Pneumocandin B₀-imprinted Polymer Using Surface-imprinting Technique for Efficient Purification of Crude Product

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In this work, we prepared surface molecularly imprinted polymer (MIP) for selective recognition of pneumocandin B₀ (PNB₀). Methacrylic acid (MAA) was first grafted onto silica gel particles (SiO₂) in the manner of “grafting from” by using 3-methacryloxypropyl trimethoxysilane as intermedium, and then PNB₀ molecules were imprinted on the surface of the obtained particles in the presence of ethylene glycol diglycidyl ether as the cross-linker. The prepared MIP-PMAA/SiO₂ was characterized by scanning electron microscopy, Fourier transform infrared spectroscopy and thermo-gravimetric analysis, which confirmed the successful grafting of MAA onto SiO₂ and the grafting degree was calculated to be 12.50 wt%. The binding properties of the products were investigated and it is found that the binding process of PNB₀ followed the pseudo-second-order kinetic model. The as-prepared material also displays relatively quick adsorption kinetics and decent recognition affinity toward the template over its structurally related compound.

Keywords Molecularly imprinted polymer, surface molecular imprinting, pneumocandin B₀, silica gel

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Introduction

Pneumocandin (PN) is a new type of cyclic lipopeptide compound produced by fermentation of filamentous fungi. Pneumocandin B₀ (PNB₀), a member of PN, is an important raw material to produce an echinocandin agent-caspofungin which exhibits potent activity against most species of Candida and Aspergillus.¹ Extraction and purification of PNB₀ are indispensable prior to its application in industry. However, due to complexity of fermentation solution and existence of a large number of analogues,² liquid-liquid extraction and traditional solid-phase extraction³ often show insufficient competence in this task owing to their poor specificity and low efficiency.⁴ Therefore, developing a convenient, low-cost, highly efficient and environmental friendly route to extract and purify PNB₀ is extremely meaningful in the pharmaceutical industry.

The molecular imprinting technique has become a powerful approach for preparing robust materials that have the ability to recognize specific chemical species.⁵⁻¹² This method concerns formation of cavities and functional sites in polymer matrix with the memory of a template, which are able to rebind template molecules in a highly selective manner. Because of its specific recognition ability,¹³⁻¹⁵ molecularly imprinted polymer (MIP) has been extensively involved in the fields such as solid-phase extraction, chem/bio-sensor, chromatography, enzyme-mimic catalysis, etc.¹⁶,¹⁷ MIP prepared by the conventional technique has some disadvantages: (1) the bulk polymer matrices must be ground before use, which could damage some binding sites; (2) the deep location of the binding sites in the polymer network hinders the mass transfer rate of the template and even causes waste of the sites.¹⁷,¹⁸ In order to overcome these defects, the surface molecular imprinting technique has been developed, which enables the template-imprinting sites situated at or in proximity of a polymer surface, allowing for more accessible sites and fast association/dissociation kinetics.¹⁹,²⁰

In this work, surface imprinting polymer with core-shell architecture was prepared for PNB₀ with methacrylic acid as the functional monomer, ethylene glycol diglycidyl ether as the cross linker and silica as the inner core. Binding thermodynamics, kinetics and selective adsorption were studied in order to gain deep insight of the synthesized materials and provide important theoretical instruction for further application of the product.

Experimental

Reagents and chemicals

Pneumocandin B₀ (PNB₀, 99%) was provided by Devote.
Instrumental Science & Technology Co. Ltd. (Jiangsu, China). Silica gel (75 - 150 μm) was purchased from Qingdao Ocean Chemical (Shandong, China). Methacrylic acid (MAA), daptomycin, sodium dodecyl benzene sulfonate (SDBS) and tunicamycin were obtained from Adamas Reagent Co. Ltd. (Shanghai, China). Ammonium persulfate and γ-methacryloypropyl trimethoxysilane (MPS) were supplied by Sigma-Aldrich (Shanghai, China). Ethylene glycol diglycidyl ether (EGDE) was purchased from Alfa Aesar Agent (Shanghai, China). Erythromycin was bought from Jiqi Pharmaceutical Co. Ltd. (Guangdong, China). MAA was distilled twice under reduced pressure before use. Other chemicals were used as received without further purification.

**Apparatus**

HPLC was performed with a Shimadzu (Japan) system comprising LC-10A pumps and an SPD-10A UV-detector. LC condition was as follows: chromatographic separation was performed on a WondaSil C18 column (150 × 4.6 mm i.d., 5 μm) which was purchased from Dalian Elite Analytical Instruments Co. (Dalian, China). The mobile phase for PNB0 was methanol-water (87:13, v/v) with a flow rate of 1.0 mL min⁻¹, and the detection wavelength was 230 nm. Infrared spectra were recorded on a Nicolet EXUS-470 FTIR apparatus (Shimadzu, Japan). Thermo-gravimetric analysis (TGA) was carried out simultaneously using an STA 409PC Luxx (Germany) instrument. Surface morphology was characterized with a Zeiss Supra55VP scanning electron microscope (SEM) operating at 20 kV. A KQ3200E ultrasonic cleaner (Kunshan Instrument Co. Ltd., Jiangsu, China) was set at 40 kHz. PHS-2 acidimeter (the Second Analytical Instrument Factory, Shanghai, China), TDL-40B high-speed centrifuge (Shanghai Ai Electronic Technology Co. Ltd., Shanghai, China), and NR-03K thermostat water bath (Yuyao Xaying Instrument Co. Ltd., Zhejiang, China) were employed in this work.

**Preparation of PNB0-imprinted polymer**

Silica gel particles were first activated by concentrated nitric acid and then about 10 g of silica was weighed into 400 mL mixture of ethanol and water (1:1, v/v) containing 10 mL MPS. The reaction was carried out at 50°C for 24 h. After that, the products were washed with anhydrous ethanol repeatedly to remove remaining MPS and the surface-modified particles MPS-SiO₂ were obtained.

About 3 g of MPS-SiO₂ and 10 mL of MAA were added into 200 mL of water, and the grafting polymerization was initiated with ammonium persulfate under N₂ atmosphere for 24 h at 70°C. The resultant particles were extracted with ethanol in a Soxhlet extractor to get rid of the polymers physically attached to silica. The grafting particles PMAA/SiO₂ were then dried under vacuum.

Next, 1 g PMAA/SiO₂ was added into 8 mmol L⁻¹ PNB₀ methanol solution, and the pH value was adjusted to 8.0 by diluted NaOH solution. The mixture was shaken on a constant temperature shaker for 5 h to ensure complete swelling of the grafted PMAA film and the complete adsorption of PMAA/SiO₂ towards PNB₀. Afterwards, the mixture was filtered and dried and 1 g of the particles was placed in 100 mL ethanol. Then, 0.1 mL EGDE was added and the reaction was performed at 50°C for 6 h. The products were rinsed repeatedly with ethanol and acetic acid (8:2, v/v) to remove the template and residual crosslinker. The obtained PNB₀ molecule-imprinted material MIP-PMAA/SiO₂ was then filtered and dried. Non-imprinted polymer (NIP-PMAA/SiO₂) was synthesized using the same procedure, except for the addition of template PNB₀.

**Batch binding experiment**

In an adsorption kinetic test, 20.0 mg polymers were placed in 600 mg L⁻¹ PNB₀ standard methanol solution and determination of PNB₀ in the solution was made at different time points (1, 2, 4, 6, 8, 10, 20, 30, 45, 60 min) at room temperature. The samples were centrifuged and filtered, and the concentration of free PNB₀ after adsorption was measured by HPLC-UV. The adsorption quantity (Q) was calculated through Eq. (1), where C₀ (mg L⁻¹) is PNB₀ concentration in the initial solution and C (mg L⁻¹) is the equilibrium concentration of PNB₀; v (L) is the volume of the PNB₀ solution; m (mg) is the mass of polymer particles. Adsorption isotherm experiments were carried out in a similar way except that the initial concentration of PNB₀ was 70 to 800 mg L⁻¹ and the incubation time was fixed according to the binding equilibrium time obtained from the above kinetic test.

\[
Q = (C₀ - C)v/m
\]  

**(1)**

**Selective adsorption**

Next, 20 mg of polymers were added into 2.0 mL standard solution containing 400 mg L⁻¹ of PNB₀ and structural analogues, respectively. These mixtures were shaken and centrifuged after reaching binding equilibrium. The concentration of PNB₀ and structural analogues in the supernatants was determined by HPLC-UV.

**Application of MIPs to extract PNB₀ from crude product**

Then, 0.2 g PNB₀-MIPs or NIPs particles were added into an empty solid phase extraction (SPE) cartridge between two polyethylene cribiform plates. The cartridges were washed with water and methanol prior to use.

Next, 1.5 mg of crude product of PNB₀ (chromatographic purity 75%) was added into a polypropylene centrifuge tube and suspended with 10 mL methanol. The sample was vortexed for 1 min and sonicated for 10 min, followed by centrifugation at 10000 rpm for 10 min.

The supernatant was percolated through the SPE column. Typically, 1.0 mL of sample solution was loaded onto the column at the speed of 1.0 mL min⁻¹ under pressure. After that, the column was washed with 2.0 mL acetonitrile and then eluted with 3.0 mL methanol/acetic acid (9:1, v/v). The eluate was collected and dried with nitrogen, and the residue was redissolved into 0.5 mL of methanol for HPLC analysis. The SPE cartridges were regenerated by using methanol/acetic acid (9:1 v/v) and methanol successively, and then dried under vacuum.

**Results and Discussion**

**Preparation of MIPs**

Grafting polymerization of MAA onto silica gel particles was conducted by “the grafting from” method with the help of MPS. Functionalization of silica with MPS provided a polymerizable surface with double bonds, allowing for subsequent formation of PMAA/SiO₂ particles. The particles were then placed in a solution of PNB₀, and strong adsorption of PNB₀ by PMAA/SiO₂ occurred as a result of electrostatic and hydrogen bonding interactions. Afterwards, the PMAA/SiO₂ particles with adsorbed PNB₀ met crosslinking agent EGGE and ring-opening reaction between the two terminal epoxy groups of EGGE and the carboxyl groups of the grafted PMAA was initiated in an alkaline environment. As a result, PNB₀ molecules were imprinted in the cross-linked network on the silica surface. After the template was leached out, cavities that are
complementary in size, shape and functionality to PNB, were left behind in the MIP matrix. The schematic diagram of MIP-PMAA/SiO₂ preparation is shown in Fig. 1.

Morphology characterization

Figures 2a and 2b display the morphology of silica gel and MIP-PMAA/SiO₂. The SEM image of silica gel shows a smooth surface, while that of MIP-PMAA/SiO₂ illustrates a rough surface morphological feature with tiny particle coating, implying the wrapping of MIP layer on silica.

FT-IR analysis

FT-IR spectra for SiO₂, MPS-SiO₂ and MIP-PMAA/SiO₂ was obtained via KBr pellet method and shown in Fig. 2c. The peak at 3430 cm⁻¹ arose from stretching vibration of O–H, suggesting that a number of activated hydroxyl groups existed on the silica surface and provided theoretical possibility for subsequent grafting. Peak intensity of hydroxyl groups of MPS-SiO₂ was significantly reduced, indicating that the surface modification of silica was successful. The peaks at 1717 and 3028 cm⁻¹ were attributed to the stretching vibration of C=O and O–H in carboxyl of MAA. This showed that the PMAA have been grafted to the surface of silica gel successfully.

Thermogravimetric analysis

TGA curves of SiO₂, MPS-SiO₂, PMAA/SiO₂ and MIP-PMAA/SiO₂ are shown in Fig. 2d. With increasing temperature, all of them underwent different levels of mass loss. The first mass loss occurring at ~45 until ~200 °C can be assigned to the evaporation of water. The second mass loss for MPS-SiO₂, in the temperature range of 300 - 550 °C corresponds to pyrolysis of MPS. The second mass loss for PMAA/SiO₂ starts at ~250 and ends at ~590 °C, and is ascribed to pyrolysis of PMAA and it can be calculated that the grafting content of MAA onto the polymer is 12.50 wt%. As for MIP-PMAA/SiO₂, its second mass loss is larger than PMAA/SiO₂, which can be the result of...
thermal decomposition of EGGE and PMAA that constitute the polymer skeleton. Then the cross-linking ratio of PMAA chains can be calculated at 19.6 wt%. Furthermore, the amount of free carboxylic groups left on MIP surface can be estimated to be 0.93 mol in 1 g MIP, which is useful information to evaluate binding capacity of MIP towards target molecules.

Adsorption kinetics

The kinetics of PNB₃ adsorption on MIP-PMAA/SiO₂ and NIP-PMAA/SiO₂ were studied, and the results are shown in Fig. 3. It is obvious that MIP-PMAA/SiO₂ displays much higher adsorption capacity than NIP-PMAA/SiO₂. Moreover, both polymers exhibit fast binding process in the initial period (about 8 min), and then the adsorption rate levels off to sorption equilibrium.

To further explore the kinetic mechanism of MIP-PMAA/SiO₂ for PNB₃ adsorption, the kinetic experimental data were fitted with the pseudo-first-order and the pseudo-second-order model. The pseudo-first-order model is given in Eq. (2), where \( k_1 \) (g min⁻¹) is the adsorption rate constant, and \( Q_e \) and \( Q_t \) (mg g⁻¹) are the amount of adsorbed PNB₃ at equilibrium and at time \( t \), respectively.

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1t
\]

The pseudo-second-order model is given in Eq. (3), where \( k_2 \) (g mg⁻¹ min⁻¹) is the adsorption rate constant, and all the other variables are the same as described in the pseudo-first-order equation.

\[
t/Q_t = 1/(k_2Q_e^2) + t/Q_e
\]

The adsorption kinetic parameters and regression coefficients are listed in Table 1. The calculated equilibrium adsorption capacity \( (Q_{e,cal}) \) obtained from the pseudo first-order model is 0.382 mg g⁻¹ with correlation coefficient \( (R_{1st}^2) \) of 0.9123 (the inset a of Fig. 3). By contrast, \( Q_{e,cal} \) estimated from the pseudo-second-order model is 9.771 mg g⁻¹ with wonderful correlation coefficient \( (R_{2nd}^2) \) of 0.9990 (the inset b of Fig. 3). Therefore, it is safe to conclude that adsorption of MIP-PMAA/SiO₂ towards PNB₃ fits well with the pseudo-second order kinetic model, implying that the process was controlled by chemical adsorption. The related discussion for adsorption models of NIP-PMAA/SiO₂ are presented in Supporting Information (Table S1 and Fig. S1).

![Figure 3](image_url)

Fig. 3 Adsorption kinetics curves of MIP-PMAA/SiO₂ and NIP-PMAA/SiO₂ towards PNB₃ at the concentration of 600 mg L⁻¹. The insets are pseudo-first-order kinetics model (a) and pseudo-second-order kinetics model (b) of MIP-PMAA/SiO₂.

![Figure 4](image_url)

Fig. 4 Binding isotherms of MIP-PMAA/SiO₂ and NIP-PMAA/SiO₂ to PNB₃ at a series of concentrations (a), Scatchard plots (b) for MIP-PMAA/SiO₂ for PNB₃ adsorption, and Langmuir model (c), Freundlich model (d), D-R model (e) and Temkin model (f) for MIP-PMAA/SiO₂ at 25°C.
Adsorption capacity

Figure 4a presents the adsorption isotherms of MIP-PMAA/SiO2 and NIP-PMAA/SiO2 for PNB0. It can be seen that adsorption capacities for MIP-PMAA/SiO2 and NIP-PMAA/SiO2 both increase significantly with increasing the concentration of PNB0 from 40 to 600 mg L–1. Afterwards, the rise in concentration from 600 to 800 mg L–1 brings about slight Q enhancement, which is probably due to sorption saturation of the binding sites. The maximum static adsorption capacities (Qmax) of the imprinted and the non-imprinted polymers to PNB0 are 9.78 and 5.42 mg g–1, respectively, indicating the existence of the imprinting effect in adsorption behavior.

To further investigate the binding properties of MIP-PMAA/SiO2, the obtained data were processed with Scatchard analysis according to Eq. (4):

\[ \frac{Q}{C} = \frac{Q_{\text{max}}}{K_d} - \frac{Q}{Q_{\text{max}}} \]  

(4)

where Q and Qmax (mg g–1) are the experimental adsorption capacity and the theoretical maximum adsorption capacity to PNB0, respectively; C (mg L–1) is the concentration of PNB0 in equilibrium solution, and Kd is the dissociation constant.

As shown in Fig. 4b, there are two distinct sections within the Scatchard plot that can be regarded as straight lines, so it might be rational to assume that the binding sites can be classified into two apparent groups with specific-binding properties. From the Scatchard equation, the dissociation constant (Kd) and the maximum-binding quantity (Qmax) of PNB0 were 0.35 mg mL–1 and 14.21 mg g–1 for high-affinity binding sites and 2.03 mg mL–1 and 58.9 mg g–1 for lower ones, respectively. We assume that the formation of two types of binding sites with different affinity might originate from varied interactions between functional monomers and imprinted molecules, the complexes of which therefore are of diverse composition. After the complex structure was immobilized into the polymeric network, binding sites with different affinity would arise when the template molecules were extracted from the cross-linked network. All the above factors contribute to the variation in apparent-binding performance.

In order to further investigate adsorption behavior of MIP-PMAA/SiO2 toward template, Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms are used to fit the experimental data.

The Langmuir adsorption isotherm model28,31 assumes that adsorbate molecules surround a series of equivalent sites on solid surface without any interaction between the adsorbed molecules. The linear Langmuir equation is expressed as:

\[ \frac{C}{Q} = \frac{1}{Q_{\text{max}}} + \frac{1}{K_I} \]  

(5)

where C (mg L–1) and Q (mg g–1) are the concentration and the amount of adsorbed PNB0 at adsorption equilibrium; Qmax (mg g–1) is the Langmuir saturation sorption capacities; Ki (L mg–1) is the Langmuir constant. A relationship is observed between C/Q and C with the linear fitting equation of C/Q = 0.0678C + 21.3771, R2 = 0.9852, Ki = 0.0317 L mg–1, and Qmax = 14.74 mg g–1.

In contrast to the Langmuir isotherm that is appropriate for homogeneous distribution of binding sites, the Freundlich isotherm32,33 basically assumes heterogeneous adsorption due to the diversity of adsorption sites and is valid for multilayer coverage on adsorbent surface. The linearized Freundlich equation is given as:

\[ \ln Q = \ln C + \ln K_f \]  

(6)

where \( K_f \) (L g–1) and n are Freundlich constants related to adsorption capacity and intensity, respectively. A relationship is examined between \( \ln Q \) and \( \ln C \) with the linear fitting equations of \( Q = 0.6389\ln C - 1.8334 \) with \( R^2 = 0.9676 \), n = 1.56, and \( K_f = 0.16 \) L g–1.

The D-R isotherm model14 is a general model for the physical adsorption processes. It follows a pore filling mechanism and is related to the porous structure of the sorbent. It assumes heterogeneity of adsorption heat over the adsorbent surface and adsorption exhibits a multilayer feature. The linear form of the D-R isotherm model is expressed as:

\[ \ln Q = -K_{\text{DR}}C^2 + \ln Q_{\text{DR}} \]  

(7)

\[ \varepsilon = RT \ln(1 + 1/C) \]  

(8)

\[ E = (-2K_{\text{DR}})^{1/2} \]  

(9)

where QDR (mg g–1) KDR (kJ mol–2) are the D-R saturation sorption capacities and D-R constant; \( \varepsilon \) (kJ) is the Polanyi potential; R is the gas constant of 8.314 × 10–3 kJ mol–1 K–1; T (K) is the absolute temperature; E (kJ mol–1) is the mean adsorption energy. A relationship is studied between \( \ln Q \) and \( \varepsilon^2 \) with the linear fitting equation of \( \ln Q = -2.7023 \times 10^{-4} \varepsilon^2 + 1.8099 \) with \( R^2 = 0.7319, K_{\text{DR}} = 2.7023 \times 10^{-4} \) kJ mol–2; QDR = 6.11 mg g–1, and E = 43.01 kJ mol–1.

The Temkin isotherm model30 is based on the assumption that the adsorption energy of all molecules in the layer would decrease linearly with the surface coverage due to some indirect sorbate/sorbent interactions. The Temkin isotherm has been generally applied in the following form:

\[ Q = (RT \ln K_t)/b + (RT \ln C)/b \]  

(10)

where Kt (L g–1) and b (kJ mol–1) are Temkin constants and Temkin constant related to the heat of sorption; R and T are the same as D-R isotherm. A relationship is viewed between \( Q \) and \( \ln C \) with the linear fitting equations of \( Q = 0.3806ln C + 3.1199, R^2 = 0.9864, K_t = 3604.72 \) L g–1, and b = 6.5096 kJ mol–1.

The calculated parameters of the above four models are summarized in Table 2. Comparing the Langmuir isotherm (Fig. 4c) with the Freundlich (Fig. 4d) model, one can find that the experimental data of MIP-PMAA/SiO2 are in better conformity with the Langmuir isotherm model \( R^2 = 0.9852 \), indicating that the binding sites of the prepared polymer towards PNB0 are mainly homogeneously distributed in the polymeric network and the type of adsorption is monolayer adsorption. On the other hand, the experimental data obtained for the adsorption of PNB0 on present sorbents are not presented graphically on the basis of the D-R isotherm model (Fig. 4e), revealing that the adsorption process of MIP-PMAA/SiO2 with PNB0 is not based on physical adsorption. On the whole, it can be concluded that the experimental data fit better with Langmuir isotherm model (Fig. 4c) and Temkin isotherm (Fig. 4f) model, reflecting that the adsorption process might feature the dual nature of both physisorption and chemisorption, in which chemisorption is predominant.36 The related models discussion for NIP-PMAA/SiO2 were given in Supporting Information (Table S2 and Fig. S2).

Selectivity

To evaluate the specific recognition ability of different polymers, erythromycin, daptomycin, SDBS and tunicamycin were selected as the competitive molecule due to their similar structure and functional groups with PNB0 (their chemical
structures are shown in Fig. S3. As shown in Table 3, the adsorption capacity of MIP-PMAA/SiO2 toward PNB0 is twice higher than that of NIP-PMAA/SiO2. With respect to structural analogues, both polymers show similar binding capacities, implying the specific recognition ability of MIP towards template molecules and the existence of imprinting effect. The binding behavior of NIP towards substances can be ascribed to the non-specific adsorption provided by the residual functional groups in polymeric chains.37,38

To better assess the sorption performance of MIP-PMAA/SiO2 and NIP-PMAA/SiO2, distribution coefficient (Kd), selective coefficient (α) and relative selective coefficient (β) were calculated with the following equations:

\[ K_d = \frac{C_p}{C_s} \] (11)

where \( K_d \) represents the distribution coefficient, and \( C_p \) (mg g\(^{-1}\)) and \( C_s \) (μg L\(^{-1}\)) are the adsorption capacity and equilibrium concentration, respectively.

\[ \alpha = \frac{K_{di}}{K_{dj}} \] (12)

where \( \alpha \) is the selectivity factor, and \( K_{di} \) and \( K_{dj} \) are the static distribution coefficient of adsorbents to template and competitive molecule, respectively.

\[ \beta = \frac{\alpha_m}{\alpha_n} \] (13)

where \( \alpha_m \) and \( \alpha_n \) are the selectivity factor of MIP-PMAA/SiO2 and NIP-PMAA/SiO2.

The results of the competitive binding experiments are also summarized in Table 3. The value of \( \alpha \) is 2.53 – 3.13 for MIP-PMAA/SiO2, while that for NIP-PMAA/SiO2 is 1.04 – 1.18, reflecting that MIP has high selectivity for PNB0 yet NIP does not.

This can be explained by molecular the imprinting theory that during MIP-PMAA/SiO2 preparation, PNB0 was incorporated into polymeric networks via several kinds of non-covalent interactions and the following elution of PNB0 left behind the imprinting cavities that are complementary to the template in size, shape and functionality.39 In terms of NIP-PMAA/SiO2, it did not experience such a process and hence did not possess imprinting cavities. The fact that \( \beta \) is more than 1.0 is indicative that there are more binding sites existing in MIP-PMAA/SiO2 than in NIP-PMAA/SiO2, which create more transmission channels to promote sorption process and capacity towards template molecules.40

Application of MIP-SPE for real sample purification

To further study the practical application of MIP-PMAA/SiO2, the samples with three different concentrations were extracted according to the method in the Experimental. The HPLC chromatogram and the corresponding results are presented in Fig. 5. It shows that PNB0-MIP SPE realized the cleanup of most impurities in the sample and played an effective role in enriching PNB0. After MIPs column treatment, the recoveries of the spiked samples were in the range of 93.56 – 95.34%, and the purities of PNB0 reached 91.66 – 93.43%, both of which were much higher compared with the data obtained from NIPs column. The results are in accordance with the above binding experiments and further prove the existence of imprinting effect in MIP polymeric architecture, which allows for high affinity of MIP-PMAA/SiO2 toward PNB0.

Conclusions

In this work, micron-sized MIP-PMAA/SiO2 has been prepared
successfully for imprinting PNB0 for the first time via surface molecular imprinting technique. The MIP-PMAA/SiO2 adsorbent exhibits good characteristics including fast adsorption kinetics and specific selectivity towards PNB0. The experimental data fit well with the pseudo-second-order kinetic model, and might be on the basis of dual nature of both physisorption and chemisorption, of which the latter one is predominant.

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Conflict of Interest

The authors have declared no conflict of interest.

Supporting Information

Supporting Information includes the related models discussion for NIP-PMAA/SiO2 and chemical structures of PNB0 and its structural analogues. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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