Asian Journal of Chemistry; Vol. 25, No. 5 (2013), 2875-2880

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14166

Comparative Study of Adsorption Ability of Ni(II) and Zn(II) Ionic Imprinted Amino-Silica Hybrid Toward Target Metal in Solution

BUHANI*, SUHARSO and ANDI YULI FITRIYANI

Department of Chemistry, Faculty of Mathematic and Natural Sciences, University of Lampung, Lampung, Indonesia

*Corresponding author: Fax: +62 721 770422; Tel: +62 721 770422; E-mail: buhani_s@yahoo.co.id

(*Received*: 6 June 2012; *Accepted*: 26 November 2012) AJC-12473

This research investigated comparative study of adsorption ability from Ni(II) and Zn(II) ionic imprinted polymer [Ni(II)-IIP and Zn(II)-IIP] amino-silica hybrid to each Ni(II) and Zn(II) ion as a target metal. Adsorbent synthesis was carried out *via* sol-gel process with an active compound 3-aminopropyltrimethoxysilane and a silica matrix from tetraethylorthosilicate. Series of experiments with batch method were performed to determine adsorption kinetics, isotherm and selectivity of adsorbent Ni(II)-IIP toward Ni(II) target ion and Zn(II)-IIP toward Zn(II) target ion in solutions. Kinetic models of Ni(II) and Zn(II) ion for all adsorbents tend to follow a pseudo second order kinetic model and a Dubinin-Raduskevich (D-R) isotherm adsorption model. The adsorption capacity value (q_{DR}) of Ni(II) ion on non-imprinted polymer (NIP) and Ni(II)-IIP is each 21.674 and 31.478 mg g^{-1}, while the adsorption capacity value of Zn(II) ion on Zn(II)-NIP and Zn(II)-IIP is 19.255 and 24.633 mg g^{-1}. The selectivity coefficient (α) value for each adsorbent shows that Ni(II)-IIP adsorbent is more effective upon its Ni(II) ion target metal than Zn(II)-IIP adsorbent with Zn(II) ion as its target.

Key Words: Ionic imprinting, Adsorption selectivity, Amino-silica hybrid, Metal ion.

INTRODUCTION

Success of heavy metal adsorption process is much influenced on adsorbent ability in interacting with heavy metals. Effective adsorbent has to possess big adsorption capacity, chemically stable and reusability for several times[1,2]. In addition, if the adsorbents will be used for separation or preconcentration of specific metals, so the adsorbents have to be selective characteristic[3,4].

In recent years, it has been developed a technique of selective adsorbent synthesis using target metal ion as a printing known with ionic imprinting technique[5]. The technique of ionic imprinting material synthesis is an appropriate technique to produce selective material to metal ions. In the ionic imprinting technique, adsorbent will be selective upon target metals because in the adsorbent synthesis exists metal ions playing a role a template and a monomer containing functional groups[6,7].

Metal ionic imprinting synthesis process occurs through metal ionic releasing as template from polymer matrix. This causes formation of ionic imprinted cavities and arrangement of ionic imprinted material which will adsorb target ions selectively[8-11]. In addition, on adsorbent, beside active groups playing a role as ligands in adsorbing metal ions, there are active sites as metal ion imprinting which are selective toward target metals.

In order to know relationship between interaction force of target metal ions and active groups playing a role as modifier agent in synthesis of selective adsorbent, so that in this research it was performed comparative study of adsorption ability from Ni(II) and Zn(II) ionic imprinted amino-silica hybrid toward each Ni(II) and Zn(II) ion as the target. Ionic imprinting process role in increasing of adsorption ability upon target metal was investigated *via* batch method experiment to identify adsorption kinetics, isotherm and selectivity.

EXPERIMENTAL

Template metal ion is obtained from $Ni(NO_3)_2{\cdot}6H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$. $CoCl_2$, $CdCl_2{\cdot}H_2O$, $CuCl_2{\cdot}2H_2O$, TEOS, NH_4OH, HCl, CH_3COOH, CH_3COONa, Na_2EDTA and ethanol were supplied from E-Merck. Amino functional group is derived from active compound of 3-aminopropyltrimetoxysilane from Aldrich.

Ni(II) and Zn(II) ionic imprinting amino-silica hybrid material synthesis: Solution of X consisting of 4 mL Ni(II) and Zn(II) 0.1 M, each was dissolved in 4 mL of ethanol. Then, each was mixed with 2 mL of 3-aminopropyltrimetoxysilane. The mixtures obtained were stirred with magnetic stirrer and heated up to homogeneous. The homogeneous mixtures were added solution of Y (4 mL of TEOS and 4 mL of water) placed in plastic cube and they were added several

drops of HCl 0.1 M up to pH of 2 with stirring by magnetic stirrer for 0.5 h. Gel produced was kept for 24 h and it was filtered and washed by ethanol. For releasing of imprinting metal ion from polymer matrix, it was done elution with Na_2EDTA 01 M and followed with HCl 0.5 M. The material found was cleaned with water up to pH≈7 and it was dried with oven at 60 ºC for 6 h[7].

Spectrophotometer of IR (Prestige-21 Shimadzu) was used to identify functional groups of ASH material before and after ionic imprinted. Chemical compositions of adsorbent before and after ionic imprinted were investigated by energy dispersive X-ray spectrometer (EDX) JSM) 6360 LA. Analysis of metal concentration was done with atomic adsorption spectrophotometer (AAS) Model Perkins Elmer 3110.

Adsorption: Adsorption process was performed with experiment series using batch method covering determination of kinetic model and adsorption isotherm model. 50 mg of adsorbent were interacted with 0-250 mg L^{-1} solution of metal ion for 5-60 min and at pH of 5.6. Adsorption selectivity was determined with interacting 50 mg of adsorbent and 20 mL of solution containing 0.5 mmol L^{-1} ion Ni(II) with its ionic pairs Ni(II)/Zn(II), Ni(II)/Cu(II), Ni(II)/Co(II) and Ni(II)/Cd(II or Zn(II) with its ionic pairs Zn(II)/Ni(II), Zn(II)/Cu(II), Zn(II)/Co(II) and Zn(II)/Cd(II). Amount of metal ion adsorbed was identified using this equation below;

$$q_t = (C_o\text{-}C_a)V/W \quad (1)$$

where, q is amount of metal adsorbed (mg g^{-1}), C_o and C_a are initial and equilibrium concentrations from metal ion (mg L^{-1}), W is adsorbent mass (g), V is solution volume of metal ion (L).

In order to evaluate suitability of experimental results with kinetic equation theory and adsorption isotherm model, for each their parameter was investigated a value of the root mean squared error and Chi-square test (χ^2)[12,13] with using eqns. 2 and 3.

$$RMSE = \sqrt{\left(\frac{1}{m-2}\right)\sum_{i=1}^{m}\left(q_{i,exp} - q_{i,cal}\right)^2} \quad (2)$$

$$\chi^2 = \sum_{i=1}^{m}\frac{\left(q_{i,exp} - q_{i,cal}\right)^2}{q_{i,exp}} \quad (3)$$

where, $q_{i,exp}$ and $q_{i,cal}$, each was obtained from experiment and estimation results through adsorption isotherm and kinetic model equation, m is the number of observation in the experimental isotherm. A smaller root mean squared error value indicates a better curve fitting, moreover, if the data produced from the model are close to the experimental results, χ^2 may be a small number[12,14].

RESULTS AND DISCUSSION

Characterization results with IR spectrophotometer on NIP, Ni(II)-IIP and Zn(II)-IIP adsorbent as seen in Fig. 1 showed that silica modification process with 3-aminopropyltrimethoxysilane were run successfully. These are shown with the existence of adsorption band at 2939.52 cm^{-1} indicating stretching vibration of -CH_2 group and they are also supported by appearance of adsorption band at 1473.62 cm^{-1} derived from asymmetry bending vibration of -CH- (methyl)[15]. In addition, decreasing of adsorption at 964.41 cm^{-1} (stretching vibration of Si-O from Si-OH) is caused by decreasing of an amount of silanol groups resulted condensation formation with amine compound. Appearances of broad adsorption around 1640-1560 cm^{-1} are predicted from bending vibration of primer amine (N-H)[16-18] overlapping with -OH group. These indicate that although it was found ionic imprinting *via* bounding process and metal ion releasing on imprinting process, it does not change character of active groups existing on Ni(II)-IIP and Zn(II)-IIP adsorbent.

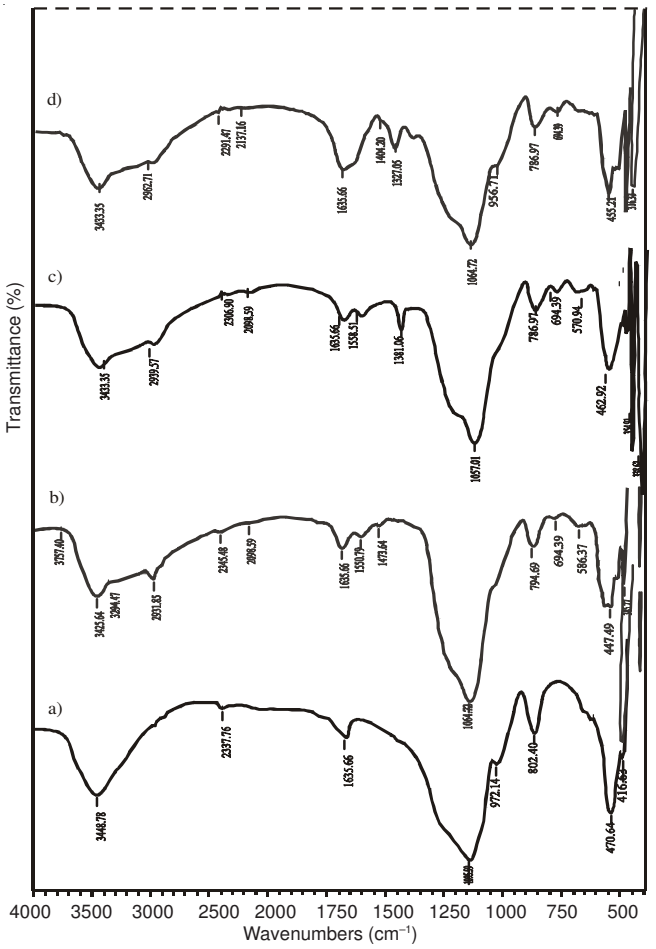


Fig. 1. Infrared spectra of a) Silica, b), NIP, c) Ni(II)-IIP and d) Zn(II)-IIP

The energy dispersive X-ray analysis (EDX) was applied to analyze element composition of Ni(II)-IIP and Zn(II)-IIP adsorbent (Fig. 2). In Fig. 2, it is observed that on NIP-Ni material (Fig. 2a) still exists Ni metal, while on Ni(II)-IIP there is no Ni metal again (Fig. 2b). Likewise on NIP-Zn material (Fig. 2c) still exists Zn metal and on Zn(II)-IIP there is nothing anymore (Fig. 2d). Ni(II) and Zn(II) metal on Ni(II)-IIP and Zn(II)-IIP were removed *via* elution process with EDTA and HCl solution.

Adsorption kinetics: Adsorption kinetic models of Ni(II) and Zn(II) ion on Ni(II)-IIP, Zn(II)-IIP and NIP adsorbent were studied with pseudo first order (eqn. 4) and pseudo second order kinetic model (eqn. 5)[19,20]. Where q_t and q_e (mg/g) are Ni(II) and Zn(II) ions adsorption capacity at time t and at

equilibrium, as well as k_1 and k_2 are the first order and second order of rate constants.

$$q_t = q_e - q_e \exp(-k_1 t) \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Linear equation of pseudo first order and pseudo second order kinetic model can be seen in Figs. 3 and 4. Kinetic parameters of pseudo first order and pseudo second order were determined based on plot of ln (q_e-q_t) *vs.* t and t/q_t *vs.* t as shown on Figs. 3 and 4 and summarized in Table-1.

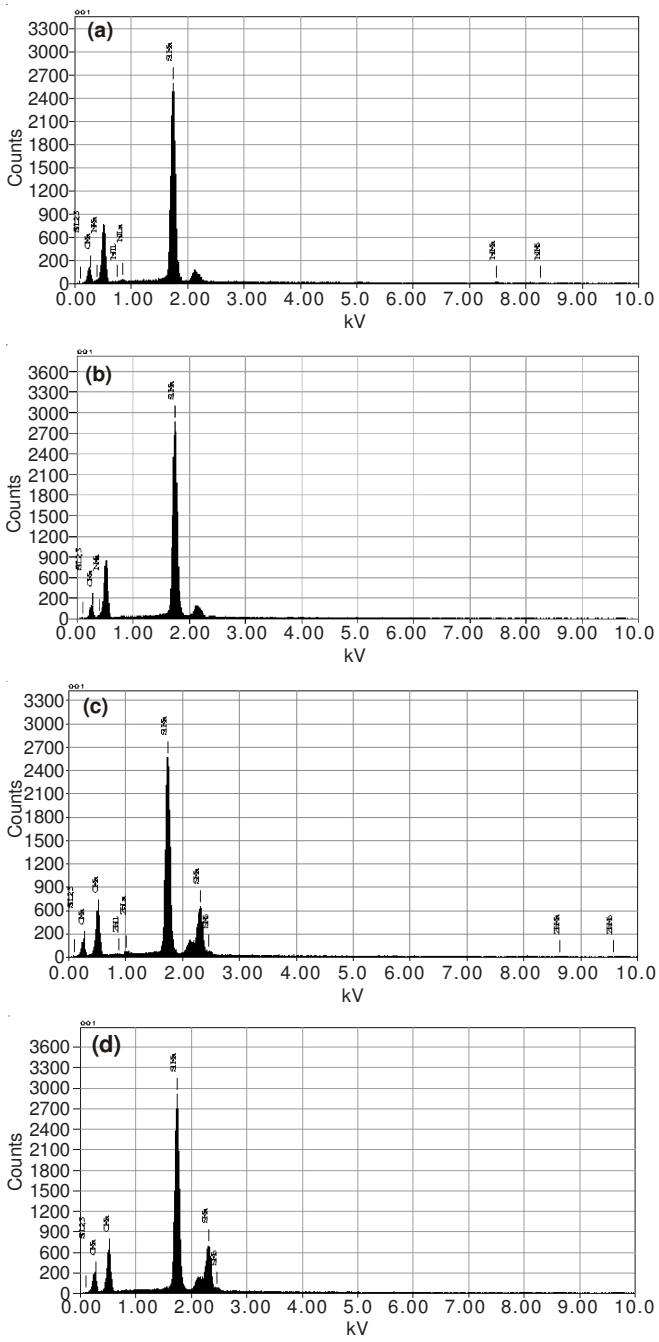


Fig. 2. EDX Analysis of a) NIP-Ni, b) Ni(II)-IIP, c) NIP-Zn and d) Zn(II)-IIP

From Table-1, it can be seen that kinetic models of Ni(II) and Zn(II) on all adsorbents tend to follow pseudo second order kinetic with correlation coefficient (R^2) of 0.99 higher than pseudo first order kinetic model. Besides that, values of root mean squared error and χ^2 on pseudo second order kinetic model are smaller than pseudo first order kinetic model. These facts show that pseudo second order kinetic model fits in describing adsorption kinetic of Ni(II) and Zn(II) target ion on ionic imprinting amino-silica hybrid and non-ionic imprinting material. Pseudo second order kinetic model is based on assumption that adsorption rate stages are controlled by chemical interaction between adsorbent functional group superficial and metal ions[20,21].

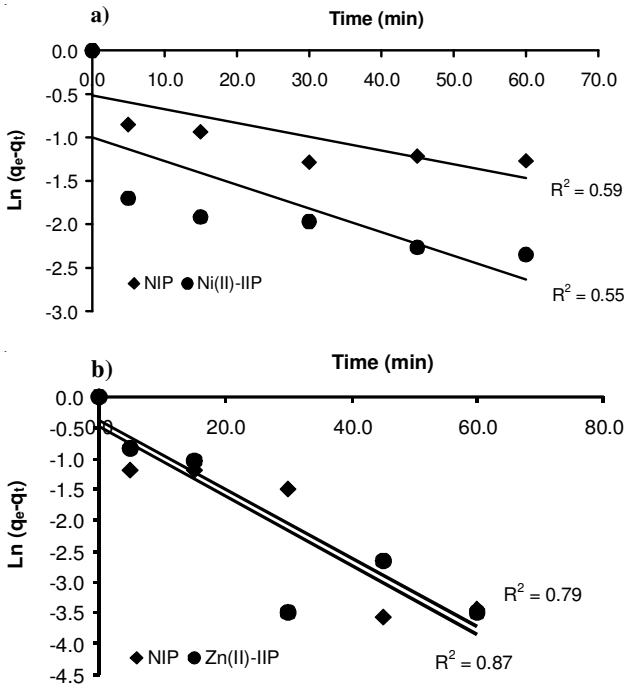


Fig. 3. Kinetic linear model of pseudo first order on adsorption of Ni(II) and Zn(II) target ions by adsorbents

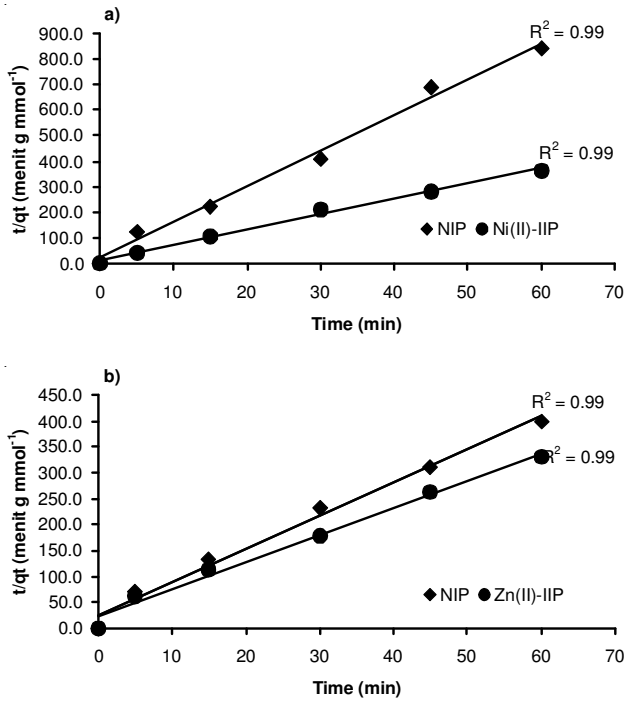


Fig. 4. Kinetic linear model of pseudo second order on adsorption of Ni(II) and Zn(II) target ions by adsorbents

TABLE-1
ADSORPTION KINETIC PARAMETERS OF Ni(II) AND Zn(II) TARGET METAL ION ON IONIC IMPRINTING AMINO-SILICA HYBRID AND NIP

Kinetic Models	Interaction of target metals with adsorbents			
	Ni(II) Ion		Zn(II) Ion	
	NIP	Ni(II)-IIP	NIP	Zn(II)-IIP
Pseudo-first-order				
k_1 (min^{-1})	0.016	0.027	0.056	0.056
q_e cal (mg g^{-1})	0.721	0.612	0.326	0.419
R^2	0.586	0.552	0.870	0.790
RMSE	1.228	1.336	1.015	1.256
X^2	7.892	13.42	2.215	3.357
Pseudo–second–order				
k_2 x 10^{-3} (g $mmol^{-1}$ min^{-1})	9.302	2.979	1.534	1.258
q_e cal (mg g^{-1})	0.276	0.247	0.239	0.287
R^2	0.902	0.940	0.931	0.918
RMSE	0.336	0.216	0.206	0.192
X^2	0.926	0.487	0.455	0.410
qe_{Exp} (mg g^{-1})	0.355	0.260	0.207	0.321

Adsorption isotherm: If adsorption process is in equilibrium condition system, adsorption capacity of Ni(II) target metal ion on Ni(II)-IIP adsorbent and Zn(II) target metal ion on Zn(II)-IIP is one of important fundamental parameters to be known. Because adsorption capacity will give a distribution describing between target metal ion and adsorbent, so in this research adsorption isotherm models of Ni(II) and Zn(II) target metal ions with adsorbents were studied with using 4 adsorption isotherm equations namely; Langmuir (eqn. 6), Freundlich (eqn. 7), Dubinin-Raduskevich (D-R) (eqn. 8) and Temkin adsorption isotherm (eqn. 9)[12,22,23].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (6)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (7)$$

$$q_e = q_{DR}\exp(-BD[RT\ln(1+\frac{1}{C_e})]^2 \quad (8)$$

$$q_e = \frac{RT}{b_{Te}}\ln(K_{Te}C_e) \quad (9)$$

With, q_m is the amount of maximum metal ion adsorbed (mg g^{-1}), C_e is the equilibrium concentration of metal ion (mL g^{-1}), n is the Freundlich exponent, K_L (L mol^{-1}) and K_F (mg g^{-1}) are each the Langmuir and Freundlich constant. q_{DR} and B_{DR} are the D-R isotherm constants in mg g^{-1} and mol^2 kJ^{-2} respectively, b_{Te} is the Temkin constant related to the heat adsorption (J mol^{-1}), K_{Te} is the equilibrium binding constant L g^{-1}, R is the gas constant (8.314 kJ mol^{-1}) and T is the absolute temperature (K).

Several adsorption isotherm models used to study interaction of target metal ion and ionic imprinting amino-silica hybrid adsorbent can be evaluated with determining correlation coefficient (R^2), root mean squared error value and χ^2 from adsorption parameters at every model as listed in Table-2. In Table-2, generally it can be seen that adsorption process of Ni(II) and Zn(II) ions on all adsorbents applied in this research tend to follow D-R isotherm model with the value of R^2 higher than Langmuir, Freundlich and Temkin isotherm models. Besides that, the value of root mean squared error and χ^2 in D-R adsorption isotherm is smaller than the other isotherm models. These facts show that D-R adsorption isotherm model fits to illustrate adsorption process of Ni(II) and Zn(II) target ions by Ni(II)-IIP, Zn(II)-IIP and NIP adsorbent. D-R adsorption isotherm model assumes that a fixed volume of sorption space closes to the sorbent surface and the existence of sorption potency over these spaces[12].

TABLE-2
ADSORPTION PARAMETERS OF Ni(II) AND Zn(II) TARGET METAL ION ON IONIC IMPRINTING AMINO-SILICA HYBRID AND NIP

Adsorption Parameters	Metal ions			
	Ni(II) ion		Zn(II) ion	
	NIP	Ni(II)-IIP	NIP	Zn(II)-IIP
Langmuir				
q_m (mg g^{-1})	24.454	34.524	23.354	27.246
$K_L \times 10^3$ (L mol^{-1})	4.053	6.599	4.228	5.027
R^2	0.972	0.988	0.978	0.982
RMSE	2.089	2.194	2.951	2.611
χ^2	1.203	1.105	1.855	0.951
Freundlich				
K_F (mg g^{-1})	4.058	6.610	3.725	4.545
n	2.843	2.861	3.002	2.792
R^2	0.958	0.957	0.945	0.978
RMSE	9.487	13.252	8.227	10.531
χ^2	23.657	32.904	20.254	26.425
Dubinin-Raduskevich				
q_{DR} (mg g^{-1})	21.674	31.478	19.255	24.633
B_{DR} x 10^{-6}	4.600	3.043	4.994	3.935
R^2	0.984	0.988	0.984	0.971
RMSE	1.931	1.313	0.777	1.346
χ^2	0.842	0.248	0.128	0.346
Temkin				
bTe (J mol^{-1})	2.152	2.824	1.794	2.388
aTe (L g^{-1})	1.016	1.032	1.011	1.021
R^2	0.949	0.946	0.955	0.968
RMSE	7.844	10.980	5.925	9.211
χ^2	15.986	34.953	10.883	22.354
q_{exp} (mg g^{-1})	23.561	32.667	19.992	25.848

Although it was studied from the value of root mean squared error and χ^2 at D-R adsorption isotherm model smaller than Langmuir isotherm model but the value of R^2 at Langmuir isotherm equation is not too different significantly with D-R isotherm. Fig. 5 showed that there is similar model at relationship between amounts of target metal ion adsorbed experimentally (q_{exp}) and calculation result (q_{cal}) with the equations of D-R adsorption isotherm and Langmuir isotherm. These are also supported with the value of experimentally adsorption capacity (q_{exp}), which is consistent with the value of q_{D-R} and q_m in Langmuir isotherm (Table-2). These indicate that commonly the adsorption process of Ni(II) ion on Ni(II)-IIP and Zn(II) ion on Zn(II)-IIP are inclined to obey D-R and Langmuir isotherm model compared with Freundlich and Temkin isotherm models.

Adsorption selectivity: Adsorption selectivity of Ni(II) ion on Ni(II)-IIP and Zn(II) ion on Zn(II)-IIP was studied with performing adsorption competition with its metal ion pairs

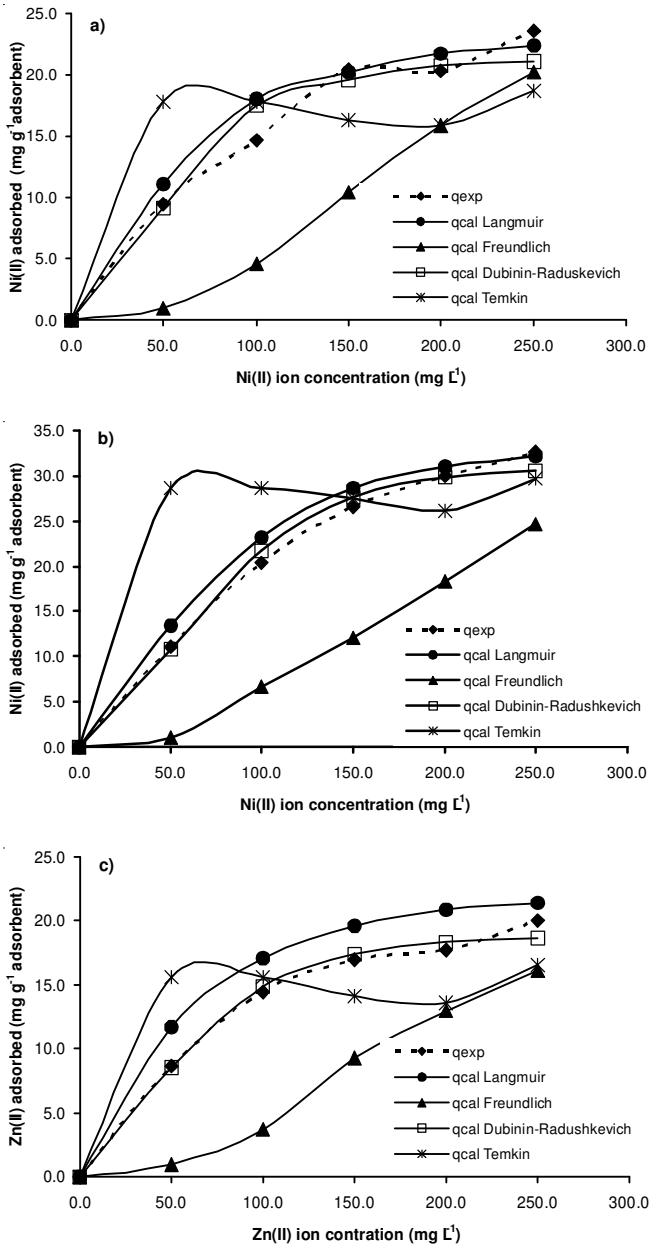
namely; ion pairs of Ni(II)/Zn(II), Ni(II)/Cu(II), Ni(II)/Co(II) and Ni(II)/Cd(II). For Zn(II) ion on Zn(II)-IIP consisted of ion pairs of Zn(II)/Ni(II), Zn(II)/Cu(II), Zn(II)/Co(II) and Zn(II)/Cd(II). The metal ions was selected based on ionic radius difference such as Ni(II) ion = 83, Zn(II) ion = 88, Cu(II) ion = 87, Co(II) ion = 79 and Cd(II) ion = 109 pm[24]. In addition, acidic characteristic difference from the metal ions is compared with Cd(II) or Cu(II) ion.

Distribution ratio, selectivity coefficient and relative selectivity coefficient of adsorbent material were determined with using distribution ratio equation (eq. 10).

$$D = q / C_a \quad (10)$$

Adsorbent selectivity factors of Ni(II)-IIP upon Ni(II) ion and Zn(II)-IIP upon Zn(II) ion with the present of other metal ions in solution were determined with calculating selectivity coefficient (α) (eq. 11).

$$\alpha = D_{M2} / D_{M2} \quad (11)$$



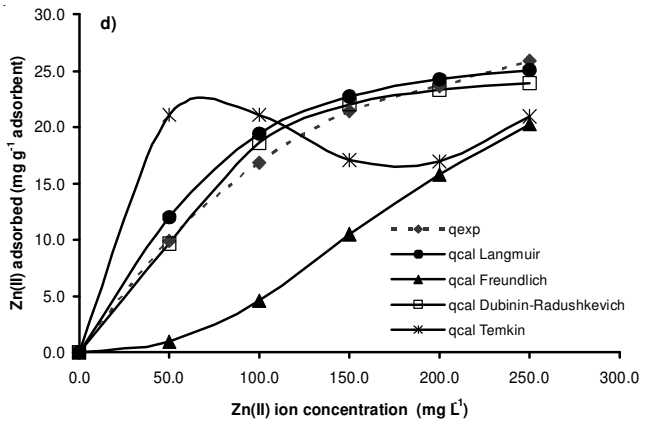


Fig. 5. Relationship between amounts of target metal ion adsorbed experimentally (q_{exp}) and calculation result (q_{cal}) with using adsorption isotherm equations on interaction of a) NIP with solution of Ni(II) ion, b) Ni(II)-IIP with solution of Ni(II) ion, c) NIP with solution of Zn(II) ion and d) Zn(II)-IIP with solution of Zn(II) ion

where, D_{M1} and D_{M2} are distribution ratio of target metal ions and other metal ions in solutions. In order to know adsorbent relative selectivity of Ni(II)-IIP and Zn(II)-IIP upon NIP, it was determined relative selectivity coefficient (α_n) (eq. 12) with α_i dan α_n representing selectivity factor of ionic imprinted and non imprinted material. Adsorption selectivity parameters of Ni(II)-IIP to Ni(II) and Zn(II)-IIP to Zn(II) were displayed in Tables 3 and 4.

$$\alpha_r = \alpha_i / \alpha_n \quad (12)$$

Tables 3 and 4 summarized that Ni(II)-IIP and Zn(II)-IIP adsorbent are more selective to target metal ions when they were competed with their ionic pairs or other metals in solution ($\alpha > 1$) than NIP adsorbent. These are supported with the value of adsorption capacity (q_{exp}, q_m and q_{D-R}) for adsorbent Ni(II)-IIP and Zn(II)-IIP adsorbent bigger than NIP adsorbent (Table-2). These also show existence of imprinting process with Ni(II) and Zn(II) template ions on amino-silica hybrid material has increased adsorption capacity and selectivity of Ni(II)-IIP and Zn(II)-IIP adsorbent with their target ions.

Generally, based on the value of q_{exp} and q_{cal} with using Langmuir and D-R isotherm (Table-2) as well as supported by the value of α of each adsorbent (Tables 3 and 4) show that

TABLE-3
SELECTIVITY PARAMETERS OF Ni(II)-IIP FOR Ni(II) ION

Metal Ions	D_i Ni(II)-IIP (mL g^{-1})	D_n NIP (mL g^{-1})	α_i	α_n	α_r
Ni(II)	4246.00	282.30			
Cu(II)	290.90	232.20	14.60	1.22	12.01
Zn(II)	242.80	214.10	17.49	1.32	13.26
Cd(II)	220.50	211.20	19.26	1.34	14.41
Co(II)	161.10	168.00	26.36	1.68	15.68

TABLE-4
SELECTIVITY PARAMETERS OF Zn(II)-IIP FOR Zn(II) ION

Metal Ions	D_i Zn(II)-IIP (mL g^{-1})	D_n NIP (mL g^{-1})	α_i	α_n	α_r
Zn(II)	3800.00	300.00			
Cd(II)	700.00	520.00	5.43	0.58	9.41
Co(II)	240.00	210.00	15.80	1.43	11.08
Ni(II)	250.00	230.00	15.20	1.30	11.65
Cu(II)	330.00	360.00	11.52	0.83	13.82

Ni(II)-IIP adsorbent is more effective upon its target metal ion [Ni(II) ion] than Zn(II)-IIP with Zn(II) ion as its target. These can be explained with HSAB concept from Pearson[25]. It explains active groups of amino-silica hybrid dominated amine group characterized as a hard base and Ni(II) ion classified as a harder acid than Zn(II) ion. Therefore, active groups of amino-silica hybrid dominated amine group tend to interact with Ni(II) ion. In synthesis of ionic imprinted adsorbent, interaction force between active groups and target metal ions is very determined synthesis success of selective metal adsorbent.

Conclusion

Imprinting process of Ni(II) and Zn(II) target metal ion in amino-silica hybrid synthesis has increased adsorption capacity and selectivity for each adsorbent upon target metal ions compared with NIP adsorbent. Based on comparative study result of adsorption selectivity and capacity determination shows that Ni(II)-IIP adsorbent is more effective upon its target metal, Ni(II) ion, than Zn(II)-IIP upon Zn(II) ion in solution. Existence of similar characteristic from hard-soft acid-base between target metal ions and active groups playing a role as ligands from modifier agent will determine interaction force of metal ions and adsorbent influencing selective adsorbent synthesis success.

ACKNOWLEDGEMENTS

Authors are grateful for financial support of this research (National Priorities in Strategic Research/Penelitian Strategis Sesuai Prioritas Nasional) from Directorate of Research and Community Services, Directorate General of Higher Education (DIKTI), National Education Department of Indonesia, with contract number: 411/SP2H/PL/Dit.Litabmas/IV/2011, 14 April 2011.

REFERENCES

1. X. Chang, N. Jiang, H. Zheng, Q. He, Z. Hu, Y. Zhai and Y. Cui, *Talanta*, **71**, 38 (2007).
2. F. Li, H. Jiang and S. Zhang, *Talanta*, **71**, 1487 (2007).
3. N. Zhang, B. Hu and C. Huang, *Anal. Chim. Acta*, **597**, 12 (2007).
4. M. Shamsipur, J. Fasihi, A. Khanchi, R. Hassani, K. Alizadeh and H. Shamsipur, *Anal. Chim. Acta*, **599**, 294 (2007).
5. P.T. Rao, R. Kala and S. Daniel, *Anal. Chim. Acta*, **578**, 105 (2006).
6. Y. Zhai, Y. Liu, X. Chang, X. Ruan and J. Liu, *React. Funct. Polym.*, **68**, 284 (2008).
7. Buhani, Narsito, Nuryono and E.S. Kunarti, *Desalination*, **251**, 83 (2010).
8. A. ErsÖz, R. Say and A. Denizli, *Anal. Chim. Acta*, **502**, 91 (2004).
9. J. Zhao, B. Han, Y. Zhang and D. Wang, *Anal. Chim. Acta*, **603**, 87 (2007).
10. J.H. Chen, G.P. Li, Q.L. Liu, J.C. Ni, W.B. Wu and J.M. Lin, *Chem. Eng. J.*, **165**, 465 (2010).
11. M.H. Arbab-Zavar, M. Chamsaz, G. Zohuri and A. Darroudi, *J. Hazard. Mater.*, **185**, 38 (2011).
12. M.M. Montazer-Rahmati, P. Rabbani, A. Abdolali and A.R. Keshtkar, *J. Hazard. Mater.*, **185**, 401 (2011).
13. N. Chen, Z. Zhang, C. Feng, M. Li, D. Zhu and N. Sugiura, *Mater. Chem. Phys.*, **125**, 293 (2011).
14. L. Vijayaraghavan, T.V.N. Padmesh, K. Palanivelu and M. Velan, *J. Hazard. Mater.*, **B133**, 304 (2006).
15. J. Coates, Interpretation of Infrared Spectra, A Practical Approach in Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., Chichester., pp. 10815-10837 (2000).
16. R.S.A. Machado, M.G. da Fonseca, L.N.H. Arakaki, J.G.P. Espinola and S.F. Oliveira, *Talanta*, **63**, 317 (2004).
17. N. Jiang, X. Chang, H. Zheng, Q. He and Z. Hu, *Anal. Chim. Acta*, **577**, 225 (2006).
18. H. Yang, R. Xu, X. Xue, F. Li and G. Li, *J. Hazard. Mater.*, **152**, 690 (2008).
19. S. Zakhama, H. Dhaouadi and F.M. Henni, *Bioresour. Technol.*, **102**, 786 (2011).
20. D. Bulgariu and L. Bulgariu, *Bioresour. Technol.*, **103**, 489 (2012).
21. E. Romera, F. Gonzales, A. Ballester, M.L. Blázquez and J.A. Munoz, *Bioresour. Tech.*, **98**, 3344 (2007).
22. Y.S. Ho, J.F. Porter and G. McKay, *Water Air Soil Pollut.*, **141**, 1 (2002).
23. J. Peric, M. Trgo and V. Medvidovic, *Water Res.*, **38**, 1893 (2004).
24. G.L. Miessler and D.A. Tarr, Inorganic Chemistry, Prentice Hall, New Jersey, pp. 587-588 (1991).
25. R.G. Pearson, *J. Chem. Educ.*, **45**, 581 (1968).