

CHEMICAL STABILITY AND ADSORPTION SELECTIVITY ON Cd²⁺ IONIC IMPRINTED *Nannochloropsis* sp MATERIAL WITH SILICA MATRIX FROM TETRAETHYL ORTHOSILICATE

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ABSTRACT

Chemical stability, reusability, and adsorption selectivity of Cd²⁺ ionic imprinted Nannochloropsis sp with silica matrix (Cd(II)-IIP) from precursor tetraethyl orthosilicate (TEOS) have been studied through adsorption experiment series with batch method. Nannochloropsis sp (Cd(II)-IIP) material was characterized with an infrared spectrophotometer (IR) to identify the functional groups in this material and identification of metal ion concentration was analyzed with an atomic absorption spectrophotometer (AAS). Chemical stability was determined in solution media of acid, neutral, and base. Adsorption selectivity was obtained with determination of selectivity coefficient (α) of Cd²⁺ ion toward its ionic pair such as Ag⁺, Zn²⁺, Cu²⁺, and Ni²⁺ ions. Nannochloropsis sp Cd(II)-IIP material is very stable in acid media and lack stable in base media as well as it can be reused for extraction 4 cycles with adsorption capacity value > 95% using eluent of 0.1 M Na₂EDTA. Selectivity of Cd(II)-IIP material upon Cd²⁺ ion is higher than non imprinted polymer (NIP) and it increases with these orders; Cd²⁺/Ag⁺ < Cd²⁺/Zn²⁺ < Cd²⁺/Cu²⁺ < Cd²⁺/Ni²⁺ for each α at metal ionic ratio of 1:1; 0.887; 20.180; 28.053; 33.417, respectively.

Keywords: ionic imprinted; Nannochloropsis sp; adsorption selectivity

ABSTRAK

Stabilitas kimia, kemampuan penggunaan ulang, dan selektivitas adsorpsi material Nannochloropsis sp imprinted ionik Cd²⁺ (Cd(II)-IIP) dengan matriks silika dari prekursor tetraetil orthosilikat (TEOS) telah dipelajari melalui serangkaian eksperimen adsorpsi dengan metoda batch. Material Nannochloropsis sp Cd(II)-IIP dikarakterisasi dengan spektrofotometer inframerah (IR) untuk identifikasi gugus fungsi dan analisis kadar logam dengan spektrofotometer serapan atom (AAS). Stabilitas kimia ditentukan dalam media larutan asam, netral dan basa. Selektivitas adsorpsi diketahui dengan menentukan koefisien selektifitas (α) ion Cd²⁺ terhadap pasangan ionnya, yaitu ion Ag⁺, Zn²⁺, Cu²⁺, dan Ni²⁺. Material Cd(II)-IIP Nannochloropsis sp sangat stabil pada media asam dan kurang stabil pada media basa serta dapat digunakan dalam ekstraksi berulang sebanyak 4 kali pengulangan dengan harga kapasitas adsorpsi > 95% menggunakan eluen 0,1 M Na₂EDTA. Selektivitas material Cd(II)-IIP Nannochloropsis sp terhadap ion Cd²⁺ lebih besar dari NIP dan meningkat dengan urutan pasangan ion Cd²⁺/Ag⁺ < Cd²⁺/Zn²⁺ < Cd²⁺/Cu²⁺ < Cd²⁺/Ni²⁺ dengan masing-masing α pada perbandingan ion logam 1:1 adalah: 0,887; 20,180; 28,053; 33,417.

Kata Kunci: imprinted ionic; Nannochloropsis sp; selektivitas adsorpsi

INTRODUCTION

Analysis technique of metal ion such as an atomic absorption spectrophotometer has a relatively high selectivity and sensitivity, however solid phase extraction (SPE) material for metal concentration with very low concentration or for metal separation from mixture with complex matrix is still used [1-3]. In addition, increasing used of metals, especially heavy metal in several live aspects causes environment damage. Characteristics of good SPE material are insoluble in water and organic solvent, relatively big specific surface area, high capacity

and selectivity toward metal separation, and reusability for several cycles in extraction.

Several works in synthesis of SPE material have been done by several researchers. One of their works is silica modification with active sites containing donor atom as a function of ligand derived from synthesis compounds or natural product like fungi, algae or other biomass from agro industrial waste in increasing of adsorption capacity of materials upon metal ions [4-9]. In addition, improving of chemical stability and adsorption selectivity is also very important of these materials. The improving of the adsorption selectivity

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can be performed through ionic imprinting process using metal ion as a template to increase material selectivity upon a target metal.

Synthesis technique of ionic imprinted material is a potential technique to produce material which is selective upon metal ion. In the ionic imprinted technique, adsorption selectivity of metal ion can occur because there are metal ions playing a role as a template and a monomer containing functional groups in polymer synthesis. A releasing of metal ions as template from polymer matrix will cause formation and arrangement of ionic imprinted cavities on ionic imprinted material which will adsorb selectively target ion [10-13].

In this research, it was carried out modification of silica using organic compound derived from *Nannochloropsis* sp algae biomass. *Nannochloropsis* sp algae biomass was chosen because this biomass has some active groups such as; hydroxyl, carbonyl, and amide. These active groups have a role as ligands to bind metal ions [14-16]. However, the use of algae biomass only as adsorbent has some problems. These problems of algae biomass are low density, degradable, and not selective toward metal ions in adsorption process [17-18]. Because of these, the algae biomass is lack of effective to be applied as a column filling material to be continuously adsorption process.

In order to control these problems, the immobilization of the algae biomass using silica as a supporting matrix and continued with imprinting process using a target ion to increase its adsorption selectivity were carried out in this research. In addition, the ionic imprinting process used Cd^{2+} ion as a template. This can cause the immobilization of the algae biomass using silica as matrix to be most selective upon Cd^{2+} ion in its adsorption process. To produce specific material which can be used in SPE, the material resulted from synthesis of Cd^{2+} ionic imprinted *Nannochloropsis* sp with silica matrix from TEOS precursor was examined. The examinations covered chemical stability in solution media, adsorption selectivity, and reusability in adsorption of target metal ion.

EXPERIMENTAL SECTION

Materials

Materials used in this research consist of TEOS, $\text{CH}_3\text{CH}_2\text{OH}$, Na_2EDTA , $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, ZnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, AgCl , CH_3COOH , filter paper Whatman 42, universal indicator paper, and CH_3COONa from commercial products of E-Merck, Germany. NaOH , NH_4OH , and HCl (37%) were purchased from Alba Chemical.

Nannochloropsis sp algae biomass was taken from Lampung Sea Cultivation Bureau/Balai Budidaya Laut

Lampung, Province of Lampung, Indonesia. The matter was cleaned with distilled water to remove dirt and was kept on a filter paper to minimize the water content. Furthermore, the biomass was dried for 3 days continued by drying in an oven at 60°C for 12 h. Then the material was ground and sieved to collect the particles around 100 – 200 mesh size.

Instrumentation

Supporting and analysis apparatus were used in this research besides standard glass and plastic apparatus. Supporting apparatus consist of analytical balance (Mettler AE 160), sieve (200 mesh), and oven (Fisher Scientific), magnetic stirrer, Centrifuge (OSK 6474B), pH meter (Orion 4 Star), vacuum pump (Buchi VacR V-500). Analysis instrumentations used in this work are atomic absorption spectrophotometer (AAS) (Perkin Elmer 3110) applied to analysis the metal concentration and IR spectrophotometer (Prestige-21 Shimadzu) used to determine the functional groups.

Procedure

Synthesis of Cd(II)-IIP

In the synthesis of Cd(II)-IIP, the interacted solutions were made into 2 parts (Solution A and B). Solution A (TEOS and water) was filled into plastic glass and added with HCl 1 M up to pH 2, then it was stirred by magnetic stirrer for 30 min. Solution B ($0,097\text{ g CdCl}_2 \cdot \text{H}_2\text{O}$ and ethanol) was filled into plastic glass, heated, and stirred by magnetic stirrer until dissolved. Then, it was added with 0.4 g biomass continued by stirring for 1 h. Solution A was mixed with solution B by stirring until gel was obtained. The obtained gel was left for a night and rinsed by mixture of water/ethanol 60/40%, followed with soaking the gel for 24 h in Na_2EDTA 0.1 M continued with stirring for 30 min in HCl 0.5 M. The resulted material was neutralized with water up to $\text{pH} \approx 7$, dried in oven for 6 h at 60°C , grounded, and sieved into size of 200 mesh.

Chemical stability

In order to know chemical stability of Cd(II)-IIP material, 0.1 g of material was mixed in 100 mL of each solution, consisting of HNO_3 0.1 M (pH 1.35), CH_3COONa 0.1 M (pH 5.22), and water (pH 9.34) with various of time 1–6 days. Concentration of Si dissolved in filtrate was analyzed using AAS. The residue left was dried and analyzed by IR spectrophotometer. Percentage of Si left in ionic imprinted material was calculated following the equation; % Si left = $\frac{[\text{Si}]_t}{[\text{Si}]_0} \times 100$, with $[\text{Si}]_0$ = initial concentration of Si in ionic imprinted material and $[\text{Si}]_t$ = concentration of Si dissolved at time (t) in mg L^{-1} .

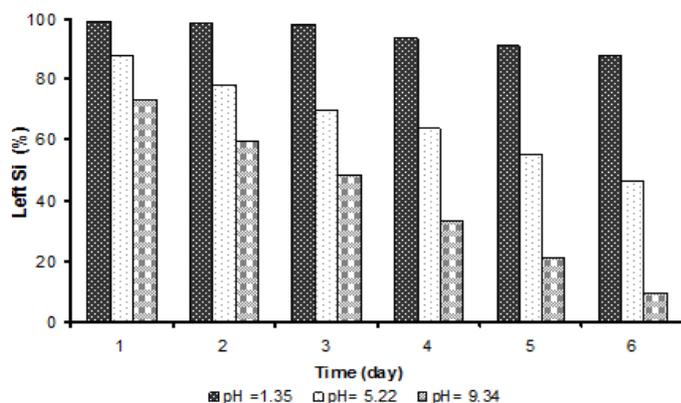


Fig 1. Relation between interaction time in solution media and % [Si] left on Cd(II)-IIP

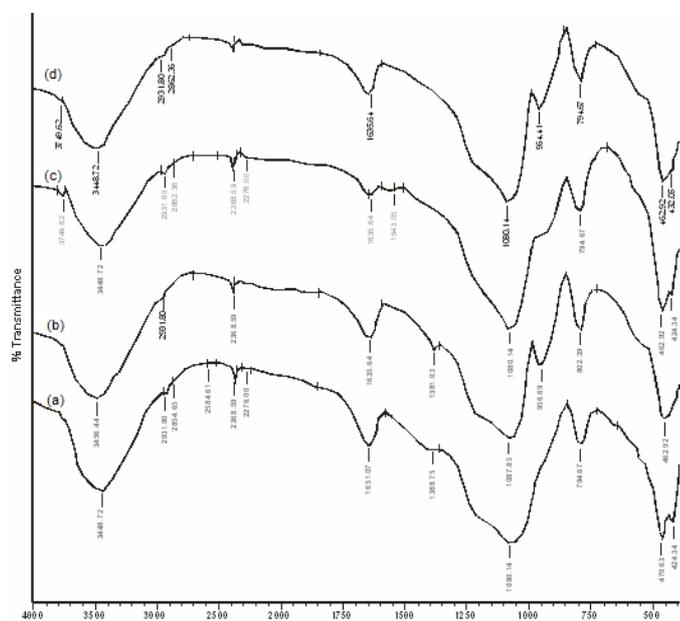


Fig 2. IR spectra of a) material Cd(II)-IIP *Nannochloropsis* sp, b) after interaction 6 days in solution media with pH = 1.35, c) pH = 5.22, and d) pH = 9.34

Reusability

Metal ion adsorbed on Cd(II)-IIP material was released using HCl 0.1 M, Na₂EDTA 0.1 M, and HNO₃ 0.1 M. After washed with water up to neutral, the material was reused to adsorb Cd(II) ion using batch method until 10 cycles.

Adsorption selectivity

50 mg of Cd(II)-IIP material and NIP was interacted with 20 mL of solution containing ion pairs; Cd²⁺/Ag⁺; Cd²⁺/Zn²⁺; Cd²⁺/Cu²⁺; Cd²⁺/Ni²⁺ with the concentration of 0.5 mmol L⁻¹ Cd(II) and 0.5 or 1.0 mmol L⁻¹ of the metal ion pairs. The adsorption was carried out in batch system using magnetic stirrer at optimum pH and time.

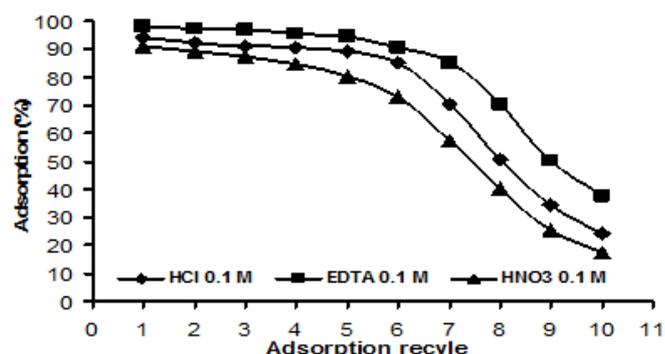


Fig 3. Adsorption recycle of Cd²⁺ ion on Cd(II)-IIP material with each eluent of HCl 0.1 M, EDTA 0.1 M, and HNO₃ 0.1 M

Solution was centrifuged and filtrate was taken to be determined the concentration of metal ion left in solution by AAS.

RESULT AND DISCUSSION

Chemical stability

One of the parameters to determine a quality of ionic imprinted material produced is chemical stability in solution media. Chemical stability of Cd(II)-IIP material was studied by interacting the material with acid, neutral, and base media condition by determining the concentration of Si left as function of time (Fig. 1).

In Fig. 1, it can be seen that the amount of Si left at after the interaction time of 6 days is the much for acid solution media (pH = 1.35). This shows that the Cd(II)-IIP material is very stable in acid condition. The stability of Cd(II)-IIP occurs because of protonation of active groups from *Nannochloropsis* sp biomass. This can protect bond cutting between functional group and silica matrix [19].

At the base condition (pH = 9.34), the concentration of Si left is the smallest while the interaction time increases. The amount of soluble Si comes from silica net hydrolysis with releasing of active groups. This occurs because of hydrolysis on chemical bonds between *Nannochloropsis* sp and silica surface. If the data of Si left concentration gives evidence of Cd(II)-IIP material stability supported by IR spectrum data in Fig. 2, so it can be stated that acid-base media condition determines strongly the material stability.

In Fig. 2, it can be seen generally that the interaction result for 6 days does not change the functional groups on Cd(II)-IIP *Nannochloropsis* sp material left in acid, neutral, and base media (Fig. 2b-d). However, on Cd(II)-IIP material in acid and base media appears several new adsorption bands. These cases do not appear in neutral media. In acid media

Table 1. Adsorption competition of Cd²⁺ metal ion upon Ni²⁺, Cu²⁺, Zn²⁺, and Ag⁺ on NIP and Cd(II)-IIP

Materials	Concentrations (mmol L ⁻¹)		Adsorption (%)		<i>D</i> (L g ⁻¹)		α	α_r
	Cd	Ni	Cd	Ni	Cd	Ni		
Cd(II)-IIP	0.5	0.0	98.36		23.965			
	0.5	0.5	97.76	58.53	17.447	0.522	33.417	34.594
	0.5	1.0	96.68	48.85	11.641	0.353	32.947	32.769
NIP	0.5	0.0	88.62		3.115			
	0.5	0.5	87.29	88.49	2.746	2.843	0.966	
	0.5	1.0	84.08	85.03	2.113	2.102	1.005	
Cd(II)-IIP	Cd	Cu	Cd	Cu	Cd	Cu		
	0.5	0.5	97.55	58.62	15.896	0.567	28.053	30.040
	0.5	1.0	96.20	48.28	10.132	0.373	27.138	28.538
NIP	0.5	0.5	87.29	88.03	2.746	2.941	0.934	
	0.5	1.0	84.08	84.75	2.113	2.222	0.951	
Cd(II)-IIP	Cd	Zn	Cd	Zn	Cd	Zn		
	0.5	0.5	96.42	56.46	10.788	0.535	20.180	22.422
	0.5	1.0	94.90	47.70	7.449	0.376	19.812	18.991
NIP	0.5	0.5	89.15	89.86	3.288	3.653	0.900	
	0.5	1.0	87.02	86.18	2.682	2.570	1.043	
Cd(II)-IIP	Cd	Ag	Cd	Ag	Cd	Ag		
	0.5	0.5	89.69	85.24	3.481	3.922	0.887	4.565
	0.5	1.0	88.38	84.40	3.043	3.679	0.827	6.478
NIP	0.5	0.5	75.01	90.09	1.201	6.182	0.194	
	0.5	1.0	81.68	95.36	1.784	13.976	0.128	

exists sharply adsorption band at 1381.03 cm⁻¹ derived from interaction of Cd(II)-IIP material with nitric acid. This is resulted from nitrate ion adsorption left [20-21]. In addition, in acid media appears adsorption band at 956.69 cm⁻¹ (Fig. 2b) and in base media at 964.41 cm⁻¹ (Fig. 2d) derived from stretching vibration of Si-O from Si-OH.

Reusability

Reusability of material for adsorption of metal ions for several cycles without damage of material structure and decreasing adsorption capacity is one of the important parameters in determining the material quality produced. In order to obtain the best quality of the material, the material should be reused for several times. Adsorption reusability with Cd²⁺ ion on Cd(II)-IIP material can be seen in Fig. 3.

From the data of Fig. 3, it can be observed that reusability of adsorption for 4 cycles does not reduce significantly the adsorption capacity. This fact shows that Cd(II)-IIP is stable enough to be reused for 4 cycles with using solutions of 0.1 M HCl; 0.1 M Na₂EDTA; 0.1 M HNO₃. The adsorption capacity of this adsorbent decreases after used 4 cycles. Decreasing of this adsorption capacity occurs because of decreasing of active sites on material caused by a desorption performed to release Cd(II) ion adsorbed.

Fig. 3 also shows that Cd(II)-IIP adsorption ability upon Cd(II) ion with using 0.1 M Na₂EDTA as eluent is the highest among of 0.1 M HCl and 0.1 M HNO₃. Cd(II) ion is an ion grouped as soft acid, while Cd(II)-IIP contains functional groups of -OH, carbonyl, and amide grouped as hard bases. In addition, interaction of coordination covalent between Cd²⁺ ion and EDTA will be more dominant. This is supported by the data of complex stability constant (*log k_f*) Cd-EDTA 16.36 [22].

It can be stated that HCl elution is more effective than HNO₃ elution. This can be explained that HCl plays a role in releasing of metal ion bounded caused by an electrostatic interaction and a complex formation. Therefore, Cd²⁺ ion sorbed on Cd(II)-IIP can be released. If the material is reused to sorb Cd²⁺ ion, amount of Cd²⁺ left on material is relatively smaller, so it does not disturb for the next adsorption. Interaction of Cl⁻ ion with Cd²⁺ ion is stronger than NO₃⁻ ion characterized as weaker donor than Cl⁻ in complex formation with Cd²⁺ [23].

Adsorption selectivity

Adsorption selectivity on Cd(II)-IIP material was studied with performing adsorption competition of Cd²⁺ ion on Cd(II)-IIP upon its ion pair (Ni²⁺, Cu²⁺, Zn²⁺, and Ag⁺ ion) in solution. The metal ions were chosen based on difference of ionic radius; Cd²⁺ = 109, Ni²⁺ = 83,

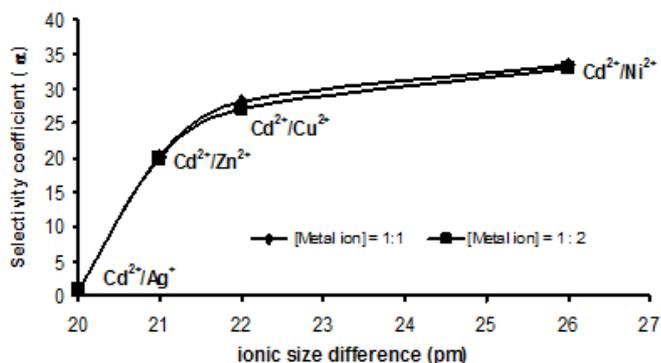


Fig 4. Relationship between metal ionic size difference and adsorption selectivity on Cd(II)-IIP

$\text{Cu}^{2+} = 87$, $\text{Zn}^{2+} = 88$, and $\text{Ag}^+ = 129$ pm [24]. In addition, the difference of acid properties from the metal ions compared to Cd^{2+} was also studied.

Percentage of metal extracted, distribution ratio, selectivity coefficient, and relative selectivity coefficient on metal ion adsorption process upon Cd(II)-IIP were determined with using these equations;

$$Q = (C_o - C_a)V/W \quad (1)$$

$$E = (C_o - C_a)/C_a \quad (2)$$

$$D = Q/C_a \quad (3)$$

$$\alpha = DM_1/DM_2 \quad (4)$$

$$\alpha_r = \alpha/\alpha_n \quad (5)$$

where, Q is amount of metal sorbed (mg g^{-1}), C_o and C_a are initial and equilibrium concentration of metal ion ($\mu\text{g mL}^{-1}$), W is adsorbent mass (g), V is metal ion solution volume (L), E (%) is extraction percentage, D is distribution ratio (L g^{-1}), α is selectivity coefficient, α_r is relative selectivity coefficient, and α_n is selectivity factor of ionic imprinted and non-imprinted adsorbent [7].

Adsorption competition data of ionic pairs, $\text{Cd}^{2+}/\text{Ni}^{2+}$, $\text{Cd}^{2+}/\text{Cu}^{2+}$, $\text{Cd}^{2+}/\text{Zn}^{2+}$, and $\text{Cd}^{2+}/\text{Ag}^+$, on NIP and Cd(II)-IIP material for each adsorption competition of metal ion pairs with concentration of 1:1 and 1:2 are listed in Table 1.

Adsorption competition of their ionic pairs on NIP and Cd(II)-IIP material (Table 1) can be observed that the adsorption selectivity of Cd(II)-IIP material for each metal ionic pairs is bigger than the adsorption selectivity of NIP material. In addition, it can be also observed that however, concentration of Cd^{2+} ionic pairs such as Ni^{2+} , Cu^{2+} , Zn^{2+} , and Ag^+ is raised 2 times bigger, selectivity coefficient value is also relatively big. This fact shows that ionic imprinting process using Cd^{2+} ion as a template can increase the adsorption selectivity upon the target ion.

The selectivity of Cd(II)-IIP material increases with ionic pair order as follow $\text{Cd}^{2+}/\text{Ag}^+ < \text{Cd}^{2+}/\text{Zn}^{2+} < \text{Cd}^{2+}/\text{Cu}^{2+} < \text{Cd}^{2+}/\text{Ni}^{2+}$. Increasing of material adsorption selectivity toward Cd^{2+} ion is strongly determined by metal ion charge and size. In this case, it can be seen in

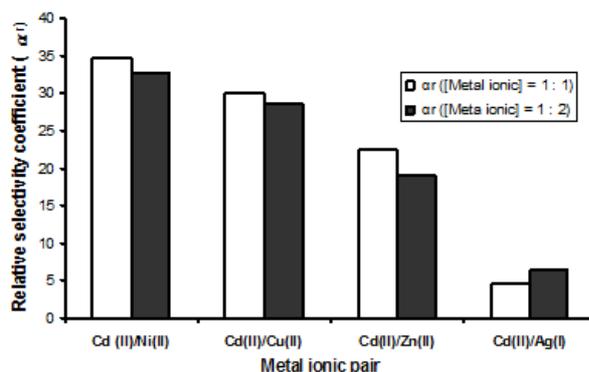


Fig 5. Relative selectivity coefficient (α_r) of Cd(II)-IIP upon NIP

Fig. 4, the larger of metal ion size difference, the bigger of the adsorption selectivity. This fact shows that adsorption selectivity is very determined by metal ion size difference. Besides that, another factor determined selectivity is metal-ligand interaction as the character of soft-hard acid-base between metal ion and ligand. Functional groups existing on Cd(II)-IIP material are $-\text{OH}$ group, carbonyl, and amide grouped hard base. If it was studied from metal cation hardness, ions of Cu^{2+} , Zn^{2+} , and Ni^{2+} are grouped more hard than Cd^{2+} and Ag^+ ion. In addition, although the material has Cd^{2+} ionic template as ionic imprinted cavities acting as active sites for Cd^{2+} ion, but it still sorbs of Cu^{2+} , Zn^{2+} , and Ni^{2+} ion through interaction of hard-soft acid-base.

For Ag^+ ion, this cation has the biggest of ionic size among Cu^{2+} , Zn^{2+} , and Ni^{2+} ion. In water media, metal cations tend to form hydrate, the larger of ionic radius the larger of distance between metal ion and oxygen in water molecules (M-O), while solvation energy is lower [22]. These facts show that Ag^+ ion is easier to be sorbed than Cd^{2+} ion. As a result of this case, Cd(II)-IIP material will be lack of selective upon Ag^+ ion as shown with selectivity coefficient value (α) $\text{Cd}^{2+}/\text{Ag}^+ \leq 1$ (Table 1).

From Fig. 5, it can be known that adsorption relative selectivity coefficient of Cd(II)-IIP upon NIP on metal ionic pairs concentration ratio of 1:1 upon Cd^{2+} ion is relatively bigger than concentration ratio of 1:2. This shows that increasing of metal ionic pairs concentration adsorbed was decreased its relative selectivity. This relative selectivity coefficient indicates how big ability of material selectivity resulted from (Cd(II)-IIP) ionic imprinting in adsorption of Cd^{2+} ion. Therefore, it can be compared with the relative selectivity coefficient of NIP.

CONCLUSION

Cd(II)-IIP material synthesized from *Nannochloropsis* sp biomass with silica matrix TEOS

precursor has chemical stability in acid and near neutral media, but low stability in base media. The ability in reextraction upon Cd^{2+} ion from solution is around 4 cycles. The Cd(II)-IIP material has higher selectivity upon Cd^{2+} ion than NIP material with adsorption selectivity order as follow; $\text{Cd}^{2+}/\text{Ag}^+ < \text{Cd}^{2+}/\text{Zn}^{2+} < \text{Cd}^{2+}/\text{Cu}^{2+} < \text{Cd}^{2+}/\text{Ni}^{2+}$. It can be concluded that Cd(II)-IIP material can be used as SPE material for preconcentration or separation of Cd^{2+} ion from the solution.

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