

PAPER • OPEN ACCESS

Comparison of cadmium adsorption onto chitosan and epichlorohydrin crosslinked chitosan/eggshell composite

To cite this article: Rahmi *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **352** 012047

View the [article online](#) for updates and enhancements.

You may also like

- [A bioprintable form of chitosan hydrogel for bone tissue engineering](#)

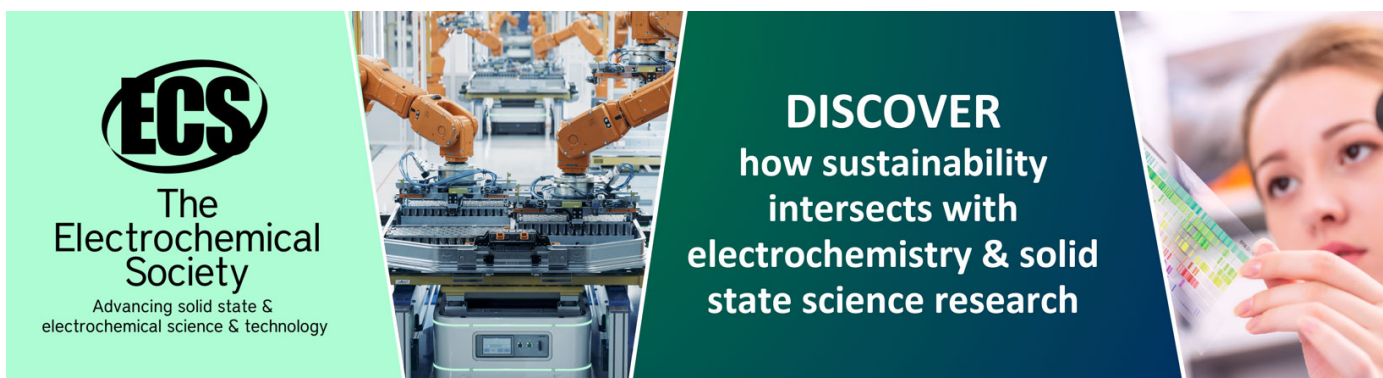
Turul Tolga Demirta, Gülseren Irmak and Meneme Gümüdereliolu

- [Characteristics of biodegradable plastic from mulu bebe banana peel starch with the addition of chitosan and glycerol plasticizer](#)

Erna Ruslana Muhamad Saleh and Sri Utami

- [Thermo-therapeutic applications of chitosan- and PEG-coated \$\text{NiFe}_2\text{O}_4\$ nanoparticles](#)

S Manjura Hoque, Mehrin Tariq, S I Liba et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Comparison of cadmium adsorption onto chitosan and epichlorohydrin crosslinked chitosan/eggshell composite

Rahmi, Marlina, Nisfayati

Department of Chemistry, Syiah Kuala University
Darussalam, Banda Aceh, 23111, Indonesia

E-mail: rahmi@fmipa.unsyiah.ac.id

Abstract. The use of chitosan and epichlorohydrin crosslinked chitosan/eggshell composite for cadmium adsorption from water were investigated. The factors affecting adsorption such as pH and contact time were considered. The results showed that the optimum pH of adsorption was pH = 6.0 and the equilibrium time of adsorption was 40 min. The adsorption isotherm of Cd ions onto chitosan and composite were well fitted to Langmuir equation. The maximum adsorption capacity (fitting by Langmuir model) of chitosan and composite were 1.008 and 11.7647 mg/g, respectively. Adsorption performance of composite after regeneration was better than chitosan.

1. Introduction

Heavy metal ions removal from polluted water is an important environmental issue. The existence of heavy metal ions will endanger to human health and environment. Some methods have been reported for heavy metal ions removal. Adsorption is one the methods that has much attention due to its effectivity and low cost [1-3]. The use of biopolymer as an adsorbent for heavy metal ions has many advantages such as availability, biodegradability and renewability. Most recent studies have focused on the seeking of effective adsorbent that locally available and cheap. One of heavy metal ion adsorbents that has much attention was chitosan [4-9].

Chitosan is deacetylated form of chitin which obtained in crustaceans and insects. Chitosan contains hydroxyl (-OH) and amine (-NH₂) groups that may form complexes with heavy metal ions and easy to modified. In order to improve the chitosan performance on heavy metal ions removal, some methods have been studied such as the use of crosslinking agent or filler on adsorbent based chitosan preparation. Some studies have been reported the use of filler for the improvement of chitosan performance such as the use of clay [10], sand [11], and cellulose [12]. However there is no study reporting the use of eggshell particles as a filler of chitosan. Meanwhile, Laus et al. (2010) reported the improvement of chitosan performance on heavy metal ion removal after crosslinking with epichlorohydrin [13]. Therefore, in this study we used both methods in order to improve the performance of chitosan on Cd ions removal from aqueous solutions. Epichlorohydrin was used as crosslinking agent and eggshell particles as a filler of chitosan based adsorbent. The availability, chemical compositions and low cost are the advantages of the utilization of eggshell as a filler on chitosan based adsorbent preparation.

The preparation and characterization of epichlorohydrin crosslinked chitosan/eggshell composite has been reported in our previous work [14]. The results showed that eggshell particles enhanced the mechanical properties and decreased the crystallinity, therefore in the present study we evaluated the



adsorption capacity of epichlorohydrin crosslinked chitosan/eggshell composite on Cd ions removal from aqueous solutions and compared with chitosan. The adsorption was conducted with various pH, agitation time and initial cadmium concentration. Langmuir and Freundlich model were used to study isotherm adsorption and adsorption kinetics were studied by using pseudo-first order and the pseudo-second order model.

2. Materials and Methods

2.1. Materials

Chitosan (degree of deacetylation: 75.0 to 85.0%) and epichlorohydrin were purchased from Tokyo Chemical Industry Co., Ltd. Japan. Eggshell particles were produced by using ball milling machine.

2.2. Preparation of epichlorohydrin crosslinked chitosan/eggshell composite

Preparation of the composite was conducted according to our previous report [10], where chitosan (1%, w/v) was dissolved in acetic acid solution (2%). The epichlorohydrin was added to the chitosan solution under vigorous magnetic stirring at room temperature for 1 h. The eggshell particles were mixed with crosslinked chitosan solution and homogenized for 3h. The mixture was spread on the petri dish. The dish was kept at room temperature. Dried composite films were peeled off from petri dish and kept for further use.

2.3. Batch Adsorption experiments

Cd(NO₃)₂ was used for stock solutions (1000 ppm) of Cd ions preparation. Appropriate concentrations of standard solutions were prepared from the stock solutions. In 250 ml beakers, 25 ml aliquots of these standard solutions were placed and 50 mg of chitosan or composite was added. Batch adsorption experiment was conducted with various pH (1-9), contact time (20, 25, 30, 35, 40, 45 and 50 min) and initial Cd ions concentration (2.4, 4.8, 9.5, 16.6, 28.5, 57.0, 95.0 ppm) in order to obtain optimum condition. Cd ions concentration was analyzed by using UV-Vis spectrophotometer.

Adsorption equilibrium and adsorption kinetic studies were conducted under optimum condition. Adsorption capacity (Q_e) was calculated based on the difference of Cd ions concentration in aqueous solution before and after adsorption (Equation 1)

$$\text{Adsorption Capacity } (Q_e) = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 is the initial Cd ions concentration, C_e is final Cd ions concentration, V is volume of Cd ions solution and W is the weight of chitosan or composite.

3. Results and Discussion

3.1. Effect of pH

In the adsorption processes, the pH of the aqueous solution is an important parameter. Batch adsorption tests were conducted in pH range of 1-9 to study the influence of pH on the adsorption capacity of Cd ions onto chitosan and composite. From the results shown in Figure1, the adsorption capacities of the chitosan and composite were dependent on the pH of solutions. The adsorption capacity of Cd ions onto chitosan or composite increased up to pH 5.0 and tended to be constant until pH 7.0 for chitosan and pH 8.0 for composite.

In acidic condition, lower adsorption capacity was observed due to the high concentration of H^+ in the solutions compete with heavy metal ions in terms of binding with NH_2 groups of chitosan. By increasing pH, the concentration of H^+ ions decreases, facilitating the adsorption of metal ions by adsorbent. It also reported that the amine groups on chitosan surfaces are easily protonated at lower pH, inducing an electrostatic repulsion of heavy metal ions. Based on zeta potential values, Calagui, et al. (2014) reported that chitosan in less acidic solution had negative surface charge where there would

be electrostatic attraction between negatively charged adsorbent surface and positively charged sorbate [15].

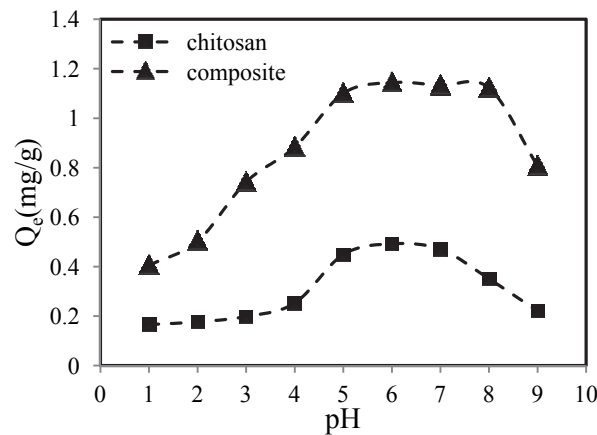


Figure 1. Effect of pH on adsorption capacity of Cd ions onto chitosan and composite

At pH 9.0, it was observed that the adsorption of Cd ions onto chitosan and composite decreased significantly. It was probably due to at alkaline solutions, amino groups of chitosan become deprotonated and allowing the shrinking of polymer chains. It reduced the possibility of heavy metal ions to contact with NH_2 groups of chitosan polymer chains and effect the decreasing of adsorption.

3.2. Adsorption Isotherms

Figure 2 shows adsorption equilibrium isotherm of Cd ions adsorption onto chitosan and composite. The adsorption capacity of Cd ions onto chitosan and epichlorohydrin crosslinked chitosan/eggshell composite increased by increasing initial concentration of Cd ions and then tended to be constant due to the saturation of the adsorbents.

Langmuir and Freundlich isotherm model were used to study the adsorption isotherm of Cd ions onto chitosan and composite. The equation for Langmuir and Freundlich model were represented in equations (2) and (3), respectively [13].

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\max}} + \frac{C_e}{Q_{\max}} \quad (2)$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Where $Q_{\max}$, K_L , K_F and n are maximum adsorption capacity (mg/g), Langmuir constant (L/mg), and adsorption intensity, respectively. Langmuir model assumes that the adsorption of adsorbate on the surface of adsorbent is monolayer adsorption. The Freundlich model does not assume monolayer adsorption, it describes the equilibrium on the heterogenous surfaces.

Table 1. Comparison of adsorption isotherm parameter for adsorption Cd ions onto chitosan and composite.

Adsorbent	Langmuir isotherm model			Freundlich isotherm model		
	R^2	$Q_{\max}$ (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n
Chitosan	0.996	1.008	0.197	0.815	43.954	0.417
Composite	0.952	11.765	0.141	0.822	0.404	0.553

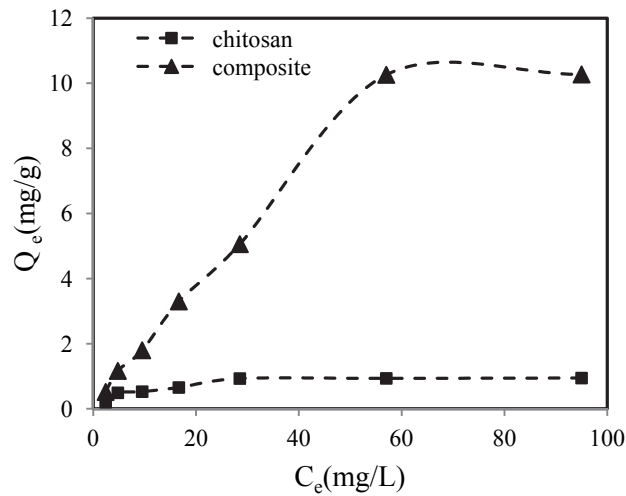


Figure 2. Adsorption equilibrium isotherm of Cd ions adsorption onto chitosan and composite.

The Langmuir and Freundlich isotherm model of Cd ions adsorption onto chitosan and composite were shown in figure 3 and 4, respectively. Comparison of adsorption isotherm parameter for adsorption Cd ions onto chitosan and composite was shown in table 1. Based on the correlation coefficient (R^2) obtained from isotherm model curves, it confirmed that the adsorption of Cd ion adsorption onto chitosan and composite were fitted to the Langmuir model. The equation of Langmuir model was employed to determine the $Q_{\max}$. $Q_{\max}$ value of Cd ions adsorption onto composite was found higher than $Q_{\max}$ value of Cd ions adsorption onto chitosan. It indicates the improvement of chitosan performance after modification with crosslinking agent and filler.

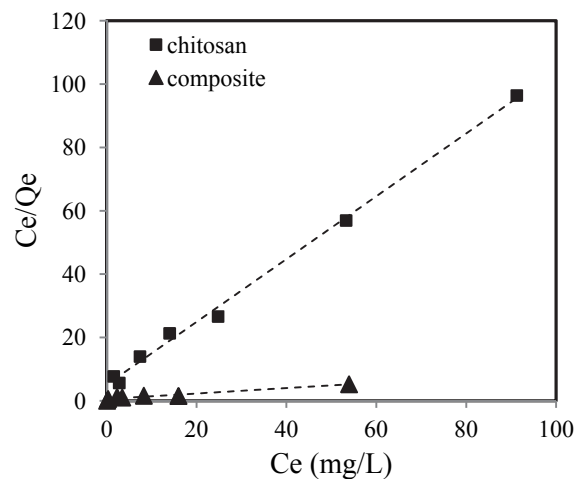


Figure 3. Langmuir isotherm model of Cd ions adsorption onto chitosan and composite.

3.3. Adsorption kinetics

Figure 5 shows the adsorption kinetics for adsorption of Cd ions onto chitosan and composite. The equilibrium time of Cd ions adsorption onto chitosan and composite were reached in the same time (40 min).

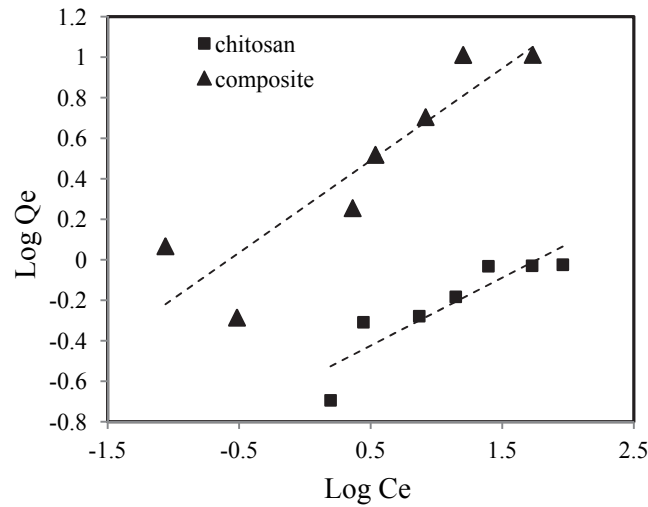


Figure 4. Freundlich isotherm model of Cd ions adsorption onto chitosan and composite.

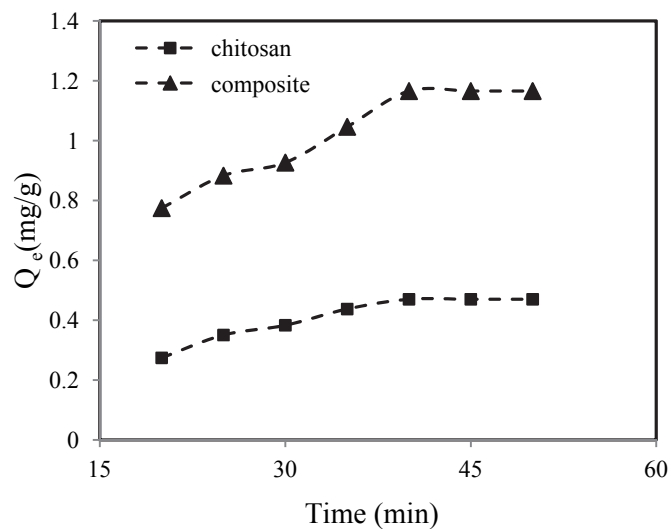


Figure 5. Adsorption kinetics of Cd ions onto chitosan and composite.

The pseudo-first order model and pseudo-second order model were used to determine the kinetic mechanism of Cd ions adsorption onto chitosan and composite. The equation for the pseudo-first order model and the pseudo-second order model are shown in Equations (4) and (5), respectively.

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (5)$$

Where Q_e is the amount adsorbed of Cd ions (mg/g) at equilibrium. Q_t is the amount adsorbed of Cd ions (mg/g) at time t (min). k_1 (min^{-1}) and k_2 (g/mg min) are the rate constant of pseudo-first order model and the pseudo-second order model, respectively. The results of parameters for the adsorption of Cd ions onto chitosan and composite are given in table 2.

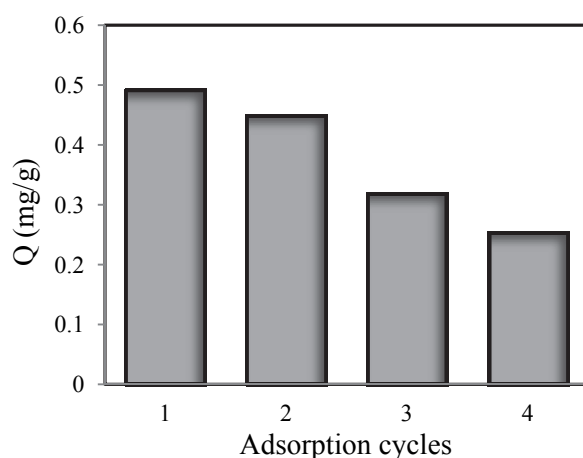
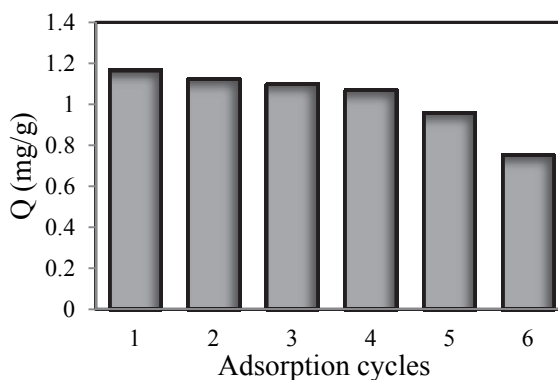
Table 2. Comparison of kinetic models for the Cd ion adsorption onto chitosan and composite.

Adsorbent	Pseudo first order			Pseudo second order		
	R^2	Q_e (mg/g)	k_1 1/min)	R^2	Q_e (mg/g)	k_2 (g/mg min)
Chitosan	0.944	0.470	0.569	0.895	0.898	1.241
Composite	0.923	1.658	0.074	0.962	1.901	0.018

Table 2 shows the correlation coefficient (R^2) values of pseudo-first order model for adsorption of Cd ions onto chitosan was higher than pseudo-second order model. It indicates that kinetic adsorption of Cd ions onto chitosan was fitted to pseudo-first order model. On the other hand, adsorption of Cd ions onto composite agreed with pseudo-second order model. It might be influenced by the addition of crosslinking agent and eggshell particles to chitosan.

3.4. Regeneration studies

Regeneration studies are important to evaluate the probability of the adsorbent for subsequent reuse. In this study, HNO_3 solution at concentration 0.05 M was used as eluent for the regeneration of composite. In this concentration, chitosan was dissolved. Therefore, the lower concentration (0.0001 M) was used for the regeneration of chitosan. Figure 6 and 7 show experimental data of regeneration efficiency of chitosan and composite for Cd ions adsorption, respectively.

**Figure 6.** Regeneration efficiency of chitosan for Cd ions adsorption.**Figure 7.** Regeneration efficiency of composite for Cd ions adsorption

The adsorption capacity of Cd ions onto chitosan and composite were decrease after adsorbent regeneration. The adsorption capacity of Cd ions onto composite was not significantly decrease after four times regeneration. The composite still showed good performance after fourth regeneration. While chitosan was only effective for once regeneration. It proves that the crosslinking agent and filler could improve chitosan performance on heavy metal ions adsorption.

4. Conclusions

It was observed that the crosslinking and addition of filler in chitosan could improve chitosan performance for Cd ions adsorption. Optimum condition for adsorption was found at pH 6 and contact time 40 minutes. Langmuir isotherm indicated that maximum adsorption capacity of Cd ions onto composite was 11.765 mg/g and this value was more than ten times larger than maximum adsorption capacity of Cd ions onto chitosan. Regeneration studies showed that the adsorbents can be used several times for adsorption of Cd ions.

References

- [1] Mansour M S, Ossman M E and Farag HA 2011 *Desalination* **272** 301–305
- [2] Barakat M A 2011 *Arab. J. of Chem.* **4** 361-77
- [3] Cataldo S, Gianguzza A, Pettignano A and Villaescusa I 2013 *React.Funct. Polym.* **73** 207-217
- [4] Laus R, Favere V T, 2011, *Bioresour. Technol.* **102**, 8769–8776
- [5] Vieira R S and Beppu M M 2005 *Adsorption* **11**(1) 731-736
- [6] Zhao F, Yu B, Yue Z, Wang T, Wen X, Liu Z 2007 *J. Hazard. Mater.* **147** 1-2 67-73
- [7] Rahmi, Fathurrahmi, Irwansyah and Purnaratrie A 2015 *Orient. J. Chem.* **31**(4) 2071-2076
- [8] Rahmi 2016 *Asian J. Chem.* **28**(10) 2267-2271
- [9] Rahmi, Lelifajri, Julinawati and Shabrina 2017 *Carbohydrate Polymers* **170** 226-233
- [10] Tirtom VN, Dincer A, Becerik S, Aydemir T, and Celik A 2012 *Chemical Engineering Journal* **197**(8) 379-386
- [11] Wan M, Kan C, Rogel B D and Dalida M L P 2010 *Carbohydrate Polymers* **80**(9) 891-899
- [12] Khan A, Khan R A, Salmieri S, Tien C L, Riedl B, Bouchard J, Chauve G, Tan V, Kamal MR and Lacroix M 2012 *Carbohydrate Polymers*, **90**(4) 1601-1608
- [13] Laus R, Costa T G, Szpoganicz B and Favere V T 2010 *J. Hazard. Mater.* **183** 233-241
- [14] Rahmi, Marlina and Nisfayati 2017 *Orient. J. Chem.* **33**(1) 478-482
- [15] Calagui M J, Senoro D B Kan C-CJ, Salvacion W L, Futralan C M and Wan M W 2014 *J. Hazard. Mater.* **277** 120-126