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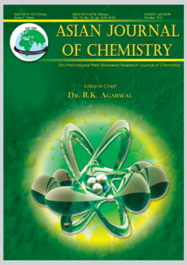

Production of Ionic Imprinted Polymer from *Nannochloropsis* sp Biomass and its Adsorption Characteristics Toward Cu(II) Ion in Solutions

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Material of Cu(II) ionic imprinted polymer from (Cu(II)-IIP) *Nannochloropsis* sp was synthesized *via* an immobilization of *Nannochloropsis* sp biomass with silica matrix from tetraethyl-orthosilicate (TEOS) precursor with a sol gel process followed with an ionic imprinting process using Cu(II) ion as a template. Characterizations of material were carried out using IR, XRD and surface area analyzer. Adsorptions of Cu(II) ions on non imprinted polymer (NIP) and Cu(II)-IIP are optimum at pH 5. Adsorption equilibrium follows Langmuir isotherm adsorption with the adsorption capacity of Cu(II) ion on NIP and Cu(II)-IIP of 54.24 and 94.71 mg g^{-1}, respectively. The adsorption energies of Cu(II) ion on NIP and Cu(II)-IIP are 23.67 and 27.26 kJ mol^{-1}. The adsorption competition data in an ionic pair solutions, Cu(II)/Cd(II); Cu(II)/Ni(II); Cu(II)/Zn(II); Cu(II)/Ag(I), show that Cu(II)-IIP is more selective than NIP with relative selectivity coefficient (α_τ) of 40.16, 37.65, 31.74, 15.20 for concentration ratio of metal ions 1:1 and 38.48, 37.56, 29.25, 12.61, for concentration ratio of metal ions 1:2, respectively. The material of Cu(II)-IIP is stable chemically and it can be reused on the adsorption of Cu^{2+} in solutions with the recovery percentage higher than 97 %.

Key Words: Ionic imprinted, Immobilization, Adsorption, Heavy metal.

INTRODUCTION

The specific problem of the existence of heavy metals in the environment is because of their accumulation in a food chain and an increasing of their concentration in the environment. Cu is one of the heavy metals used widely in several industries. The existence of Cu in the industrial waste is usually in Cu(II) ion as a hydrolytic product. Some industries as colouring, paper, oil and metallurgy release copper(II) in atmosphere[1,2].

Several methods have been developed to minimize the concentration of heavy metals from liquid waste as chemical precipitation, coagulation, complexation, solvent extraction, membrane separation, ion exchange and adsorption. The adsorption has some advantages because of simple process and low cost[3-5].

The success of the adsorption process is determined by an adsorbent selecting used. Recently, it is much more developed an adsorbent specific containing a ligand specifically interacting with metal ions derived from a supporting solid modification like an inorganic material (silica) or a polymer. Modification of the adsorbent surface is performed with immobilizing of organic functional groups which are able to be as heavy metal complex derived from natural product (like algae and fungi biomass) or an organic compound synthesis containing an active group played a role as a ligand toward metal ions[6-9].

The algae biomass from several algae species is effective to bind metal ions from a water environment[10] because the algae biomass contain several functional groups which are able to play a role as a ligand upon metal ions[4,11,12]. But, the use of these biomass have some problems because these biomass have low density causing ineffective to be used as column filling material to adsorb continually and they are easily degraded chemically or biologically[10,13]. In addition, the algae biomass is not selective toward metal ions adsorbed because not all metal ions in the water environment are dangerous for live as metal ions from alkaline group and earth alkaline (K^+, Na^+, Mg^{2+}, Ca^{2+}).

Nannochloropsis sp is one of potential algae as an adsorbent to adsorb heavy metal ions because it contains functional groups playing a role as a ligand[9] and it has abundance in Indonesian watering especially in Province of Lampung. Increasing of adsorption capacity and selectivity is performed with an immobilization of algae biomass using a silica gel supporting matrix through an ionic imprinting technique. The ionic imprinted polymer technique (IIP) can raise the adsorption selectivity because metal ions can play a role as a template to form a polymer *via* imprinted[5,14,17]. The ionic imprinted technique is based on copolymerization from monomer either isolated or non-isolated or complex ion with a crosslinking agent[18,19]. Furthermore, the metal ions will be released as a template and if there are interactions with the same metal ion (target), it will increase its interaction to be stronger and also its selectivity to be more selective upon target metal ions[20-22]. Several researches were carried out to produce the Cu(II) ionic imprinted material using an active compound as complex agent derived from synthesis material such as; ion-imprinted polymer based on salen-Cu complex[19], double-imprinted polymer[23], Cu(II)-imprinted polymetharcrylic microbeads[24], ionic imprinting on surface silica gel particles[2], imprinted chelating resin (DBDA15C4)[25], magnetic Cu(II) ion imprinted composite adsorbent[26], imprinted polymer microbeads[27], metal ion imprinted nano-porous polymer[28]. In this work, *Nannochloropsis* sp biomass was used as the Cu(II) metal ion complex agent with the silica supporting matrix derived from the TEOS precursor and it was used to determine adsorption characteristics upon Cu(II) ion from solutions.

EXPERIMENTAL

Tetraethylorthosilicate (TEOS), CH_3CH_2OH, $CuCl_2{\cdot}2H_2O$, Na_2EDTA, $CdCl_2{\cdot}H_2O$, $ZnCl_2$, $NiCl_2{\cdot}6H_2O$. AgCl, HNO_3, CH_3COOH and CH_3COONa used are commercial products of Merck, Germany. NaOH, HNO_3, NH_4OH and HCl (37 %) were ordered from Alba Chemical. Algae biomass was taken from Lampung Sea Cultivation Bureau/Balai Budidaya Laut Lampung, Province of Lampung, Indonesia. It was cleaned with distilled water to remove dirt and was kept on a filter paper to minimize the water content. Furthermore, the biomass was sun dried for 3 days continued by drying in an oven at 60 ºC for 12 h and then ground and sieved. The biomass was then sieved to collect the particles around 100-200 mesh sizes for use.

Analysis intrumentation performed in this work consisted of an atomic adsorption spectrophotometer (AAS) (Perkin Elmer 3110) used to count the metal consentration, IR spectrophotometer (Prestige-21 Shimadzu) used to determine the functional groups, the XRD (Shimadzu 6000) used to analize the material of synthesis result and a Quantachrome Nova 1200e used to analize the surface area.

Preparation of Cu(II)-imprinted polymer (Cu(II)-IIP): In the synthesis of the imprinted ionic Cu(II) with *Nannochloropsis* sp biomass, the interacted solutions were divided into two part consisting of solution A: filling 5 mL of TEOS and 2.5 mL water filled in plastic glass and added 2 drops of 1 M HCl solution up to pH 2, then they were stirred with a magnetic stirrer for 0.5 h until homogeneous. Solution B: 0.17048 g of $CuCl_2{\cdot}2H_2O$ and ethanol was added into plastic glass, heated and stirred by a magnetic stirrer until it was dissolved. Then, it was added biomass and stirred for 1 h. Solution A and B were mixed and stirred again for 0.5 h until a homogeneous gels were formed. Formed gels were kept for a night and rinsed by water/ethanol 60/40 % continued with soaking the gels for 24 h in Na_2EDTA solution 0.1 M and HCl 0.5 M followed with neutralizing using water up to pH 7. Further, the adsorbent was dried in an oven at 70 ºC for 2 h. The Cu concentrations in the gels before and after loosed were identified by an atomic adsorption spectrophotometer (AAS). The obtained adsorbents was grounded and sieved by 200 mesh size. Non-imprinted polymer (NIP) was also prepared under similar experimental conditions without adding $CuCl_2{\cdot}2H_2O$. The adsorbent materials were analyzed using an infrared (IR), XRD and a Quantachrome Nova 1200e.

Sorption experiments: A total of 50 mg Cu(II)-IIP adsorbent was suspended with a constant stirring for 1 h in 20 mL of 100 mg L^{-1} of Cu(II) at various pH. The pH of solution was adjusted using the following buffer: sodium acetate/hydrochloric acid for pH (2-3) and sodium acetate/acetic acid for pH 4-7. Further, it was stirred using a stirrer for 1 h in order to be well adsorbed. The metal solutions were analyzed using an atomic absorption spectrophotometer (AAS) (Model Perkins Elmer 3110, Made in USA) at conditions of wavelength of 228.8 nm, slit of 0.7 nm, lamp current of 8 mA, flow rates of flame gases (air; 9.5 L min^{-1} and acetylene; 2.2 L min^{-1}).

Selectivity of adsorption was evaluated based on the data of binary competitive metal ion adsorption for Cu(II)/Cd(II); Cu(II)/Ni(II); Cu(II)/Zn(II); Cu(II)/Ag(I) aqueous solutions at pH 5. An amount of 50 mg portion of NIP adsorbent and Cu(II)-IIP adsorbent were equilibrated with 20 mL of the buffered solution containing 0.5 mmol L^{-1} of Cu(II) and 0.5 or 1.0 mmol L^{-1} of Cd(II), Ni(II), Zn(II) and Ag(I), respectively.

The adsorption capacity, the distribution ratio, the selectivity coefficient and the relative selectivity coefficient were counted using following equations:

$$Q = \frac{(C_o - C_e)V}{W};$$

$$D = \frac{Q}{C_e};$$

$$\alpha = \frac{D_{Cu(II)}}{D_{M(II)}};$$

$$\alpha_r = \frac{\alpha_i}{\alpha_n}$$

where Q represent the adsorption capacity (mg g^{-1}), C_o and C_e represent the initial and final concentrations of metal ions, W is the mass of non-imprinted polymer (NIP) adsorbent or Cu(II) imprinted ionic polymer (Cu(II)-IIP) adsorbent (g), V is the volume of metal ion solution (mL), D is the distribution ratio (mL g^{-1}), α is the selectivity coefficient, $D_{Cu(II)}$ and $D_{M(II)}$ represent the distribution ratios of Cu(II) to Cd(II), Ni(II), Zn(II) or Ag(I). α_r is the relative selectivity coefficient, α_i and α_n represent the selectivity factor of imprinted adsorbent and non-imprinted adsorbent.

RESULTS AND DISCUSSION

Characterization of Cu(II)-IIP adsorbent: In order to investigate *Nannochloropsis* sp biomass existed on NIP, CuP (Polymer with Cu) and Cu(II)-IIP material, the functional groups were characterized using IR. From Fig. 1, the bands of 1087.85 and 956.69 cm^{-1} indicate asymmetric stretching vibration of Si-O-Si and stretching vibration of Si-O from

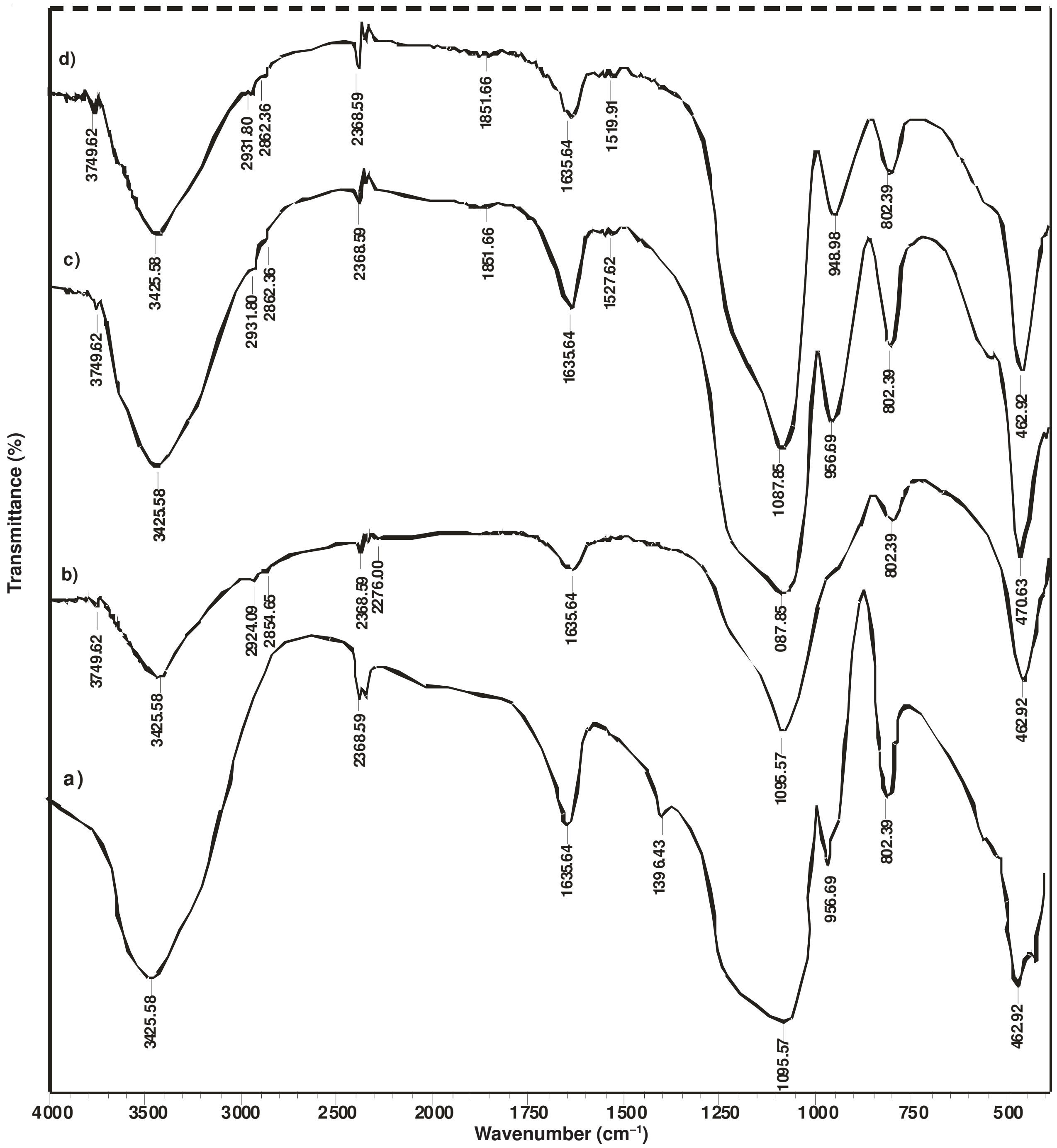

Fig. 1. (a) Infrared spectra of (a) Silica gel, (b) NIP, (c) CuP and (d) Cu(II)-IIP

silanol, respectively. The existence of water adsorbed is represented by OH vibration at 3425.58 cm^{-1}. The bands at around 802.39 and 462.92 cm^{-1} are resulted from each symmetric stretching vibration and bending vibration of Si-O from siloxane. Characteristic adsorbent bands for NIP, CuP and Cu(II)-IIP can be seen at the bands around 2931.80-2862.36 cm^{-1} assigned to the CH asymmetric and symmetric stretching vibration modes, respectively, from the *Nannochloropsis* sp biomass[7,29]. These facts indicate that the *Nannochloropsis* sp biomass exist on the silica surface derived from TEOS precursor.

The nitrogen adsorption-desorption isotherm for NIP and Cu(II)-IIP are shown in Fig. 2. In the graph at low P/Po area, it is seen that a nearly horizontal-shape shows an adsorption on a small porous volume. Generally, NIP and Cu(II)-IIP material follow a type IV adsorption isotherm according to IUPAC classification and an H1 hysteresis loop showing a mesoporous material. Adsorbate volume for all the isotherm types increases sharply upon (P/Po) at around 0.7 indicating a nitrogen caviler condensation in the mesoporous structure arranged. The hysteresis loop for Cu(II)-IIP is weaker than NIP because of decreasing of the porous volume after functionalized and ionic imprinting process[29,30].

In addition, from the data obtained of specific surface area of silica, NIP and Cu(II)-IIP, 199.80, 170.58 and 98.54 m^2 g^{-1}, respectively, show decreasing of the specific surface area from silica to Cu(II)-IIP after the immobilization and ionic

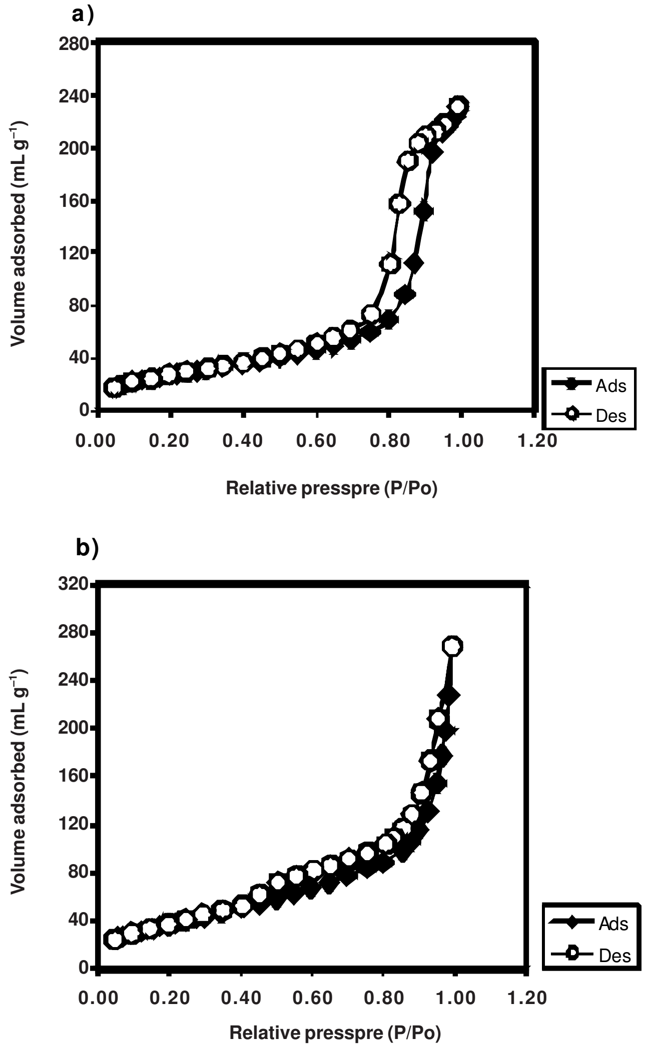

Fig. 2. Nitrogen adsorption-desorption isotherms of (a) NIP and (b) Cu(II)-IIP

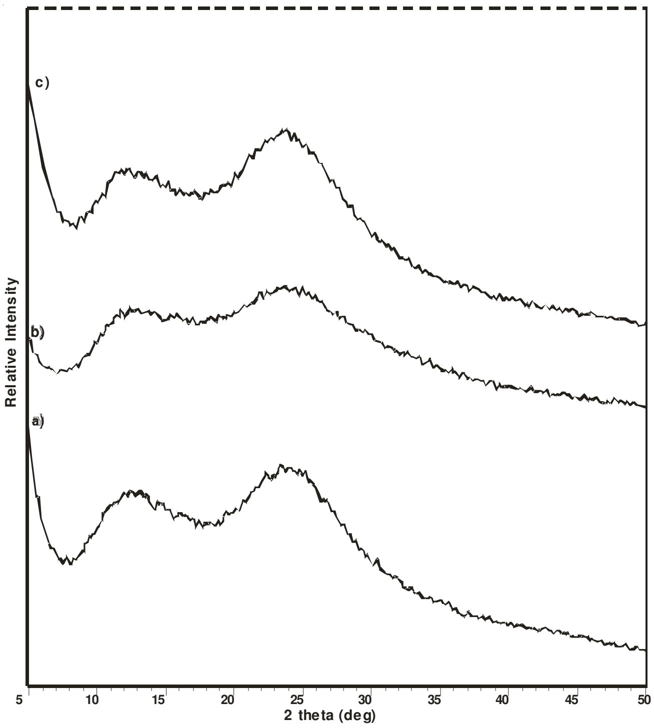

Fig. 3. XRD pattern of (a) NIP, (b) CuP and (c) Cu(II)-IIP

imprinting process performed on the materials. These facts show that after the immobilization between silica and *Nannochloropsis* sp biomass causes the silica surface covered by the active compounds from the organic groups of the *Nannochloropsis* sp biomass. Therefore, the specific surface area will decrease. In other word, it can be stated that the decreasing of surface area is caused by the occurring of organic molecule interaction on the silica surface explaining the existence fact of pendant group hindering nitrogen gas adsorption[29,31].

Fig. 3 shows that all diffraction peaks from NIP, CuP and Cu(II)-IIP are in 2θ peak at around 24°. The wide peaks at 2θ angle between 15-35° are a characteristic peak of an amorphous compound, which was the amorphous diffraction peaks of the silica gel[32,33], namely showing the Si-O short order structure. In addition, it can be observed that the XRD diffraction model on NIP and Cu(II)-IIP material is relatively similar. This indicates that the ionic imprinting process does not change the material structure.

Adsorption pH: pH (acidic parameter) is one of important factors on an adsorption process because an acidic solution changing can cause changing of an adsorbent surface charge and metal ion species in solution[34]. In order to study the effect of pH on Cu(II) metal ion adsorption, a metal ion solution is interacted with NIP and Cu(II)-IIP (Fig. 4).

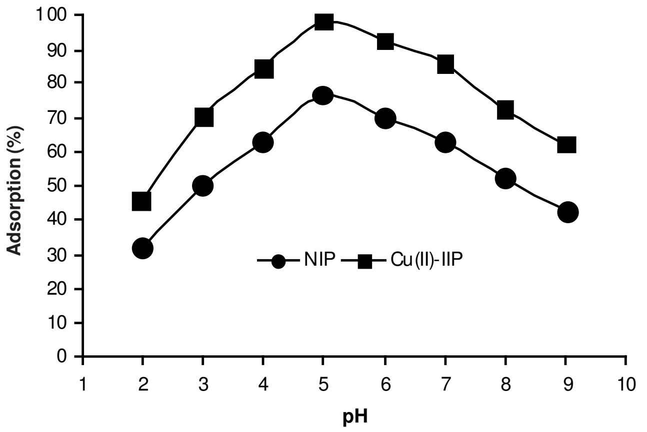

Fig. 4. Effect of pH on adsorption of 100 mg L^{-1} Cu(II) ion on NIP and Cu(II)-IIP. Other conditions: contact time of 1 h and temperature of 27 °C

Effect of the solution pH on Cu(II) ion adsorption process on NIP and Cu(II)-IIP is generally observed that the higher the pH, the higher the adsorption of Cu(II) ion and it is optimum at pH 5 followed with decreasing of pH. At low pH (< 5), the adsorption of Cu(II) ion is relatively small. This can be explained that at acid condition, the functional groups on NIP and Cu(II)-IIP occur protonation causing binding of hydrogen ion (H^+) and hydronium ion (H_3O^+). In addition, the metal ions in solution before adsorbed by an adsorbent occur a hydrolysis producing a proton as the equation this follow;

$$M^{2+} + nH_2O \longrightarrow [M(OH)_n^{2-n}]H^+ + nH^+$$

Hydroxo complex $[M(OH)_{n2-n}]^+$ obtained from above reaction will be more adsorbed than free metal cation (M^{2+})[35].

At acid condition, the reaction from the equation above will move to left, therefore it results the amount of the metal hydroxo complex formed to be lower than the amount of the free metal cations. At acid condition also, the adsorbent surface has a positive charge resulting repulsion between the adsorbent surface and the metal ion. Therefore, this causes low adsorption.

At pH 5, the adsorption is relatively high because the metal hydroxo complex (MOH^+) formed in solution is much more and also the adsorbent surface will be negative charge with releasing proton causing increasing of the adsorption through an electrostatic interaction. At pH > 7, the amount of Cu(II) adsorbed starts to decrease because Cu^{2+} have been starting to precipitate resulting decreasing of Cu^{2+} in solution and the precipitation process to be more dominant than the adsorption process[23,25-27].

Effect of stirring time: The effect of stirring time is another important factor in evaluation the affinity of Cu(II)-IIP upon Cu^{2+}. To determine the rate of loading of Cu^{2+} on the Cu(II)-IIP, the recommended batch procedure was carried out at pH of 5 and temperature of 27 ºC. The contact times are varied from 5-120 min and the results are shown in Fig. 5. The stirring time of 5 min for Cu^{2+} raises sharply up to 0.5 h equilibrium happening at pH of 5. This shows that the adsorption of Cu^{2+} on Cu(II)-IIP runs quickly. In addition, the stirring time of 1 h is enough to produce the maximum adsorption of Cu^{2+}.

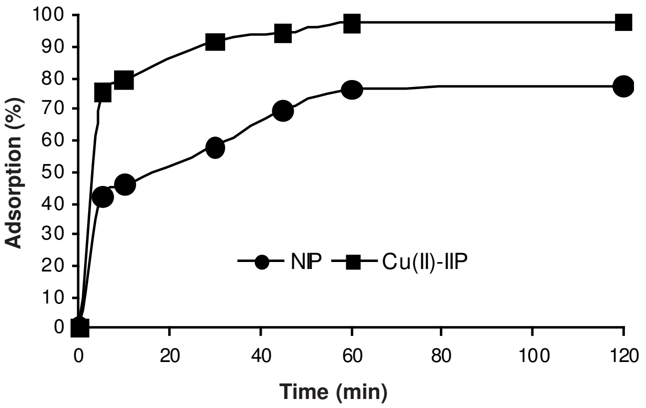

Fig. 5. Effect of stirring time of 100 mg L^{-1} Cu^{2+} on NIP and Cu(II)-IIP. Other conditions: pH of 5.0, temperature of 27 ºC

Adsorption capacity: Adsorption capacity of adsorbent is also important factor to know how much the adsorbent amount needed in adsorbing the metal ions from solutions. The adsorption capacity is determined by a batch procedure at the conditions; 50 mg of the adsorbent, 20 mL of Cu^{2+}, contact time of 1 h, pH of 5 and temperature of 27 ºC. From Fig. 6, it can be observed that the Cu^{2+} adsorption by NIP and Cu(II)-IIP indicates an adsorption tendency increasing sharply as raising of metal ion concentration and at the highest concentration, the increasing of metal ion concentration does not followed with the increasing of Cu^{2+} adsorption significantly.

Data in the Fig. 6 were evaluated using the isotherm adsorption Langmuir and Freundlich equations (eqns. 1 and 3)[35,36] as follow;

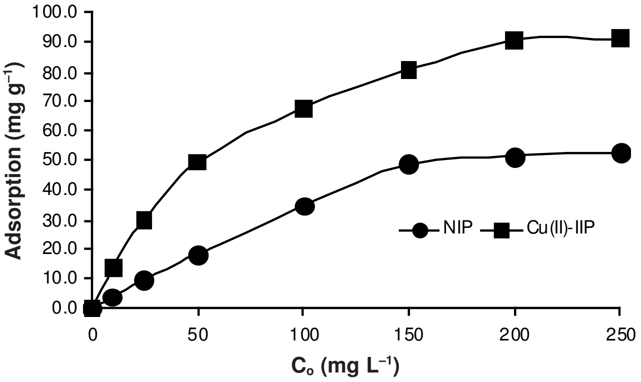

Fig. 6. Effect of Cu(II) initial concentration on the adsorption quantity of NIP and C(II)-IIP. Other conditions: 50 mg of the adsorbent; 20 mL of Cu(II) ion; Contact time of 1 h; pH of 5; temperature of 27 ºC

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{max}} + \frac{1}{Q_{max}} C_e \qquad (1)$$

where C_e (mg L^{-1}) is the equilibrium liquid phase concentration of total Cu^{2+}, q_e (mg g^{-1}) is the total Cu^{2+} adsorption capacity at equilibrium, Q_{max} is the monolayer adsorbent capacity and K_L is the energy constant of adsorption (L mol^{-1}). Therefore, a plot of log $1/q_e$ *versus* C_e gives a straight line resulting slope and intercept. In order to determinate the adsorption energy, the equation 2 was used;

$$\Delta G = -RT \ln K_L \qquad (2)$$

where ΔG is change in Gibbs free energy (kJ mol^{-1}), R is universal gas constants (8.314 J K^{-1} mol^{-1}) and T is temperature (Kelvin).

Freundlich equation is based empirically on a heterogeneous surface. The formula of the Freundlich equation is $q_e = K_f C_e^{1/n}$, where K_f is Freundlich capacity factor and n is the Freundlich's intensity factor with the value of n in the range of 1-10[36-38]. The linear form of the Freundlich's equation is given by:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3)$$

Therefore, a plot of log q_e *versus* log C_e enables the constant K_f and exponent n. Data of Cu^{2+} adsorption on NIP and Cu(II)-IIP obtained from analysis result using the Langmuir and Freundlich equations are given in Table-1.

From Table-1, it can be seen that the adsorption model of Cu^{2+} on NIP and Cu(II)-IIP tends to follow the Langmuir isotherm adsorption with a linear regression coefficient (r^2) around 0.98 higher than a linear regression coefficient (r^2) of the Freundlich isotherm adsorption. Then, the adsorption capacity of Cu^{2+} increases around 40 % on Cu(II)-IIP. This happens because the Cu(II) ionic imprinted process on *Nannochloropsis* sp biomass produces an adsorbent surface to be more selective and specific in case of Cu^{2+} caused by the ionic imprinting technique based on copolymerization from monomer either isolated or non-isolated or a complex ion[18]. A coordination geometry shape, a coordination number, a charge and a metal ionic size play an important role in producing the adsorbent selectivity[19]. The success of the metal ionic template synthesis on ionic imprinting adsorbent is also determined by

TABLE-1
PARAMETERS OF LANGMUIR AND FREUNDLICH ISOTHERM FOR Cu^{2+} BY NIP AND Cu(II)-IIP

Adsorbent	Langmuir				Freundlich		
	Q_{max} (mg g^{-1})	$K_L \times 10^{-3}$ (L mol^{-1})	ΔG (kJ mol^{-1})	r^2	K_f (mg g^{-1})	n	r^2
NIP	54.24	13.22	23.67	0.99	9.98	2.60	0.88
Cu(II)-IIP	94.71	55.83	27.26	0.98	32.55	2.55	0.91

use of appropriate ligand for a complex formation with a metal ion, because the appropriate ligand will effect directly to the adsorbent selective. The selectivity on the Cu-IIP adsorbent can be attained because the polymer synthesis with an ion template and a functional monomer occurs at the metal ion released from a polymer matrix causing the metal ion to be more selective to identify the template ion from other component in sample[21].

If the adsorption capacity of Cu^{2+} on Cu(II)-IIP from *Nannochloropsis* sp biomass compared with the Cu(II) ionic imprinted adsorbent from other researches (Table-2) can be known that the Cu(II) ionic imprinted adsorbent produced from *Nannochloropsis* sp biomass in this research has a relatively high adsorption capacity value.

Adsorption selectivity: The adsorption selectivity on NIP and Cu(II)-IIP material were studied with performing adsorption competition of Cu^{2+} on Cu(II)-IIP toward its pair with Cd(II), Ni(II), Zn(II) and Ag(I) in solution. These metal ions was chosen based on an ionic radius difference namely; Cu(II) = 87, Cd(II) = 109, Ni(II) = 83, Zn(II) = 88 and Ag(I) = 129 pm[39]. Besides that, an acidity characteristic difference from their metal ions was compared with Cu(II) ion. The adsorption competition data of ion pairs for Cu(II)/Cd(II), Cu(II)/Ni(II), Cu(II)/Zn(II) and Cu(II)/Ag(I) on Cu(II)-IIP and NIP material with concentration ratio of 1:1 and 1:2 are listed in Table-3.

The adsorption selectivity on Cu(II)-IIP for each ion pair of Cu(II)/Cd(II), Cu(II)/Ni(II), Cu(II)/Zn(II) and Cu(II)/Ag(I) are higher than the adsorption selectivity on NIP. These cases show that the ionic imprinted process using Cu^{2+} as the template can increase the adsorption selectivity to Cu^{2+} as the target. The increasing selectivity occurred is because of the existence of the Cu(II) ionic template on the Cu(II)-IIP material. The selectivity coefficient of the Cu(II)-IIP material increases

TABLE-2
Cu(II) IONIC ADSORPTION CAPACITIES FROM SEVERAL Cu(II) IONIC
IMPRINTED POLYMER ADSORBENTS WITH BATCH METHOD

Adsorbent	Adsorption capacity of Cu(II) ion (mg g^{-1})	References
Cu(II)(poly(EGDMA-MAH/Cu(II) microbead	48.00	[27]
Cu^{2+}- ion imprinted material IIP-PEI/SiO_2	40.69	[2]
Double-imprinted polymer chitosan-Cu^{2+}	45.35	[23]
Copper(II) ion-imprinted porous polymethacrylate	16.14	[5]
Cu(II)–IIP from *Nannochloropsis* sp. biomass	94.71	This work

TABLE-3
ADSORPTION COMPETITIONS OF Cu(II) *versus* Cd(II), Zn(II), Ni(II) AND Ag(I) ON Cu(II)-IIP AND NIP
MATERIAL OTHER CONDITION: pH of 5.0; CONTACT TIME OF 1 h; TEMPERATURE OF 27 °C

Material	Initial concentration (mmol L^{-1})		D (mL g^{-1})		α	$α_r$
	Cu	Cd	Cu	Cd		
Cu(II)-IIP	0.50	0.00	66,490			
	0.50	0.50	21,630	530	40.81	40.16
	0.50	1.00	17,000	440	38.64	38.48
NIP	0.50	0.00	3,990			
	0.50	0.50	3,120	3,070	1.02	
	0.50	1.00	2,440	2,430	1.00	
	Cu	Ni	Cu	Ni		
Cu(II)-IIP	0.50	0.50	10,360	300	34.53	37.65
	0.50	1.00	8,370	260	32.19	37.56
NIP	0.50	0.50	3,430	3,740	0.92	
	0.50	1.00	2,640	3,080	0.86	
	Cu	Zn	Cu	Zn		
Cu(II)-IIP	0.50	0.50	6,910	390	17.72	31.74
	0.50	1.00	5,430	340	15.97	29.25
NIP	0.50	0.50	2,640	4,730	0.56	
	0.50	1.00	2,370	4,340	0.55	
	Cu	Ag	Cu	Ag		
Cu(II)-IIP	0.50	0.50	2,530	440	5.75	15.20
	0.50	1.00	2,400	470	5.11	12.61
NIP	0.50	0.50	1,960	5,180	0.38	
	0.50	1.00	1,960	4,840	0.40	

with the order of the ion pairs as follow; Cu(II)/Ag(I) < Cu(II)/Zn(II) < Cu(II)/Ni(II) < Cu(II)/Cd(II). The increasing of the Cu(II)-IIP adsorption selectivity toward Cu(II) ion is very determined by a metal ionic charge and size, the bigger the metal ionic size difference, the higher the selectivity, except to the ionic pair of Cu(II)/Ag(I).

Chemical stability: One of parameters to determine the ionic imprinted material quality from *Nannocholoropsis* sp biomass produced is a chemical stability in a solution media. The stability of the Cu(II)-IIP material was studied through a suspension of 0.1 g Cu(II)-IIP in 100 mL of acid solution (pH = 1.35), close to neutral (pH = 5.40) and base (pH = 9.34) with determining Si concentration left as function of time as described in Fig. 7.

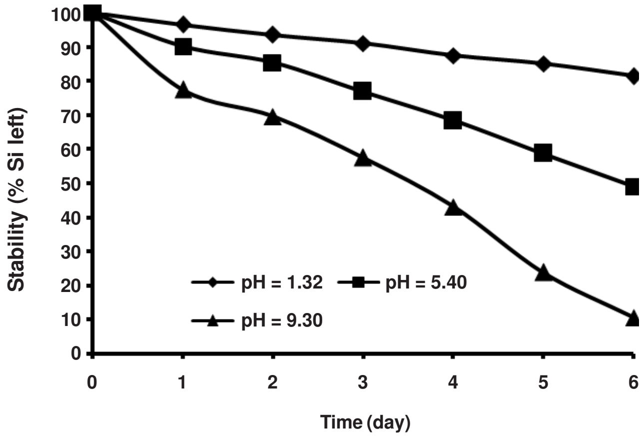

Fig. 7. Relationship between the interaction time in solution media and stability of percentage [Si] left on Cu(II)-IIP

Fig. 7 shows that the amount of Si left until the longest interaction time for 6 days is the acid solution media indicating very stable material at acid condition (pH = 1.32). Protonations of active groups as amine and hydroxyl[9] increase the stability of the material significantly in a water solution media. Other possibility, the existence of the protonation limits a water interaction with the organo-silica hybrid material which have been imprinted with Cu(II)[40]. The characteristics of Cu(II)-IIP surface depend on the pH condition of the solution media. At the base condition (pH = 9.34), a percentage of Si left is the lowest while the interaction time increases. The amount of Si dissolved is derived from a silica net hydrolysis with releasing of organic groups from *Nannochloropsis* sp biomass because the hydrolysis occurs on a chemical bonding of the organo-silica hybrid from silica with an organic compound from *Nannochloropsis* sp biomass on Cu(II)-IIP material.

Reusability: Reuse of the material to adsorb metal ions for several times without a damage of the material structures and a decreasing of the adsorption capacity is one of the important parameters in determining the material quality synthesized. The much more reusability of material, the material will be more quality. The Cu(II)-IIP material can be reused for 5 times to adsorb Cu(II) ion with the value of adsorption capacity higher than 97 %.

Elution condition: In order to know the recovery ability of Cu(II)-IIP toward Cu^{2+} from solutions, Elution was performed toward Cu^{2+} with using HCl and Na_2EDTA as eluents (Table-4). From Table-4, it can be seen that the elution using HCl with the concentrations of 1.0-2.0 M or Na_2EDTA with the concentrations of 0.1-0.2 M are effective enough to elute Cu(II) ion from the adsorbent with percentage recovery > 97 % at the same volume.

TABLE-4
ELUTION RECOVERY (%) FOR Cu(II) ADSORBED ON Cu(II)-IIP

Eluent HCl (M)	Recovery[a] (%)	Eluent Na_2EDTA (M)	Recovery[a] (%)
0.1	76.24 ± 0.79	0.01	80.24 ± 0.45
0.5	87.34 ± 0.88	0.05	87.34 ± 0.60
1.0	97.16 ± 0.61	0.10	97.43 ± 0.52
2.0	99.05 ± 0.19	0.20	99.89 ± 0.09

10 mL eluent was used to select eluent concentration. [a]$\bar{x} \pm \sigma$ (n = 3), $\bar{x}$ average value for three determination, σ standard deviat.

Conclusion

The adsorbent of Cu(II)-IIP has higher adsorption capacity and selectivity in adsorbing of Cu(II) ion in solutions than the adsorbent of NIP. In addition, the Cu(II)-IIP material from *Nannochloropsis* sp biomass is stable chemically in acid media and close to neutral in a time period for several days and it can be reused in the adsorption process with Cu(II) ionic recovery ability in solution higher than 97 %. The proposed method in this work has been applied successfully to determination of copper in/from aqueous solutions.

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