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Removal of Cadmium from Aqueous Solutions by Polyethylene Glycol Diglycidylether Crosslinked Chitosan-Coated Cristobalite

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This study describes the adsorption of Cd(II) ions onto polyethylene glycol diglycidylether (PEGDE) crosslinked chitosan-coated cristobalite. Chitosan was modified by crosslinked with PEGDE and immobilized to cristobalite. The adsorbent was used in batch experiments with various operating parameters such as pH and agitation period. The adsorption of Cd(II) ions increased with an increase in pH. The optimum solution pH of Cd(II) ions adsorption was found to be 5. The equilibrium adsorption data for Cd(II) were fitted to Langmuir and Freundlich models. The maximum adsorption capacity of Cd(II) was 1.452 mg/g inferred from Langmuir model. The kinetics process of Cd(II) ions adsorption onto PEGDE crosslinked chitosan-coated cristobalite was found to fit the pseudo-first order model.

Keywords: Chitosan, Cristobalite, Polyethylene glycol diglycidylether, Cd(II), Adsorption.

INTRODUCTION

Cadmium has drawn much attention due to its toxicity and potential hazard to the environment and organisms. There are several industries that pollute the environment with high level of Cd(II) ions such as battery industries, metal plating, textile printing, electroplating, lead mining, paint industry and metallurgy. The most common method to remove Cd(II) ions from the environment is chemical precipitation, but it produces large amount of sludge. Membrane technology, evaporation, ion exchange and electrochemical technique are well known methods for removal heavy metal ions from polluted water but most of them are ineffective and expensive. Adsorption is one of the most effective, economical and widely used method for removal of heavy metal ions [1-3]. One of adsorbents that has been used widely is chitosan [4-8].

Chitosan has been studied extensively as an adsorbent of heavy metal ions due to its high capacity, low cost, biodegradability, biocompatibility, renewability, non-toxicity and efficiency. Chitosan contains chemically active functional groups such as amine ($-NH_2$) and hydroxyl groups (-OH) that serve as an efficient sites to bind with heavy metal ions. However, chitosan has low chemical stability. Consequently, its stability needs to be reinforced. Several studies have been reported the use of crosslinking agents to reinforce chemical stability of chitosan such as glutaraldehyde and polyethylene glycol diglycidylether (PEGDE) [9]. The use of chitosan alone as an adsorbent will be costly. Immobilizing chitosan on a low cost material would result in less amount of chitosan being used without affecting the over all metal adsorption capacity [10-13].

In this study, chitosan was crosslinked with PEGDE and coated on cristobalite particles through precipitation procedure to prepare adsorbent of Cd(II) ions from aqueous solutions. The effect of PEGDE concentrations in adsorbent preparation on performance of Cd(II) ions uptake was examined. The optimum operating conditions, equilibrium data and kinetic data were determined to understand the adsorption mechanism of Cd(II) onto PEGDE crosslinked chitosan-coated cristobalite.

EXPERIMENTAL

The raw materials were shrimp shells seafood wastes of city of Banda Aceh and natural cristobalite from Sabang, Aceh, Indonesia. Shrimp shells seafood wastes were processed in three steps (demineralization, deproteinization and deacetylation) to obtain chitosan. Natural cristobalite was sieved become 40-60 mesh in size.

Preparation of PEGDE crosslinked chitosan-coated cristobalite: Chitosan (1 %, w/v) was dissolved in 2 % aqueous acetic acid solution. Polyethylene glycol diglycidylether (with a series of concentration) was added to chitosan solution and the mixture was stirred continously at 60 °C for 4 h. Then, cristobalite particles were added to the solution at room tempe-

rature for 1 h and subsequently soaked in a NaOH (2 mol/L) solution for 24 h to allow the development and solidification of PEGDE crosslinked chitosan-coated cristobalite. Finally, the coated particles were washed extensively with cold and hot distilled water to remove the remaining NaOH. Dried at 49 °C for 48 h and stored in a desiccator for further use.

Cadmium(II) ions adsorption experiments: Investigation of Cd(II) adsorption onto PEGDE crosslinked chitosan-coated cristobalite was carried out in bath adsorption experiments. For this purpose, 1 g of adsorbent was placed into 20 mL aqueous solution with desired concentrations of Cd(II) ions. The mixtures were shaken by a rotary shaker at room tempe-rature. The adsorption process was observed by varying pH of the solution, agitation period and Cd(II) ions concentration. The amount of metal adsorbed per unit mass (Q) is calculated as eqn. 1:

$$Q = \frac{(C_i - C_f)}{m} V \quad (1)$$

where m is the weight of the adsorbent, V is the volume of Cd(II) ions solution, C_i (mg/L) and C_f (mg/L) are the concentration of heavy metal ions before and after adsorption experiments, respectively.

RESULTS AND DISCUSSION

Effect of polyethylene glycol diglycidylether (PEGDE) on adsorption of Cd(II) ions: In order to investigate the optimum concentration of PEGDE, the adsorbent preparation was conducted with various concentration of PEGDE. The effect of the adsorbents were evaluated for removal Cd(II) ions from aqueous solutions. The results of these experiments are summarized in Fig. 1.

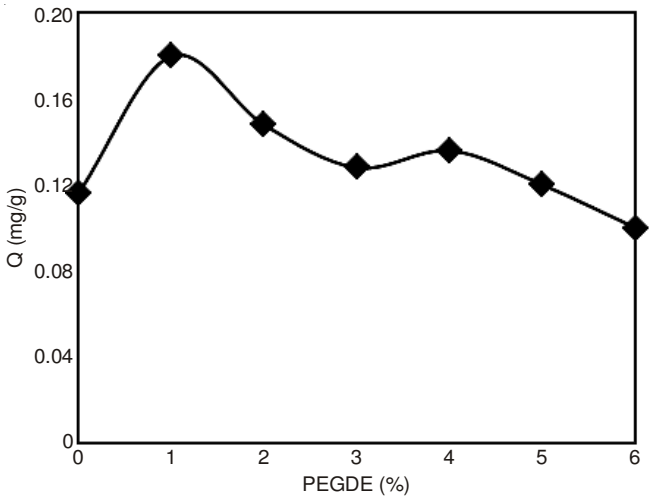

Fig. 1. Effect of PEGDE concentration on the adsorption of Cd(II) ions

Fig. 1 shows the adsorption capacity of Cd(II) onto PEGDE crosslinked chitosan-coated cristobalite was influenced by PEGDE concentration. Adsorption capacity of Cd(II) was higher onto PEGDE crosslinked chitosan-coated cristobalite comparing chitosan-coated cristobalite without crosslinking. Hsien and Rorrer [14] reported the crosslinking can enlarge the space between the chitosan chains improving the accessibility of amino groups for metal ions. Another explanation is that crystallinity of chitosan decreased by crosslinking and influence accessability of internal sites for metalic ions where a decrease in crystallinity can improve adsorptive characteristic [5,13,15].

The optimum concentration of PEGDE was found to be 1 % (v/v). However, after increasing the concentration above 1 % the adsorption capacity decreased. It was probably due to the free hydroxyl groups present in the chitosan reduced, where the crosslinking was taking place on the hydroxyl groups of chitosan as shown in Fig. 2.

Effect of pH on adsorption of Cd(II) ions: One of the factors affecting the adsorption process is pH. Optimum pH of Cd(II) ions adsorption of PEGDE crosslinked chitosan-coated cristobalite was 5. This is consistent with the research conducted by Zhao *et al.* [16] on the adsorption of Cd(II) by modified chitosan. The adsorption capacity of PEGDE crosslinked chitosan-coated cristobalite at optimum pH was 0.172 mg/g (Fig. 3).

At low pH environment the adsorption capacity of the PEGDE crosslinked chitosan-coated cristobalite was low because the number of H^+ ions in solution was large causing more NH_2 has a tendency to bind to H^+ rather than with Cd(II) ions. The increasing number of H^+ in the solution of Cd(II) cause NH_2 protonated with H^+ from the acid becoming NH_3^+. When chitosan was at alkaline pH, free amino group in chitosan was deprotonated and effect the decreasing of adsorption. Calagui *et al.* [17] reported that based on zeta potential values, chitosan had negative surface charge at pH > 2.8 where as solution become less acidic, there would be electrostatic attraction between positively charged sorbate and negatively charged adsorbent surface.

Adsorption capacity of non crosslinked chitosan-coated cristobalite was also examined at pH 1 and 2. The adsorption capacity values of Cd(II) ions were obtained lower than the PEGDE crosslinked chitosan-coated cristobalite.

Effect of agitation period on adsorption of Cd(II) ions: Agitation period (contact time) between the adsorbate and adsorbent greatly affect the adsorption capacity. The results showed that the adsorption capacities of Cd(II) ions onto PEGDE crosslinked chitosan-coated cristobalite increase by increasing agitation period and tend to be constant after 0.5 h implying that equilibrium has been reached (Fig. 4).

Initially, adsorption occured rapidly due to the presence of vacant active sites of chitosan. However after 0.5 h, less active sites were available to be occupied due to the repulsive force between the solute molecules on the solid and bulk phases, resulting Cd(II) ion uptake remain constant [18].

Adsorption isotherms and kinetics: Langmuir and Freundlich adsorption isotherms were used to analyze equilibrium adsorption of Cd(II) ions onto PEGDE crosslinked chitosan-coated cristobalite. The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. Its linearized form is represented by eqn. 2:

$$\frac{1}{Q} = \frac{1}{Q_{max}} + \frac{1}{K_a Q_{max} C} \quad (2)$$

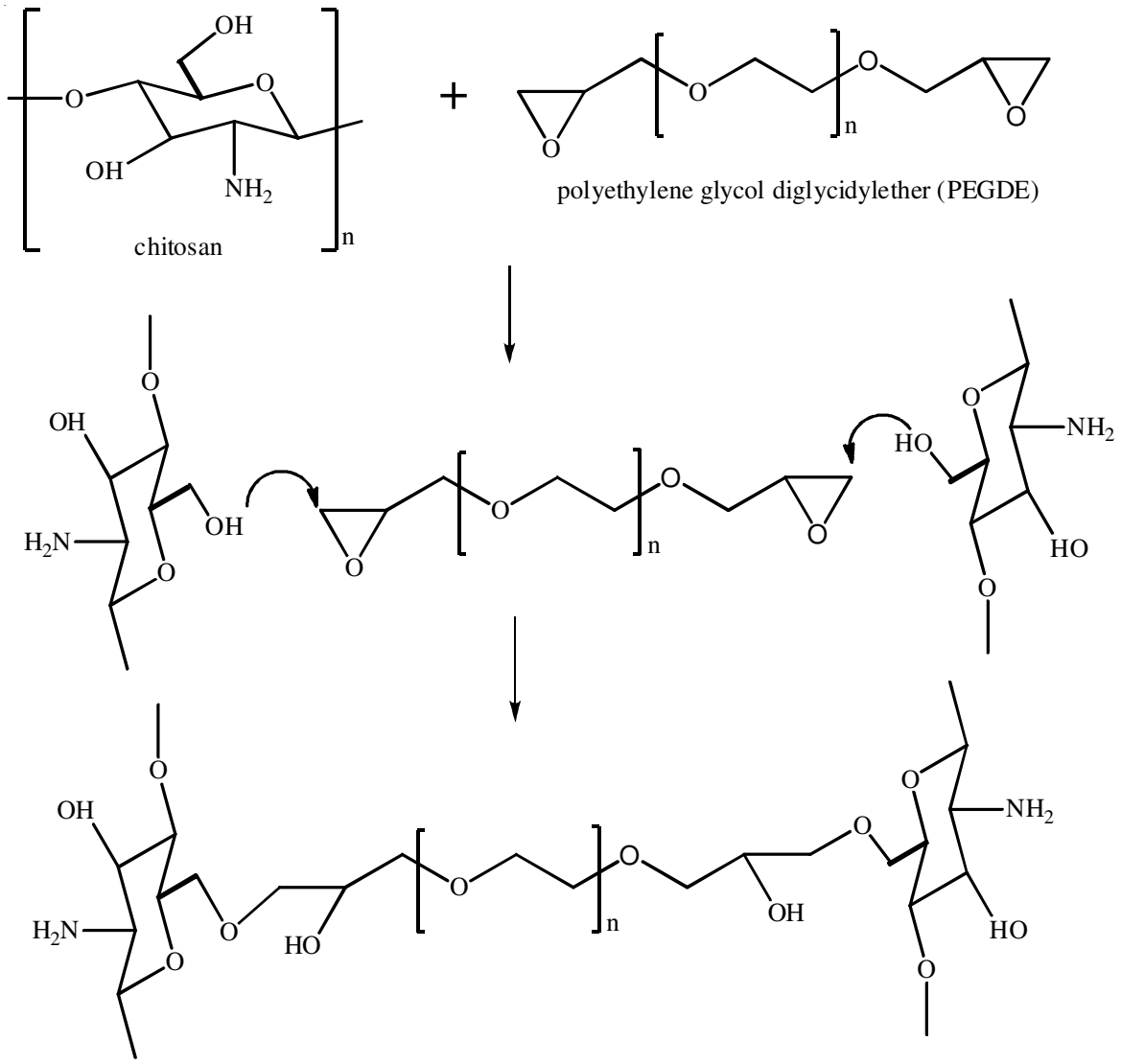

Fig. 2. Schematic representation of cross-linking reaction between PEGDE and chitosan

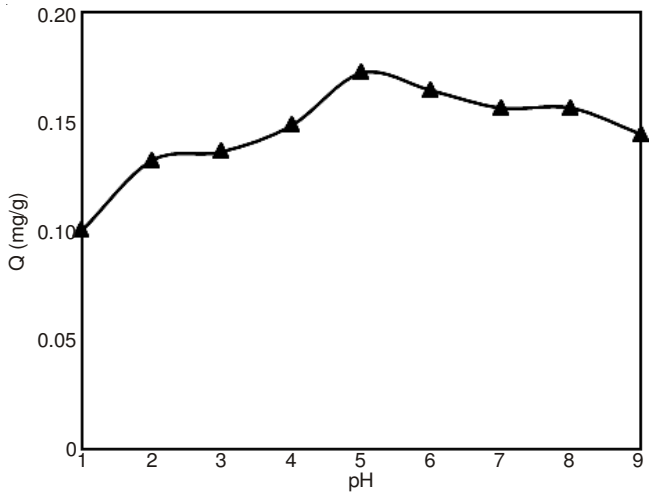

Fig. 3. Effect pH on the adsorption Cd(II) ions onto PEGDE cross-linked chitosan-coated cristobalite

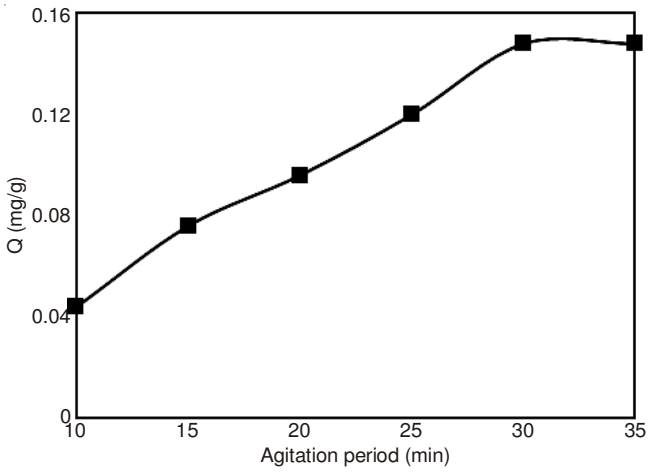

Fig. 4. Effect agitation period on the adsorption Cd(II) ions onto PEGDE cross-linked chitosan-coated cristobalite

where Q is the amount of adsorbate adsorbed per unit weight of PEGDE crosslinked chitosan-coated cristobalite at equilibrium concentration (mg/g), C is the final concentration in the solution (mg/L), Q_{max} is the maximum adsorption at monolayer coverage (mg/g). The Langmuir constant K_a is related to the energy or net enthalpy of adsorption [19]. Langmuir isotherm curve of Cd(II) ions adsorption onto PEGDE crosslinked chitosan-coated cristobalite is shown in Fig. 5.

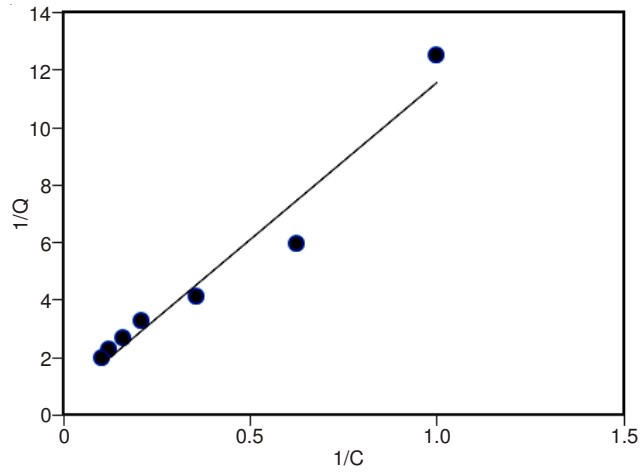

Fig. 5. Langmuir isotherm curve

The affinity between PEGDE crosslinked chitosan-coated cristobalite and Cd(II) ions can be predicted using the Langmuir parameter K_a from the dimensionless separation factor R_L as shown in eqn. 3:

$$R_L = 1/(1 + K_aC_0) \quad (3)$$

The adsorption process may be described as follows: $R_L > 1$ unfavourable, $R_L = 1$ linear, $0 < R_L < 1$ favourable and $R_L = 0$ irreversible. The calculated R_L values for adsorption of Cd(II) onto PEGDE crosslinked chitosan-coated cristobalite were 0.312-0.760, which indicates favourable adsorption of Cd(II) onto PEGDE crosslinked chitosan-coated cristobalite.

Another widely used empirical equation, the Freundlich equation, is based on adsorption on a heterogeneous surface as shown in eqn. 4:

$$\log Q = \frac{1}{n}\log C + \log K_f \quad (4)$$

where Q and C have the same definitions as in eqn. 2, K_f is a Freundlich constant representing the adsorption capacity and n is a constant depicting the adsorption intensity. Therefore, K_f and 1/n can be determined from the linear plot of log Q *versus* log C. Freundlich isotherm curve of Cd(II) ions adsorption onto PEGDE crosslinked chitosan-coated cristobalite is shown in Fig. 6.

Both of adsorption isotherm models fit with experimental data of Cd(II) ions adsorption onto PEGDE crosslinked chitosan-coated cristobalite (Figs. 5 and 6). Table-1 shows the comparison data of Langmuir and Freundlich isotherms. Where the maximum adsorption capacity (Q_{max}) was found to be 1.463 mg/g and n value of Freundlich model indicates the strength interaction between adsorbent and adsorbate.

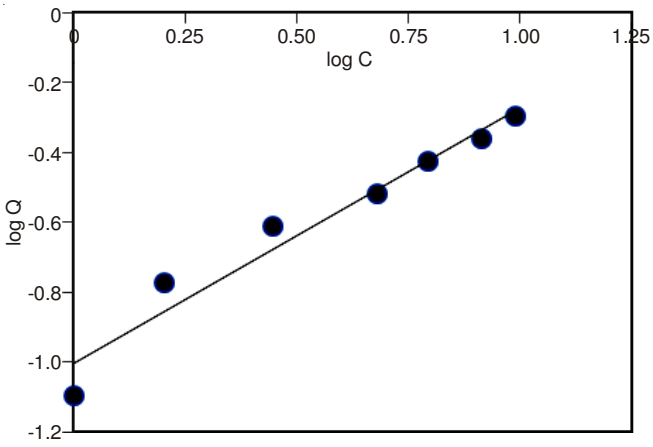

Fig. 6. Freundlich isotherm curve

TABLE-1
COMPARISON DATA OF LANGMUIR AND FREUNDLICH ISOTHERMS

Langmuir isotherm		
Q_m (mg/g)	K_a	R^2
1.452	0.063	0.954
Freundlich isotherm		
K_f (mg/g)	n	R^2
0.099	1.37	0.956

In order to investigate the mechanism of sorption, the rate constans were determined by using pseudo-first order and pseudo-second order kinetic models. The pseudo-first order rate equation is expresses by eqn. 5:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2}.303t \quad (5)$$

where k_1 (min^{-1}) is the pseudo-first order rate constant, q_e and q_t are the adsorption capacities (mg/g) at equilibrium and time t (min), respectively. This model considers the rate of occupation of the adsorption sites which assumed to be proportional to the number of occupied sites. The values of ln (Q_e-Q_t) were plotted *versus* t and the plot was found to be linear as shown in eqn. 6:

$$\log (Q_e - Q_t) = -0.653 - 0.034t \; R^2 = 0.978 \quad (6)$$

The plot indicates that the pseudo-first order model is applicable for the adsorption of Cd(II) ions onto PEGDE crosslinked chitosan-coated cristobalite where the value of k_1 and Q_e were 0.078 min^{-1} and 0.222 mg/g, respectively.

The pseudo-second order rate equation is expresses by eqn. 7:

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{t}{Q_e} \quad (7)$$

where k_2 (g/mg min) is the pseudo-second order rate constant, Q_e (mg/g) is the maximum adsorption capacity and Q_t (mg/g) is the amount of adsorption at time t (min). The values of t/Q_t were plotted against t and the plot shows the very low correlation function as shown in eqn. 8. The plot indicates that second order model is not applicable for Cd(II) ions adsorption.

$$\frac{t}{Q_t} = 548.9 - 17.04t \; R^2 = 0.526 \quad (8)$$

It is evident that the kinetics is only well described using pseudo-first order model ($R^2 > 0.9$). This implies that physical adsorption is the rate determining step of the adsorption Cd(II) using PEGDE crosslinked chitosan-coated cristobalite.

Conclusion

Adsorption capacity of Cd(II) ions onto PEGDE crosslinked chitosan-coated cristobalite was investigated in this study. Effects of the concentration of PEGDE in adsorbent preparation, pH, agitation period and initial concentrations on

Cd(II) ions adsorption were determined. The results showed that PEGDE optimum concentration was 1 % (v/v), optimum pH was 5 and equilibrium of adsorption was reached in 0.5 h. The Langmuir and Freundlich models were suitable to the experimental data of Cu(II) adsorption onto PEGDE crosslinked chitosan-coated cristobalite. The adsorption kinetics obeyed the pseudo first-order model.

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