

CADMIUM ADSORPTION ON CHITOSAN/CHLORELLA BIOMASS SORBENT PREPARED BY IONIC-IMPRINTING TECHNIQUE

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ABSTRACT

Ionic-Imprinted Chitosan/Chlorella biomass sorbent (IICCb) has been synthesized for selective adsorption of Cd(II) adsorption. IICCb was prepared by coating Cd(II)-complexed-chitosan hydrogel on the biomass surface followed by cross-linking procedure. Cd(II)-imprinting ions were then eluted using Na₂EDTA solution to provide a specific template for binding sites of Cd(II). Batch adsorption was carried out as function of initial pH, contact time, and initial concentration of the Cd(II) solution. Result showed that the optimum adsorption of Cd(II) was found at pH 4-6. Study of pseudo-second order kinetic showed that the adsorption of Cd(II) on IICCb went faster than that on Ionic-Imprinted Chitosan (IIC) or Non-Imprinted Ionic Chitosan/Chlorella sorbent (NIICCb). The maximum Cd(II) adsorption capacity as obtained from Langmuir adsorption isotherm was found to be 53.76 mg/g on IICCb, that was comparatively higher than that on IIC (44.44 mg/g) or on NIICCb (51.02 mg/g) adsorbent.

Keywords: *Ionic-Imprinted Chitosan/Chlorella biomass sorbent; adsorption; Cd(II)*

ABSTRAK

Biosorben Kitosan Tercetak Ion pada Biomasa Chlorella (IICCb) telah disintesis untuk adsorpsi selektif Cd(II). IICCb dibuat dengan cara melapiskan hidrogel kitosan-terkompleks-Cd(II) pada permukaan biomasa dilanjutkan dengan prosedur crosslinking. Ion-ion umpan Cd(II) dielusi menggunakan larutan Na₂EDTA untuk menyediakan templat spesifik bagi situs pengikatan Cd(II). Adsorpsi dilakukan sebagai fungsi pH, waktu kontak dan konsentrasi awal larutan Cd(II). Hasil penelitian menunjukkan bahwa adsorpsi Cd(II) terjadi pada pH optimum 4-6. Studi kinetika pseudo-orde 2 menunjukkan bahwa adsorpsi Cd(II) pada IICCb berlangsung lebih cepat dibandingkan pada Kitosan Tercetak Ion (IIC) atau Kitosan Tidak Tercetak Ion/Biomasa Chlorella (NIICCb). Kapasitas maksimum adsorpsi yang dihitung berdasarkan persamaan isotherm Langmuir menghasilkan nilai sebesar 53,76 mg/g pada IICCb, lebih tinggi dibandingkan pada IIC (44,44 mg/g) atau pada NIICCb (51,02 mg/g adsorben).

Kata Kunci: *Kitosan Tercetak Ion pada Biomasa Chlorella, adsorpsi, Cd(II)*

INTRODUCTION

Cadmium (Cd), together with mercury (Hg) and lead (Pb) are classified as the top three most toxic heavy metal pollutants for environment. There are many sources of industries waste water causing the pollution of cadmium e.g. cadmium electroplating, mining, battery and ceramics [1-3]. Several techniques have been developed to remove those heavy metals from waste water including precipitation, ion exchange, adsorption, membrane process, solvent or solid extraction, etc. These processes are generally complicated, costly and bearing much disposal which makes dangerous to environment. It has been demonstrated that biosorption

is a potential alternative method for removal of heavy metals. Many kinds of biosorbents have been applied for adsorption of heavy metals such as fungi [4-5], sludge [6], bacteria [7], seaweed and algae [8-10]. One of the most popular and potential biosorbent for heavy metal is chitosan. Chitosan or poly (N-acetyl-D-glucosamine) is deacetylated product of chitin that is the second most abundant polysaccharides in nature [11]. Chitosan has been widely applied for removal heavy metal ions in wastewater due to its large content of -NH₂ and -OH groups that can chelate many heavy metal ions such as Cu(II), Cd(II), Zn(II), Ni(II), Co(II), Hg(II), Fe(II), Fe(III) and Cr(III), [12-13]. The main drawback of using chitosan for industrial wastewater

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treatment is its solubility in dilute acids. This problem can be avoided by crosslink chitosan with many kinds of bi/poly-functional agent e.g. glutaraldehyde [14-17], epichlorohydrin [18-21], or ethylene glycol diglycidyl ether (EGDE) [18,22-23]. Crosslinking procedure can improve the stability of chitosan in acid media but the adsorption capacity significantly decreased because most of active sites consumed by crosslinking agent [18,24-25].

Tan et al. [18], Chen et al. [24-25] and Nishad et al. [26] prepared Ionic-Imprinted Chitosan to characterize the adsorption of Ni(II), Cu(II), Zn(II), Pb(II) and Co(II) ions using molecular imprinting method introduced by Ekberg and Mosbach. Ionic-imprinting is an inexpensive technique for preparing adsorbent which has a specific template for ion recognition. By this method, active sites of chitosan were firstly shielded with metal ions before crosslinking them, so the adsorption capacity and selectivity of this adsorbent increased without losing of its stability. All above researchers found that adsorption capacity of ionic-imprinted chitosan to targeted metal ions was significantly increased. The resulting adsorbent could also be regenerated and used again for more than five adsorption-desorption cycle.

Su et al. [27-28] and Li et al. [29] developed this imprinting technique to create a Surface Molecular Imprinted Adsorbent (SMIA) using biomass of *Penicillium Chysogenum* fungi as core material. SMIA prepared by Su et al. does not only possess high selectivity but also avoids the problem of mass transfer. Adsorption capacity of Ni(II) on SMIA reported to be increased almost twice compared to un-treated biomass. According to Su and co-workers, SMIA has combination advantages of chitosan and biomass mycelium, so the resulted SMIA exhibits enhancement of ability and stability that allows reusing it for up to 15 cycles.

In this paper, we report the study of adsorption of Cd(II) by Chitosan/*Chlorella* biomass prepared by surface ionic-imprinting technique, named as Ionic-Imprinted Chitosan/*Chlorella* biomass sorbent (IICCb). This includes synthesis and characterization of imprinted-biosorbent and its application for selective adsorption of the Cd(II) target ions. Utilization of *Chlorella* biomass as support material for ionic-imprinted chitosan is interesting because it is built on the main components of polysaccharide which has some similarities with the chemical structure of chitosan. In the cell wall of biomass, there are chemical compounds with charged functional groups such as carboxyl, phosphate, thio, hydroxyl and amine [30-31]. The combination of abundance and sorption capability of *Chlorella* biomass with the unique properties of imprinted-chitosan hydrogel will provide advantages in terms of high bioavailability, elution of imprinting ions facility, and enhancement of sorption capacity of the resulting biosorbent.

Characterization of Cd(II) adsorption was conducted to assess the effect of initial pH, initial metal ion concentration and contact time on the effectiveness of the IICCb. Selectivity of the resulting biosorbent towards Cd(II) target ions was examined in the solution containing competitor ions of Cu(II) and Cr(III). The sorption mechanism and surface characteristics of biosorbent were investigated using Fourier Transform Infrared Spectrophotometry (FTIR) and Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDAX) analysis.

EXPERIMENTAL SECTION

Materials

The materials used were chitosan medium molecular weight (Sigma), CH₃COOH, CdCl₂·H₂O, Na₂EDTA, HNO₃ and NaOH from Merck, epichlorohydrin 99% from Aldrich, and Whatman No. 42 filter paper.

Biomass of *Chlorella* sp was collected from Lampung Sea Cultivation Bureau (*Balai Budaya Laut Lampung*, Indonesia). Microalgae was washed thoroughly with distilled water, sun dried for 3 days followed by drying at 60 °C for 12 h then grounded on agate stone mortar. The resulted biomass was then sieved by 100-mesh sieve for further use.

Instrumentation

The characteristic of functional groups among adsorbents was confirmed by Fourier-Transform infrared Spectrophotometer (Shimadzu FTIR Prestige-21). The surface morphological image and elemental composition of biosorbents were obtained by scanning electron microscopy-energy dispersive X-Ray (SEM-EDAX JSM 6360 LA) after 300 μ gold plating at accelerating voltage of 15 kV, 0.5 A. The metal solution was analyzed using an atomic absorption spectrophotometer (AAS Model Perkins Elmer 3110).

Procedure

Preparation of Ionic-Imprinted Chitosan/*Chlorella* Biomass Adsorbent (IICCb)

IICCb was prepared according to the reported procedure [18,27-28]. Firstly, 1.0 g chitosan (dry weight) was dissolved in 20 mL dilute acetic acid solution of 2.5% (v/v). Then 10 mL CdCl₂ with concentration of 5000 mg/L was added into the chitosan solution and stirred for 60 min to get an equilibrium adsorption of Cd(II) ions. The complex solution was stayed overnight to remove any bubbles and then 1.0 g (dry weight) of *Chlorella* biomass slowly

added into the hydrogel and mechanically stirred using rotary shaker for about an hour. The mixture was dropped into 1.0 M NaOH (with a little added ethanol) solution to get beads formation and stand for 2 h with stirring before filtered and washed thoroughly until the washing was neutral. Crosslinking procedure was carried out by soaking the beads in epichlorohydrin solution (pH 10) for 12 h at room temperature.

Elution of imprinted-ions

The elution of Cd(II) imprinted ions from adsorbent surface was conducted using solution of 0.2 M Na₂EDTA for 2 h in a rotational shaker. To analyze the role of biomass during elution of imprinting ions, this experiment also compares Cd(II)-complexed chitosan without biomass surface, named Ionic-Imprinted Chitosan (IIC). Regeneration was carried out by dipping the biosorbents into 0.1 M NaOH solution for 1 h. The beads were filtered using vacuum filtration, then washed several times with deionized water until the washings were neutral, after that dried in an oven at 60 °C to get Ionic-Imprinted Chitosan/*Chlorella* biomass hybrid (IICCb) biosorbent. The dry biosorbent was sized by an 80-mesh sieved and stored at a sealed bottle for further use.

Adsorption experiments

The effect of pH was evaluated by determining the Cd(II) adsorbed in the range pH of 2-9. Amount of 0.05 g IICCb adsorbent was added into 10 mL at 100 mg/L Cd(II) solutions, adjusted to desired pH with 0.1 M hydrochloric acid or 0.1 M NaOH solution, and then stirred for 2 h at room temperature. The solution was filtered and its remaining of Cd(II) ion was measured by atomic absorption spectrophotometer.

The adsorption kinetic was studied by mixing 0.05 g (dry weight) adsorbent with 10 mL of 100 mg/L metal solution at pH 5.0 ± 0.2 and shaking them at 120 rpm using a rotational shaker at room temperature. Effect of contact time was evaluated by varying interaction time at 5-240 min. The pseudo-second order kinetics model supported by Ho and Mc.Kay [32] was applied to determine the rate of adsorption.

$$\frac{1}{C_t} = \frac{1}{k_2 C_e^2} + \frac{1}{C_e} t \quad (1)$$

With t is contact time (min), C_e and C_t are concentration at equilibrium and time t , respectively, and k_2 is rate constant of second order adsorption ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$). The adsorption rate constant (k_2) was determined from the intercept of linear curve intercept t/q_t versus t .

Adsorption isotherm study was conducted by mixing 0.05 g (dry weight) adsorbent with 10 mL metal solution with concentrations which varied in the range of 0-500 mg/L (pH 5.0 ± 0.2) and shaking it at 120 rpm for 2 h using a rotational shaker at room temperature. The

relation between varying concentration of metal ions in equilibrium and the number of Cd(II) adsorbed was studied by Langmuir isotherm. Adsorption capacity was calculated based on the equation 2 [19].

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

With C_e is the equilibrium concentration of Cd(II) (mg/L), Q_e is amount of Cd(II) adsorbed per unit weight of adsorbent (mg/g), Q_{max} is the theoretical maximum adsorption capacity (mg/g) and b is the Langmuir adsorption equilibrium constant (L/g). A linearized plot of C_e/Q_e versus C_e gives Q_{max} and b .

Selectivity test

IICCb selectivity towards Cd(II) target ions was studied by competing adsorption in a solution containing a mixture of Cd(II)/Cu(II) and Cd(II)/Cr(III) ions. The volume of each metal ion solution was 10 mL with a concentration of 1.0 mmol/L. Solution containing mixture of metal ions was then interacted with 0.01 g of IICCb adsorbent for 2 h at pH 5. The amount of adsorbed ions, the ratio of distribution, and the coefficient of adsorption selectivity were calculated based on the Equation 3-5.

$$Q = \frac{(C_0 - C_e) V}{W} \quad (3)$$

$$D = \frac{Q}{C_e} \quad (4)$$

$$\alpha_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (5)$$

With Q is the amount of adsorbed ions (mmol/g), C_0 is initial concentration of metal ion (mmol/L), C_e is equilibrium concentration of metal ion (mmol/L), V is volume of solution (mL), W is weight of adsorbent (mg), D is distribution ratio (L/g), and α is selectivity coefficient.

RESULT AND DISCUSSION

Characterization of IICCb

The FTIR spectra of *Chlorella* biomass (Chlo), chitosan beads (Chit), Non-imprinted Chitosan/*Chlorella* biomass (NIICCb), Cd(II)-complexed-Chitosan/*Chlorella* biomass (Cd(II)-CCb) and Ionic-Imprinted Chitosan/*Chlorella* (IICCb) were determined to find out the various functional groups of adsorbents that change during the preparation of IICCb. These spectra are presented in Fig. 1.

The spectra in Fig.1 show the characteristic peaks at 3100-3400 cm^{-1} (overlapping of -OH and -NH₂ stretching), 2924 cm^{-1} (-CH stretching of methyl or methylene) and 1580 cm^{-1} (-NH₂ bending). The spectrum of *Chlorella* biomass (Fig. 1a) shows two

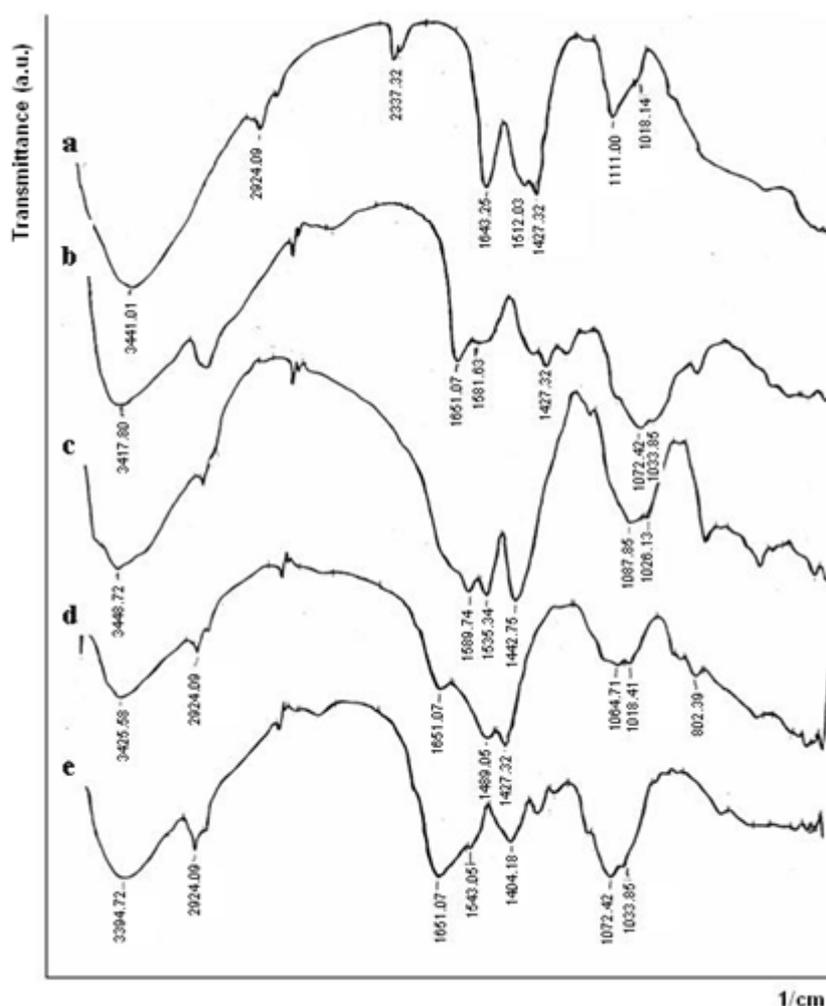


Fig 1. FTIR spectra of (a) Chlo, (b) Chit, (c) NIICCb, (d) Cd(II)-CCb and (e) IICCb

obvious peaks at 1643 cm^{-1} and 1427 cm^{-1} . These peaks are attributed to the stretching of C=O and C-O of carboxyl, the functional group of *Chlorella* biomass that is thought to be the main active sites in the binding of metal ions [31,33]. The free amine group belong to chitosan is confirmed by peak of 1581 cm^{-1} in Fig. 1b. The FTIR spectrum of NIICCb (Fig. 1c) shows characteristic peaks that different from those of chitosan (Fig. 1b) and *Chlorella* biomass (Fig. 1a). The peaks of 3417 cm^{-1} and 1581 cm^{-1} of chitosan shift to 3448 cm^{-1} and 1535 cm^{-1} , while peaks of 1643 cm^{-1} and 1427 cm^{-1} of biomass shift to 1589 cm^{-1} and 1442 cm^{-1} , respectively. The changing of those peaks position indicates that formation of NIICCb composite involves an electrostatic interaction of protonated amines of chitosan and carboxyl groups of biomass.

FTIR of NIICCb (Fig. 1c), Cd(II)-CCb (Fig. 1d) and IICCb (Fig. 1e) show the expected peaks at 1535 cm^{-1} , 1489 cm^{-1} and 1543 cm^{-1} , respectively. The existence of those peaks indicates that chitosan has actually been

coated on the surface of biomass during the preparation of IICCb. Another interesting observation is the considerable shift of the $-\text{NH}_2$ and $-\text{OH}$ stretching and $-\text{NH}$ bending vibration before elution (Fig. 1d) and after elution of Cd(II)-imprinting ions (Fig. 1e). Shifting of those peaks indicates the involvement of $-\text{NH}_2$ and $-\text{OH}$ in the binding of Cd(II) metal ions. Our research confirms the studies conducted by previous researchers that suggest the role of amines and hydroxyl groups of chitosan in the binding of transition metal ions through complex formation mechanism [18-19].

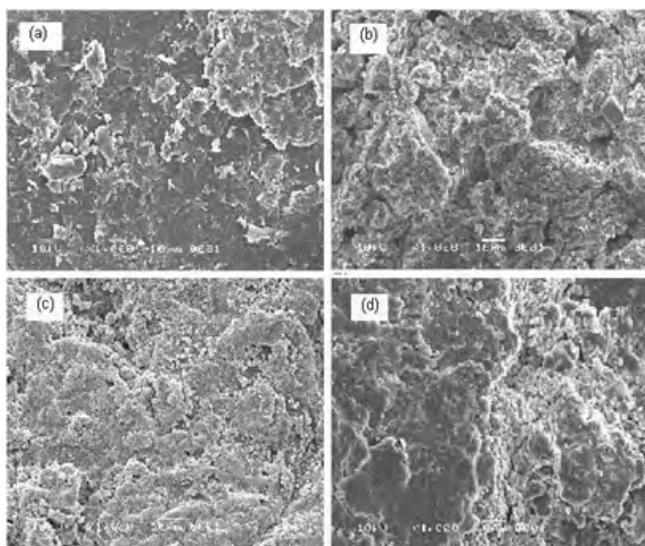
The IICCb, NIICCb, raw chitosan and biomass were also characterized using Scanning Electron Microscopy with energy dispersive X-Ray analysis (SEM-EDAX) to observe the different surface morphology and elemental composition of those materials. The SEM-images and EDAX results are presented in Fig. 2 and Table 1, respectively.

Table 1. Elemental composition of chitosan, *Chlorella* biomass, NIICCb, Cd(II)-CCb, and IICCb

Element	Dispersive energy (keV)	% mass of				
		Chitosan	<i>Chlorella</i> biomass	NIICCb	Cd(II)-complexed CCb	IICCb
C	0.277	44.25	24.16	34.09	27.53	48.07
N	0.392	16.79	-	1.45	-	18.23
O	0.525	38.37	40.85	42.16	22.33	30.37
Na	1.041	0.13	4.38	1.08	8.55	0.49
Mg	1.253	-	20.46	16.91	10.52	1.50
Cl	2.621	0.146	10.15	3.45	28.72	1.34
Cd	3.132	-	-	-	1.34	-

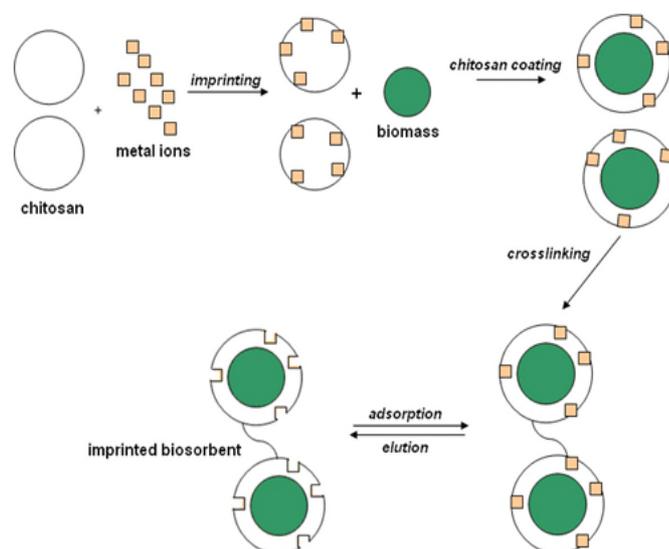
Table 2. Percentage of total Cd(II)-imprinting ions that eluted by 0.2M Na₂EDTA

Adsorbent	Concentration of Cd(II) (mg/L)		% total ion eluted
	initial	after	
Cd(II)-complexed Chitosan/ <i>Chlorella</i>	4989.57	4718.45	94.57
Cd(II)-complexed Chitosan	5145.98	3832.12	73.56

**Fig 2.** SEM images of (a) chitosan, (b) *Chlorella* biomass, (c) NIICCb, and (d) IICCb

The SEM images of chitosan coated *Chlorella* biomass in the form of NIICCb (Fig. 2c) and IICCb (Fig. 2d) physically look more compact than chitosan (Fig. 2a) or biomass (Fig. 2b). In principle, IICCb and NIICCb are composed by two materials i.e. chitosan and *Chlorella* biomass. The interaction of these two materials is expected to increase the density of the resulting composite adsorbent, so that IICCb and NIICCb display better mechanical properties than their constituent materials.

Chitosan and *Chlorella* biomass are mainly composed by C, O, and N elements with addition minerals on biomass composition (Mg, Na, and Cl). The EDAX result showed by Table 1 reveals that Cd(II)-imprinting ions are indeed adsorbed by chitosan adsorbent during the synthesis of IICCb. It is indicated by the presence of Cd element on the composition of

**Fig 3.** Illustration of formation of ionic-imprinted Chitosan/*Chlorella* biosorbent

Cd(II)-CCb complex, and after elution process, this element is no longer found on IICCb composition.

The result of Cd(II) imprinting ions elution which conducted by atomic absorption spectrophotometric method is presented on Table 2. The total percentage of Cd(II) imprinting ions eluted from Cd(II)-complexed chitosan/*Chlorella* biomass is 28.5% higher than that from Cd(II)-complexed chitosan. It is estimated due to difference in the morphology of the two materials. On Cd(II)-complexed chitosan, imprinting ions may be trapped in crosslinking results, so that only about 73% can be leached out using EDTA solution. Coating the hydrogel imprinted-chitosan on the biomass surface is believed can improve the arrangement of the active sites of the adsorbent which makes it much easier for eluting the imprinting ions.

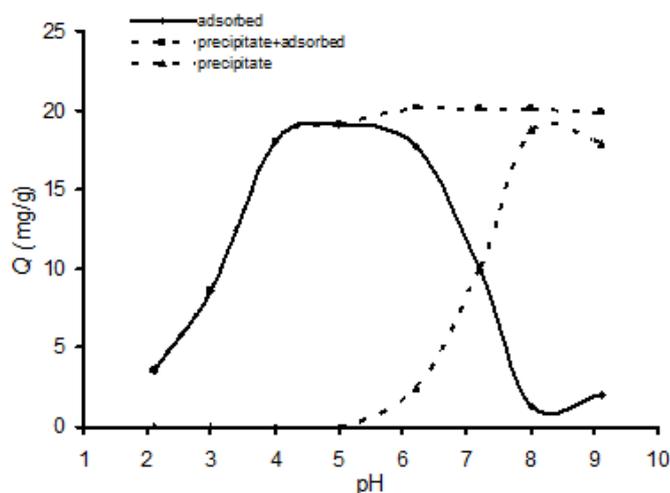


Fig 4. Effect of pH on the adsorption of Cd(II) on IICCb

It allows the formation of specific templates on the biosorbent surface corresponding to the characteristic of target ions. The formation of specific templates on IICCb structure based on the procedure developed by Su et al. [18] is illustrated in Fig. 3.

Fig. 3 shows the stages of the preparation of IICCb. Firstly, chitosan was interacted with imprinting ions to prepare kind of templates that would be easily recognizable by target ions in the subsequent process of adsorption. The metal-complexed chitosan in hydrogel form was then coated on the surface of biomass, followed by crosslinking it using epichlorohydrin reagent. Crosslinking has been proved to improve the stability of the biosorbent as the formation of polymer networks that make it resistant to acid attack [24]. Elution of imprinting ions was performed using EDTA solution to provide specific spatial configurations on the biosorbent surface with the appropriate orientation for target ions. Regeneration of the adsorbent was conducted by immersing it in dilute NaOH solution to restore the active sites into free forms, thus it can increase their activity in binding metal ions.

Effect of Initial pH on Cd(II) Adsorption

The effect of initial pH on Cd(II) adsorption capacity was investigated to determine the optimum pH and adsorption characteristics on pH alteration. The study was conducted on the range pH of 2-9 and the result is presented on Fig. 4.

Fig. 4 shows that adsorption is strongly influenced by initial pH of medium. At pH below 3, adsorption of Cd(II) is relatively low due to the fierce competition between protons and Cd(II) ions to reach the biosorbent active sites. On the other hand, the functional groups of IICCb are protonated into positively charged species which induce an electrostatic repulsion with the Cd(II)

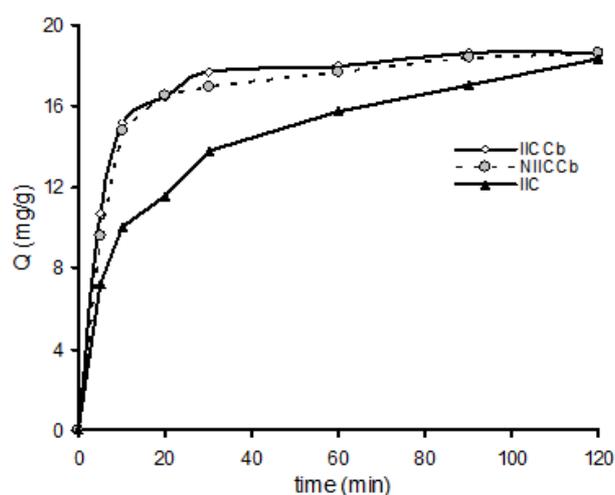


Fig 5. Effect of contact time on the adsorption of Cd(II)

ions. The amount of adsorbed ions then increases sharply with the rising of pH. Under this condition, the protonation degree of the adsorbent is reduced so that the accessibility of ligands toward metal ions increases. Adsorption of Cd(II) reaches its optimum at pH 4-6. At pH above 7, adsorption decreases significantly because there are large amounts of OH⁻ ligands in the solution. Metal ions would prefer to bind to the OH⁻ ligand and forming species complex of Cd(OH)₂ [33]. It makes the precipitation process becomes more dominant than adsorption which characterized by the sharp decline of Cd(II) adsorbed ions.

Kinetics of Cd(II) Adsorption

Kinetics study was conducted to investigate how fast an adsorption process can take place by evaluating the effect of contact time. The result of Cd(II) adsorbed as function of contact time is presented as Fig. 5.

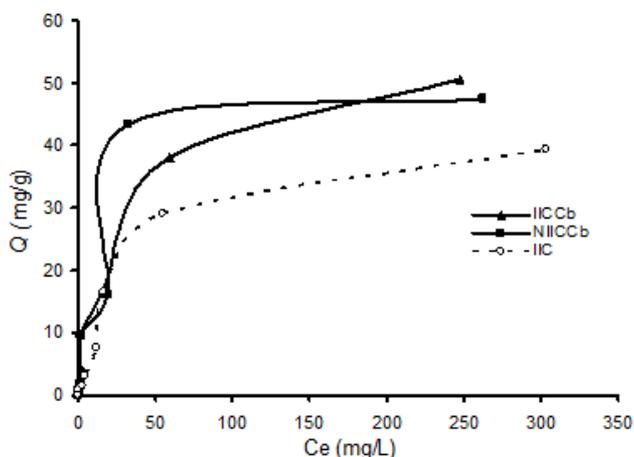
Adsorption of Cd(II) on IICCb and NIICCb takes place quickly in the first 30 min and then remains relatively constant thereafter. Equilibrium is reached within 30 min. Fig. 5 displays the quite large gap between the number of adsorbed ions on IICCb and IIC in the early contact time. The difference between IIC and IICCb lies on the addition of biomass on the latter material, thereby the rapid attainment of adsorption equilibrium on IICCb considered as contribution of hydrogel chitosan coating on the biomass surface. The role of biomass on the adsorption kinetics of metal ion by composite of chitosan/biomass was also reported by Liu et al. who studied the adsorption of Cu(II) on Ionic-Imprinted Chitosan/*Sargassum* biomass [34], and also Fan and Xu who study the adsorption of Ni(II) on chitosan-immobilized *Laminaria japonica* biomass [35].

Table 3. Pseudo-second order kinetic parameter of Cd(II) adsorption

Adsorbent	Parameter of pseudo 2 nd order kinetics	
	k_2 (g.mg ⁻¹ .min ⁻¹)	R^2
IICCb	2.22×10^{-2}	0.999
NIICCb	1.79×10^{-2}	0.999
IIC	0.86×10^{-2}	0.993

Table 4. Langmuir constants for Cd(II) adsorption

Adsorbent	Q_{max} (mg/g)	b (L/g)	R^2
IICCb	53.76	55.32	0.984
NIICCb	51.02	51.38	0.975
IIC	44.44	25.91	0.941

**Fig 6.** Isotherm adsorption of Cd(II) on IICCb, NIICCb and IIC

From the data of contact time, it can be expected that Cd(II) adsorption rate on IICCb will faster than that on IIC. This hypothesis was examined using pseudo-second order kinetics model suggested by Ho and Mc. Kay [32]. The kinetic parameters are presented on Table 3.

The pseudo-second order rate constant (k_2) of Cd(II) adsorption on IICCb is almost 3 times higher than that on IIC, and about 1.3 higher than that on NIICCb. On the IICCb, the specific templates were initially prepared by imprinting process and the active sites were then arranged on the biosorbent surface. When the imprinted biosorbent contacted again with ions which have similar characteristics to the templates, they would quickly recognize them. This can shorten the equilibrium time, and so it is kinetically advantageous.

The experimental kinetics data on all IICCb, NIICCb or IIC shown by Table 3 follow the pseudo-second order kinetics model as indicated by the high correlation coefficient ($R^2 > 0.99$). It reflects that rate-determining step involves the characteristics of both adsorbate and adsorbent. The pseudo-second order kinetic also successfully describes the adsorption of Ni(II) on Ionic-Imprinted Chitosan/*Penicillium* [27-28],

Cu(II) on Ionic-Imprinted Chitosan/*Sargassum* [34], Au(III), Pt(IV) and Pa(II) on glycine modified chitosan [36], and Ni(II) on alginate modified chitosan [37].

Isotherm of Cd(II) Adsorption

The functional groups of chitosan ($-NH_2$ and $-OH$) are known to have high capability to bind transition metal ions [13,18-19]. According to Hassan et al. [38], though these sites are quite effective for metal ion binding, they are not readily available for adsorption in flake or gel form. The adsorption capacity can be enhanced by dispersing chitosan hydrogel on various support materials. Hassan et al. [38] and Boddu et al. [39] coated chitosan to alumina and perlite, and reported that adsorption sites of chitosan became more reactive and readily interact with metal ions when they were dispersed on those kind of surfaces. In this research, we used *Chlorella* biomass as support material for imprinted chitosan to study the characteristic adsorption of Cd(II). The isotherm adsorptions of Cd(II) on the IICCb, NIICCb and IIC are presented on Fig. 6.

The isotherm adsorption curves of all type of adsorbents on Fig. 6 have similar patterns. Adsorption occurs rapidly in the initial concentrations of metal ions because there are still much active sites opened. On increasing the concentration, adsorption takes place slowly and then remains constant after a concentration of about 100 mg/L. This indicates the equilibrium of adsorption-desorption processes in solution. The adsorption parameters which calculated from the Langmuir equation (Eq. 2) are presented in Table 4.

Table 4 shows that correlation coefficients of Langmuir model for IICCb, NIICCb and IIC are relatively high ($R^2 > 0.94$), which indicate that adsorption of Cd(II) on those all adsorbents occur at monolayer surface with chemisorption as dominant mechanism. The Q_{max} calculated from Langmuir model for IICCb is about 21% higher than IIC. This enhancement is considered as a role of biomass in IICCb structure. Coating hydrogel chitosan on biomass surface is expected to expose more active sites of biosorbent, so their adsorption potentiality towards metal ions is increased. Table 4 also reveals that adsorption capacity of IICCb is slightly greater than NIICCb. It confirms the contribution of imprinting process which may create a specific of template for Cd(II) ions.

The adsorption capacities of some adsorbents prepared with surface-ionic imprinting technique on chitosan using some kinds of support materials are summarized in Table 5. The capacity values for some surface-imprinted biosorbents are varied depend on research condition.

Table 5. Adsorption capacity of several adsorbents prepared with surface-ionic imprinting technique

Metal ions target	Crosslinking reagent	Core Material	Adsorption capacity (mg/g)		Adsorption method	References
			Imprinted	non-imprinted		
Ce(III)	KH-560	Attapulgitite	38.02	About 16	Column	[40]
Ni(II)	ECH	Biomass of <i>Penicillium</i>	82.50	56.20	batch	[27-28]
Cu(II)	ECH	Biomass of <i>Sargassum</i>	68.58	31.12	batch	[34]
Cd(II)	ECH	Biomass of <i>Chlorella</i> sp	53.76	51.02	batch	This research

Table 6. Selectivity parameters of IICCb, NIICCb and IIC towards Cd(II) in the Cd(II)/Cu(II) mixture

Adsorbent	Q (mmol/g)		D (L/g)		α
	Cd(II)	Cu(II)	Cd(II)	Cu(II)	
IICCb	0.065	0.071	0.097	0.110	0.879
NIICCb	0.036	0.089	0.044	0.160	0.272
IIC	0.065	0.066	0.096	0.099	0.978

*C₀ = 1.0 mmol/L; volume 10 mL; contact time 120 min; Weight of adsorbent = 0.1 g; pH 5.0 ± 0.2

Table 7. Selectivity parameters of IICCb, NIICCb and IIC towards Cd(II) in the Cd(II)/Cr(III) mixture

Adsorbent	Q (mmol/g)		D (L/g)		α
	Cd(II)	Cr(III)	Cd(II)	Cr(III)	
IICCb	0.077	0.064	0.125	0.095	1.324
NIICCb	0.055	0.086	0.075	0.151	0.500
IIC	0.078	0.063	0.129	0.092	1.404

*C₀ = 1.0 mmol/L; volume 10 mL; contact time 120 min; Weight of adsorbent = 0.1 g; pH 5.0 ± 0.2

Selectivity of IICCb Towards Cd(II) Target Ions

Selectivity of an adsorbent towards certain type of metal ion is influenced by many factors, one of them is competition of ions. In this study, we used Cu(II) and Cr(III) ions as competitors for Cd(II) adsorption. It is mainly based on the difference of ionic size with the similar characteristic as transition metal ions. The ionic size of Cd(II), Cu(II) and Cr(III) are 1.09 nm, 0.87 nm and 0.75 nm, respectively [41]. Selectivity of IICCb prepared on this study towards Cd(II) target ions was examined by doing competitive adsorption on the solution containing a mixture of Cd(II)/Cu(II) and Cd(II)/Cr(III) ions. The data was compared to NIICCb and IIC and the results are presented in Table 6 and 7.

Table 6 and 7 clearly show that selectivity of imprinted biosorbents (IIC and IICCb) towards Cd(II) ions is much higher than of non-imprinted biosorbent (NIICCb) in both mixtures of Cd(II)/Cu(II) or Cd(II)/Cr(III). The formed spatial configurations in the ionic imprinted chitosan have proven to be selective for target ions that have similar ionic size characteristics with their templates ions. From the tables, selectivity (α) of IIC and IICCb towards Cd(II) target ions in the Cd(II)/Cr(III) system is greater than that in the Cd(II)/Cu(II) system. As the size differences (Δ) of Cd(II)-Cr(III) is 0.34 nm and Δ of Cd(II)-Cu(II) is 0.22 nm, it can be inferred that selectivity of ionic-imprinted biosorbent is greatly influenced by the size of the ions. The greater size difference of the competitor ions towards template ions, the greater selectivity of biosorbent towards target ions, and vice versa.

Comparison of two types of adsorbents that equally treated with ionic-imprinting process, i.e. IICCb and IIC shows that selectivity of the IIC is higher than IICCb. IICCb which is composed of at least two adsorbent materials have active sites which are more heterogeneous than the IIC which only composed of chitosan adsorbent. The existence of biomass is thought to be involved in the process of Cd(II) adsorption, so that adsorption takes place more complex and reduces the selectivity of IICCb compared to IIC. This data consistent with the kinetic and capacity results which reveals the involvement of biomass in the Cd(II) adsorption process.

CONCLUSION

The ionic-imprinted chitosan coated on *Chlorella* biomass (IICCb) has been synthesized through a relatively simple method. FTIR spectra and EDAX results confirm the involvement of amine and hydroxyl groups of chitosan as the main sites for metal ion adsorption. Adsorption of Cd(II) ions on IICCb occurs optimally at pH 4-6 and follows the pseudo-second order kinetic. The adsorption capacity of Cd(II) ions on IICCb is higher than that on IIC, considered as biomass contribution to open more active sites and arrange them on the surface of biosorbent. Selectivity of IICCb and IIC towards Cd(II) ions is higher than that on non-imprinted biosorbent (NIICCb). This confirms the role of imprinting process in the formation of specific templates that correspond to the characteristics of the target ion.

REFERENCES

1. Jha, I.N., Iyenger, L., and Rao, A.V.S.P., 1988, *J. Environ. Eng.*, 114(4), 964–974.
2. Debbaudt, A.L., Ferreira, M.L., and Gschaidner, M.E., 2004, *Carbohydr. Polym.*, 56(3), 321–332.
3. Beigi, S.M., Babapoor, A., Maghsoodi, V., Mousavi, S.M., and Rajabi, N., 2009, *Iran. J. Chem. Chem. Eng.*, 28(3), 81–89.
4. Guangyu, Y., and Viraraghavan, T., 2000, *Water. SA*, 26(1), 119–123.
5. Bayramoğlu, G., Bektaş, S., and Arica, M.Y., 2003, *J. Hazard. Mater.*, 101(3), 285–300.
6. Chen, J.P., Lie, D., Wang, L., Wu, S., and Zhang, B., 2002, *J. Chem. Technol. Biotechnol.*, 77(6), 657–662.
7. Hussein, H., Ibrahim, S.F., Kandeel, K., and Moawad, H., 2004, *Electron. J. Biotechnol.*, 7(1), 38–46.
8. Dönmez, G.Ç., Aksu, Z., Öztürk, A., and Kutsal, T., 1999, *Process Biochem.*, 34(9), 885–892.
9. Dönmez, G.Ç., and Aksu, Z., 2002, *Process Biochem.*, 38(5), 751–762.
10. Chen, J.P., and Yang, L., 2006, *Langmuir*, 22(21), 8906–8914.
11. Domard, A., 1996, *Proceedings of the 2nd Asia Pacific Symposium on Chitin and Chitosan*, 21-23 November 1996, Bangkok, 3–11.
12. Guibal, E., 2004, *Sep. Purif. Technol.*, 38(1), 43–74.
13. Rinaudo, M., 2006, *Prog. Polym. Sci.*, 31(7), 603–632.
14. Hsien, T.Y., and Rorrer, G.L., 1997, *Ind. Eng. Chem. Res.*, 36(9), 3631–3638.
15. Guibal, E., Milot, C., and Tobin, J.M., 1998, *Ind. Eng. Chem. Res.*, 37(4), 1454–1463.
16. Gao, Y., Lee, K.H., Oshima, M., and Motomizu, S., 2000, *Anal. Sci.*, 16(12), 1303–1308.
17. Yan, Z., Haijia, S., and Tianwei, T., 2007, *Korean J. Chem. Eng.*, 24(6), 1047–1052.
18. Tianwei, T., Xiaojing, H., and Weixia, D., 2001, *J. Chem. Technol. Biotechnol.*, 76(2), 191–195.
19. Wan Ngah, C.S., Endud, C.S., and Mayanar, R., 2002, *React. Funct. Polym.*, 50(2), 181–190.
20. Chen, A-H., Liu, S-C., Chen, C-Y., and Chen, C-Y., 2008, *J. Hazard. Mater.*, 154(1-3), 184–191.
21. Li, N., and Bai, R., 2006, *Water Sci. Technol.*, 54, 103–111.
22. Li, N., and Bai, R., 2005, *Sep. Purif. Technol.*, 42(3), 237–247.
23. Cui, Z., Xiang, Y., Si, J., Yang, M., and Zhang, T., 2008, *Carbohydr. Polym.*, 73(1), 111–116.
24. Chen, A-H., Yang, C-Y., Chen, C-Y., Chen, C-Y., and Chen, C-W., 2009, *J. Hazard. Mater.*, 163(2-3), 1068–1075.
25. Chen, C-Y., Yang, C-Y., and Chen, A-H., 2011, *J. Environ. Manage.*, 92(3), 796–802.
26. Nishad, P.A., Bhaskarapillai, A., Vemurugan, S., and Narasimhan, S.V., 2012, *Carbohydr. Polym.*, 87(4), 2690–2696.
27. Haijia, S., Zhixing, W., and Tianwei, T., 2005, *J. Chem. Technol. Biotechnol.*, 4(80), 439–444.
28. Haijia, S., Ying, Z., Jia, Li., and Tianwei, T., 2006, *Process Biochem.*, 41(6), 1422–1426.
29. Xiang, L., Haijia, S., and Tianwei, T., 2007, *J. Environ. Manage.*, 85(4), 900–907.
30. Aksu, Z., and Dönmez, G.Ç., 2006, *Process Biochem.*, 41(4), 860–868.
31. Doshi, H., Ray, A., Kothari, I.L., and Gami, B., 2006, *Curr. Microbiol.*, 53(2), 148–157.
32. Ho, Y.S., and McKay, G., 2000, *Water Res.*, 34(3), 735–742.
33. Srivastava, V.C., Mall, I.D., and Mishra, M., 2009, *Chem. Eng. Process. Process Intensif.*, 48, 370–379.
34. Liu, H., Yang, F., Zheng, Y., Kang, J., Qu, J., and Chen, J.P., 2011, *Water Res.*, 45(1), 145–154.
35. Fan, W., and Xu, Z., 2011, *Chem. Biochem. Eng. Q.*, 25(2), 247–254.
36. Ramesh, A., Hasegawa, H., Sugimoto, W., Maki, T., and Ueda, K., 2008, *Bioresour. Technol.*, 99(9), 3801–3809.
37. Vijaya, Y., Popuri, S.R., Boddu, V.M., and Krishnaiah, A., 2008, *Carbohydr. Polym.*, 72(2), 261–271.
38. Hasan, S., Ghosh, T.K., Viswanath, D.S., and Boddu, V.M., 2008, *J. Hazard. Mater.*, 152(2), 826–837.
39. Boddu, V.M., Abburi, K., Talbott, J.L., and Smith, E.D., 2003, *Environ. Sci. Technol.*, 37(19), 4449–4456.
40. Li, C.X., Pan, J.M., Gao, J., Yan, Y.S., and Zhao, G.Q., 2009, *Chin. Chem. Lett.*, 20(8), 985–989.
41. Huheey, J.E., Keiter, E.A., and Keiter, R.L., 1993, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., Harper Collins College Publishers, New York.