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KINETICS AND ISOTHERM STUDIES OF Pb(II) IMPRINTED CARBOXYMETHYL CHITOSAN–PECTIN-PEGDE

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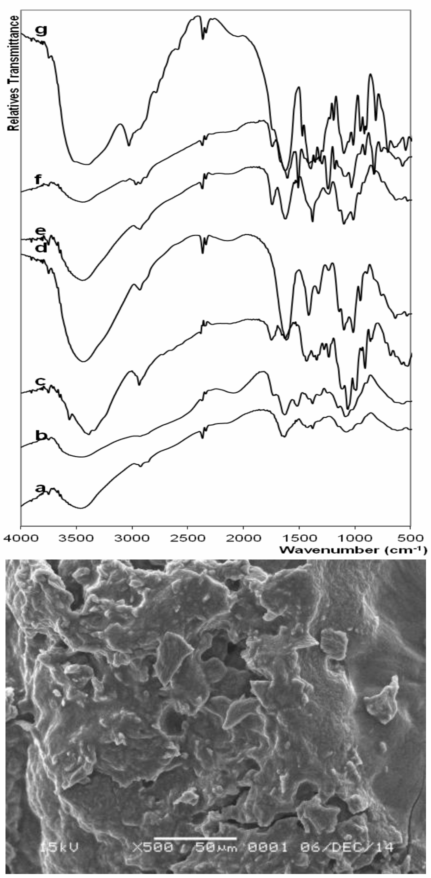
Graphical abstract



Abstract

Pectin and chitosan are biomaterials that capable to act as biosorbent. Pectin has active groups, such as carboxyl, methoxyl, and hydroxyl (OH), while chitosan has amine group (–NH_2) and hydroxyl (OH) as the active site metal ion absorber. Integration of two biopolymers is conducted by using a suitable cross-linker agents that are expected to form stable and more organized structure. This structure facilitate metal ions to enter and to form chelation reaction. Thus, it has great capacity for metal adsorption. A modified natural adsorbent pectin-chitosan has been synthesized by reacting of -OH group among pectin (Pec) and chitosan with Poly(ethylene glycol) Diglycidyl Ether (PEGDE) crosslinker agent to form a stable and an acidic medium-resistance adsorbent. Prior to increasing the active group of the adsorbent, chitosan was attached with acetate to form Carboxymethyl Chitosan (CMC). Furthermore, the CMC-Pec-PEGDE adsorbent was imprinted with Pb (II) to afford Pb(II) imprinted-CMC-Pec-PEGDE adsorbent in order to improve the selective sorption of Pb(II) metal ion. All of the functional groups attached on the synthesized adsorbents were characterized by Fourier Transform Infrared (FT-IR) Spectrometry. The kinetics and thermodynamics bath sorption of Pb(II) on Pb(II) imprinted-CMC-Pec-PEGDE film adsorbent have been investigated including the optimal condition for adsorption. The pseudo first-order and second-order kinetic model were investigated in order to determine the adsorption mechanism. The results indicated that all of the three adsorbent, CMC, CMC-Pec-PEGDE, and Pb(II) imprinted-CMC-Pec-PEGDE followed a pseudo-second-order kinetic model. Furthermore, adsorption studies of Pb(II) ion on CMC and CMC–Pec-PEGDE found to follow Langmuir adsorption while on imprinted-CMC-Pec-PEGDE followed Freundlich adsorption isotherm. The adsorption isotherm parameters of CMC and CMC-Pec-PEGDE adsorbents were ΔG° of 24.8 and 23.1 kJ mol^{-1}, respectively. While Pb(II) imprinted- CMC-Pec-PEGDE followed isotherm model with ΔG° of 9.6 kJ mol^{-1}.

Keywords: Adsorption, Pb(II), carboxymethyl chitosan(CMC), pectin(Pec), Pb(II) imprinted-CMC-Pec-PEGDE

1.0 INTRODUCTION

Pollution of the water environment that caused by heavy metal pollution rises in a row with developments in technology and industry. Therefore, efforts should be made to solve the problem of heavy metal pollution by lowering the metal ions concentration in the aquatic environment, based on the accurate monitoring records to the heavy metal content. Lead (Pb) is one of the harmful heavy metals that are dangerous to human life and also to the environment, which is toxic, could accumulate in the human body, and cause the metabolic and tissue function disorders. In the cases of lead poisoning in human, it could cause severe damage to the central and peripheral nervous system, reproductive system, kidney, brain, and liver [1, 2]. The other reported toxic effects of the Pb metal are visual disturbances, convulsions, nausea, vomiting, anemia, loss of appetite, constipation, severe abdominal pain, antisocial behaviors, tenderness, and gradual paralysis in the muscles [3].

Recently, there were many reported methods for removing heavy metals from aqueous solutions such as adsorption, chemical precipitation, membrane filtration, ion exchange, and reverse osmosis [4–6]. However, a removal of metal ion from the aquatic environment are quite difficult, expensive, incomplete, and also could generate a large amount of solid waste. Therefore, a method that is easy to apply, environmentally friendly, biodegradable, and relatively low at cost would be favorable for being developed [7–9]. One of those methods which are relatively effective to conquer of heavy metal pollution problems is developed based on the adsorption method. Generally, adsorption method is held by contacting metals ion solution with the adsorbent and the interaction could occur between the metal ions and the surface of solids which is abundant with functional groups, such as –OH, –NH, –SH and –COOH [10]. Adsorption material that can be developed as biosorbent includes pectin and chitosan.

Pectin is a polysaccharide in the plant middle lamella and primary cell wall that is cross-linked with cellulose and hemicellulose fibers. The pectin polysaccharide is composed of D-galacturonic acid units with α–(1,4) bonds, which constitute the "smooth regions" and has the main functional groups i.e. hydroxyl, carboxyl, amide, and methoxyl. Carboxyl functional groups have been reported to be potential for biosorption of heavy metal ion [11]. Heavy metal ions could react with free carboxyl groups of pectin to form insoluble complexes [6].

Chitosan, a poly(β–1,4)–2–amino–2–deoxy–D–glucopyranose, is one of the common adsorbent utilized in the metal ions removal process. Some studies reported the chemical and physical modifications of chitosan in order to improve the metal ion adsorption properties such as selectivity, capacity, chemical stability in acidic media, and the resistances to the biochemical and also microbiological degradation [12–15]. The imprinting technique was performed to improve the selectivity of adsorbent in bonding with metal ions. This method was carried out using metal ion as a template, then utilizing a crosslinker, and finally releasing the metal ion to form a specific cavity [16–18]. The adsorption process of the imprinted adsorbent is determined by the specificity of ligand, coordination number and geometry, charge and also the metal ion size. Therefore, the imprinted adsorbent supposed to have higher selectivity and adsorption capacity to the certain metal ions and quite stable in acidic media.

This report presented the preparation of the Pb(II) imprinted- CMC–Pec–PEGDE adsorbent by crosslinked the –OH group of pectin and Carboxymethyl Chitosan (CMC) with Poly(ethylene glycol) Diglycidyl Ether (PEGDE) as a crosslinking agent. In the process, Pb(II) ion was used as a template ion, and after the crosslinking process, it was released using a chelating agent. The imprinting technique could preserve the availability of the active groups in both pectin and chitosan so it can adsorb metal ions optimally. Furthermore, the adsorption capacity and selectivity of the adsorbent could be improved. In this study were also investigated the pH and contact time effect to the adsorption of Pb(II) ion on the Pb(II) imprinted-CMC–Pec-PEGDE film, included the kinetics and isotherms adsorption properties.

2.0 METHODOLOGY

2.1 Materials

Chitosan (deacetylation degree around of 75–85%) and Poly(ethylene glycol) Diglycidyl Ether (PEGDE) were purchased from Sigma–Aldrich (Germany). The others chemical i.e. chloroacetic acid, acetone, 37% HCl, fumed HNO_3, pectin from apple peel, NaEDTA, NaOH, ethanol, isopropanol, metals standard solution (Pb) were purchased from E. Merck (Germany).

2.2 Procedure Preparation of Pb(II) Imprinted-CMC-Pec-PEGDE Film Adsorbent

The Pb(II) imprinted–CMC–Pectin–PEGDE adsorbent was prepared according to the previously reported procedure with slight modification [19]. Chitosan(3.0 g) was dispersed in 80 mL isopropanol(0.2 M) and stirred for 30 min. NaOH 40% was added dropwisebfor 30 min and followed by drop by drop for addition of chloroacetic acid in isopropanol. The reaction mixture was stirred at room temperature for 12 h. The mixture was filtered and washed with ethanol and then dried in oven to obtain CMC. The next step 1 g pectin(pec) and 1 g CMC was dispersed in 50 mL acetic acid 2.5 % respectively and homogenized. Pb(II) 500 ppm(25 mL) was added into pec-CMC gel than shaked for 1 h. After that 1 g Poly(ethylene glycol) Diglycidyl Ether (PEGDE) was mixed and shaked for 1 h and filtered, the filtrate analyzed using AAS to detect Pb adsorbed in the adsorbent whereas the gel was washed with distilled water. Desorption of Pb(II)-imprinted pec-CMC-PEGDE gel was done by stirring 25 mL of 0.2 M NaEDTA for 2 h. Gel filtration residue was washed with distilled water. Then 25 mL of 0.05 M NaOH was added to the film further the gel was washed with distilled water and dried at 60°C. Characterization of the functional groups of the synthesized materials was conducted using Fourier Transform Infrared (FT-IR) Spectrophotometer.

2.3 Procedure Interaction of Pb(II) Ion on the Pb(II) Imprinted-CMC-Pec-PEGDE Adsorbent Film Adsorbent

The sorption capacity of adsorbent to metal ions was determined by adding 10 mg of adsorbent into 10 mL of 50 mg/L Pb ion with the variation of pH, contact time, and concentration of Pb(II). For each variation, the solutions were filtered and Pb concentrations were measured by atomic absorption spectrophotometry (Hitachi 170-30 atomic absorption spectrophotometer).

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Pb(II) Imprinted-CMC-Pec-PEGDE Film Adsorbent

FT-IR spectroscopy analysis was carried out to see the functional group attached to the synthesized adsorbent and also to predict the binding interaction of Pb (II) metal ions with the adsorbents (as seen in Figure 1). Actually, in the process of preparation, Pb(II) metal ions will be released subsequently from the adsorbent to form Pb(II) imprinted-CMC-Pec-PEGDE adsorbent. In this work, Pb(II) imprinted-CMC-Pec-PEGDE adsorbent was synthesized through four reaction stages involves: synthesis of CMC–Pectin (CMC-Pec) film; imprinting of Pb(II) ion on CMC-Pec film (CMC-Pec-Pb); Cross-linking of CMC-Pec-Pb with PEGDE to form CMC-Pec-PEGDE-Pb; and releasing of Pb(II) ion to afford Pb(II) imprinted-CMC-Pec-PEGDE adsorbent.

Figure 1 showed the FT-IR spectra of synthesized adsorbent compared to the raw material chitosan **(a)** and pectin **(c)**. Typical characteristics of the hydroxyl group of chitosan and pectin were seen by a broadband at 3464 and 3387 cm^{-1} respectively [20]. The presence of the amide group (–NHCO) on the chitosan was observed at a wave number of 1636 cm^{-1}. Meanwhile, the stretching vibration of C-O and the methylene group on chitosan was indicated by the absorption band at 1080 and 2924 cm^{-1} respectively. The presence of absorption peak at 1751 cm^{-1} from the FT-IR spectra of pectin indicate the presence of C=O ester group [21]. Furthermore, the band at 1065 and 1628 cm^{-1} corresponded to –CO– group stretching vibration and–COOH group respectively.

The CMC adsorbent **(b)** showed a characteristic peak at 1605 and 1412 cm^{-1} as a proof of the presence of a carboxylic group (–COOH). This result indicates the grafting process of chitosan to attach the carboxylate group, as an active site of the adsorbent for Pb(II) ion, using chloroacetic acid was successful. Generally, FT-IR spectra of the synthesized adsorbent CMC-Pec, CMC-Pec-Pb, CMC-Pec-PEGDE-Pb and Pb(II) imprinted-CMC-Pec-PEGDE showed similar active functional groups to the CMC, pectin, and chitosan as the main compounds. For example, characteristics of carboxylate and amine functional group from CMC was seen at 1760–1700 cm^{-1} and 1657–1550 cm^{-1} respectively. Meanwhile, the absorption peak of –OH group appeared at 3402-3441 cm^{-1} and –COOH group of pectin was shown at 1630–1600 cm^{-1}. On the other hand, the adsorption peak at 2931 cm^{-1} could be assigned as vibration of. –CH–CH group and –CH2 group.

The successful imprinting process of the CMC-Pec with Pb(II) ion was shown by a new peak at 1381 cm^{-1} which are assigned to the binding of the carboxylate group with Pb(II) ion (COO–Pb). Moreover, the binding interaction of the Pb(II) ions with the functional group $–COO^{-}$ was shown by the weakening peak at 1600 cm^{-1}. Meanwhile, the crosslinking process of CMC-Pec-Pb with PEGDE resulted in the absorption peak at 1103 cm^{-1} which attributed to the ether C–O as well as the C–C stretches. Characteristics spectra of Pb(II) imprinted- CMC-Pec–PEGDE film was indicated by the appearance of a peak at 1628 cm^{-1}, which also seen on stage b and c when Pb(II) ion was separated from the carboxylate group. In addition, the reappearance of $–COO^{-}$ ion indicated by a peak at 1450 cm^{-1}.

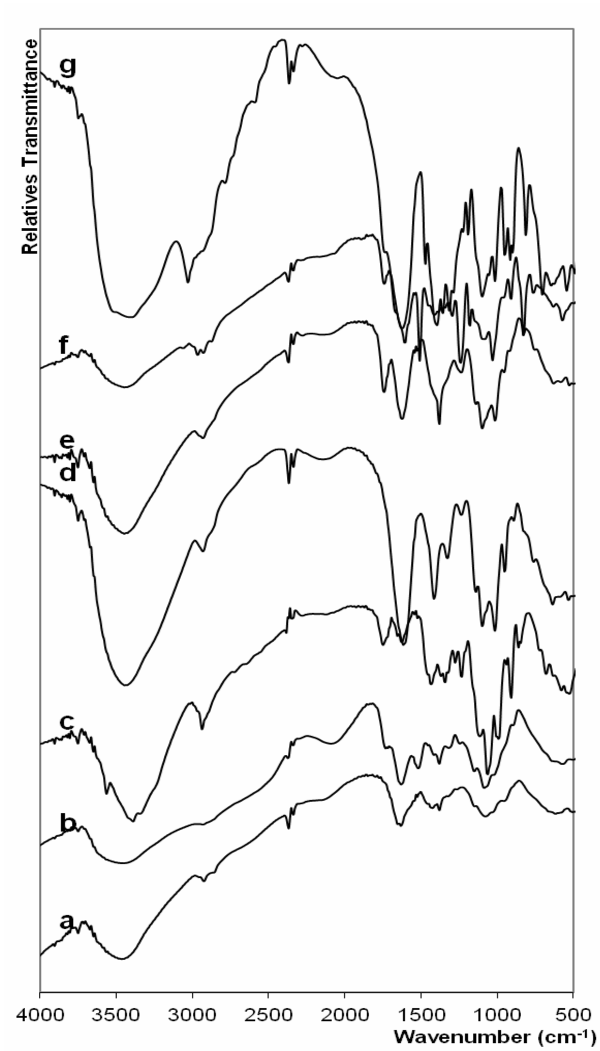


Figure 1 FT-IR spectra of Chitosan (a), CMC (b), Pectin (c), CMC-Pec (d), CMC- Pec-Pb (e), CMC-Pec–PEGDE–Pb (f), and Pb(II) imprinted-CMC–Pec– PEGDE film (g)

3.2 Adsorption Kinetic of Pb(II) Ion on Pb(II) Imprinted-CMC-Pec-PEGDE Film Adsorbent

The adsorption kinetics of Pb(II) on CMC, CMC-Pec-PEGDE, and Pb(II) imprinted-CMC-Pec-PEGDE adsorbents were studied at various contact times and at optimum pH of 5. The profile of the contact time effect on the adsorption of Pb(II) ions was shown in Figure 2. Initially, the adsorption of Pb(II) (in mg Pb(II)/g adsorbent) is quickly increased due to the unoccupied most of the adsorbent active sites. Adsorption equilibrium was reached at 180 min after contact with the adsorbent, while no adsorption changes occurred on a longer contact time on CMC and CMC-Pec-PEGDE adsorbents. Otherwise, adsorption of Pb(II) on Pb(II) imprinted-CMC-Pec-PEGDE adsorbent is decreased because of the Pb (II) ions are still occupying the cavity encounter desorption where Pb (II) ions were contacted to the adsorbent.

The effect of contact time on the adsorption capacity of Pb(II) ion on CMC, CMC-Pec-PEGDE, and Pb(II) imprinted-CMC- Pec-PEGDE was shown in Figure 2.

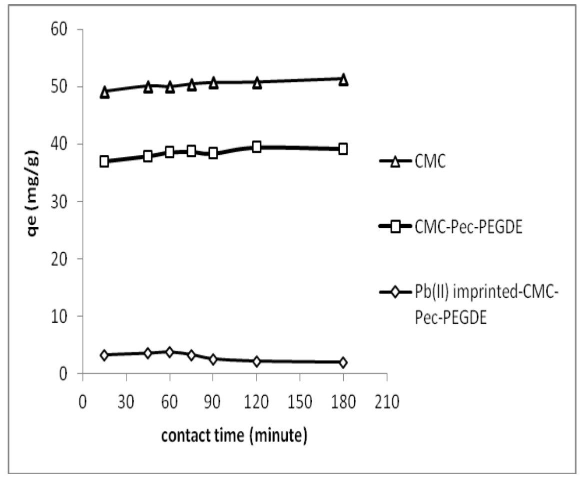


Figure 2 Effect of contact time (min) on adsorption capacity (qe) (mg/g) of Pb(II) ion on CMC, CMC-Pec-PEGDE, and Pb(II) imprinted-CMC- Pec-PEGDE

The mechanism of sorption kinetics was determined by investigating two kinetics models, which then being used to test the experimental data. Adsorption kinetics was studied by modeling the data into pseudo first-order kinetics equation (Lagergren) and pseudo second order kinetics equation (Ho) [21]. Pseudo first-order (i) and pseudo second order (ii) kinetics equation are formulated as follows:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad \text{(i)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \text{(ii)}$$

where q_e and q_t are the sorption capacity at equilibrium (mmol g^{-1}) and at time t (min). Meanwhile, k^1 is a pseudo first order rate constants (min^{-1}) and k^2 is a rate pseudo second order constant (g $mmol^{-1}$ min^{-1}).

Table 1 Kinetic parameters of Pb(II) adsorption onto CMC, CMC-Pec-PEGDE and Pb(II) imprinted-CMC-Pec-PEGDE

Adsorbent	Pseudo-order 1		
	q_{e1} (mmol g^{-1})	k_1 (L min^{-1})	R^2
CMC	5.98×10^{-5}	5.5×10^{-3}	0.995
CMC-Pec- PEGDE	3.11×10^{-5}	5.0×10^{-3}	0.882
Pb(II) - CMC-Pec-PEGDE	2.35×10^{-4}	6.8×10^{-3}	0.402

Adsorbent	Pseudo-order 2		
	q_{e2} (mmol g^{-1})	k_2 (g $mmol^{-1}$ min^{-1})	R^2
CMC	1.2031	1.110	1
CMC-Pec- PEGDE	20.165	0.884	0.999
Pb(II) - CMC-Pec-PEGDE	1.,804	5.028	0.997

The results of the evaluation of kinetic constants of the adsorption are presented in Table 1. It is noticeable that the adsorption of Pb(II) ions on CMC and CMC-Pec-PEGDE adsorbent fit well with the pseudo-second-order kinetic equation while on Pb(II) imprinted-CMC-Pec-PEGDE appropriate with the pseudo-first order kinetic equation. This result could be explained from the correlation coefficient (R^2) for each adsorbent.

All of the three film adsorbent, CMC, CMC-Pec-PEGDE and Pb(II)-CMC-Pec-PEGDE were well-suited with a pseudo-second-order kinetic model with an R^2 value of 1.0, 0.999 and 0.997 respectively. Pseudo-first order kinetic was required when the adsorption processes are controlled by hydrogen bonding between the adsorbent and the adsorbate and by processes of electrostatic adsorption. Meanwhile, pseudo-second order kinetic was required when the adsorption processes are controlled by chemical bonding between adsorbent and adsorbate [22]. Therefore, the adsorption mechanism of Pb(II) ion by three adsorbent, CMC, CMC-Pec-PEGDE and Pb(II) imprinted CMC-Pec-PEGDE would fit with the combination of chemisorption and physisorption, e.g. chelation and electrostatic adsorption.

3.3 Adsorption Isoterm of Pb(II) Ion on Pb(II) Imprinted-CMC-Pec-PEGDE Film Adsorbent

Influence of pH on Adsorption

The pH of aqueous solution is a very important factor that has a great impact on sorption of heavy metal ions. The influence of pH on adsorbents are illustrated in Figure 4. The structure of chelating groups can be changed by protonation at different pH values. The optimal adsorption occur on pH 5, made functional group have negative charge and able to bind metal ions. In the higher pH, Pb(II) ions precipitated become $Pb(OH)_2$ that can't be adsorbed and therefore the adsorption ability decrease because adsorption process takes place simultaneously with the precipitation process. The influence of pH media on the adsorption capacity of Pb(II) ion on CMC, CMC-Pec-PEGDE, and Pb(II) imprinted-CMC-Pec-PEGDE was shown in Figure 3.

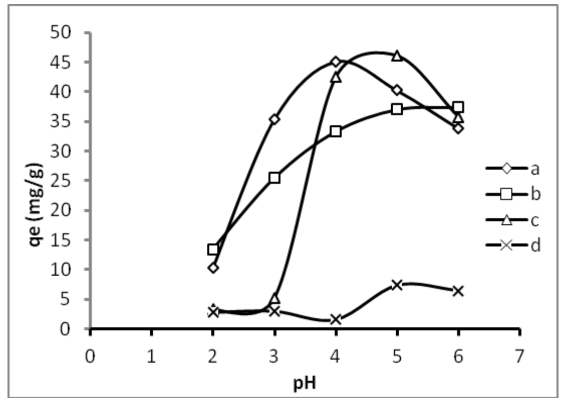


Figure 3 Effect of pH media on adsorption capacity (qe) (mg/g) of Pb(II) ion on a. Pectin, b. Chitosan, c. CMC and d. Pb(II) templated CMC-Pec-PEGDE

Adsorption isotherm describes the correlation between the concentration of solute (Pb(II) ions) in solution and total of adsorbed solute on the adsorbent when the two phases reach the equilibrium stage. The equations that often used to determine the adsorption isotherm are Langmuir, Freundlich, and Langmuir-Freundlich models. In this study, Langmuir and Freundlich adsorption isotherm models were considered to describe the interaction between the solute and the adsorbent. Table 2 presented the related parameters of Langmuir and Freundlich isotherm to the adsorption of Pb(II) using CMC, CMC-Pec-PEGDE and Pb(II) imprinted-CMC-Pec-PEGDE adsorbents.

Table 2. Parameters of Langmuir and Freundlich adsorption isotherm of Pb(II) using CMC, CMC-Pec-PEGDE and Pb(II) imprinted-CMC-Pec-PEGDE

Adsorbent	Isoterm Adsorption			
	b (mol/g)	K (L/mol)	R2	ΔG (kJ/mol)
CMC	1.638×10^{-3}	10310.8	0.69	23.049
CMC-Pec-PEGDE	6.878×10^{-1}	21069.6	0,98	24.831
Pb(II) - CMC-Pec- PEGDE	4.0×10^{-2}	47.801	0.07	9.645

Adsorbent	Pseudo Second Order		
	q_{e2} (mmol g^{-1})	k_2 (g $mmol^{-1}$ min^{-1})	R^2
CMC	2.187	2.053	0.48
CMC-Pec-PEGDE	2,044	1.132	0,95
Pb(II) - CMC-Pec- PEGDE	0.98	0.524	0.88

Based on Table 2, the adsorption of Pb(II) using Pb(II) imprinted-CMC-Pec-PEGDE adsorbent gave a better fit to the Freundlich adsorption isotherm due to its higher R^2 value (0.883) than the Langmuir. It is clearly revealed that the interaction between Pb(II) with Pb(II) imprinted-CMC-Pec-PEGDE film adsorbent probably occurs in multi-layers. On the other hand, the adsorption of Pb(II) using CMC and CMC-Pec-PEGDE film adsorbent were suited to the Langmuir isotherm adsorption model with an R^2 value of 0.691 and 0.998 respectively. The interaction between Pb(II) metal ions with these two adsorbents is a chemical adsorption where the adsorption occurs at the active sites of the adsorbent. This result indicates that grafting and the cross-linking process of chitosan and pectin might produce the homogeneous active sites on the surface of the adsorbent that may be dominated by carboxylate groups. The grafting process of chitosan with chloroacetic acid also could improve the active site of adsorbent where the carboxylate groups on the CMC and CMC-Pec-PEGDE are able to bind well with Pb(II) ion. Furthermore, a combination of chloroacetic acid- grafting and PEGDE-cross-linking process to afford CMC-Pec-PEGDE adsorbent have been proven could increase the adsorption of Pb(II) ion.

Adsorption energy (E_{ads}) of CMC, CMC-Pec-PEGDE, and Pb(II) imprinted-CMC-Pec-PEGDE adsorbent toward Pb(II) ions could be calculated with the following equation:

$$E_{ads} = -\Delta G° = RT \ln K \qquad \text{(iii)}$$

where R is the general gas constant (8.314 J K^{-1} mole), T is the absolute temperature (K), and ΔG° is Gibbs energy (kJ mol^{-1}). In general, physisorption free energy (ΔG°) is lower than -20 kJ mol^{-1}, chemisorption is at a range of -80 to -400 kJ mol^{-1}, while the physisorption along with chemisorption is at a range of -20 to -80 kJ mol^{-1} [25]. In Table 2, ΔG° value for adsorption of Pb(II) ion on CMC, CMC-Pec-PEGDE and Pb(II) imprinted- CMC-Pec-PEGDE adsorbents are in order of -23.1, -24.8 and -9.6 kJ mol^{-1}. This result means that the adsorption of Pb(II) onto Pb(II) imprinted- CMC-Pec-PEGDE involves a physisorption whereas of CMC and CMC-Pec-PEGDE incriminate a physisorption and chemisorption simultaneously. This finding also suggests that the crosslinking process of PEGDE to pectin and CMC increases the strength of the interaction between Pb(II) and the adsorbent.

4.0 CONCLUSION

Adsorption kinetic and equilibrium parameters of Pb(II) imprinted-CMC-Pec-PEGDE film as biosorbent of Pb(II) were obtained in a batch system. Dependent variables of the adsorption capacity of Pb(II) were found to be the Pb(II) ion concentration, contact time and pH of the Pb(II) solution. An increasing of the initial Pb(II) concentration lead to the increasing of the adsorption capacity of Pb(II) on Pb(II) imprinted-CMC-Pec-PEGDE film adsorbent at the optimum contact time (at 60 min) and optimum pH of 5.

The experimental data revealed the adsorption kinetics of CMC and CMC-Pec-PEGDE adsorbent were fitted well to the second-order kinetic while Pb(II) imprinted-CMC-Pec-PEGDE was first-order kinetic models. This result indicates the adsorption of Pb(II) on CMC and CMC-Pec-PEGDE controlled by the chemisorption process, whereas on Pb(II) imprinted- CMC-Pec-PEGDE by physisorption. The work also revealed that the Pb(II) ion uptake could be well described by the Langmuir and Freundlich adsorption model. The adsorption isotherm of CMC and Pec-CMC-PEGDE adsorbents with respective ΔG° of 24.8 and 23.1 kJ mol^{-1} were followed Langmuir models, while the Pb(II) imprinted- CMC-Pec-PEGDE was Freundlich isotherm model with ΔG° of 9.6 kJ mol^{-1}.

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