



Removal of Copper (II) from Aqueous Solutions using Cuttlebone as Bio-adsorbent

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Abstract

Biosorption is an effective process for removal and recovery of heavy metal ions from aqueous solutions. In the present study, batch adsorption experiments were carried out for the removal of copper (Cu II) from aqueous solutions using cuttlebone powder (<100 μm) as a bio-adsorbent. The effects of initial pH, adsorbent dosage, initial concentration, and contact time on adsorption efficiency and capacity were studied to evaluate the optimum conditions for copper removal. The results found optimal conditions at initial pH of 5.0, 10 g/L cuttlebone, 500 mg/L initial concentration of Cu II in solution, and 150 min of equilibrium time. The Langmuir isotherm and pseudo-second order kinetic model were fitted to the experimental adsorption data. The maximum adsorption capacity calculated from the Langmuir isotherm was 54.05 mg/g. This result shows that cuttlebone is an effective bio-adsorbent, constituting a promising, efficient, low-cost, and eco-friendly technology bio-sorbent for reducing copper pollution during wastewater treatment.

Keywords: Copper removal; Cuttlebone adsorbent; Adsorption kinetic; Adsorption isotherm

Introduction

Heavy metal pollution is one of the most important environmental problems worldwide as various industrial and agricultural activities produce and discharge wastes containing different heavy metals into the environment [1-3]. Although some heavy metals are essential micro-nutrients for living organisms, high levels of contamination are associated with bioaccumulation

and biomagnification in the food chain [4-5]. The toxicity and non-degradability of heavy metals are of great concern to human health as heavy metals can inhibit cellular function, stimulate cancer risk, and cause several chronic health problems [6]. Therefore, various methods for heavy metal removal from aqueous solutions have been developed using physical, chemical, and biological technologies. Well-known methods

for removing metal ions from aqueous solutions include chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, and evaporation among others [7-8]. Applications of these conventional methods, however, are sometimes restricted because of technical or economic constraints [9]. Recently, biological methods for removing heavy metals have gained considerable momentum due to their high efficiency, low operating cost, and simplicity. Biosorption is one such method which utilizes inactive bio-logical materials to eliminate toxic heavy metal contaminants from industrial effluents [10-11].

Cuttlebone, the internal skeleton of the cuttlefish (*Sepia officinalis*), can be found in large quantities in coastal areas. Additionally, many fish processing industries in Thailand have used cuttlefish as a major export product. After processing cuttlefish, the majority of cuttlebones are discarded into the environment as waste by-product. The major component of cuttlebone, accounting for 88% to 97% of its composition, is an aragonite crystalline form of CaCO_3 , while another component is a composite containing 1% to 7% protein and 3% to 7% β -chitin [12-14]. Due to their chemical compositions and lower utilization, cuttlebone can be used as a bio-adsorbent for heavy metal removal in wastewater treatments. Moreover, utilization of cuttlebone is not only low cost and easily available for the removal of heavy metals but also reduces environmental pollution. Therefore, the present study aimed to evaluate the potential of cuttlebone for removal of Cu (II) ion from aqueous solutions and to investigate optimal conditions for adsorption.

Materials and methods

1) Preparation of bio-adsorbent and aqueous solutions

Cuttlebone samples were collected from Laem Charoen and Mae Rumphueng beaches

in Rayong Province of Thailand. The samples were first rinsed several times with ion-free double distilled water to remove impurities and interfering materials such as salt and sand, then dried at 80 °C for 48 hours. The dried materials were then ground using a laboratory mill and sieved through a 100 μm size fraction sieve (American Society for Testing and Materials, ASTM). The cuttlebone powder was again rinsed with ion-free double distilled water, then dried at 80 °C for 48 hours and stored in desiccators until further use. In this study, the powdered material was directly used as bio-adsorbent without any pre-treatment. All glassware used was immersed in HNO_3 overnight, then washed with ion-free double distilled water. Copper stock solution (10,000 mg/L) was prepared by dissolving an appropriate amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ salt in 0.5 M HNO_3 as an electrolyte to control ionic strength of metal ions. The solution was prepared by diluting the copper stock solution with ion-free double distilled water to the required concentrations using 0.5 M HNO_3 . Copper concentrations in all experiments were determined using an atomic absorption spectrophotometer (Agilent 240AA, Santa Clara, CA, USA) with 0.03-10.0 mg/L copper detection limit and deuterium background corrector.

2) Batch adsorption experiment

Adsorption experiments for copper removal were carried out as a function of initial pH value, adsorbent dosage, initial concentration, and contact time. Batch biosorption assays were carried out in 125 mL Erlenmeyer flasks containing 25 mL of Cu (II) solution at a constant shaking speed (100 rpm). The optimum initial pH for copper removal was investigated by adding 0.25 g of cuttlebone powder into 25 mL of 150 mg/L Cu (II) solutions, which were pre-adjusted to various pH values (2, 3, 4, 5, and 6) using 0.1 M NaOH or 0.1 M HNO_3 . To investigate the optimum adsorbent dosage, cuttlebone powder was weighed in a dosage range of 0.05-0.35 g

(corresponding to 2-14 g/L), then added to different flasks containing 50 mL of 150 and 500 mg/L copper solution under the optimum pH value. In the experiment to determine optimum initial pH and adsorbent dosage, the cuttlebone-copper solutions were shaken on an orbital shaker for 120 min at room temperature. For the experiment to determine contact time, a quantity of the optimum dosage of cuttlebone powder was added to 500 mg/L of copper solution under the optimum initial pH. Cuttlebone-copper solutions were shaken to react for 10, 20, 40, 60, 80, 100, 120, 150, 180, and 240 min

at room temperature. All samples were filtered with filter paper (Whatman No.5) to separate cuttlebone from the Cu (II) solution. The remaining Cu (II) in the filtrate sample was analyzed using the previously mentioned atomic adsorption spectrophotometer. All experiments were done in triplicate. Control treatments were carried out using adsorbent-free copper solutions for each experiment. To determine the optimum conditions, adsorption efficiency and adsorption capacity were calculated using Eq.1 and Eq.2.

$$\text{Adsorption efficiency (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (\text{Eq.1})$$

$$\text{Adsorption capacity (mg/g)} = \frac{(C_i - C_f)}{S} \quad (\text{Eq.2})$$

Where C_i and C_f are the initial and final concentrations of copper (mg/L), respectively. S is the concentration of bio-sorbent in the mixing solution (g/L). Analytical values were statistically analyzed according to Duncan's multiple range tests.

3) Adsorption models

The adsorption equilibrium was analyzed according to the Langmuir and Freundlich adsorption isotherms using Eq.3 and Eq.4, respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (\text{Eq.3})$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (\text{Eq.4})$$

Where C_e is the equilibrium concentration of Cu (II) ions (mg/L), q_e is the equilibrium adsorption capacity (mg/g), K_L and K_F are the Langmuir and Freundlich adsorption isotherm constants, respectively, q_m is the maximum adsorption capacity (mg/g), and n is the adsorption intensity.

For investigation of Cu (II) adsorption kinetics, the pseudo-first-order and the pseudo-second-order kinetic models (Eq.5 and Eq.6) were used to test the data from the batch experiment in the study on the effect of contact time.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (\text{Eq.5})$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (\text{Eq.6})$$

Where q_e is the adsorption capacity at equilibrium (mg/g), K_1 and K_2 are the pseudo-first- and second-order rate constants, respectively, and q_t is the adsorption capacity (mg/g) at time t (minutes).

Results and Discussion

1) Effect of initial pH

Solution acidity is known to play the most important role in the biosorption of heavy metals as it strongly influences availability of metal binding sites at the surface and chemical reactions of heavy metal in solution such as hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation, speciation, and biosorption availability [15-18]. The effect of initial pH on copper biosorption was investigated in this study using 150 mg/L Cu (II) solution at pH 2-6. The pH values above 6 were

not considered as heavy metals precipitated above this pH [19]. The experimental results of copper biosorption by cuttlebone at different initial pH conditions are shown in Figure 1. The adsorption efficiency at pH 3-6 was insignificantly different with a maximum of 99.39% at pH 5, while adsorption capacity was also highest at pH 5 (14.42 mg/g). The reaction of adsorbent material, ions in aqueous solutions, and Cu (II) speciation describes the correlation between solution pH and copper uptake onto the cuttlebone, which was composed of aragonite (a crystallized form of calcium carbonate, CaCO_3) and β -chitin [12-14], which are the functional groups of the adsorption process. Adsorption efficiency was low at wastewater pH 2 due to the reaction of the high concentration of H_3O^+ with CaCO_3 , which is the major component of the adsorbent, which resulted in dissolution to bicarbonate ions (HCO_3^-) and carbonic acid (H_2CO_3) and a lower adsorbent mass. In addition, calcium carbonate crystals and β -chitin on the cuttlebone surface also adsorbed the excess H_3O^+ ; therefore, there are fewer binding sites available on the biosorbent to bind the metals.

Considering pH of the zero point charge (pH_{zpc}), or the pH when the charge of the adsorbent surface was zero, can also explain the stronger adsorption mechanism in terms of the

effect of pH on cation and anion adsorption. When the solution pH was higher than pH_{zpc} , the surface was negatively charged. Similarly, when the solution pH was lower than pH_{zpc} , the surface was positively charged [20-21]. In comparison to a previous experiment by Ben Nasr et al. (2011) which reported that cuttlebone adsorbent has a $\text{pH}_{\text{zpc}} = 9.8$ [21], in this study, the pH of all experiments was lower than pH_{zpc} , indicating the presence of a positive charge on the adsorbent surface. The high adsorption efficiency and capacity at pH 5 (Figure 1) should be discussed as the result of a lower level of positive charge on the adsorbent surface. However, at pH 6, we observed a significant drop in adsorption capacity, which can be assumed to be caused by precipitation occurring through complexation between Cu (II) and hydroxide ions, leading to decreasing metal ion solubility to be taken up by the adsorbent [21]. In addition, pH 5 has been reported by several researchers to be optimal for absorption of several heavy metals onto chitin and other types of functional groups [15, 18, 20, 22]. Thus, there is great potential during wastewater treatment processes to combine various adsorbents together to remove more than one type of heavy metal. Therefore, in this study, Cu (II) adsorption by cuttlebone adsorbent was optimized at an initial value of pH 5.

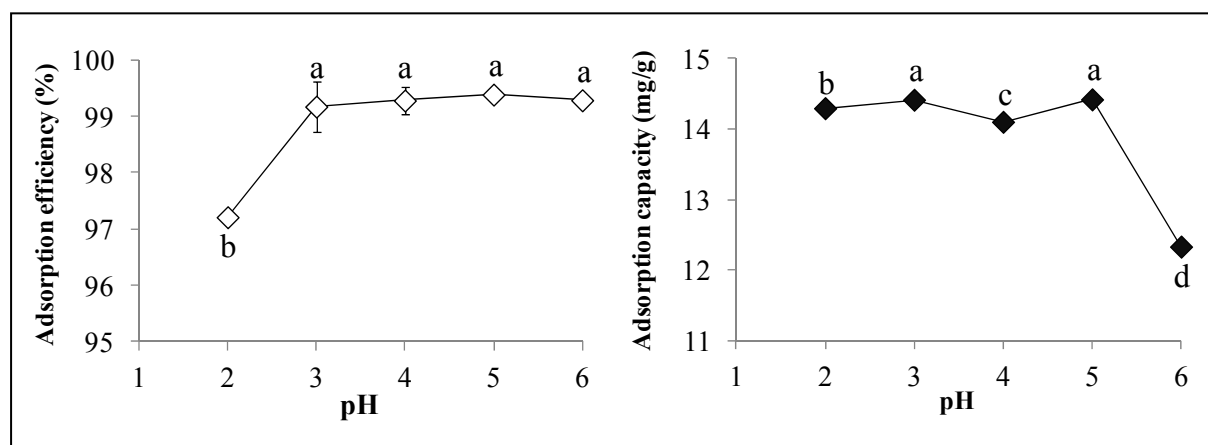


Figure 1 Effect of pH on copper adsorption efficiency and adsorption capacity (Initial concentration 150 mg/L, adsorbent dosage 10 g/L and contact time 120 minute)
a, b, c and d shows statistical difference with 95% confidence intervals

2) Effect of adsorbent dosage and initial concentration

The optimum adsorbent dosage was determined experimentally using 150 and 500 mg/L of initial Cu (II) concentration at initial pH 5 using different adsorbent dosages in the range of 2-14 g/L (Figure 2). The results showed that adsorption efficiency increased, dependent on the increase in adsorbent dosage of solutions in both initial Cu (II) concentrations. This phenomenon is explained by an increase in surface area of the adsorbent, which in turn increased the number of binding sites [23]. When we treated 150 mg/L Cu (II) solution, adsorption efficiency was low at 77.56% when using an adsorbent dosage of 2 g/L, while the efficiency markedly increased, up to 98.78%–99.30%, with an adsorbent dosage of 4-14 g/L. Adsorption capacity decreased when higher adsorbent dosages were applied. Absorption efficiency and capacity of differential adsorbent dosage were largely influenced by Cu (II) concentrations [22]. Generally, adsorption occurs at specific sites that are saturated as the concentration increases until the site gradually reaches the point where the adsorption rate at the exchange sites reaches a stable equilibrium [22]. When the ratio of initial moles of metal ions and available surface area is low, the quantity of metal removed will increase at a rate proportional to the initial concentration [16, 24]. Nevertheless, at higher metal concentrations, the number of available adsorption sites is reduced in comparison to the moles of metal ions present in the aqueous solutions. Therefore, the percentage of metal removal is relatively dependent upon the initial metal ion concentration [25]. To investigate the effect of adsorbent dosage and optimum dose suitable for practical usage, higher concentrations of Cu (II) adsorption were considered. In 500 mg/L Cu (II) adsorption, adsorption effi-

ciency increased when a higher dosage of the adsorbent was added because of the increasing number of active sites; however, the increase was insignificant when the adsorbent dosage was higher than 10 g/L. The adsorption capacity results showed a decreasing trend at higher dosages. This could be attributed to removal of Cu (II) by the excessive adsorbent dose, because the adsorptive capacity of the available adsorbent was not fully utilized at a higher adsorbent dosage in comparison to lower adsorbent dosages. Therefore, adsorption capacity may actually decrease at higher adsorbent dosages. As a result, the optimum dosage in this study was found to be 10 g/L, as the minimum dosage with high efficiency.

3) Effect of contact time

The experimental results of biosorption of Cu (II) ions onto cuttlebone at different contact times are shown in Figure 3. The efficiency and capacity of the adsorption during contact times of 10-240 min significantly increased and most of the processes were completed within 150 min, followed by slow attainment of equilibrium. As a result, a contact time of 150 min was sufficient to achieve equilibrium as the adsorption did not change significantly with further increased contact time. Therefore, the uptake concentration and unadsorbed concentration of Cu (II) at the end of 150 min were given as the equilibrium values. The studies of adsorption pattern with contact time showed a trend similar to that of several previous studies, but other works seems to have a longer optimum contact time for adsorption [15-16, 24]. The possible reasons can be derived from the properties of adsorbent materials and the initial concentrations of the tested heavy metal.

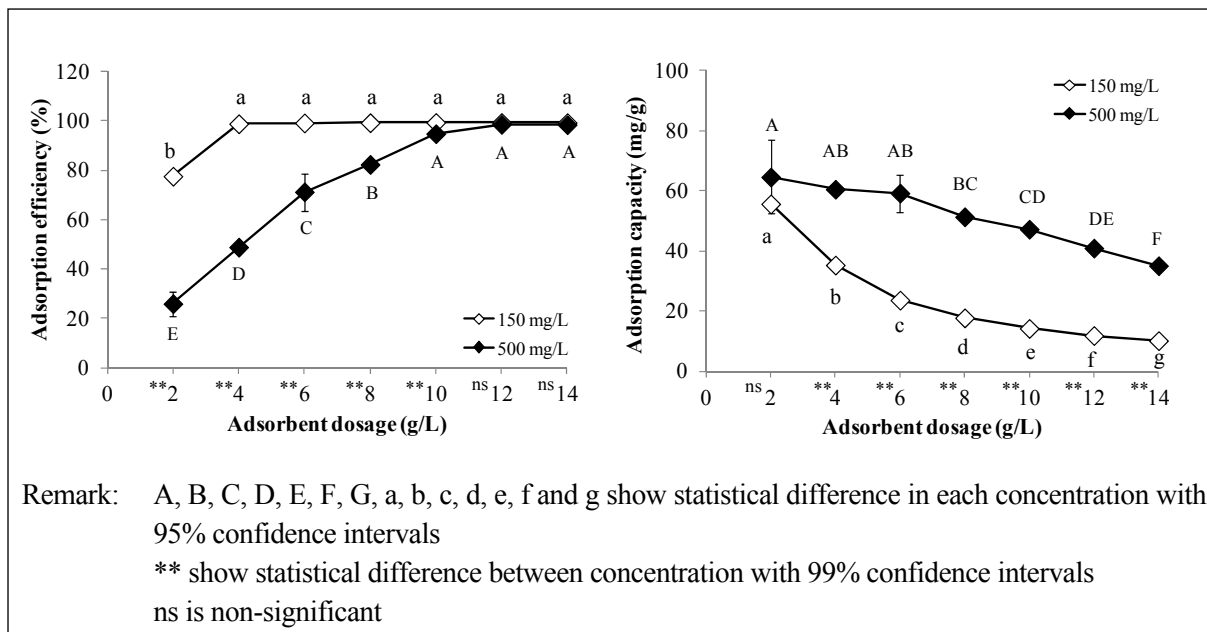


Figure 2 The effect of adsorbent dosage on copper adsorption efficiency and adsorption capacity (Initial Cu concentration 150 and 500 mg/L, pH 5 and contact time 120 minute)

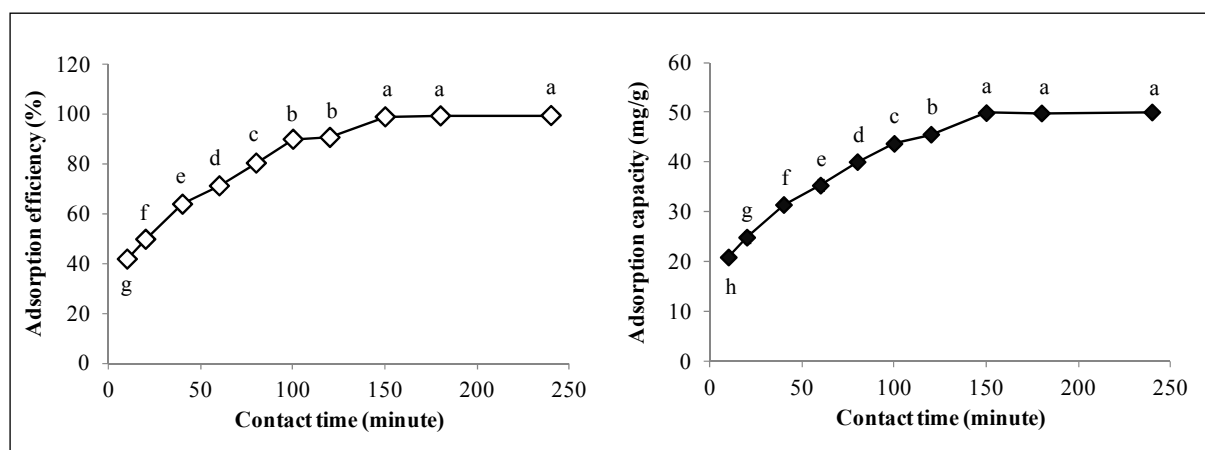


Figure 3 The effect of contact time on copper adsorption efficiency and adsorption capacity (Initial Cu (II) concentration 500 mg/L, pH 5 and adsorbent dosage 10 g/mL).
 a, b, c, d, e, f, g and h show statistical difference with 95% confidence intervals

4) Adsorption models

An adsorption isotherm is a model describing the mobility of a substance from fluid media or aquatic environments to a solid phase at a constant temperature and pH [26]. The Langmuir and Freundlich models are the most widely accepted and used in the literature [7]. In the present study, the experimental data were compared with linear correlation in the Langmuir and Freundlich isotherms (Table 1). The best-fit model was determined based on the linear

regression correlation coefficient (R^2). As a result, the adsorption of Cu (II) onto the cuttle-bone surface correlated well with the Langmuir isotherm ($R^2 = 0.967$). This model assumed that the adsorption characteristics according to the Langmuir isotherm are based on the chemical adsorption or monolayer adsorption of solute, which only occurs at a finite number of definite localized sites with no lateral interactions or steric hindrance between the adsorbed molecules [7, 26]. From the Langmuir isotherm equa-

tion, the constant (K_L) and maximum capacity (q_m) were determined as 0.0282 L/mg and 54.05 mg/g, respectively. The q_m of cuttlebone Cu (II) adsorption is compared to that of other adsorbents in Table 2. Due to CO_3^{2-} precipitation and adsorption onto the surface of cuttlebone, the adsorption capacity of the tested ad-sorbent was higher than that of most raw biomass adsorbents, but it was lower than adsorbents modified to have different chemical characteristics using complicated methods. However, the difference in adsorption capacity can be related to the difference in physical and chemical characteristics of the adsorbents.

The parameters of pseudo-first- and -second-order kinetic models and their coefficients of correlation are presented in Table 1. The calculated capacity at equilibrium (q_e) for the pseudo-second-order kinetic model was 56.18 mg/g, in agreement with the experiment (50.05 mg/g), and the correlation coefficient value was very high ($R^2 = 0.994$), indicating that the pseudo-second-order kinetic model can be used to model cuttlebone adsorption of Cu (II). Moreover, this result indicated that the rate-limiting step in heavy metal adsorption is chemisorption involving valence forces through the sharing or exchanging of electrons between sorbent and sorbate, complexation, coordination, and/or chelation [27].

Table 1 Cu (II) adsorption with adsorption isotherm and kinetic model

Adsorption kinetic						Adsorption isotherm					
pseudo first order			pseudo second order			Langmiur isotherm			Freundlich isotherm		
k_1	q_e	R^2	k_2	q_e	R^2	q_m	K_L	R^2	n	K_F	R^2
(1/min)	(mg/g)		(g/mg/min)	(mg/g)		(mg/g)	(L/mg)			(mg/g)	
0.022	38.34	0.702	0.037	56.18	0.994	54.05	0.028	0.967	6.41	19.84	0.712

Table 2 Comparison of Cu (II) adsorption capacity of cuttlebone with other adsorbent

Adsorbent	pH	Adsorption capacity (mg/g)	Reference
<i>Ulva fasciata</i> (Green algae)	5.0	26.88	[13]
Chitosan/perlite beads	4.5	104	[14]
Cellulose/chitin beads	5.0	32.41	[15]
Black gram husk	5.0	25.73	[20]
<i>Portunus sanguinolentus</i> (Crab shell)	6.0	243.9	[23]
<i>Chinonecetes opilio</i> (Crab shell)	5.0	62.28	[26]
Sawdust	4.0	6.585	[27]
Modified peanut husk	4.0	10.15	[27]
Coconut tree sawdust	6.0	3.89	[28]
Egg shell	6.0	34.48	[28]
Sugarcane bagasse	6.0	3.65	[28]
Cuttlebone	5.0	54.05	This study

Conclusions

The present study found that cuttlebone has strong potential as an adsorbent for Cu (II) removal under optimum conditions of pH 5 and adsorbent dosage 10 g/L. The Langmuir isotherm was fixed and maximum capacity was calculated to be 54.05 mg/g. In the adsorption kinetic study, the biosorption rate was rapid and most of the process was completed within 150 minutes, according to the pseudo-second-order model. As a result, cuttlebone, a natural, renewable, cost-effective biomass, could be used as a biosorbent for Cu (II) removal from industrial effluents due to its high capacity for Cu uptake. Moreover, the study of cuttlebone in the removal of other metal ions or pollutants and larger scale adsorption systems could be interesting alternative developments for wastewater treatment processes.

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