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To cite this article: Noorhidayah Ishak *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **864** 012184

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Optimization of Different Parameter in Synthesis Ion Imprinted Polymers via Precipitation Polymerization for Nitrate Adsorption

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Abstract. An important issue in synthesis of ion imprinted polymers (IIP) is optimization of the main parameters that involved during polymerization process as those parameters can influence the performance of IIP. In this study, IIP was synthesized by precipitation polymerization using allylthiourea (ATU) as monomer, nitrate as template ion, ethylene glycol dimethacrylate (EGDMA) as crosslinker, 2,2'-azobisisobutyronitrile (AIBN) as initiator with 365 nm ultraviolet (UV) light and mixture of acetonitrile and dimethylsulfoxide (DMSO) as porogenic solvent. The influences of various polymerization parameters in the synthesis of IIPs were investigated. The parameters studied included: ratio of monomer-template, amount of crosslinker and amount of porogenic solvent. These parameters were optimized using response surface methodology (RSM) coupled with central composite design CCD). Results showed that IIP with an optimum adsorption capacity of 156.233 mg/g of nitrate ion (NO_3^-) can be obtained under the following polymerization conditions: 3.90 mmol of ATU, 18.67 mmol of EGDMA and 38.30 mL of porogenic solvent. The nitrate imprinted polymer and non-imprinted polymer were characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The SEM micrograph showed microparticles ranging from 14.05 – 16.17 μm in diameter and the surface was rough and porous. The sorption of IIP followed Langmuir adsorption isotherm model. In this study, the binding capacity indicated that nitrate imprinted polymer recognized NO_3^- in aqueous solution more effectively compared to non-imprinted polymer and this polymer particles portrayed better adsorption as compared other adsorbent.

1. Introduction

Nitrate ion, NO_3^- is a stable and highly soluble form of nitrogen in aqueous solution [1]. Nitrate is an important element and major nutrient that necessary for plant growth. Moreover, it is used as nitrogenous fertilizer in agriculture in order to increase crop production. However, extensive use of nitrate fertilizer will lead to contamination of the valuable groundwater [2]. This is the main cause of nitrates contamination in water resource. Surface water and groundwater can be contaminated by nitrate ions through the natural sources such as atmospheric precipitation and local mineral deposits as well as disposal of untreated municipal and industrial wastes [3]. This in turn affected the quality of fresh water supplied for human consumption. The elevation of NO_3^- concentration in drinking water is a serious hazard to human health, causing abnormalities such as methemoglobinemia (also known as blue baby



syndrome for infants less than six months old) and cancerous growths in human digestion system. In addition, the presence of nitrates in water resources can cause eutrophication through the growth of algae, causing depletion of dissolved oxygen and eventually endanger animal's health [4,5]. Thus, it is important to remove excess nitrates from the aquatic environment.

Various methods have been developed for NO_3^- removal in water resources including adsorption, ion exchange, reverse osmosis, coagulation, filtration and lime softening [6]. The conventional technologies such as coagulation, filtration and lime softening processes suffer from limitations of high energy consumption and high operating cost [7]. Thus, several physico-chemical processes have been used to remove the dissolved nitrates in drinking water and wastewater. Among these, adsorption has been hailed as the potential technology in the removal of NO_3^- due to its simplicity, high efficiency, less sludge production, easiness in handling and cost effective [8]. In general, a number of materials including activated carbons and ion imprinted polymers have been used to serve as adsorbent for adsorption process. IIPs appear to be the potential candidate to serve as adsorbent in the removal of NO_3^- from contaminated water resources due to their unique features such as high selective affinity, large number of binding sites, faster binding and rebinding kinetics, lower cost, large surface area as well as high chemical and mechanical stability [9].

IIPs are new generation tailor-made synthetic materials with artificially generated recognition sites that can specifically rebind with target ion. Their high selectivity and affinity are because of the memory effect of the polymer towards the ion interaction with specific ligand, coordination number of metal ion, ion charge, coordination geometry, size and shape [10]. IIPs are prepared by copolymerization of functional monomer with crosslinker in the present of initiator and template in a suitable solvent (commonly non-polar and aprotic solvent) [11]. During polymerization, functional monomers will be mixed with template ion to form complexes. Then, the complexes will be surrounded and stabilized by cross-linker, forming a three-dimensional polymer network where the template ions are trapped. After polymerization, the template ion are extracted from the three-dimensional polymer network, leaving sites corresponding to the template in size, shape and interaction [12]. The resultant IIPs possess a permanent memory for the imprint ion that are formed. This enables the IIPs to selectively rebind the imprint ion from various compounds in the mixture [13].

Polymerization methods that are commonly used in the synthesis of IIPs included bulk polymerization and precipitation polymerization [14]. Bulk polymerization is most widely used in preparation of IIPs. However, the resulting material possessed non-uniform distribution of particle size. Hence it must be crushed and sieved to obtain the desired dimension. However, crushing and sieving processes are not only time consuming but also causing destruction of binding sites and contamination of the polymer [15]. Thus, precipitation polymerization which can achieve high yield of IIPs has been employed recently. This method can produce particles that are cross-linked and rigid to avoid coagulation [16]. Therefore, stabilizers were not required in the synthesis of IIPs via precipitation polymerization. The composition used for the preparation is very similar to bulk polymerization, except that the amount of porogen used is much higher [12]. The important parameters during precipitation polymerization are ratio of template-monomer, the amount of crosslinker and solvent.

To optimize the process parameters, response surface methodology (RSM) is an effective tool as it requires less resources and quantitative data use suitable experimental design to determine and solve multivariate equation simultaneously [17-18]. It is helpful to study the interactive effect of process parameters [19-20]. The experimental design usually used is central composite design (CCD) to fit an empirical with full second-order polynomial model. The combination of CCD with a full second order polynomial model is very powerful and normally a sufficient representation of most of the continuous response surface provided over a wide range of factor domain.

In this study, IIPs was prepared via non-covalent imprinting technique and nitrate was used as template. The parameters of polymerization process such as ratio of monomer-template, amount of crosslinkers and amount of porogenic solvent were studied and optimized using RSM couple with CCD to produce IIPs with optimum recognition ability for NO_3^- .

2. Experimental

2.1. Material

Allythiourea (ATU) and dimethylsulfoxide (DMSO) were purchased from Merck. Sodium nitrate (NaNO_3) and methanol were purchased from HmbG Chemicals. Acetonitrile and hydrochloric acid (HCl) were purchased from Fisher Scientific. Ethylene glycol dimethacrylate (EGDMA) and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich and Acros Organic respectively. All chemicals used were analytical reagent grade.

2.2. Instrumentation

The effect and optimization of polymerization process parameters in the synthesis of IIPs were studied using Design of experiment (DOE). The DOE selected was RSM coupled with CCD using Design-Expert version 7.1. software. SEM (JSM-6460) was used to determine the surface morphology of the imprinted polymer. FTIR (Perkin Elmer) spectroscope was used to characterize the functional group presence in the imprinted and non-imprinted polymer (NIPs). The concentration of NO_3^- solution was determined using UV-Vis spectroscopy (Shimadzu UV-1800). Thermo Heraeus Megafuge 16R centrifuge was used to centrifuge sample during binding test. Shaker-Daihan Scientific: SHO-1D was used during binding analysis.

2.3. Preparation of IIPs and NIPs

IIPs was prepared by precipitation polymerization. Pre-polymerization solution was prepared by dissolving NaNO_3 (1 mmol) in the solution mixture containing acetonitrile and DMSO (in the ratio of 1:1 v/v, 3.07 – 61.93 mL), ATU (1.32 – 4.00 mmol), EGDMA (6.48 – 48.52 mmol) and 100 mg of AIBN. The solution was stirred for 10 min to make sure it was well-mixed and then purged with nitrogen for 10 min to eliminate oxygen that trapped radicals and then slowed down the polymerization process. The solution was sealed immediately and exposed to UV lamp with wavelength of 365nm for 24 hours to complete the UV polymerization. Meanwhile, the corresponding NIPs were prepared using similar method mentioned above but without the template ion.

After polymerization, the supernatant was removed while the precipitate was dried in oven overnight at 50 °C. 2g of the as-synthesized polymer was measured and placed in centrifuge tube. Then, it was washed several times with 50 ml of mixture of 0.5 mol/L of HCl and methanol solution (1:1 v/v). This washing step was performed by constant shaking at 130 rpm using orbital shaker for one hour. Then, it was centrifuged at 5000 rpm for 5 min. The supernatant was removed and subjected to UV-Vis spectrophotometer analysis for NO_3^- detection in the wavelength of 301 nm. The washing step was repeated until no NO_3^- was detected in UV-Vis spectrophotometer analysis. Next, the polymer was washed repeatedly with double distilled deionized water until neutral pH was reached. Finally, the as-synthesized polymer was dried in oven overnight at 50 °C.

2.4. Adsorption Capacity Tests

The adsorption capacity of IIP and NIP was studied by batch rebinding technique. 10 mg of dried adsorbents (IIPs or NIPs) was placed in a centrifuge tube and mixed with 10 mL of 600 mg/L of NaNO_3 solution. The centrifuge tube was placed in Shaker-Daihan Scientific at 130 rpm to agitate the solution orbitally for nitrate ion rebinding for 1 hour at room temperature. After that, the adsorbent was removed from the mixture by centrifugation at 5000 rpm for 5 min. The adsorbent was filtered using 0.45 μm syringe filter and the filtrate was analyzed using UV-Vis spectrophotometer to determine the concentration of NO_3^- . From that, the final concentration of NO_3^- in the solution after contact with adsorbent was obtained. Then, the adsorption capacity, Q was calculated. The adsorption capacity test was repeated for the polymers (NIPs and IIPs) synthesized under optimum polymerization conditions with different concentration of NO_3^- ranged from 200 mg/L to 1000 mg/L. Each experiment was performed in triplicate.

3. Experimental

3.1. Statistical Analysis and Model Fitting

Table 1 showed the adsorption capacity of IIPs prepared using precipitation polymerization method with various process parameters.

Table 1. Experimental design matrix of three parameters with experimental responses

Run	Factor A	Factor B	Factor C	Response
	ATU (mmol)	EGDMA (mmol)	Acetonitrile-DMSO solvent (mL) (ratio 1:1)	Adsorption Capacity, Q (mg/g)
1	3.00	48.52	32.50	118.444
2	3.00	27.50	32.50	146.222
3	2.00	15.00	15.00	125.111
4	4.00	40.00	15.00	84.000
5	3.00	27.50	3.07	122.889
6	3.00	27.50	32.50	150.667
7	4.00	40.00	50.00	131.778
8	2.00	40.00	15.00	120.667
9	2.00	40.00	50.00	129.556
10	3.00	27.50	32.50	152.889
11	4.00	15.00	50.00	149.556
12	1.32	27.50	32.50	127.333
13	4.68	27.50	32.50	141.778
14	3.00	27.50	32.50	152.889
15	3.00	27.50	61.93	128.444
16	4.00	15.00	15.00	138.444
17	3.00	6.48	32.50	130.667
18	2.00	15.00	50.00	94.000
19	3.00	27.50	32.50	156.222
20	3.00	27.50	32.50	145.111

Multiple regression analysis gave the following quadratic model indicating an empirical relationship between adsorption capacity and process variables in coded values:

Adsorption capacity can be calculated by using the following formula,

$$150.84 + 4.30A - 4.52B + 3.37C - 12.92AB + 10.14AC + 9.58BC - 6.81A^2 - 10.34B^2 - 9.95C^2 \quad (1)$$

Where A is amount of monomer (mmol), B is amount of crosslinker (mmol) and C is amount of porogenic solvent (mL). Normally, the model with larger F-value and lower probability value with significant terms (p-value < 0.05) was chosen [21]. Therefore, based on table 2, the suggested experimental design was a quadratic model with the highest F-value (47.02) and the lowest p-value (<0.0001) as compared to other models.

Table 2. Sequential model sum of squares

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob>F	
Mean vs Total	3.502E+005	1	3.502E+005			
Linear vs Mean	686.08	3	228.69	0.59	0.6287	
2FI vs Linear	2891.82	3	963.94	3.82	0.0366	
Continued.						
Quadratic vs 2FI	3062.98	3	1020.99	47.02	<0.0001	Suggested
Cubic vs Quadratic	37.38	4	9.34	0.31	0.8604	Aliased
Residual	179.76	6	29.96			
Total	3.571E+005	20	17855.01			

3.2. Analysis of Variance

The analysis of variance (ANOVA) for response surface quadratic model was shown in Table 3. Fisher's F test and p-value was used to check the statistical significant of the regression model. Larger F-value and smaller p-value implied higher significant terms of the model [22]. As shown in Table 3, the F-value of 33.98 and the "prob > F" value of < 0.001 indicated that the developed model was significant. It exhibited that only 0.01% of chance that model F-value might happen due to noise. The linear coefficient (A, B, C), the interaction coefficient (AB, AC, BC) and quadratic term coefficient (A^2 , B^2 , C^2) were found to be significantly affect the adsorption capacity of IIPs since the p-values were less than 0.05 [23]. Moreover, it was reported that the coefficient with the highest F value showed the most significant effect [24]. Therefore, by referring to Table 3, the parameter with most significant effect on adsorption capacity of IIPs in decreasing order was B (amount of crosslinker) followed by A (amount of monomer) and lastly C (amount of porogenic solvent). However, the interaction term with most significant effect on adsorption capacity of IIPs in decreasing order was AB, followed by AC and BC. The "Lack of Fit F-value" of 1.38 indicates the lack of fit was not significant correspond to the pure error. The chance that "Lack of Fit F-value" might happen due to noise was 36.71%. The absence of lack of fit ($p > 0.05$) strengthened the reliability of the model.

The coefficient of determination, R^2 was important to judge statistically the quality of the polynomial model equation. The statistical significant was evaluated by F-test within 95% confidence level [22]. The R^2 shown in Table 3 was very close to unity (0.9683) revealing that the developed model equation successfully expressed the correlation between process parameter to adsorption capacity of IIPs towards NO_3^- . The corrected value for R^2 after eliminating of unnecessary model terms was adjusted R^2 . The adjusted R^2 would be obviously smaller than the R^2 [25]. In this research, the adjusted R^2 of 0.9398 was very close to R^2 . It indicated high significance of the model [21]. The predicted R^2 of 0.8418 implied that 15.82% of the total variables were not interpreted by the model. The predicted R^2 was in reasonable agreement with adjusted R^2 . Adequate precision measures the ratio of signal to noise. It is considered desirable value if the ratio is greater than 4 [26]. Thus, the adequate precision of 19.217 showed an adequate signal. Furthermore, coefficient of variation (CV) is an expression of standard deviation as percentage of mean. A small CV value of less than 10% implied better reproducibility. However, a high CV value states that the variation in the mean value is large and does not sufficiently demonstrate an acceptable response model [21, 27]. The value of CV obtained in this research was just 3.52% and thus the response of the model was satisfactory.

Table 3. Analysis of variance for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob>F	
Model	6640.89	1	737.88	33.98	<0.0001	significant
A-Monomer	252.62	1	252.62	11.63	0.0066	
B-Crosslinker	278.45	1	278.45	12.82	0.0050	
C-Solvent	155.01	1	155.01	7.14	0.0234	
AB	1334.72	1	1334.72	61.47	<0.0001	
AC	822.38	1	822.38	37.87	0.0001	
BC	734.72	1	734.72	33.84	0.0002	
Continued.						
A ²	667.62	1	667.62	30.75	0.0002	
B ²	1541.35	1	1541.35	70.99	<0.0001	
C ²	1426.48	1	1426.48	65.70	<0.0001	
Residual	217.14	10	21.71			
Lack of Fit	125.78	5	25.16	1.38	0.3671	not significant
Pure Error	91.36	5	18.27			
Corrected Total	6858.02	19				
Std. Dev.	4.66				R ²	0.9683
Mean	132.33				Adj R ²	0.9398
C.V (%)	3.52				Pred R ²	0.8418
					Adeq Precision	19.217

3.3. Diagnostic Study

Diagnostic plots were used to evaluate the suitability of the selected model to approximate the real situation. Figure 1 showed the graph of the predicted versus actual value for the response of adsorption capacity of IIP. The graph displayed that the actual value were scattered relatively close to the straight line. This was in good agreement with the high value of R^2 as shown in table 3. This indicate that the quadratic model was significant to predict the adsorption capacity under the studied experimental parameters [22].

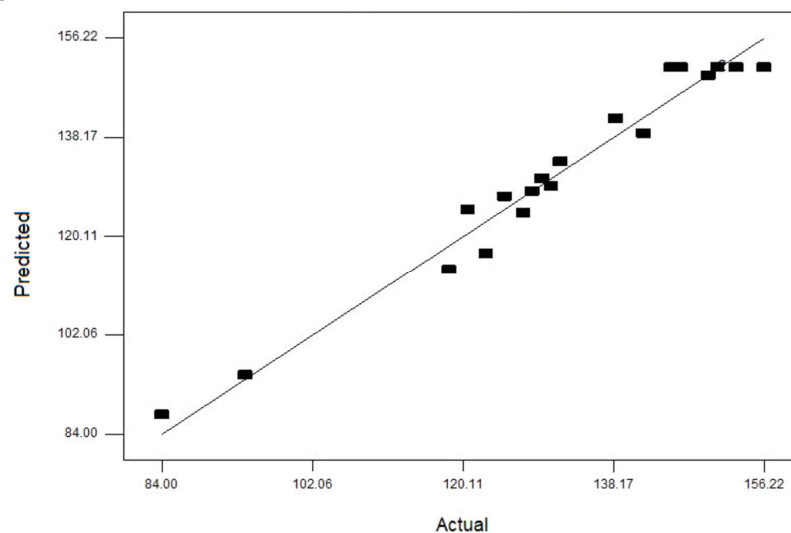


Figure 1. Graph of predicted versus actual values for adsorption capacity

3.4. Response Surface Analysis

Figure 2(a) exhibits the effect of amount of monomer and crosslinker on the adsorption capacity of IIPs. It can be seen that the adsorption capacity of IIPs increased with the increase of the amount of monomer and the decrease of the amount of crosslinker. This was due to additional of sufficient amount of ATU to interact with all of the potential locations for hydrogen bonding with NO_3^- , maximizing the interaction of NO_3^- with ATU and thus increased the quality of the binding sites [28]. However, when the amount of monomer exceeded 3.90 mmol and the amount of crosslinker less than 18.67 mmol, the adsorption capacity decreased. This was because the excessive functional monomer would increase the non-selective binding sites, which produced by the residues of non-assembled monomer. The insufficient amount of crosslinker caused the binding sites fail to maintain their original shape during the process of removing template ion [29, 30]. This result was supported by N.Ishak and her co workers who focused in understanding the interaction of functional monomer and template at molecular level. Since NO_3^- possesses six hydrogen bond acceptor sites, thus in order to saturate all the binding sites of NO_3^- , at least four mol functional monomers were required to form a stable complex [31]. Hence, only suitable amount of monomer and crosslinker could lead to maximum adsorption capacity.

The interaction effect between amount of monomer and porogenic solvent on adsorption capacity of IIPs was presented in figure 2(b). The adsorption capacity was observed to increase with an increase in the amount of monomer and porogenic solvent. This was due to higher amount of monomer increased the chance of pre-assembled interaction between functional monomer and template ion. An increment in the amount of porogenic solvent created more nitrate cavities within polymer network for binding purpose [29]. Nevertheless, after the optimum point of 3.90 mmol monomer and 38.30 mL of porogenic solvent, the adsorption capacity decreased. This was due to the excessive functional monomer caused the formation of non-specific binding sites and the polymer chains which could embed the binding sites and thus reduce the selectivity. High porogenic solvent would dilute the solution causing more defects to the binding sites [29, 32]. Moreover, it was observed that low adsorption capacity occurred at low amount of monomer and porogenic solvent. This was owing to insufficient amount of monomer could not lead to fully assemble the template ion and low volume of porogenic solvent caused the polymer to form precipitate early and thus reduce the formation of binding sites [29, 32]. Hence, an appropriate amount of monomer and porogenic solvent was important to obtain a maximum adsorption capacity of IIPs.

Figure 2(c) shows the interaction between amount of crosslinker and porogenic solvent on the IIPs adsorption capacity. The amount of crosslinker and porogenic solvent used in polymerization process were found to affect the adsorption capacity of IIPs significantly. From the figure, it can be noticed that the increased in the amount of crosslinker and porogenic solvent increased the adsorption capacity. The maximum adsorption capacity (156.233 mg/g) occurred when the amount of crosslinker and porogenic solvent at 18.67 mmol and 38.30 mL respectively. The adsorption capacity of IIPs dropped after the optimum amount of crosslinker and porogenic solvent. Excessive amount of crosslinker caused difficulty in template ion adsorption due to strong steric hindrance effect. Meanwhile, excessive amount of solvent caused dilution of the solution and defects on the binding sites [30, 32]. In contrast, low amount of crosslinker failed to maintain the three-dimensional structure corresponding to the shape of the template after the template was removed and low volume of porogenic solvent caused precipitation of polymers at early stage of polymerization [13, 31] Thus, suitable amount of crosslinker and solvent are important in polymerization process in order to obtain IIPs with high adsorption capacity.

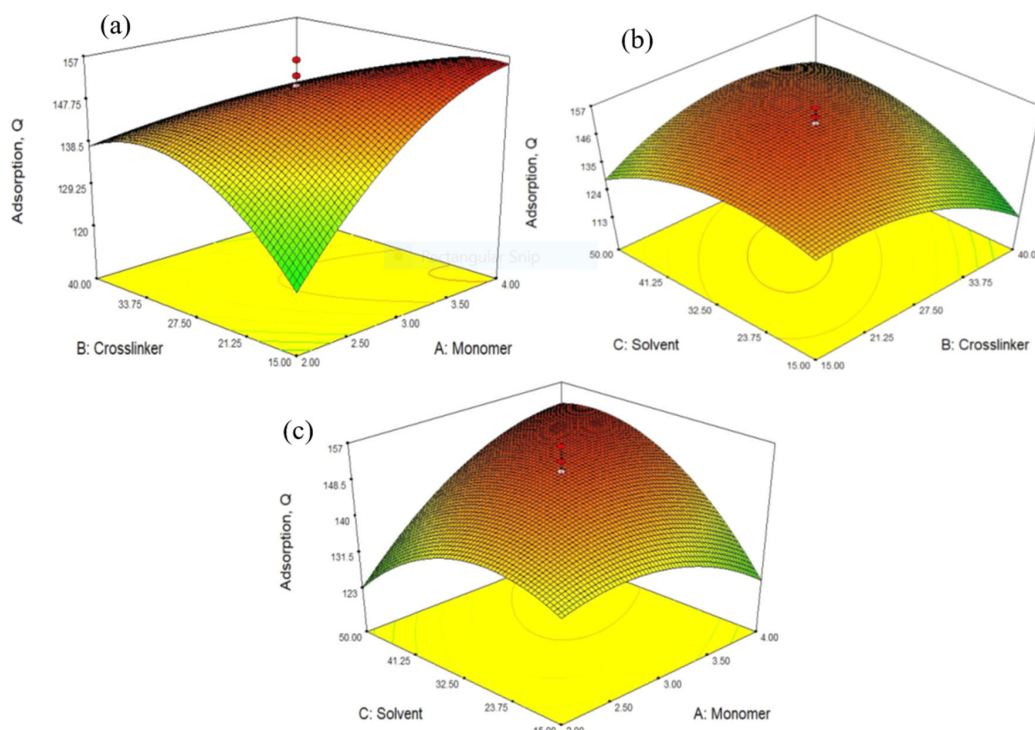


Figure 2. Response surface plot of IIP adsorption capacity versus interaction between two factors. (a) monomer and crosslinker (b) monomer and solvent (c) crosslinker and solvent

3.5. Optimization of Process Parameter

Based on the results of ANOVA analysis, all the process parameters studied were proven to affect the synthesis of IIPs significantly. Therefore, the following step was to optimize the process parameters to synthesize the IIPs with highest adsorption capacity. The optimization process must take into consideration both the individual process parameters and the interaction between parameters. This was performed with the aid of the optimization function embedded in Design Expert software 7.1.5 using the developed model shown in equation 1. Table 4 displayed the limits for each of the process parameters utilized in the optimization process. Based on the 95% confidence interval, the software predicted that IIPs with an optimum adsorption capacity of 156.233 mg/g can be obtained with the following process parameters; 3.90 mmol of monomer, 18.67 mmol of crosslinker and 38.30 mL of porogenic solvent. Three repeated experiments were carried out to verify the predicted optimum process parameters used to synthesize the IIPs. As shown in table 5, an average optimum adsorption capacity of 151.778 ± 1.283 mg/g with only 2.85 % error (comparing to predicted value) can be achieved by the IIPs synthesized under the predicted optimum process parameters. This proved that the predicted optimum process parameters were valid in this study.

Table 4. Constraints used to optimize adsorption capacity of ion imprinted polymers

Variable	Goal	Lower Limit	Upper Limit
A: Monomer	in range	2	4
B: Crosslinker	in range	15	40
C: Solvent	in range	15	50
Q: Adsorption Capacity	in range	84	156.222

Table 5. Three repeated experiment using suggested optimum process parameters

Adsorption Capacity (mg/g)					Percentage Error (%)
Experimental Data			Average	Predicted Data	
1	2	3			
144.000	149.556	151.778	151.778 ± 1.283	156.233	2.85

The optimum adsorption capacity obtained in this study was found to be higher than other similar studies. Ishak, et al. [33] reported that the preparation of nitrate imprinted polymer using isobutyl nitrate as template, methacrylic acid (MAA) as monomer and only acetonitrile as solvent. Meanwhile the crosslinker and initiator used were similar with this study: EGDMA and AIBN. As reported, the maximum adsorption capacity using bulk polymerization method was only 30.21 mg/g which was much lower than the optimum adsorption capacity 151.778 ± 1.283 mg/g achieved by the IIPs synthesized in this study via precipitation polymerization. This indicated that precipitation polymerization method produced IIPs with better adsorption capacity than bulk polymerization [14]. In another study by Zhang, et al. [34] who used activated carbon (prepared from rice husk and activated by NaOH) as adsorbent to remove NO₃⁻, a maximum adsorption capacity of 70.2 mg/g was achieved. It was also lower than the maximum adsorption capacity obtained in this study. This revealed the fact that IIP showed better potential in removing NO₃⁻ compared to activated carbon. This was because of the selective nature of IIPs to NO₃⁻ as compared to the non-selective nature of activated carbon.

4. Adsorption Capacity at Different Concentration of Nitrate Solution

The batch binding test for target NO₃⁻ adsorption was conducted to examine the binding capacity of IIPs and NIPs. Adsorption capacity, Q was calculated using following equation:

$$Q = \frac{v(C_i - C_f)}{m} \quad (\text{mg/g}) \quad (2)$$

where C₀ is initial concentration (mg/L), C_t is the final concentration (mg/L), V is the volume of solution used for extraction (L) and m is the mass of polymer used for extraction (g) [35]. The specificity of IIPs and NIPs towards template nitrate ion was defined by imprinting factor (IF):

$$IF = \frac{Q_{IIP}}{Q_{NIP}} \quad (3)$$

where Q_{IIPs} and Q_{NIPs} are the adsorption capacity of IIPs and NIPs respectively [36].

As shown in figure 3, the adsorption capacity of IIP increased rapidly with initial concentration increased from 200 to 600 mg/L and became saturated over 800 mg/L with the maximum adsorption amount of NO₃⁻ of 232.333 mg/g. However, it was noticed that adsorption capacity of NIP for nitrate ion was much lower than that of IIP and reached the maximum adsorption amount at 154 mg/g. This implied that the specific recognition sites have been successfully created on the surface of IIP in the imprinting process. In contrast, due to the absence of imprinted cavities on the surface of NIP and thus, non-specific adsorption became dominant effect. Therefore, it was reasonable that the adsorption capacity of NIP for nitrate was significantly lower than IIP [37].

In this study three types of models were considered for predictive modeling adsorption of nitrate ion by IIP. Langmuir, Freundlich and Langmuir-Freundlich (L-F) adsorption isotherm models were applied to study the binding characteristic of both IIPs. The related constants of each model were calculated based on nonlinear equation using solver function and shown in Table 6. The experiment was carried out at various concentrations of nitrate ion (200, 400, 600, 800 and 1000 ppm). For IIP-NaNO₃, the Langmuir model has a higher correlation coefficient, R² as compared to Langmuir-Freundlich and Freundlich model. Based on this, it can be concluded that the adsorption of nitrate imprinted polymer followed Langmuir adsorption isotherm model. Langmuir adsorption isotherm model is used to describe homogeneous adsorption of the layer of polymer where ion adsorption process has uniform adsorption activation energy. This suggested the imprinting site for nitrate ions are homogeneously distributed on the IIP-NaNO₃ polymer particle surface [38]. Furthermore, the theoretical value of maximum adsorption

capacity (291.12 mg/g) obtained from the Langmuir equation was close to the experimental value of 232.333 mg/g.

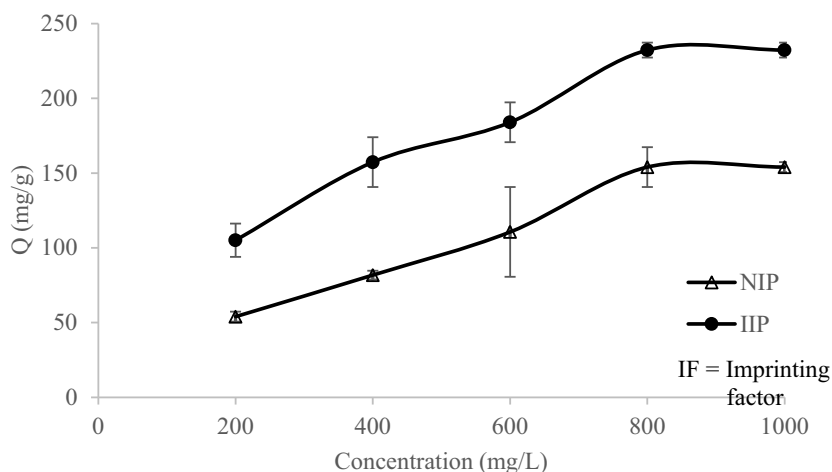


Figure 3. Adsorption capacity, Q (mg/g) of ion imprinted polymers and non-imprinted polymers at different concentration of nitrate solution (mg/L)

Table 6. Fitting parameter of each adsorption isotherm model for nitrate ion sorption

Fitting parameter	Isotherm models		
	Freundlich	Langmuir	Langmuir-Freundlich
Non linear equation	$Q = aC_e^m$	$Q = \frac{N_t a C_e}{1 + a C_e}$	$Q = \frac{N_t a C_e^m}{1 + a C_e^m}$
R^2	0.996	0.997	0.964
N_t (mg/g)	-	291.12	482.27
^a Adsorption constant	18.69	0.005	0.017
m	0.385	-	0.608

5. Characterization of Polymers

5.1. FTIR Spectra Analysis

Figure 4(a) displays the FTIR spectra of ATU, NaNO_3 . Meanwhile, Figure 4(b) showed the FTIR spectra of NIPs and IIPs. It was observed that NIP and IIP shared similar polymer backbone because of high level of EGDMA crosslinking reagent used in the polymerization process. Distinctive bands of poly(EGDMA) backbone was found on both NIP and IIP spectra: the typical C=O stretching at the peak of 1730 cm^{-1} and C—O—C stretching at the peaks around 1257 and 1159 cm^{-1} [39, 40]. The adsorption peaks of poly(ATU) in poly(ATU-co-EGDMA) were indistinguishable in FTIR spectra because of overlapping with the peaks of poly(EGDMA). One of the overlapping peak was C=C stretch at 1634 cm^{-1} . As a result of the binding of NO_3^- with $-\text{NH}_2$ group in ATU, the N-H stretching vibration at 3440 cm^{-1} in NIPs was found to be shifted to 3427 cm^{-1} in IIPs after IIPs were subjected to NO_3^- adsorption test [41]. Moreover, the vibration adsorption peak at 3440 cm^{-1} was assigned to the overlapping of $-\text{NH}_2$, $-\text{NH}-$ (contributed by the amino groups in the monomer) and $-\text{OH}$ groups (contributed by the hydroxyl groups in EGDMA) [42]. On the other hand, the adsorption peak at 3075 cm^{-1} in ATU (Figure 1(a)) was

assigned to alkenyl C–H stretching. However, due to the crosslinking of ATU by EGDMA, it shifted to alkyl C–H stretching at 2958 cm^{-1} in IIPs spectra (Figure 1(b)) [43]. Moreover, N–O stretching vibration at the peak of 1381 cm^{-1} was found only in IIPs. This means that sodium nitrate was present in IIP while absent in NIP. This confirmed the presence of NaNO_3 in IIPs and the absence of NaNO_3 in NIPs which further implied that IIPs were successfully synthesized via precipitation polymerization process.

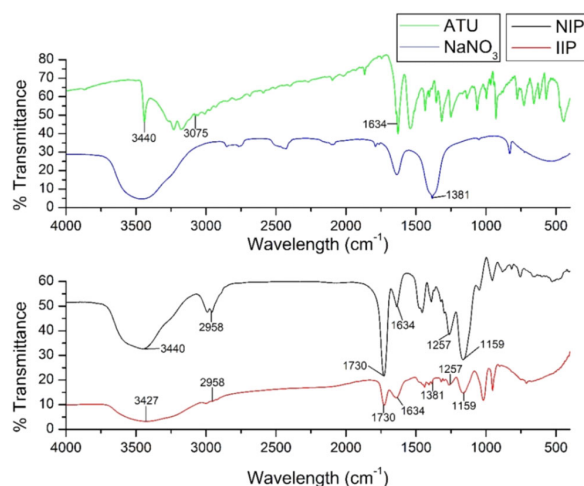


Figure 4. FTIR spectrum of ATU, NaNO_3 , NIP and IIP

5.2. SEM Analysis

SEM was used to analyze the surface morphology and the particle size of IIPs. Figure 5 shows the SEM micrograph of leached IIPs sample at magnification of 2000 times. As shown in the figure, rough and porous structure was observed on the surface of nitrate imprinted polymer. This was due to the presence of recognition sites in IIPs after the removal of template [44]. The particle size of polymers formed during the polymerization was found in the range of 14.05 to $16.17\text{ }\mu\text{m}$.

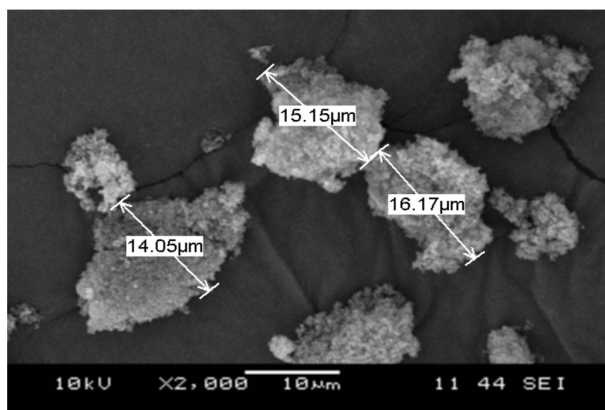


Figure 5. SEM image of leached ion imprinted polymers

6. Conclusion

In this study, nitrate imprinted polymers were successfully prepared via precipitation polymerization by using allylthiourea as monomer, EGDMA as crosslinker, AIBN as initiator and acetonitrile and dimethylsulfoxide as porogenic solvent. RSM coupled with CCD was used to study and optimize the

process parameters in polymerization process. The ANOVA of quadratic model showed the model was significant with low probability ($p < 0.0001$). The optimum process parameter obtained were as follows: 3.90 mmol of monomer, 18.67 mmol of crosslinker and 38.30 mL of porogenic solvent with 156.233 mg/g of predicted optimum adsorption capacity. The experimental result gave an average optimum adsorption capacity of 148.445 mg/g which was very close to the predicted value (percentage error of 2.85%). This proved that the predicted optimum process parameters were valid in this study. While the adsorption mechanism behavior indicated that IIPs followed isotherm model. In short, IIPs synthesized via precipitation polymerization can be a break through adsorbent in NO_3^- removal.

Acknowledgements

The author would like to thank to Faculty Engineering Technology, University Malaysia Perlis. Financial support from the Fundamental Research Grant Scheme (FRGS) (FRGS/1/2019/TK05/UNIMAP/03/2) is gratefully acknowledged.

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