by X-ray fluorescence (Philips PW2400) showed that the powder contained 83.13% of CaO and X-ray diffraction spectrometer (Philips X'Pert MPD) imaged as HAp and some calcium oxide and calcium hydroxide, similar to that reported by Aungchotipun M [9].

3.2 Physical state of HAp adsorbent and adsorption isotherm data fitting

Powder and pellet Hap adsorbents, both the eggshell and commercial types, were investigated for their effects on Cu(II) removal. Figure 1 and Table 1 show that the efficiency of powder was about 4 times higher than that of pellet; and that HAp from eggshell performed better than those from commercial. The maximum Cu(II) removal efficiencies found from this research are 92.72%, 82.91%, 77.27%, and 75.43%, respectively for eggshell HAp powder, commercial HAp powder, eggshell HAp pellet, and HAp commercial pellet. Those 3 types of adsorption isotherms and their parameters descriptions are noted in Table 2.

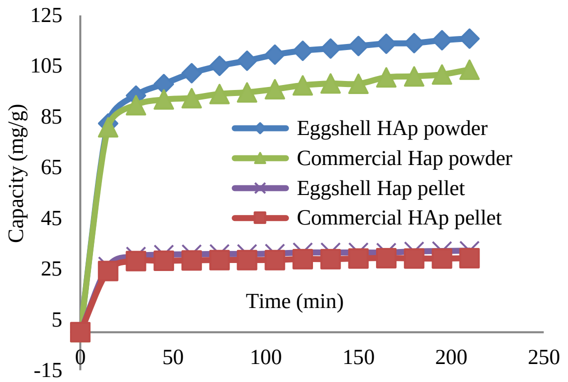

Figure 1 Time dependence of Cu(II) adsorption capacities on various type adsorbent at initial concentration 200 mg/L

Table 1 Efficiency of Cu(II) adsorption on adsorbent (at initial concentration 200 mg/L)

Type of adsorbent	%Removal	Capacity (mg/g)
Eggshell HAp powder	92.7230	115.9030
Eggshell HAp pellet	77.2660	32.1960
Commercial HAp powder	82.9110	103.6350
Commercial HAp pellet	75.4330	29.2440

Table 2 Isotherm parameter of Cu(II) adsorption on eggshell HAp pellet*

Freundlich			Langmuir			Temkin			
1/n	k_f	R^2	q_m(mg/)	B(L/g)	R^2	A(L/g)	B(J/mol)	bT	R^2
1.309	0.186	0.969	13.021	12.111	0.959	0.238	0.017	26.855	0.937

*N.B: 1/n, an empirical parameter related to adsorption intensity; K_f , the Freundlich constant; q_m, the maximum uptake capacity (mg/g); b, the Langmuir equilibrium constant (mg/L); A, the equilibrium binding constant (L/g); B, the heat of adsorption (J/mol); b_T, the Temkin isotherm constant.

Table 3 Parameter of Cu(II) adsorption kinetic on eggshell HAp pellet

Initial Conc. (mg/L)	Pseudo-first-order			
	q_e(cal)	q_e(exp)	k_1	R^2
10	1.42	0.97	6.36	0.89
20	3.96	4.61	0.004	0.84
50	6.73	11.46	1.53	0.55
100	18.22	22.28	0.00001	0.70
200	29.24	32.19	0.03	0.63
	Pseudo-second-order			
	q_e(cal)	q_e(exp)	k_2	R^2
10	1.02	0.97	0.012	0.99
20	4.34	4.61	0.012	0.99
50	11.69	11.47	0.013	0.99
100	22.81	22.28	0.013	0.99
200	32.69	32.19	0.014	0.99

The higher capacities of eggshell HAp than that of commercial Hap might come from inherit eggshell properties such as its porosity and mineral composition which can be noticed from XRD comparison [9]. Additionally, for industrial wastewater treatment, Hap pellet is more suitable to operate than the powders in that isotherms and kinetic parameter of powders were not investigated.

3.3 Kinetics and thermodynamic parameters

Results of data fitting of kinetic investigations are illustrated in Table 3. Thermodynamic parameters of Cu(II) adsorption are shown in Figure 2 and Table 4. The positive value of ΔH^0 obtained indicated that the adsorption process is endothermic; inferring that adsorption on the eggshell HAp pellets gets more efficient with increasing temperature. The positive value of ΔS^0 obtained is consistent to the increase in degree of freedom of the adsorbed species. Finally, the obtained negative value of ΔG^0 indicates feasibility and spontaneity of the adsorption process. The positive/negative signs are agreeable with literature [10].

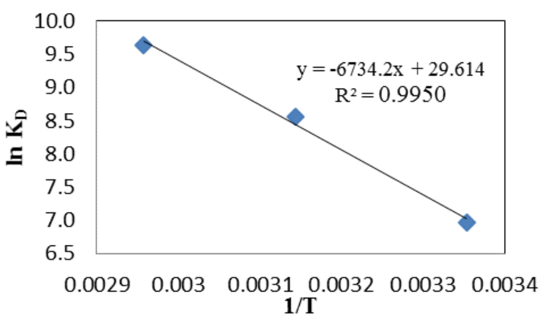

Figure 2 Thermodynamic correlation of Cu(II) adsorption on eggshell HAp pellet

Table 4 Thermodynamic parameter of Cu(II) adsorption for the initial concentration of Cu(II) solution of 10 mg/L

ΔH^0 (kJ/mol)	ΔS^0 (J/molK)	ΔG^o (kJ/mol)		
		25 °C	45 °C	65 °C
61.02	185.92	-17.29	-22.63	-27.10

4. Conclusion

This study reports adsorption of Cu(II) onto pellets and powder of hydroxyapatite derived from eggshell. Equilibrium contact time was found to be most practical at 210 min, and the higher initial concentration performed better. For adsorption isotherm, data obtained fitted best employing Freundlich, and pseudo-second-order kinetic was better than first-order. Adsorption of Cu(II) was found to be spontaneous and physical adsorption type according to adsorption energy. Obtained positive values of entropy and enthalpy confirmed random Cu(II) attachments onto the adsorbent surface with endothermic process. Negative values of Gibbs energy obtained indicated that adsorptions were applicable. In adsorption performance, powder eggshell HAp was much better than its pellet form, hence, improvement method of pellet surface characteristics needs to be further explored.

5. Acknowledgements

The authors are grateful to Graduate school and faculty of engineering, Prince of Songkla University (PSU) for financial assistance and support to this research.

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