Kinetic and thermodynamic biosorption of Pb(II) by using a carboxymethyl chitosan–pectin–BADGE–Pb(II)-imprinted ion polymer adsorbent

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Abstract. Pb(II)-imprinted pectin-carboxymethyl chitosan-BADGE or Pb(II)-CPB was synthesized by mixed pectin (Pec) and carboxymethyl chitosan (CC) and then crosslinked with a crosslinking agent bisphenol A diglycidyl ether (BADGE) to form a stable adsorbent and resistant to acidic media. As a first step, the synthesis was performed by reacting the –OH group among Pec and CC with BADGE to form CPB. The Pb(II) ion was then imprinted with the Pec–CC gel and formed Pb(II)-CPB. Furthermore, the release of Pb(II) ions from the adsorbent was performed using the chelating agent, Na_2EDTA. The kinetic and thermodynamic equilibrium of the batch sorption of Pb(II) onto Pb(II)-CPB were investigated. The results of this study showed that the adsorption process of the Pb(II)-CPB adsorbent could be well described by the pseudo-second order model. The thermodynamic biosorbent in adsorption of the Pb(II) ion follows Freundlich isotherm. The adsorption energy of the adsorbent was 15.59 kJ mol^{-1}. This proves that the mechanism process of the adsorbent to Pb(II) ions occurs by physical adsorption. The Pb(II)-CPB adsorbent shows a significantly higher capacity compared to Pec and chitosan. Adsorption capacity of Pb(II)-CPB was 664.44×10^{-3}. The Pb(II)-CPB adsorbent has higher selectivity on Pb^{2+} ions compared to Pec and CC with the adsorption selectivity order Pb(II)/Zn(II) < Pb(II)/Cu(II).

Keywords. CC; Pec; Pb(II)-CPB adsorbent; Pb(II); adsorption selectivity.

1. Introduction

Environmental issues involving heavy metal pollution are related to the excessive use of lead (Pb) materials by human activities, such as mining, smelting and their various uses in the industry. Pb is a cumulative toxic heavy metal that has multiple adverse effects on body systems, including the central nervous system, kidneys, liver and reproductive system. Pb poisoning is characterized by symptoms of anemia, muscle weakness, insomnia, headache, dizziness, irritability and hallucinations. Pb exposure may also cause nephropathy and chronic renal failure [1]. Pb is a dark grey powder mainly used as the raw material for batteries and ammunition, in paint making components, tetraethyl lead plants, radiation shields, pipe layers, cable wrappers, ceramic glass, electronic goods, tubes or containers and also in brazing processes.

There are a number of different waste treatment technologies available for the treatment of metal-contaminated wastewater, including filtration, precipitation and adsorption. The utilization of low-cost adsorbents is one method of waste treatment that widely applied recently. Adsorption is the interaction of a substance (molecule or ion) on the surface of the adsorbent. The mechanism of application can be distinguished into physical and chemical sorptions. In the physisorption process, adsorbates binded by the adsorbents held by van der Waals forces [2]. The molecular bond is very weak and the energy involved in the physical adsorption is < 20 kJ mol^{-1} [3].

Pectin (Pec) is a natural substance present in the primary cell walls of terrestrial plants and the main component of the middle lamella in plants cells. It is an anionic polysaccharide and composed of a-(1,4)-linked D-galacturonic acid [4]. Pec has many active groups such as hydroxyl, carboxyl, amide and methoxy [5]. Recently, Pec is widely used across many fields of industries especially in food, pharmaceutical and cosmetics, and it also used as an alternative biosorbent material for heavy metal remediation [6,7]. The functional groups which can be used to bind heavy metals are especially hydroxyl groups [8].

Besides Pec, the other biomaterial that has significant attention as metal biosorbent is chitosan (CS). CS is a natural biopolymer synthesized from crustacean and its adsorption properties are primarily due to the presence of amine (–NH$_2$) and hydroxyl (–OH) which are the main reactive groups for metal ions. However, the main drawback of CS is its poor solubility at physiological pH, i.e., neutral pH. Otherwise,
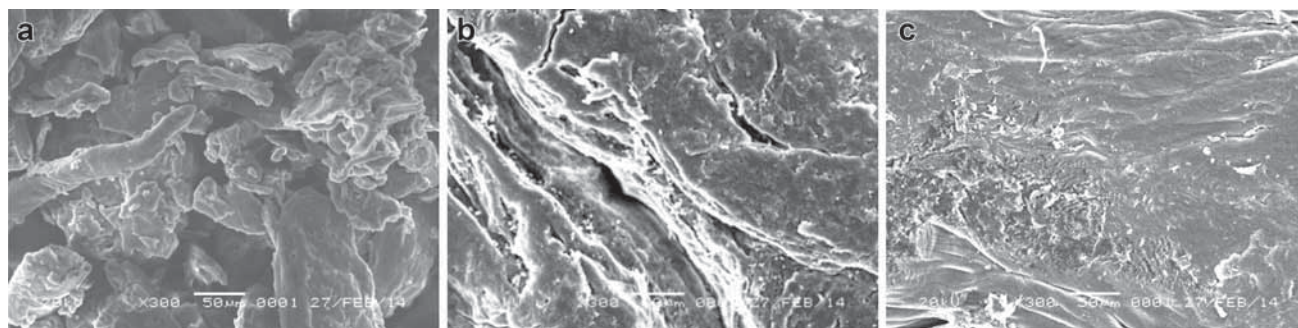
Figure 1. SEM images of (**a**) Pec, (**b**) CS and (**c**) CC.

CS is highly soluble in acidic solution, such as acetic acid and dilute HNO_3, HCl and $HClO_4$, in which the number of amine groups that are active groups for metal will be reduced. Crosslinking is a common method to enhance the chemical stability of CS under acidic conditions. Reagents such as glutaraldehyde, epichlorohydrin, chloromethyl oxirane, polyethylene glycol and ethylene diamine diglycidyl ether are several suitable cross-linking agents for CS. Crosslinked CS has an improved stability and solubility and thus also has wider applicability as a metal adsorbent in the environment [9].

2. Materials and methods

2.1 *Materials*

CS with a deacetylation degree of 75–85%, local Pec, bis phenol A diglycidyl ether (BADGE) (Sigma-Aldrich, Germany), chloroacetic acid, acetone, sodium hydroxide, ethanol and Pb(II) standard solution were purchased from E Merck (Germany).

2.2 *Procedure*

2.2a *Preparation of adsorbent*: Three grams CS was dissolved in 80 ml of isopropanol and 28 ml of sodium hydroxide (40%, w/v) was added carefully drop by drop. The solution was stirred for 30 min. A total of 7.65 g of chloroacetic acid was added and stirred for 12 h. The solution mixture was filtered and washed with methanol and the residue was dried using an oven at 600°C for 3 h to form carboxymethyl chitosan (CC). The obtained product was characterized using an infrared (IR) spectrophotometer [10]. Furthermore, CC and Pec were synthesized to form a Pb(II) imprinted CC-Pec-crosslink adsorbent. One gram of each CC and Pec was dispersed in 50 ml 2.5% acetic acid and it was homogenized and allowed to stand for 24 h. Twenty-five milligram Pb(II) ion (500 ppm) was added into CC-Pec gel and shaked for 1 h. Furthermore, 1 g of BADGE (50 ml) was mixed and shaked for 1 h and filtered. The filtrate was analysed using atomic adsorption spectroscopy (AAS) to determine the amount of Pb(II) absorbed in the adsorbent.

2.2b *Desorption study*: Desorption of Pb(II)-imprinted CPB gel was conducted using 0.2 M NaEDTA (25 ml) by stirring for 2 h. The gel was filtered with Whatman filter paper, and the filtrate was analysed using AAS to determine the amount of Pb(II) desorbed. The gel residue was washed with distilled water. Then, 25 ml of 0.05 M sodium hydroxide was added to the gel Pb(II)-imprinted CPB, further, the gel was washed with distilled water and dried at 60°C, and the functional group was characterized by IR and the surface morphology of the adsorbent was determined using a scanning electron microscope (SEM).

2.2c *Study of sorption capacity*: The adsorbent sorption capacity toward Pb(II) ions was determined by reacting 10 mg of Pb(II)-CPB adsorbent with 10 ml of 50 mg l^{-1} Pb(II) ion upon the variations of pH, contact time and initial concentration of Pb(II). Furthermore, Pb adsorbed was analysed using AAS.

2.2d *Study of adsorption selectivity*: Ten grams of the adsorbent was added into 10 ml of solution containing Pb(II)/Cu(II) and Pb(II)/Zn(II) ion pairs with a molar ratio of 1:1 at pH 5. Adsorption was carried out with stirring for 60 min. The mixture was filtered and the filtrate was analysed to determine the metal ion content with AAS.

3. Results and discussion

3.1 *Analysis of surface morphology and elemental content*

Analysis of the surface morphology with SEM aims to see the microstructure of the surface of the adsorbent, while the analysis of elemental content in the adsorbent is determined with energy-dispersive X-ray spectroscopy (EDX). The morphology of Pec by SEM analysis shows a coarse structure distributed into the particles. The morphology of CS and CC is much smoother than that of the Pec surface, which is flake forming, fibrous and non-porous [11]. The surface morphology of SEM of Pec, CS and CC is shown in figure 1.

The Pb(II)-CPB adsorbent is prepared by two stages of reaction. In the first step, Pb(II) ions were added as imprinting
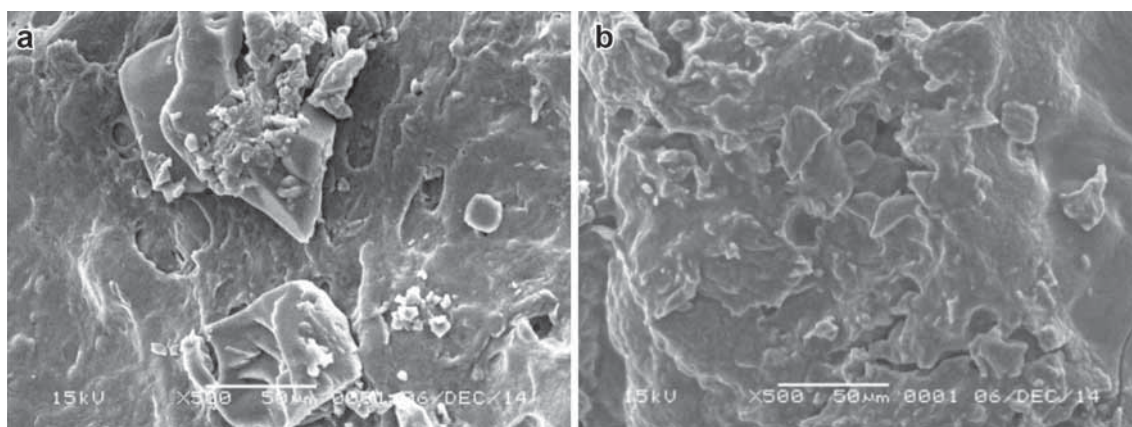
Figure 2. SEM images of the Pb(II)-imprinted CPB adsorbent: (**a**) stage 1 and (**b**) stage 2.

Table 1. Adsorption kinetic parameters of Pb(II) by CS, CC and Pb(II)-CPB.

	Parameter					
	Pseudo-first-order			Pseudo-second-order		
Adsorbent	$q_e^1 \times 10^{-6}$ (mmol g^{-1})	$k_1 (\times 10^{-3})$ (1 min^{-1})	R^2	q_e^2 (mmol g^{-1})	k_2 (g mmol min^{-1})	R^2
Pec	79.7	1,5	0,676	10.39	4.48	0,896
CS	6.39	3,4	0,995	1.204	0.60	1,000
CMC	59.8	5,5	0,676	1.203	1.11	1,000
Pb(II)-CPB	0.180	3,8	0.349	2.178	10.09	0,990

ions into CC-Pec gel, and in the second step, Pb(II) ions were released using the chelating agent Na$_2$EDTA. The image of the adsorbent during the preparation process in both stages is shown in figure 2. The Pb(II)-CPB morphology of the adsorbent looks smoother, porous and homogeneous. In the process of imprinting Pb(II) ions in step 1, CC-Pb-BADGE shows a finer surface with the presence of rounded cracks in several parts. The rounded cracks are possible as Pb(II) ions trapped in the CC-Pec crosslinked BADGE adsorbent. This conclusion is reinforced by EDX analysis which shows the presence of Pb(II) besides C, N and O atoms.

In the second step, Pb(II) ions were dissipated using Na$_2$EDTA and the obtained Pb(II)-IIP adsorbents exhibit a coarser surface due to porosity. The formed cavities are due to the release of previously bound Pb(II) ions. The Pb(II) ion was bonded in imprinted processes, which is released by Na$_2$EDTA, and produced cavities on the adsorbent. The result of elemental analysis by EDX also shows that almost all the peaks of Pb(II) were lost and the remaining content of Pb(II) was 2.02%. The SEM–EDX analysis of the NIP material shows that there were cavities as Pb-IIP, but it has a flat surface.

3.2 *Adsorption kinetics*

The adsorption mechanism is studied by modelling the data of contact time variation into the pseudo-first-order kinetics equation (Lagergren) and pseudo-second-order (Ho).

The obtained adsorption kinetic parameters are shown in table 1.

Table 1 shows the coefficient correlation (R^2) of pseudo-second-order kinetics is greater than that of the pseudo-first-order; this shows that the pseudo-second-order kinetics is more appropriate for the adsorption of Pb(II) by CS, CC and Pb(II)-CPB adsorbents. The pseudo-second-order kinetics explained that the adsorption process between the adsorbent and adsorbate is controlled by the chemical bonding mechanism. It involves in sharing of covalent bonds or exchange of electrons between the adsorbent and the Pb(II) ion. The rate constant (k_2) of Pb(II)-CPB shows the greatest value, due to the formation of cavities in the adsorbent, it facilitates that the Pb(II) ion to reach the active site. Whereas the CS adsorbent has the smallest value, because of its structure which is rigid and not well organized yet.

3.3 *Effect of the initial concentration of Pb(II) ions on Pb(II)-ion adsorption by Pec, CS, CC and Pb(II)-imprinted CPB adsorbent*

Figure 3 shows the effect of the initial concentration of Pb(II) on effectiveness of Pec, CS, CC and Pb(II)-imprinted CPB adsorption. From figure 3, it can be seen that the adsorbed Pb(II) ion increases sharply with the increase the Pb(II) ion concentration. At higher concentrations, the increase of the

adsorbed Pb(II) ions slows down, the active groups of adsorbents become more saturated and finally, no more active group of adsorbents can bind Pb(II) ions. It is caused because the active surfaces of the adsorbent have been saturated with the adsorbate and have reached their respective adsorption capacity.

Table 2 shows that the modification of the Pec–CS adsorbent by the imprinting method of the Pb(II) ion (Pb(II)-CPB) improves the adsorption capacity compared with Pec, CS or CMC. The adsorption capacity of Pb(II) ions by Pec, CS, CC and Pb(II)-CPB were 0.58×10^{-3}; 1.46×10^{-3}; 1.76×10^{-3} and 6644 mg g^{-1}, respectively. CS has a hydroxyl and an amine functional group.

The modification process by the ion imprinting method of Pb(II)-CPB has the highest adsorption capacity of the Pb(II) ion when compared with Pec, CS and CC. The Pb(II)-CPB has amine and carboxylic active groups which can increase adsorption capacity, in addition many cavities were formed to fit the size to mould Pb(II) ions. These cavities led Pb(II) ions more easily to interact with the active site of the adsorbent, thus increasing the adsorption capacity. The modified Pec–CS adsorbent, both by crosslinking methods or imprinting of Pb(II), was able to increase the adsorption ability of Pb(II), and also to improve the stability in the acid or base media. Both properties were very important when an adsorbent is used in different fields of application, such as industry.

3.4 Adsorption selectivity

In this study, the selectivity of adsorption was studied by simultaneously interacting Pb(II) ions with their partner ions. As a pair ion, Cu(II) and Zn(II) ions were selected. The number of adsorbed metal ions is determined by the selectivity coefficient (α). The results show an increase in the selectivity of Pb(II)/Cu(II) on Pb(II)-CPB. The results of the selectivity coefficient of Pb(II) ions toward Cu(II) and Zn(II) ions after adsorption by the adsorbent membrane are shown in figure 4.

To determine the amount of the adsorbed metal ions, the distribution ratio and selectivity coefficient in the adsorption process of metal ions on a membrane adsorbent used the equations following:
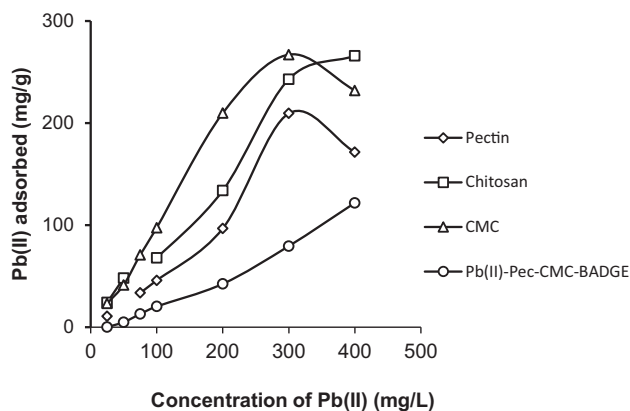
$$Q = (C_0 - C_e)V/M, \tag{1}$$
$$E = (C_0 - C_e)/C_e, \tag{2}$$
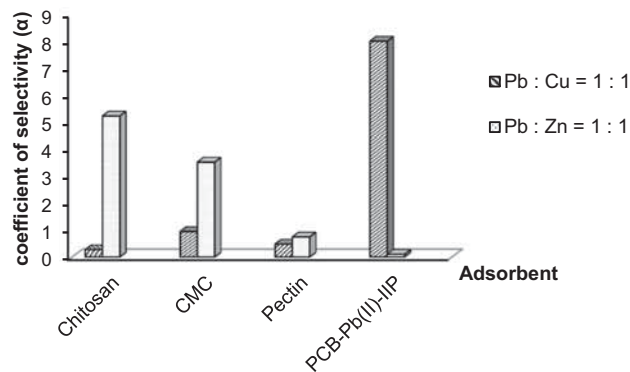$$D = Q/C_e, \tag{3}$$
$$\alpha = DM_1/DM_2, \tag{4}$$
$$\alpha_r = \alpha_1/\alpha_2, \tag{5}$$

Figure 3. Effect of the initial concentration of Pb(II) ions in solution toward effectiveness of Pb(II) adsorption by Pec, CS, CC and Pb(II) imprinted CPB.

Figure 4. Adsorption selectivity of Pb(II)/Zn(II) and Pb(II)/Cu(II) on the adsorbent.

Table 2. Isotherm Langmuir dan Freundlich parameter.

| | Parameter | | | | | | |
| | Langmuir | | | | | Freundlich | |
Adsorbent	$b \times 10^{-3}$ (mg g^{-1})	$K \times 10^3$ (l mmol^{-1})	ΔG (kJ mol^{-1})	R^2	n	Kf (mg g^{-1})	R^2
Pec	0.58	2.73	25.48	0.944	1.46	2.49	0.738
CS	1.46	2.24	19.2	0.616	1.22	1.17	0.971
CC	1.76	9.38	22.8	0.923	2.18	1.51	0.904
Pb(II)-CPB	664.4	0.518	15.59	0.08	1.04	1.76	0.571

Table 3. Selectivity coefficient value (α) on the adsorbent.

Adsorbent	Selectivity coefficient (α)	
	Pb(II)/Zn(II)	Pb(II)/Cu(II)
Pec	0.74	0.48
CC	3.54	0.95
PCB-Pb(II)-IIP	0.06	5.06

where Q is the amount of metal adsorbed (mg g^{-1}), C_0 and C_e are the initial and equilibrium concentrations of the metal ion (mg l^{-1}), W is the adsorbent mass (g), V is the metal ioning solution volume (l), $E(\%)$ is the extraction percentage, D is the distribution ratio (l g^{-1}), α is the selectivity coefficient, α_r is the relative selectivity coefficient and α_n is the selectivity factor of the ionic imprinted and non-imprinted adsorbents [12]. The complete results of the selectivity of metal ions on all adsorbents are presented in table 3.

From table 3, it can also be seen that the imprinted ion (CPB-Pb(II)-) adsorbed Pb(II) ions selectively competing with Cu(II) ions. The selectivity coefficient (α) of the adsorbent in adsorption of Pb(II) ions in competition with Zn(II) is considered selective if the α value is >1. The selectivity coefficient <1 indicates that the adsorbent is not selective. The results showed that the CPB-Pb(II)- membrane had a high coefficient value. This proved that the modified membrane adsorbent was not only made CS and Pec resistant to acidic solutions, but also increased the selectivity of Pb(II) ions.

4.   Conclusion

The Pb(II)-CPB biosorbent was prepared by imprinting Pb(II) ions into CC–Pec gel, after the addition of BADGE, the Pb(II) ion was released using Na$_2$EDTA. Adsorption kinetic and equilibrium parameters of the biosorbent toward Pb(II) take place in a batch system. The kinetic adsorption of Pec, CS, CC and Pb(II)-CPB adsorbents in adsorption to the Pb(II) ion follows the pseudo-second-order kinetics equation. The adsorption process of CC and Pec adsorbents was fitted with the Langmuir adsorption model, whereas CS and Pb(II)-CPB adsorbents were fitted with the Freundlich adsorption model. The energy ($\Delta G°$) adsorption of Pec and CC was 22.4 and 22.8 kJ mol^{-1}, respectively, which indicates that the adsorption process shows chemical adsorption behaviour. The energy ($\Delta G°$) adsorption of CS and Pb(II)-CPB was 19.2 and 15.59 kJ mol^{-1}. It indicates that the adsorption of CS and Pb(II)-CPB adsorbents comes off by physical behaviour. The Pb(II)-CPB adsorbent has higher selectivity to the Pb^{2+} ion when compared to the Pec and CC adsorbents with the adsorption selectivity order Pb(II)/Zn(II) < Pb(II)/Cu(II), whereas the adsorption selectivity order for Pec and CC is Pb(II)/Cu(II) < Pb(II)/Zn(II). It can be concluded that the Pb(II)-CPB adsorbent can be used as the SPE material for preconcentration or separation of the Pb(II) ion from the solution.

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