ASM Sci. J.Special Issue 2018(1) AiMS2018, 114-123

Synthesis and Adsorption Studies for Newly Prepared Ni^{2+}-imprinted Polymer co-Functionalized with Picolinic Acid

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The development of new adsorbent has rapidly increased in order to overcome the problem of waste water treatment from heavy metal pollution. The ability of nickel (II)-ion imprinted polymer (Ni-IIP) as an alternative adsorbent for the removal of nickel ion from aqueous has been investigated. The Ni-IIP was prepared via bulk polymerization by using functional monomers; methylacrylic acid (MAA) with picolinic acid as a co-monomer. Nickel ion was used as template, AIBN as initiator and EGDMA as cross-linking agent. Non-imprinted control polymer (NIP) was prepared in the same manner as Ni-IIP but in the absence of nickel ion. The resultant of Ni-IIP and NIP were characterized by using Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope (SEM). Result showed that, the adsorption of nickel ion onto Ni-IIP increased as the adsorbent dosage increased and contact time is prolonged. The adsorption isotherm model for Ni-IIP and NIP were fitted well with Freundlich and Langmuir, respectively. Kinetic study for both Ni-IIP and NIP were followed the pseudo-second order, indicates that the rate-limiting step is the surface adsorption that involves chemisorption. Selectivity studies showed that the distribution coefficient of Ni^{2+} was higher compared to Zn^{2+}, Mg^{2+} and Pb^{2+}. The present work has successfully synthesized Ni-IIP particles with good potential in recognition of Ni^{2+} ions in an aqueous medium.

Keywords: Adsorption isotherms, adsorption kinetic, bulk polymerization, ion imprinted polymer.

I. INTRODUCTION

The contamination of wastewater by toxic metal cations such as Cd^{2+}, Cu^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+} and Mn^{2+} is one of the main issue in environmental problems. Specifically, nickel is known as toxic, carcinogenic and causes environmental damage. The exposure to nickel compounds give bad impact to the human health such as nickel-aczema disease [1]. The synthesis development of new extractants and adsorbents for nickel has increased as an increas-

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*Corresponding author:fshimal@umt.edu.my ing demand of selective system for separation of nickel [2]. Recently, various adsorbents have been used to remove Ni^{2+} from aqueous such as complex-forming sorbent [3], biopolymer [4], activated carbon [5]-[7] and multi-walled carbon nanotubes [8]-[9]. Activated carbon is the common adsorbent to adsorb Ni^{2+} [5]. One of the promising technology namely molecular imprinting has been widely used for preparing a synthetic material mimicked biological receptor. It possesses a three-dimensional network, cross-linked polymeric chain called molecularly imprinted polymers (MIPs). The application of MIPs as high-added value compound has been a great interest to improve any drawbacks of the existing methods and produce less costly procedure in the extraction of analyte in aqueous media.

Ion imprinting polymers (IIPs) is one of the molecular imprinting studies that use metal ion as a target analyte for the main purpose of metal ion enrichment and separation. Numerous studies were successfully produced IIPs-based sensor for several of metal ions such as Cu^{2+} [10]-[11], Zn^{2+} [12]- [13], Pb^{2+} [14], Pd^{2+} [15], Pt (IV) [16] and others including Ni^{2+} [1]. The resulted IIP produced had different values of adsorption capacity, this was due to the type of ligand, monomer and porogen used.

This work highlighted the preparation of IIP using molecular imprinting methods to study the imprinting effect of Ni^{2+} ions towards the imprinted polymers (Ni-IIP), which will be extended to further development of technological appliances especially for environmental concern. The effect of adsorption dosage of imprinted polymers and the effect of contact time towards adsorption of Ni^{2+} ions was evaluated. The observation towards the surface related to the Ni^{2+} ions concentration at the constant temperature has been described by adsorption isotherm. It is as a value of quantification and general insight into the understanding of the sorption mechanism and crucial for estimating the adsorption capacity, surface properties and affinities of the imprinted polymer. The Langmuir and Freundlich model have been proposed to describe the adsorption isotherm during equilibrium state. Two kinetic theories were applied; pseudo-first order and pseudo-second order for kinetically interpreting the specific adsorption of synthesized imprinted.

II. MATERIALS AND METHODS

A. Chemicals and Instruments

Nickel(II) chloride hexahydrate, Zinc(II) chloride, Magnesium(II) chloride, Lead(II) chloride, Picolinic acid, 2,2-azobisisobutyronitrile (AIBN), Methylacrylic acid (MAA) Ethylene glycol dimethacrylate (EGDMA), Hydrochloric acid, Ethylenediaminetetraacetic acid (EDTA), methanol, acetone and silicon oil. Fourier transform- infrared (FTIR) spectroscopy was used to identify the functional groups of the polymers synthesized. Scanning Electron Microscope (SEM) was used to identify the morphology of the polymer. The Atomic Absorption Spectroscopy (AAS) was used to study the adsorption parameter of Ni^{2+} in aqueous.

B. Preparation of Nickel (II)-Ion Imprinted Polymer

Bulk polymerization method had been chosen to synthesis the polymers. $NiCl_2.6H_2O$ (1 mmol), picolinic acid (1 mmol), MAA (4 mmol) EGDMA (20 mmol) and AIBN (2 mmol) were dissolved in methanol (5 ml) in a Kimax culture tube. The solution was purged with nitrogen for 10 minutes while cooling on ice bath. The tube was sealed with screw cap and placed into an oil bath for 48 hours with constant temperature at 60 °C. The obtained monolith was crushed, ground and sieved prior storage. Non-imprinted control polymer (NIP) was prepared in the same manner as Ni-IIP but in the absence of nickel ion. To remove the unreacted monomer and the template, the Ni-IIP was treated with a liquid of 9:1 volumetric ratio of ethylenediaminetetraacetic acid (EDTA) to HCl.

C. Adsorption Process

Equilibrium batch rebinding experiment was studied using Atomic Absorption Spectroscopy (AAS). 25 ml of 10 ppm of Ni^{2+} ions solution was added to the different mass of polymers (10, 12, 15, 18 and 20 mg). The solution was shaken at different interval times (i.e. 5 to 90 minutes) to facilitate the adsorption process onto polymers. After the binding process was complete, the solution was filtered and analysed to identify the concentration of free Ni^{2+} ions in solutions.

D. Selectivity Studies

To analyze the specificity of the imprinted polymer, competitive adsorptions of other metal ions such as Zn(II), Mg(II), and Pb(II) have been study. About 18 mg of IIP were mixed with 25 ml solution containing 10 mg/L of Ni (II), Zn(II), Mg(II) and Pb(II) and shaken for 30 minutes. AAS was used to measure the residual concentration of the four metal solutions. NIP was treating with the same method except the mass used is 15 mg. The experiments were performed in three replicates.

E. Characterization Studies

The IR spectra of Ni-IIP and NIP showed the same pattern of backbone structure and functional groups. This is due to the same polymerization reagents used in the synthesis in both Ni-IIP and NIP. The FT-IR spectra (Figure 1) showed two low intensity peaks at about 2956 and 2990 cm^{-1}, attributing to the C-H stretching of CH_2- and CH_3 groups in the polymeric chain respectively. The intense absorption at 1727 cm^{-1} referred to the carbonyl groups from

EGDMA. The C-O vibration was observed at 1159 cm^{-1}. The peak at 1637 cm^{-1} was referred as C=C and C=N (ring) stretching respectively, while the peak at 1456 cm^{-1} associated to CH_2- and CH_3 deformation. The differences in strength of vibration at peak 1637 cm^{-1} referred to the bonding between nickel with picolinic acid [17]. NIP spectrum showed that there are unreacted double bond in the polymer material shows at band 1637 and 961 cm^{-1} [18].

III. RESULTS AND DISCUSSIONS

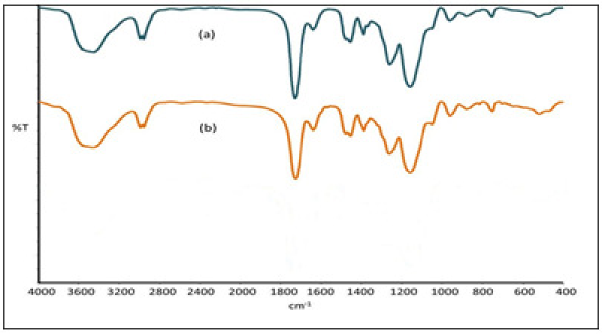

Figure 1. FT-IR spectra of (a) NIP (b) Ni-IIP

SEM in Figure 2 clearly shows the morphology of the Ni-IIP and NIP. Both polymers did not exhibit definite shape due to the bulk polymerization process. SEM images also shows both polymers possessed relatively rough surfaces which is the main factor of the mass transfer rate of metal ion toward the polymer surface as well as improving its sorption capacity [10]. However, Ni-IIP has highly porous surfaces compared to NIP due to the imprinting effect of Ni^{2+} on Ni-IIP.

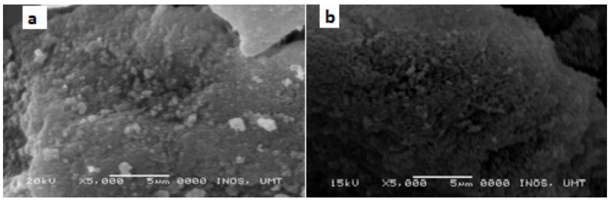

Figure 2. SEM images of (a) Ni-IIP (b) NIP

A. Adsorption Study

The amount of Ni^{2+} adsorbed by Ni-IIP and NIP was calculated according to Equations 1 and 2:

Ni^{2+} uptake=((C_o-C_e)/C_o) x 100 .....(1)

Adsorption capacity, q_e(mg/g)=((C_o-C_e)V)/W.....(2)

where C_o and C_e (mg/L) are Ni^{2+} concentrations at initial and equilibrium respectively. V (L) is the volume of the solution and W (g) is the weight of the Ni-IIP or NIP.

The variation in percentage removal of Ni^{2+} with contact time at same initial concentration; 10 mg/L with five different dosage (10 to 20 mg) of Ni-IIP and NIP is presented in Figure 3. Proving that, the amount of Ni^{2+} adsorbed increased as the adsorbent dosage increased and contact time is prolonged. Also, the maximum concentration of Ni^{2+} adsorption taking place for both polymers is within the contact time of 30 minutes then achieved equilibrium thereafter. The adsorption rate elevates sharply at the beginning of 5 minutes due to the adsorption sites are more abundant and available [19]. However after 30 minutes, it did not reach the equilibrium and the adsorption Ni^{2+} decrease as increasing the time. This might due to the non-specific cavities occurred on NIP

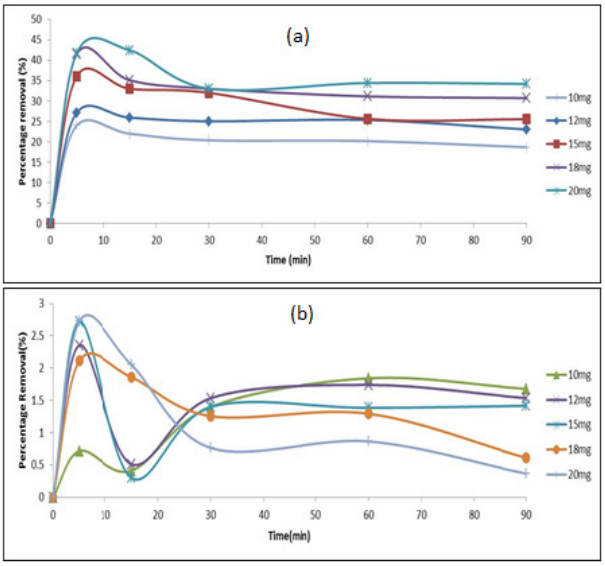

Figure 3. Effect of contact time on Ni^{2+} removal with different dosage of (a) Ni-IIP (b) NIP

For the effect of adsorbent dosage of polymers, Figure 4 shows the comparison of percentage removal of Ni^{2+} between Ni-IIP and NIP. The highest percentage of Ni^{2+} removal was found 33 % for Ni-IIP while NIP only 1.4 %. This can be proved that Ni-IIP has good adsorption behavior towards concentration of Ni^{2+} compared to NIP.

B. Adsorption Isotherm

Adsorption isotherm studies provide an adsorption capacity of adsorbent towards adsorbate and provide the effectiveness of an adsorbent. In this study, the adsorption data of Ni^{2+} onto Ni-IIP and NIP was analyze using two different types of isotherm model; Langmuir and Freundlich. The highest correlation coefficients, R_2 values are used to describe the best isotherm model that will be used.

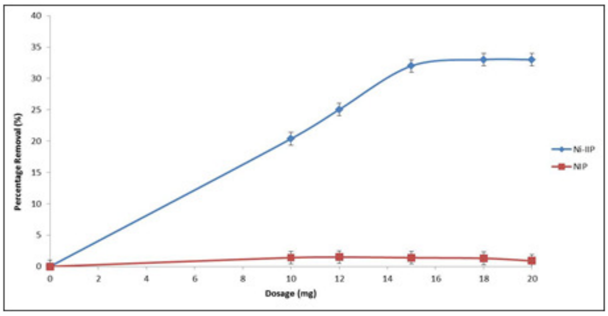

Figure 4. Effect of adsorbent dosage between Ni-IIP and NIP

Langmuir isotherm is the maximum adsorption which is corresponding to homogenous surfaces and one monolayer adsorbate molecule can be adsorbed on surface of adsorbent. The linear form of Langmuir is represented in Equation 3:

$q_e/C_e = Q_oB - Bq_e$ ....(3)

where C_e indicates equilibrium concentration of Ni^{2+} (mg L-1), qe the amount of Ni^{2+} adsorbed per unit mass of Ni-IIP (mg.g-1). Qo represent adsorption capacity and B is a Langmuir constant. Freundlich isotherm model assumes heterogenous surface energies and a heterogenous adsorption surface has unequal available sites with different energies adsorption. The linear form of Freundlich is represented in Equation 4:

$\mathrm{lnq}_e = \mathrm{lnK}_f + \mathrm{lnC}_e$ ....(4)

where K_F refer to Freundlich constant related to sorption capacity of Ni-IIP while 1/n was to determine the adsorption intensity. The value of n indicates the favourability of adsorption when $1 < n < 10$ or most favourable as $1/n < 1$ [20]. The adsorption data in the experiment were applied to both equations isotherm model. It showed that the adsorption data for Ni-IIP was fitted well with Freundlich isotherm model with $R_2 = 0.9784$ compared to R_2 for Langmuir (0.9379). Furthermore, the adsorption of Ni^{2+} onto Ni-IIP is most favorable due to the value of 1/n is less than 1 [20] as shown in Table 1. This result recommends that Ni^{2+} could be readily adsorbed on heterogenous surface caused by the various functional groups on Ni-IIP and multiple interactions of adsorbent-adsorbate like as hydrogen bonding and formation of complexes between picolinic acid with Ni^{2+}, also due to the binding sites in Ni-IIP which is difference in size, shape and rigidity [20]. Instead, Langmuir model fitted well with NIP data with the $R_2 = 0.9997$ compared to Freundlich $R_2 = 0.6145$. The negative value of Langmuir constant suggested that it gives RL value more than 1 and adsorption of Ni^{2+} onto NIP were very difficult it may be caused by the resulted cavities did not produced well during synthesis then give effect to adsorption of Ni^{2+} onto NIP as well as lower the adsorption capacity. However, the higher correlation coefficient (R_2) of Langmuir compared to Freundlich shows that the homogenous surface was occurred on NIP. The equation of RL is calculated using Equation 5:

$R_L = 1/(1+BC_o)$ .....(5)

The value of R_L show the type of isotherm either favorable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) (Jiang Kim, 2013). Therefore, the values of maximum adsorption capacity by Ni-IIP and NIP can be determined (Table 1).

Table 1. Langmuir and Freundlich isotherms constant for Ni-IIP

Polymers	Langmuir			Freundlich		
	B	Q_o	R^2	K_r	1/n	R^2
Ni-IIP	-0.14	-0.28	0.9379	0.988	0.81	0.9784
NIP	-0.10	-1.94E-03	0.9997	0.981	-0.69	0.6145

C. Kinetic Studies

Two simplified kinetic model were applied to the experimental data in order to analyze the sorption kinetics of Ni^{2+} onto Ni-IIP and NIP. The pseudo-first-order and the pseudo second order kinetics models are presented in the Equations 6 and 7 respectively.

$\ln(q_e - q_t) = -k_1 t + \mathrm{lnq}_e$........(6)

where qe and qt refer to the amount of Ni^{2+} adsorbed at equilibrium (ppm) and time (min) respectively and k_1 indicates the rate constant of pseudo first order sorption (min^{-1}).

$(t/q_t) = (t/q_e) + (1/(K_2e_2)$ ....(7)

where k_2 is the rate constant of adsorption for pseudo second order (g $mg^{-1}min^{-1}$). The kinetic results for Ni-IIP and NIP are tabulated in Table 2. It can be clearly observed that both polymers obeyed to pseudo second order model due to the higher correlation coefficient compared to pseudo first order. Furthermore, the obtained values of calculated qe for both polymers were in agreement with qe the experimental data. Pseudo second order described the adsorption process of Ni^{2+} on Ni-IIP and NIP, based on the assumptions that the adsorption involved chemisorptions through exchange or sharing of electrons between sorbate and sorbent [21].

D. Selectivity Studies

In batch adsorption experiments, the selectivity of the Ni-IIP towards the interferent metal was studies. Selectivity of the Ni-IIPs over the interferent metal ion can be measured by using Equation 8. While selectivity for the binding of Ni^{2+} in the presence of interferent metal can be evaluated by using Equation 9.

$K_d =[(C_i-C_f)/C_f]/[V/W]$.......(8)

where K_d is distribution coefficient, C_i and C_f is the initial and final concentration of metal ion.V is the volume of solution (L) and W is the weight of polymers (g).

$\alpha = K_{templatemetal}/K_{interferentmetal}$ ....(9)

where α is selectivity coefficient. Relative selectivity coefficient can be calculated by using Equation 10.

$\alpha_r = \alpha_i/\alpha_n$ ....(10)

where α_r is a relative selectivity coefficient, α_i and α_n represent the selectivity coefficient of Ni-IIP and NIP respectively.

As the equilibrium mass of Ni-IIP and NIP was obtained at 18 mg and 15 mg (Figure 4) respectively, this mass was used on this selectivity studies. The K_d values of Ni-IIP increased for Ni^{2+}, however decrease as other ions as shown in Table 3. Pb^{2+} showed a higher K_d value for both Ni-IIP and NIP compared to Ni^{2+} and Mg^{2+}. We postulate that, Pb^{2+} would not fit into the imprinting sites however it could associate with many functional sites [20]. The relative selectivity coefficient (α) is an indicator to show the adsorption affinity of recognition sites to the Ni^{2+}. The value of Ni-IIP for Ni^{2+}/Zn^{2+}, Ni^{2+}/Mg^{2+} and Ni^{2+}/Pb^{2+} were 3.51, 1.19 and 1.53 greater than NIP respectively. Hence, proving that the Ni-IIP has been imprinted with Ni^{2+}, and the selective behavior of Ni-IIP is influenced by the nature of metal ion, ionic radius and its charge.

IV. SUMMARY

In conclusion, Ni-IIP and NIP had been successfully synthesized by bulk polymerization.

Table 2. Kinetic model for Ni-IIP and NIP

Polymers	Pseudo first order				Pseudo second order		
	q_e (exp)	K_1	q_e (cal)	R^2	K^2	q_e (cal)	R^2
Ni-IIP	4.41	-0.01	0.65	0.5370	-0.18	4.06	0.9994
NIP	0.35	0.04	2.84	0.1043	0.676	0.36	0.9604

Table 3. Selective separation properties of Ni-IIP and NIP for various metal ions

Metal ions	Ionic charge	Ionic radii (pm)	K_d(IIP)	K_d(NIP)	α(IIP)	α(NIP)	α_r
Ni (II)	2	69	1.12	0.35	-	-	-
Zn (II)	2	74	0.36	0.37	3.23	0.92	3.51
Mg (II)	2	71	0.12	0.04	9.37	7.84	1.19
Pb (II)	2	119	0.92	0.44	1.21	0.79	1.53

The adsorption capacity of Ni^{2+} for Ni-IIP was higher compared to NIP due to the imprinted sites that have been formed. Also, it has been proven that the amount of Ni^{2+} adsorbed increased as the adsorbent dosage increased and contact time is prolonged. Freundlich model was the most appropriate model to describe adsorption of Ni^{2+} onto Ni-IIP, while Langmuir model fitted well with NIP data. In kinetic studies, both polymers followed pseudo second order model. The adsorption capacity for Ni-IIP (4.41 mg g^{-1}) higher than previous studies [22],[17] proving the importance of choosing of ligand and monomer in synthesis Ni-IIP. Lastly the imprinting effect of Ni-IIP showed higher efficiency and selectivity compared to NIP. As our novel by using picolinic acid as co-monomer is very suitable for imprint metal-containing. Also, this study may offer a great sustainable option into overcome the heavy metal (nickel) containing in waste water treatment.

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