Removal of Heavy Metal from Synthetic WastewaterUsing Calcined Golden Apple Snail Shells

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Abstract

Westudied the removal of heavy metals from synthetic waste water samples by using Golden Apple Snail shells,calcined at 1050°C: they were able to removeup to 30% of copper(II) ions, 88% of cadmium(II) ions and 56% of lead(II) ions. The best performance was at pH 6. Metal removal followed a stable pseudo-second order reaction equation with parameters, k_2 and q_e, with k_2 values for Cu^{2+}0.00377, Cd^{2+} 0.00278 and Pb^{2+} 0.00365 g/mg-min and q_e values of 9.65,25.9, 16.8 mg/g and we concluded that the sorption mechanism is primarily absorption into the pores of the sorbent . This adsorbing material had two advantages, that is, lower volume of the Golden Apple Snail Shell and a cost-effective absorbent. If further developed, this could lead to better and effective low cost treatment for polluted waste waters.

Keywords: Golden Apple Snail Shell, Absorption, Cadmium, Copper, Lead, Sorption kinetics

Introduction

Environmental pollution from heavy metal contamination such as cadmium, lead, and copper in the environment, due to disposal of wastes containing these metals into the environment, e.g. wastes from etching, milling, anodizing and cleaning, conversion coating, electroless depositions and electroplating, among others (Barakat, 2011), into public water sources, without detoxification or inefficient detoxification processes, is a serious health concern. Particularly as these heavy metalspermanently contaminate the water sources, sedimentary soil and living organisms in the water. The contamination therefore penetrates the food chain. In addition, these heavy metals do not decompose naturally, so they accumulate in the human body and cause bone pain, high blood pressure, kidney malfunction (Babel &Kurniawan, 2003), and eventually lead to bone deterioration and other problems.

Cadmium can enter the body directly and indirectly: it enters the body from contaminants in food, water and tobacco. It is absorbed in the stomach and spreads to the spleen, liver and intestines and accumulates in the kidneys. People, who have been exposed to dust or food, contaminated with high levels of cadmium, experience breathing difficulties, nausea, vomiting, chest pains, pulmonary edema, limb destruction, spine deformation and chronic anemia, which may be fatal. The disease caused by cadmium toxicity is called“Itai-Itai”. Lead can enter the body in three ways from food, breathing and through the skin. For acute poisoning, the symptoms include, among others, brain damage, severe vomiting, convulsions, unconsciousness, headaches, insomnia, blurred vision, anemia, damage to muscles, fatigue, liver inflammation, kidney problems, joint pain, and paralysis as well as neurological disorders children also become mentally retarded. If the body receives copper at too high levels, it can accumulate in the body. Acute copper poisoning is classifiedinto two categories: gastrointestinal toxicity and respiratory toxicity. This poisoning causes nausea, vomiting and diarrhea.

Over the years, various treatment technologies have been introduced to remove heavy metals from contaminated wastewater, for example, photocatalysis(Barakat, Chen, & Huang, 2004; Kajitvichyanukula, Ananpattarachaia, &Pongpom,2005) , electrodialysis(Mohammadi, Mohebb, Sadrzadeh, &Razmi, 2005) , chemical precipitation (Kurniawan, Chan, Lo, & Babel, 2006) and membrane filtration (Kurniawan et al, 2006). These processes can remove heavy metals but at high investment costs and also require effective management and high operating costs. Absorption is an alternative to remove heavy metals in wastewater. In general, this uses activated carbon as the absorbent material. However, the cost of producing activated carbon is still high, so this study focused on finding other lower cost materials. Previous research has exploited waste from agricultural processes, such as grape residue (Panumas, Nakorn, &Chanjam, 2008), tea residue (Orapin, 2007) and shells, mussels (Chanyaporn, 2002) and eggshells (Saowapa,2016). Shells are an excellent alternative natural sorbent material because they are waste. They are easy to find and have good properties as a sorbent: they are porous and have very sorbent surfaces. The main constituent of the shell is calcium carbonate (Jung et al., 2000), which adsorbs contaminants on the surface (Nisarat, 2013), further, high temperature incineration improves the sorption efficiency (Tabtong, &Juijuljerm, 2000). These cost-effective sorbing materials can be found in several groups (i) agricultural and household by-products, (ii) industrial by-products, (iii) sludge, (iv) sea materials, (v) soil and ore materials and (vi) novel low-cost adsorbents (Ali, Asim, & Khan, 2012).

Calcium carbonate is formed by the deposition of carbonate sediments in natural waters. White, insoluble, non-toxic and chemically stable, it is widely used as a key raw material in various industries, such as a filler in the plastics, rubber, paper and color industries. Calcium carbonate is also used as a control agent in steel manufacture (Wang et al., 2007). When calcium carbonate is heated to high temperature, it releases carbon dioxide and converts to calcium oxide. It can absorb moisture in the air well. Many natural materials contain calcium carbonate, e.g. coral, sea shells, egg shells and snails, which are 95-99% calcium carbonate and a protein content in the range 0.1-5.0% by weight (Kaplan, 1998). In shells, it is mostly calcite (Jacob et al., 2008; Hale, Drumm, Harrison, & Phillips, 1994).

Aquatic snails damage many valuable economic crops, e.g. rice and lotus, which are planted in water. In particular, golden apple snails (*Pomaceacanaliculata*) destroy the rice seedlings. It also causes ecological changes by rapidly spreading into new environments and is listed as among one hundred of the world's most invasive species, helping to reduce the number of species and organisms in the ecosystem leading to ecological changes. Further, some pathogens, such as *Angiostrongiruscantanensis*, can be transmitted to humans (Pattama, 2000). Eradication of the golden apple snail can use various techniques - both mechanical and biological. Also, the snail can also be consumed use as organic fertilizer and for animal food production, by using its shell to adjust soil pH, using the body of the snail for fertilization and by putting the whole animal into the soil, so that, after the shell has deteriorated, the plant grows quickly. However, there are still plenty of shells available, so, if the calcined snail shells could be used for heavy metal removal from the water, this would have additional benefits for the public as natural wastes are used to save cost, providing an incentive for farmers to collect the snails to reduce crop damage and the spread of the snail and additionally enhance farm income. Therefore, we aimed to find the optimum conditions for using the golden apple snail shells for calcination to remove cadmium, lead and copper out water systems and determing the sorption kinetics.

Methods and Materials

1. Chemicals and Adsorbent

Chemicals : The chemicals used were standard solutions of Cadmium(II), Lead(II), and Copper(II) with the concentrations of 1000 mg/L, concentrated nitric acid (HNO_3),and sodium hydroxide – all of analytical reagent grade, purchased fromE. Merck.

Adsorbent : Golden apple snails were collected from rice paddies in Kantarawichai, Mahasarakham Province (16°19’22”N 103°17’48”E)), washed to remove stains with tap water until clean, dried by natural air and then oven dried at 100 ± 10°C for 24 h, calcined at 1050°C for 2 h, put into a sealed dry container and stored at the room temperature for use in the next experiment. The temperature of 1050 °C follows Yijun,Shengyong, andHuimin (2014).Mustakimah, Suzana, andSaikat (2012) confirmed that calcium oxide is prepared in this process. It was stored in a desiccator. Calcium oxide was then reacted with water to produce calcium hydroxide.

2. Characterization of adsorbent

Structural properties and identities of minerals in the samples were determined by X-Ray Diffraction (XRD). A Bruker D8 diffractometer, with Cu-Kα radiation and tube voltage set to 30 kV and current to 30 mA, was used to record the diffraction spectra. Sample morphology was observed using a Scanning Electron Microscope (SEM) (Leo 1455 VP, UK), set at 15 kV. Sample chemical composition was determined by X-ray fluorescence (XRF) with a Bruker AXS SRS 3400 machine.

3. Heavy metal uptake studies

3.1 To find the optimum times for maximum metal ion removal, we prepared syntheticwaste waters consisting of a single metal: in each case, 50 mg/L metal ion solutions were prepared and adjusted to pH to 6, using nitric acid or sodium hydroxide. After, we added 0.6 g of absorbent to mix with 50 mL of the heavy metal solution, stirred at 100 rpm at room temperature, collected the solution. After intervals of 10, 20, 30, 40, 50 and 60 mins, the absorbentwas filtered from the solution. Then we analyzed the remaining metal concentrationwith anAtomic Absorption Spectrophotometer (AAS).

3.2 The experiments in section 3.1 were repeated at pHs of 2, 4, 6, 8 and 10.

3.3 To measure the affect of absorbent dosage, the procedure in 3.1 was repeated at dose of 0.2, 0.4, 0.6, 0.8, and 1 g.

3.4 We determined absorption kinetics followingYupadee(2004).

Using the optimum conditions, pH 6 and dose 0.6 g – see plots in Fig 4 and 5, we measured remaining pollutant concentrations *vs* time using AAS.

Results and Discussion

1. Characterization of adsorbent

X-Ray Diffraction (XRD) spectra (see Figure. 1) indicated that the shell mostly contained calcium carbonate. After, calcination at 1050^{O}C, XRD spectra showed that most of the calcium carbonate was transformed into calcium oxiede. This confirmed Boonyuen, Malaithong, Prokaew, Cherdhirunkorn, and Chuasantia(2015)'s report that calcium carbonate was almost entirely decomposed into calcium oxide and carbon dioxide at this temperature.

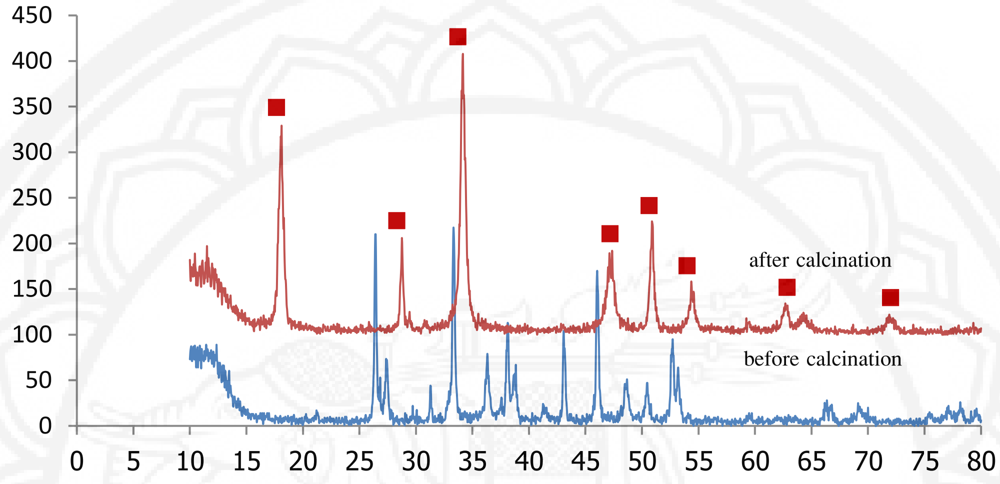

Figure1 Powder XRD patterns: Golden apple snail shell before calcinations and calcium oxide after calcinations (🟥 as calcium oxide).

Micro structure analysis by SEM indicated that, before calcination, shells possessed large crystals, with dispersed tiny pores and a slightly rough surface - see Figure 2a. After calcination, the structures were much smaller and lacked crystallinity - see Figure 2b. We attribute this to heat dissolving organic substances in the shell and transformation of calcium carbonate structure into smaller, porous and easily ground calcium oxide particles.

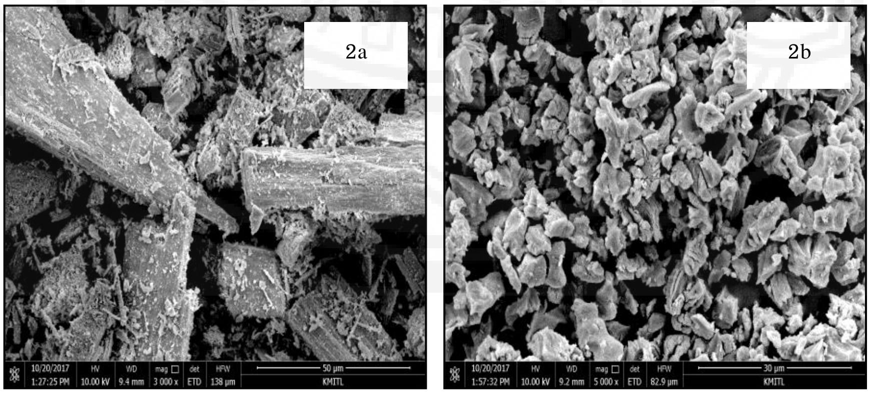

Figure2 SEM images of (2a) Golden apple snail shell and (2b) Calcium oxide.

XRF spectra showed that, before calcination, about 76% of the shell was CaO, but, after calcination, this rose to 98.6%. The full compositions are shown in Table 1.

Table 1 Chemical composition of absorbent.

Sample	Component (% weight)							
	Na_2O	CaO	Fe_2O_3	CuO	SrO	SiO_2	MnO	La_2O_3
Absorbent sample	0.530	98.6	-	-	-	0.448	0.348	-

2. Effect of contact time on heavy metals ions removal.

Results from the contact time experiments (section 3.1)are plotted in Figure 3 for all three pollutants.The best absorption were Cu^{2+} 26%, Cd^{2+}89%, and Pb^{2+}55%. These differences can be understood if we consider the atomic radii: $Cu^{2+}$are much smaller (atomic radius 0.73 nm) compared to Cd^{2+} (0.95 nm) and Pb^{2+}(1.19 nm), thus $Cu^{2+}$are able to more easily escape from the pores and exchange with the surrounding medium. Note that $Cd^{2+}$and Pb^{2+}reached equilibrium earlier (<20 min) compared to Cu^{2+}(nearly 30 min) showing the $Cd^{2+}$and Pb^{2+}were absorbed quickly and retained.

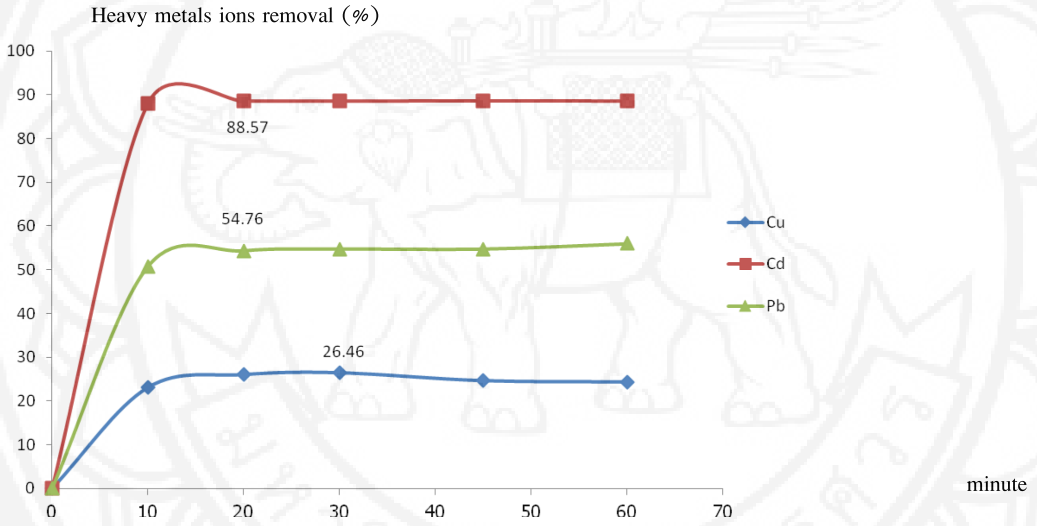

Figure3 Effect of contact time on heavy metal ion removal(dose 0.5 g, ion concentration 1 mg/L, pH 6)

3. Effect of pH on heavy metals ions removal.

Figure 4 shows the amount of metal ions removed for pH values from 2 to 10. At pH 6, 26% of Cu^{2+}, 89% of Cd^{2+} and 55% of $Pb^{2+}$was removed. For pH below 6, the hydrogen ions (H^+) covered some parts of the surface and reduced the absorption area. If pH was above 6, absorption also decreased because metal ion hydroxides precipitated and thus reduced initial metal ion concentrations (Orapin, 2007).

$$M^{n+} + xH_2O \mid \rightleftharpoons I_2O)_x]^{n+} [M(H_2 \rightleftharpoons {}_1 OH]^{(n-1)+} + H^+ \qquad (1)$$

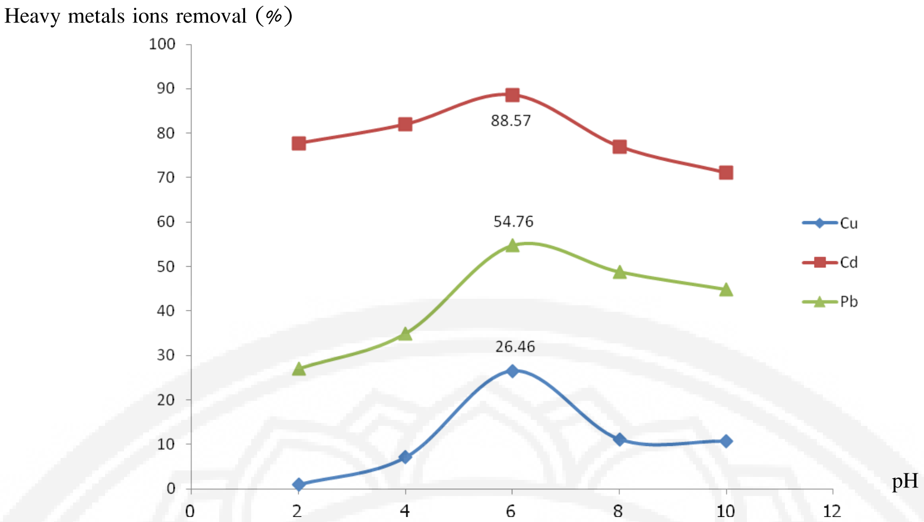

Figure4 Effect of pH on heavy metals ions removal(dose 0.5 g, metal ion concentration 1 mg/L, 30 min)

4. Effect of adsorbent dose on heavy metals ions removal.

The data in Figure 5 shows that once the dose increased beyond 0.6 g, about 30% of Cu^{2+}, 88% of Cd^{2+} and 56% of $Pb^{2+}$was removed. Further increases in dose did not significantly affect removal rates, so the surface presented by the absorbent at 40g/L was sufficient to reach an equilibrium state.

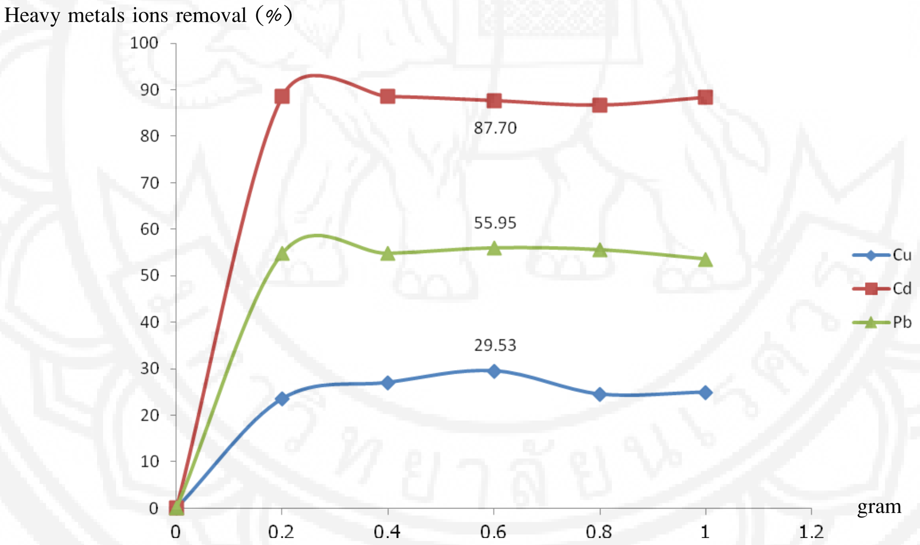

Figure5 Effect of adsorbent dose on heavy metals ions removal(metal ion concentration 1 mg/L, pH 6, 30 min)

5. Sorption kinetics

We considered two sorption mechanisms: absorption onto the surface, resulting from simple physical attraction between molecules in the liquid and molecules on the surface of the material, and absorption into the material resulting from both physical and chemical interactions between the sorbed atoms and the absorbent material. Absorption is usually characterized by a pseudo-first order equation (Ajay &Mahendra, 2015):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

whereq_e is the absorption capacities at equilibrium, q_t is the absorption capacities at time, k_1 is the rate constant and t is the time.

Thus if we plot $\ln(q_e - q_t)$ *vs* t, as shown in Figure 6, we can derive the rate constant, k_1.

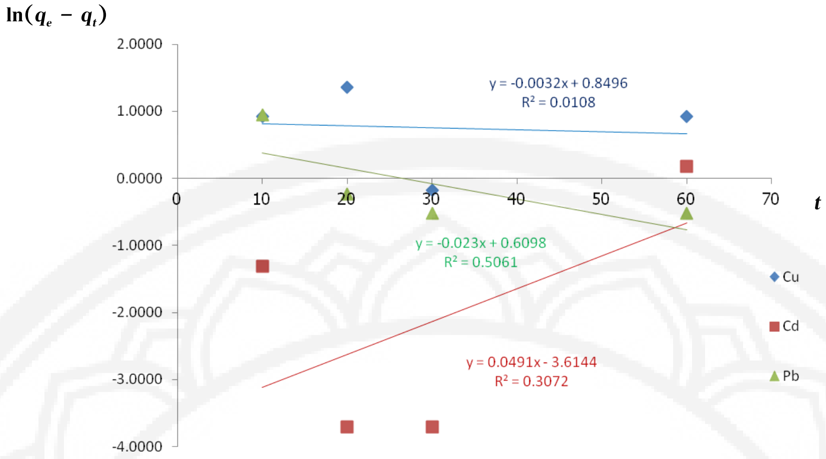

Figure6 Pseudo-first order model.

On the other hand, absorption is generally characterized by a second order equation (Ajay &Mahendra, 2015):

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (3)$$

Using this model, we plotted t/q_t *vs* t and computed the slope ($1/q_e$) and the intercept ($1/k_2 q_e^2$) to estimate k_2 – see Figure 7.

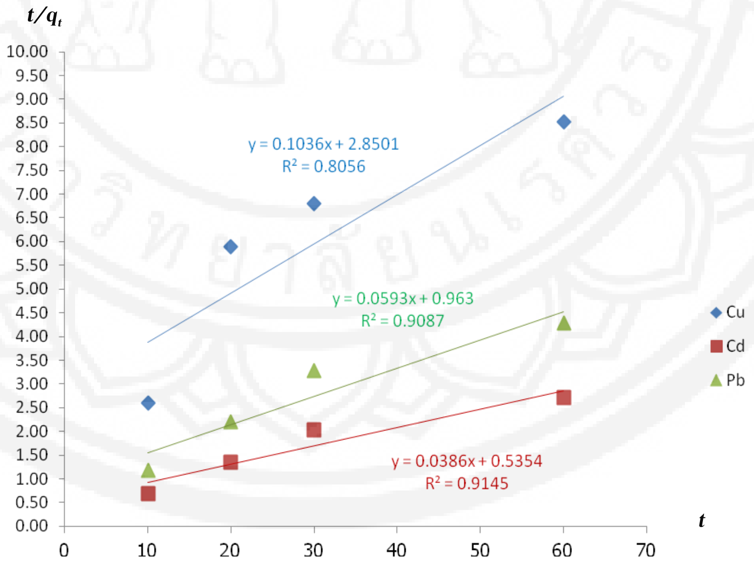

Figure7 Pseudo-second order model

R^2 values (0.8 – 0.9) taken from Figure 7 show that the pseudo-second order model is a better fit to our observations than a first-order model with R^2 values at 0.5 or lower.

The highest absorption capacity forCu^{2+}at the equilibrium point in the second order reaction model, q_e, was 9.65 mg/g and the reaction rate, k_2, was 0.00377 g/mg-min. ForCd^{2+}, q_e= 25.9 mg/g, and k_2 =0.00278 g/mg-min. For Pb^{2+},q_e = 16.86 mg/g and k_2 = 0.00365 g/mg-min - see Table 2.

Table 2 Adsorption kinetics for adsorbent

Metal ion	Pseudo-first order	Pseudo-second order		
	R^2	R^2	k_2	q_e
Cu^{2+}	0.011	0.810	$3.77x10^{-3}$	9.65
Cd^{2+}	0.307	0.914	$2.78x10^{-3}$	25.91
Pb^{2+}	0.506	0.909	$3.65x10^{-3}$	16.86

Conclusion and Suggestion

The absorbent produced from the 1050°C calcined golden apple snail shell showed significant capacity for removing copper(II) ions (30%), cadmium(II) ions (88%) and lead(II) ions (56%) from our synthesized waste water. The snail shell absorbent performed best at pH 6 with an absorbent dose of 0.6g/50mL. Cadmium and lead were quickly absorbed,reaching equilibrium within 20 min and remaining stable after that. $Cu^{2+}$was less quickly absorbed,taking 30 min to reach equilibrium. Sorption kineticsfollowed a pseudo-second order model,with the highest absorption capacitiess was for cadmium(II) ions at25.9 mg/g, followed by lead(II) ions at 16.86 mg/g and copper(II) ions at 9.65 mg/g, with corresponding second-order rate constants of 0.00278 g/mg-min for Cd^{2+}, 0.00365 g/mg-min for Pb^{2+} and 0.00377 g/mg-min for Cu^{2+}. We believe that the good metal absorption capability is related to the extent of surface modification. Thus calcined golden apple snail shells meet both critical factors for effective waste water treatment - low cost materials and good heavy metal removal. The apparent preferential absorption of cadmium ions by the snail shells may be significant: Cd^{2+} is an insidious poison and a relatively recent addition to the list of environment hazards (compared to Pb^{2+}, whose dangers have been long understood). This may justify further work to understand it and encourage further use of absorbents derived from natural shells - particularly when cadmium used in local industries.

Acknowledgement

We sincerely thank the laboratorystaff at the Science Center of Rajabhat Maha Sarakham University for allowing the research team to use their facilities and instruments whichwere critical to the success of this project.

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