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BIOSORPTION OF CADMIUM FROM AQUEOUS SOLUTION ONTO *CUTTLE BONE* OBTAINED ALONG THE PERSIAN GULF COAST AS A CHEAP AND EFFECTIVE BIOSORBENT: EVALUATION OF ADSORPTION ISOTHERMS AND KINETICS

Sina Dobaradaran[a,b,c*], Iraj Nabipour[d], Saeed Tajbakhsh[d], Maryam Khorsand[b], Mozhgan Keshtkar[b], Asma Khaledi[b], Fereshte Babaahmadi[b]

[a]The Persian Gulf Marine Biotechnology Research Centre, Bushehr University of Medical Sciences, Bushehr, Iran.
[b]Department of Environmental Health Engineering, Faculty of Health, Bushehr University of Medical Sciences, Bushehr, Iran.
[c]Systems Environmental Health, Oil, Gas and Energy Research Center, Bushehr University of Medical Sciences, Bushehr, Iran.
[d]The Persian Gulf Tropical Medicine Research Center, Bushehr University of Medical Sciences, Bushehr, Iran.
Email: S.dobaradaran@bpums.ac.ir

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Abstract

Adsorption is considered as one of promising treatment method for removal of heavy metals from aqueous solutions. Cadmium is non- biodegradable and must be eliminated from aqueous phase. The aim of this study was to determine *Cuttle bone* efficiency in removal of cadmium from aqueous phase. Adsorption was studied in a series of batch experiments at room temperature (25±1^{o}C) and the effects of experimental parameters such as biosorbent dose (0.1-10 g/L), contact time (3–120 min), pH (3-10), and initial Cd concentration (1–300 mg/L) were also investigated. The remaining concentration of Cd in solution after biosorption was determined by using an atomic adsorption spectrometr (AAS) method (Varian, spectrAA 240, Germany). The highest removal adsorption was reached at 5 g/L biosorbent dose, 3 min contact time and initial Cd concentration at 2 mg/L (100% Cd removal). The adsorption was found to be better fitted to the Freundlich isotherm which was indicative of multilayer adsorption. The biosorption kinetics was controlled by the pseudo-second order and pore diffusion models. Finally, it was concluded that the *Cuttle bone* can be used as an effective, low cost and environmental friendly biosorbent for removal of cadmium from aqueous phase.

Keywords: Adsorption isotherms, Biosorbent, Cadmium, *Cuttle bone*, Persian Gulf

Introduction: Water contamination may be originated from natural processes, man disposal practices as well as industrial activities (Dobaradaran et al. 2010). Contaminants including toxic heavy metals may be discharged into the environment by different ways and causing considerable soil and water pollution (Abdelwahab et al. 2013). Some of heavy metals including cadmium have no known major role in body living organs and are toxic even in trace levels. Cadmium has biological half-life in the range of 10–30 years, and has the capability to accumulate in human body living organisms. The U.S. Environmental Protection Agency (U.S. EPA) has categorized cadmium as a priority pollutant and has set a value of 0.005 mg/L as maximum contaminant level goal (MCLG) and maximum contaminant level (MCL).

Cadmium is non- biodegradable and must be eliminated from aqueous phase (Wu et al. 2006, Wen et al. 2011). Several methods including adsorption, chemical coagulation, membrane process and ultrafilteration, precipitation, zeolites, ion-exchange and electro-chemical, were developed to eliminate elevated cadmium concentration from water (Alferra et al. 2014, Rao 2010, Fu & Wang 2010). Among these processes, adsorption is an extensively used one for cadmium removal from aqueous solutions. Currently, considerable interests were observed on the utilization of biosorbent materials for elimination of different pollutants.

Biosorption advantages over conventional treatment processes comprise low cost, less sludge production, regeneration of biosorbent, no nutrient needs, high performance in dilute effluents, while being environmentally desirable and economically viable (Shams et al. 2013, Dobaradaran et al. 2015, Dobaradaran et al. 2014). Low cost biosorbent could be produced from numerous raw materials such as industrial, agriculture, and marine wastes. Several efforts have been described on heavy metals including Cd by biosorption (Table 1). Marine biomass is available in large quantities and can form a good basis for the development of biosorbent materials. Cuttlefish bone is a biomass marine that can be found in large amount in coastal area. Cuttlefish possess an internal structure called the *Cuttle bones*. Some studies have been conducted in relation to absorption of different pollutants such as fluoride and acid blue 158 by *Cuttle bone* (Farzana et al. 2010, Babu et al. 2014). The aim of the present study was to investigate the Cd biosorption capacity of *Cuttle bone* powder. The effect of different parameters such as biosorbent dose, contact time, pH, and initial Cd concentration were also discussed. Beside this we determined the sorption isotherms, biosorption kinetics and modeling of Cd biosorption by *Cuttle bone* powder.

Table-1: Removal efficiency of cadmium sorption by various biosorbent in some previous studies.

Biosorbent	Maximum removal percentage	Reference
Wheat	86	(Zer & Pirinc 2006)
Bagasse fly ash—a sugar	90	(Gupta et al. 2003)

Corn stalk graft Copolymers	99.2	(Zheng et al. 2010)
Peels of banana	90	(Anwar et al. 2010)
Sawdust—A green	97	(Memon et al. 2007)

Materials and Methods

Biosorbent preparation

The *Cuttle bone* was collected along the Persian Gulf in the Bushehr seaport coastal area. The biosorbent was transferred to laboratory and thoroughly washed two times by tap water and then by distillated water in order to remove clay, sand, and other impurities. The washed *Cuttle bone* were subsequently dried in an oven (Memmert, Germany) at 105˚C for 24 h and finally powdered and sieved through a 0.71 mm screen.

Batch experiment

A stock solution of 1000 mg/L was prepared by dissolving Cd $(NO_3)_2.4\ H_2O$ (Merck, Germany) in ultrapure water. Then fresh dilutions of desired concentrations of Cd were prepared by diluting the stock solution. At each experiment, 100 ml of Cd solution with a specific initial Cd concentration level was agitated at 120 rpm. The effects of three different pH values (3, 6.8, 10) seven contact times (3, 5, 10, 15, 30, 60, and 120 min), seven initial cadmium concentrations, (1, 2, 5, 10, 20, 50 and 300 mg/L), and six biosorbent dose levels (0.1, 0.5, 1, 2, 5 and 10 g/L) were studied in the batch experiments at room temperature (25±1^{o}C).

Analytical method

After each experiment, sample was filtered through a 0.45 µm membrane. The remaining concentration of Cd in solution after biosorption was determined by using an atomic adsorption spectrometr (AAS) method (Varian, spectrAA 240, Germany) with a cadmium hallow cathode lamp and an air acetylene flame at 228.8 nm. The removal efficiency was calculated using the following Eq. 1 (Bharli & Bhattacharyya 2014):

$$\text{Biosorption yield} = \frac{(C_i - C)}{C_i} \times 100 \qquad (1)$$

Where C_i and C are the concentrations of cadmium before and after the experiment in any time (mg/L).

The equilibrium biosorption capacity of *Cuttle bone* at different cadmium concentration levels was calculated by using the following Eq. 2:

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (2)$$

q_e is the equilibrium biosorption capacity (mg/L); C_i is the cadmium concentration at initial time (mg/L); C_e is the concentration of cadmium in biosolution at equilibrium time (mg/L); V is the solution volume (L); and m is the biosorbent dosage (g).

Results and Discussion

Effect of pH

The effect of pH on Cd removal was studied in the pH range of 3 to 10 and results are shown in Figure 1. pH played a key role in heavy metal biosorption. Biosorption process is dependent on the pH value of aqueous phase, the functional groups on the biosorbent, and their ionic states at specific pH value. Cadmium biosorption increased dramatically from 64% to 99% by increasing pH value from 3 to 6.8 and then was almost constant by increasing pH value from 6.8 to 10. Increasing Cd biosorption by increasing pH values could be attributed to the influencing the surface charge of the biosorbent, the degree of ionization and the species of biosorbate. The precipitation of metal hydroxide starts at a pH value of 8.5 and therefore at this pH and higher there is a competition between biosorption process and precipitation as metal hydroxide. The same results have been reported for removal of Cd by using sea urchins as biosorbents, the study results showed that the Cd sorption was negligible at pH value of 2, but increased with increasing pH value (Ben et al. 2011). Gupta et al. also reported that the maximum adsorption of Cd occurred at a concentration level of 14 mg/L and a pH value of 6.0 (Guota et al. 2003). As there was not significant difference between pH values of 6.8 and 10 for Cd sorption onto *Cuttle bone*, therefore a pH value of 6.8 has been selected as the optimum pH to perform all experiments.

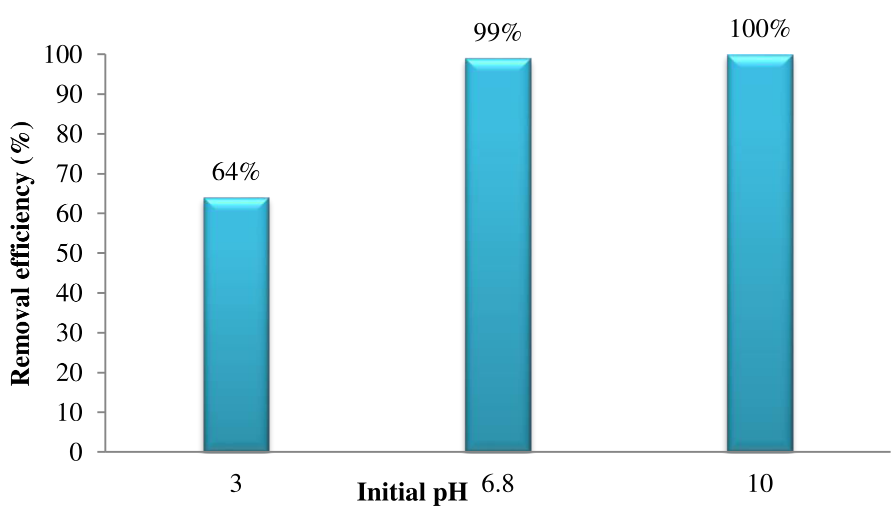

Figure-1: Effect of pH on Cd biosorption on to *Cuttle bone* (biosorbent dose= 1 g/L, initial Cd concentration = 1 mg/L).

Effect of biosorbent dose

The effect of *Cuttle bone* dosage on the Cd removal was studied using different biomass doses of *Cuttle bone* in the range of 0.1–10 g/L (Figure 2). The results indicated that the adsorption rate rapidly increased in the first 3 min and then adsorption rate was almost constant. The biosorption efficiency was depended on the increasing of *Cuttle bone* dosage in the solution. This can be attributed to the additional number of adsorption sites, which are resulted from the increase in the *Cuttle bone* dosage. Similar trends have been reported for the removal of Cd by natural biosorbent in former studies (Gupta et al. 2003, Zheng et al. 2010).

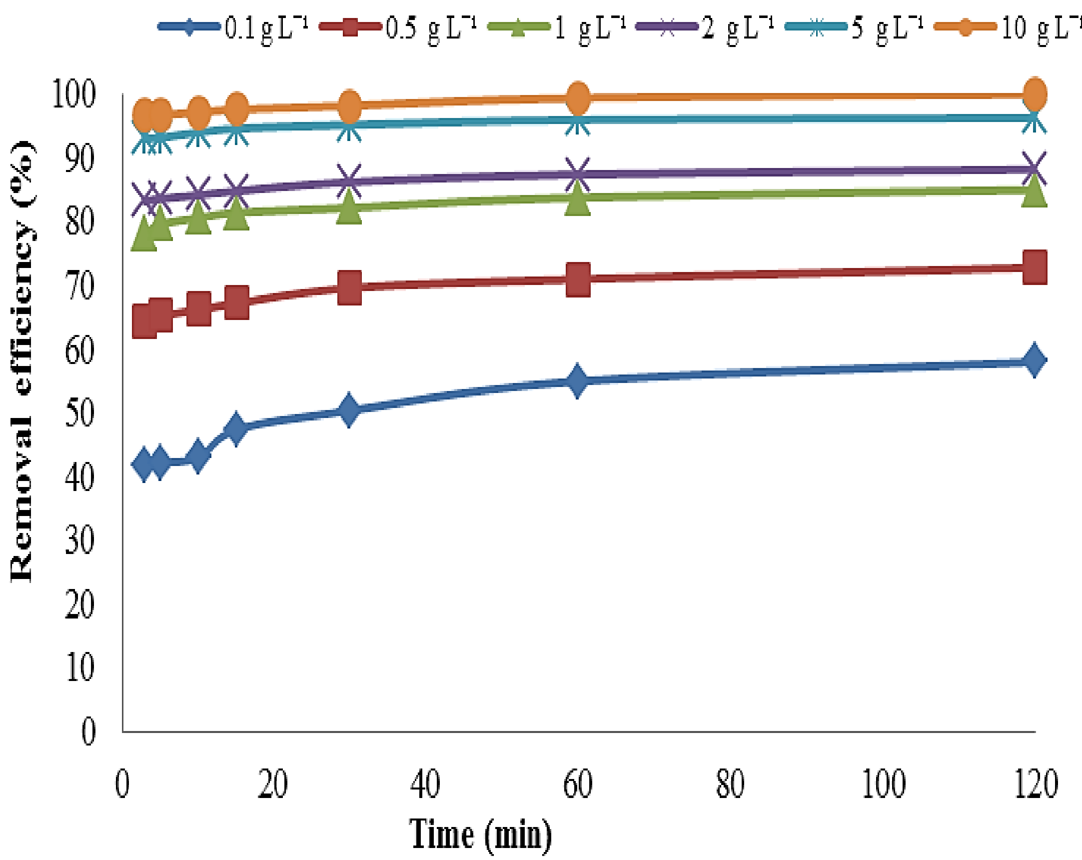

Figure-2: Cadmium adsorption as a function of biosorbent dose (initial Cd concentration: 5 mg/L, pH: 6.8).

Effect of contact time and initial cadmium concentration

The effect of initial Cd concentration on the Cd removal is shown in Figure 3. It was observed that by increasing substrate concentration from 1 to 300 mg/L the removal efficiency increased. Monika Jain et al. and Abdel et al. reported similar trends in the Cd removal from aqueous phases by using sunflower waste carbon and alga *Anabaena sphaerica*, respectively (Jain et al. 2013, Abdel-Atey et al. 2013).

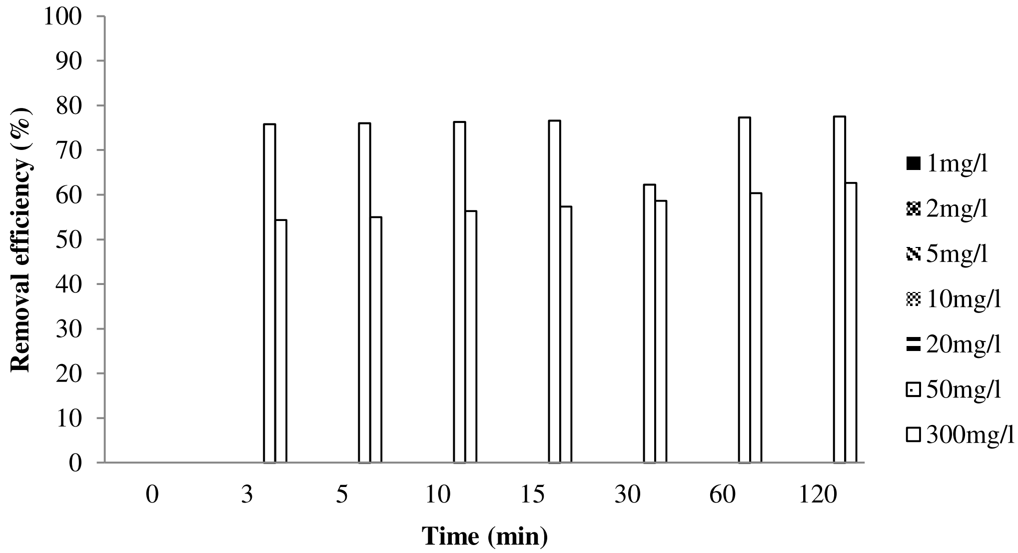

Figure-3: Cadmium adsorption as a function of initial cadmium concentration (biosorbent: 2 g/L, pH: 6.8).

Isotherms of sorption:

In order to quantify the sorption capacity of *Cuttle bone* for the cadmium removal from aqueous phases, two generally used isotherms namely Freundlich and Langmuir have been adopted. The linear form of Freundlich (Freundlich 1096) isotherm can be written as:

$$\text{Log}\,(q_e) = \text{Log}\,(K_f) + \frac{1}{n}\,\text{Log}\,C_e \qquad (1)$$

Where q_e is the mass of cadmium biosorbed per unit weight of the sorbent (mg/g), K_f is the Freundlich capacity factor and a measure of adsorption capacity, 1/n is the equilibrium concentration of cadmium in solution (mg/L) after adsorption. The values of 1/n and K_f for the biosorbent were calculated from the slope and the intercept of the linear plot of log q_e vs log C_e. Adsorption Freundlich isotherm parameters of cadmium onto *Cuttle bone* are shown in Table 2. The Langmuir adsorption isotherm (Langmuir 1916) model is defined as:

$$q_e = \frac{abC_e}{1+bC_e} \qquad (2)$$

And can be rewritten as:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{1}{q_{max}}\,C_e \qquad (3)$$

Where q_e is the mass of cadmium per unit mass of biosorbent (mg/g), q_{max} is the monolayer sorption capacity, b is the Langmuir constant related to the free energy of adsorption equilibrium concentration of cadmium in solution (mg/L) after adsorption.

The Langmuir constant can be determined by plotting $\frac{C_e}{q_e}$ versus C_e.

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \qquad (4)$$

Adsorption Langmuir isotherm parameters of cadmium onto *Cuttle bone* are shown in Table 2. As shown in Table 2, Freundlich model is better fitted than Langmuir model for removal of Cd by using *Cuttle bone* as biosorbent. Freundlich isotherm considers the heterogeneous adsorption surface and multilayer adsorption.

Table-2: Adsorption isotherm and model parameters for cadmium sorption onto *Cuttle bone*.

	Isotherm/ Modeling	Parameter	Value
Isotherm of biosorption	**Freundlich**	K_F (mg/g)	0.01726
		1/n	1.0764
		R^2	0.9495
	Langmuir	b (L/mg)	1.0469
		Q_e (mg/g)	0.3304
		R^2	0.8202
Kinetic and moleding of biosorption	**First-order kinetic**	q_e (mg/g)	0.0121
		K_1 (g/mg min)	0.5038
		R^2	0.9718
	Second-order kinetic	q_e (mg/g)	0.2347
		K_2 (g/mg min)	0.1452
		R^2	0.9999
	Intraparticle diffusion	K_d	27.168
		C	105.74
		R^2	0.9294

Biosorption kinetics and modeling

The adsorption kinetics is important in the treatment of aqueous phase, as it presents key visions into reaction and mechanisms of sorption reactions. The experimental biosorption kinetic were described by using pseudo-first-order, pseudo-second-order kinetics and intraparticle diffusion model. This kinetics can be written in their nonlinear forms, as bellow:

Pseudo-first- order model:

$$\log(q_e - q_t) = \log q_e - \frac{K_{1,ads}}{2.303} t, \qquad (5)$$

Pseudo-second- order model:

$$\frac{t}{q} = \frac{1}{q_e{}^2 K_{2,ads}} + \frac{1}{q_e} t, \qquad (6)$$

Where q_e is the mass of solute sorbed at equilibrium (mg/g), q_t is the mass of solute sorbed at time t (mg/g), K_1 is the first-order equilibrium rate constant (g/g min), K_2 is the second-order equilibrium rate constant (g/g min).

The intraparticle diffusion model equation can be defined as Eq. (7):

$$q_t = k_d\, t^{0.5} + C \qquad (7)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of sorbed cadmium on *Cuttle bone* at equilibrium and time t (min), C is the intercept and K_1 (1/min), K_2 (g/mg min) and K_d (mg/g min 0.5). The intraparticle diffusion model rate constant (K_d) and C can be calculated from the slope and intercept of the linear plot of q_t vs $t^{0.5}$, respectively (Dong et al et al. 2004).

The constants of pseudo first-order, pseudo second-order kinetic, intraparticle diffusion are shown in Table 2.

The plots were found linear with well correlation coefficients illustrating the applicability of pseudo-second-order model in the present study. Considering the drawn plots, the experimental data were well fitted to the pseudo-second kinetic model with higher correlation coefficient (Table 2). Kinetics of Cd adsorption by *Cuttle bone* followed the pseudo-second model, indicating that the adsorption limiting step may be chemisorption. This indicates that the adsorption of Cd maybe occurs via surface complexation reactions at specific adsorption sites of *Cuttle bone*.

Conclusion

In this study the efficiency of the *Cuttle bone* as a biosorbent in removal of Cd from aqueous phases was evaluated. The efficiency of cadmium removal increased by increasing the biosorbent dose, initial Cd concentration and decreased by increasing pH. The highest removal of Cd was reached only after 3 min contact time in optimum operation condition. Freundlich model was better fitted than Langmuir model for removal of Cd by *Cuttle bone*. The adsorption process was observed to follow a pseudo-second-order kinetic. Finally based on all the results in this study, it can be concluded that the *Cuttle bone* can be used as an effective, environmental friendly, low cost and easy to source biosorbent for the removal of Cd from aqueous solution.

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Corresponding Author:

Sina Dobaradaran*,

Email: *S.dobaradaran@bpums.ac.ir*