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Fabrication of Composite Material from Sea Mussel Shells and White Clay as a Versatile Sorbent

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Abstract: Problem statement: The removal of heavy metals contaminated in aqueous solution/wastewater has been causing worldwide concern. However, the adsorbent materials are usually limited due to their high cost and environmentally benign. To overcome the above-mentioned disadvantages, low-cost and effective adsorbents are in demand. **Approach:** In this study, the sea mussel shells/natural clay beads were prepared for using as low-cost sorbent to remove Cd in the synthetic wastewater. **Results:** The sorbent were characterized using Scanning Electron Microscopy (SEM). The adsorption of Cd(II) ions from aqueous solution onto adsorbent has been investigated using kinetic approach to evaluate the effect of initial concentration and contact time on the removal of Cd. In adsorption studies, residual Cd(II) ion concentration reached equilibrium in duration of 240 min for initial Cd concentration of 5 ppm. The maximum removal achieves 99.75 mg g^{-1}. **Conclusion/Recommendations:** The present results suggest that the adsorbent derived from sea mussel shells/natural clay bead is expected to be an economical material for removal of Cd(II) ions effectively from contaminated water.

Key words: White clay, composite material, sea mussel, sorbent, adsorption

INTRODUCTION

The progressive increase of industrial technology results in continuous increase of heavy metals such as Hg, Pb, Cr, Ni, Cu, Cd and Zn in the aquatic environment, so that a great effort has been devoted for minimizing these harzadous pollutants. A variety of methods have been proposed for the treatment of wastewater such as chemical precipitation (Matlock *et al*., 2001), electrochemical reduction, ion exchange (Inglezakis *et al*., 2007), membrane separation (Aravindan *et al*., 2009) and adsorption (Gupta and Sharma, 2002). Among these methods, the adsorption has been found to be superior to other techniques because of its capability of adsorbing a broad range of different types of adsorbates efficiently. In recent year, there is an increase interest in using non-chemical and low-cost adsorbent (Salim *et al*., 2007) to remove heavy metals from wastewater.

The objective of this study was to fabricate and evaluate the feasibility of using this composite material prepared from the mussel shell and natural clay for the removal of cadmium from aqueous solution. The present research also describes the batch adsorption characteristic of Cd ions on the fabricated adsorbent. Experimental data have been analyzed by adsorption isotherms.

MATERIALS AND METHODS

Raw material: The natural white clay utilized for this study was obtained from Ranong province, Thailand. The clay was ground, sieved by 45-60 mesh.

The mussel shells were obtained from Samut Prakarn province, Thailand having major ingredients $CaCO_3$. The shells obtained were dried, ground and sieved by 45-60 mesh. Then, the fine powder was heated at 850°C for 4 h.

The experimental Cd(II) solution were diluted from the standard solution (1,000 ppm Cd) with deionized water to obtain desired concentration.

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Sample preparation: The adsorbent was prepared with mussel shells powder and natural clay. The mass ratio of mussel shell to natural clay was controlled as 1:3. The blended powder was dried at 100°C for 4 h before being used.

The surface area and its porous properties were characterized by N_2 adsorption apparatus using single point Brunauer, Emmette and Teller (BET) (Autosorb-1, Quantachrome, USA) procedure. The surface structure of fabricated composite material was performed by Scanning Electron Microscope (SEM JEOL, JSM-6301F, Japan).

Determining the amount of metal removal: For batch kinetic studies, 20 g of the mussel shells/clay beads were introduced into a 180 m L solution of the Cd(II) solution of initial concentration of 5 ppm. The samples were shaken in a thermostatic shaker at a speed of 150 rpm at 30°C. After a predetermined time, each solution was filtered through Whatman filter paper. The metal concentration in supernatant was determined by using an atomic absorption spectrometer (AAS, Perkin Elmer, A Analyst 800, USA).

The amount of adsorbed Cd ions (mg metal ions/g sorbent) was calculated using Eq. 1 from the decrease in the concentration of metal ions in the medium by considering the adsorption volume and used amount of the sorbent. The Removal efficiency (R_e), determined as the Cd removal percentage relative to initial concentration, calculated using Eq. 2:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$R_e = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Where:

q_e = The amount of metal ions adsorbed into unit mass of the sorbent (mg g^{-1}) at equilibrium
C_o = The initial concentration of the metal ions (ppm)
C_e = The equilibrium concentration of the ions metal ions (ppm)
V = The volume of the metal aqueous solution (mL)
W = The weight of the sorbent (g)

RESULTS

Results: Figure 1 shows the SEM photograph of the prepared adsorbent (mussel shells: Clay = 1:3 by weight). The results revealed that the mussel shell powders have 250-355 µm in size and the natural clay have a cylindrical in shape.

Fig. 1: SEM photograph of the mussel shell and natural clay powder

To evaluate the sorption characteristics of composite materials for Cd(II) ions, the change of sorption capacity with time for different initial concentrations has been investigated. A series of experiments were undertaken by varying the initial concentration (5 and 20 ppm Cd(II) concentrations) on removal kinetics of Cd(II) from the solution. Figure 2 showed that the residual Cd(II) ion concentration reached equilibrium in duration of 240 min.

Kinetics of adsorption: In this study, the first-order kinetic model, which was used to examine the controlling mechanism of adsorption processes, is given as (Chiou and Li, 2003):

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Where:

q_e and q_t = The amount of Cd(II) adsorbed on adsorbent (mg g^{-1}) at equilibrium and at time t, respectively
k_1 = The rate constant for first-order adsorption (L min^{-1})

The straight-line plots of log (q_e-q_t) against t (Fig. 3) were used to determine the rate constant, k_1. The k_1 value and correlation coefficient R given in Table 1. The second-order equation may be expressed as (Wu *et al*., 2000):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where, k_2 is the rate constant for second-order adsorption (g mg^{-1} min^{-1}). The kinetic plot between t/q_t versus t was plotted as shown in Fig. 4. Slope and intercept values were solved to give the value of second-order rate constant given in Table 1.

Table 1: Kinetic parameter for Cd(II) adsorption on mussel shell/natural clay beads (C_o = 5 ppm)

First order	
k_1 ($\times 10^{-2}$ min^{-1})	1.3500
R	0.9735
Second order	
k_2 ($\times 10^{-5}$ g.mg^{-1}.min^{-1})	8.9000
R	0.9767

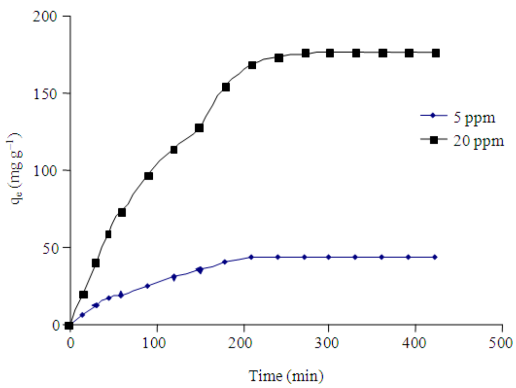

Fig. 2: Effect of initial concentration of Cd(II) adsorption by the sea mussel shell and natural clay adsorbent

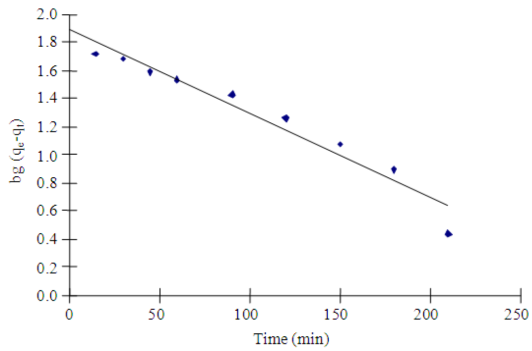

Fig. 3: Plots for first-order for Cd(II) adsorption onto the mussel shell and natural clay beads

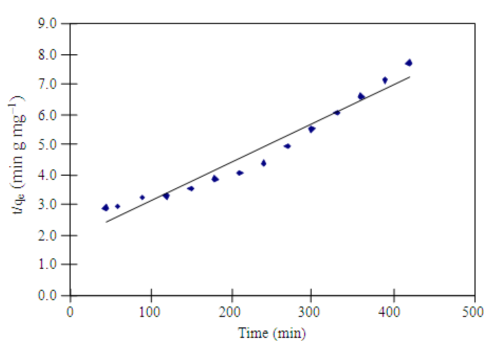

Fig. 4: Plots for second-order for Cd(II) adsorption onto the sea mussel shell and natural clay beads

DISCUSSION

As illustrated in Fig. 2, initially the amount of Cd(II) ions adsorbed increase rapidly, but then the process slows down and subsequently attains a constant value after 240 min i.e., when adsorption equilibrium is established. This phenomenon was due to a large number of vacant surface site for metal ions adsorption during the initial stage. Near the equilibrium the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phase. The adsorption of Cd(II) by composite materials increases as the initial Cd(II) concentration increased. An increase in the initial Cd(II) concentration leads to an increase in adsorption capacity of the Cd(II) onto the adsorbent. This is due to the increase in the concentration gradient between the bulk and the surface of the prepared adsorbent with the increase in initial Cd(II) concentration. Base on the correlation coefficients, the adsorption of Cd(II) is best described by the second-order equation. In many cases the first-order equation does not fit well to the whole range of contact time and is generally applicably over the initial stage of the adsorption processes.

CONCLUSION

The capability of the use of sea mussel shell and natural clay for removing Cd(II) from aqueous solution was examined. The present investigation showed that the mussel shell and natural clay beads can be effectively used as a sorbent for the removal of Cd(II) from aqueous solution. The adsorption kinetics of Cd(II) on sorbent was found to follow the second-order kinetic model.

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REFERENCES

Aravindan, V., P. Vickraman and K. Krishnaraj, 2009. Li^+ ion conduction in TiO_2 filled polyvinylidenefluoride-co-hexafluoropropylene based novel nanocomposite polymer electrolyte membrane with LiDFOB. Curr. Appli. Phys., 9: 1474-1479. DOI: 10.1016/J.CAP.2009.04.001

Chiou, M.S. and H.Y. Li, 2003. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. Chemosphere, 50: 1095-1105. DOI: 10.1016/S0045-6535(02)00636-7

Gupta, V.K. and S. Sharma, 2002. Removal of cadmium and zinc from aqueous solution using red mud. Environ. Sci. Technol., 36: 3612-3617. DOI: 10.1021/es020010v

Inglezakis, V.J., M.A. Stylianou and D. Gkantzou, 2007. Removal of Pb(II) from aqueous solution by using clinoptilolite and bentonite as adsorbents. Desalination, 210: 248-256. DOI: 10.1016/J.DESAL.2006.05.049

Matlock, M.M., B.S. Howerton and D.A. Atwood, 2001. Irreversible precipitation of mercury and lead. J. Hazard Mater., 84: 72-83. DOI: 10.1016/S0304-3894(01)00190-X

Salim, M., Y. Munekage and K.M. Naing, 2007. Arsenic removal from contaminated water using silica ceramic: A batch adsorption study. J. Applied Sci., 7: 2314-2320. http://scialert.net/qredirect.php?doi=jas.2007.2314.2320&linkid=pdf

Wu, F.C., R.L. Tseng and R.S. Juang, 2000. Comparative adsorption of metal and dye on flake- and bead-types of chitosans prepared from fishery wastes. J. Hazard Mater., 73: 63-75. DOI: 10.1016/S0304-3894(99)00168-5