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Hydrophilic molecularly imprinted phenol-amine-formaldehyde resins

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Abstract

Hydrophilic molecularly imprinted resins (MIR), which are produced using hydrophilic monomers such as phenols, aldehydes, melamine or urea, have recently attracted increasing attention for use in separation and preconcentration. Among their obvious advantages are good sorption capacity, high recovery and selectivity, as well as their reusability in aqueous solutions. In this work we applied the bulk molecular imprinting method to produce quercetin-imprinted phenol-amino-formaldehyde resin. For this purpose, phloroglucinol and melamine solutions were mixed with formaldehyde and then polyethylene glycol and quercetin (Qu) were added to the obtained solution as a porogen and a template, respectively. The mixture was stirred under heating, then left in the thermostat for a continuous time. The optimum ratio of phloroglucinol to melamine was 3:1. The average molecular mass of porogen (M_w) varied between 4000–10000 Da. The obtained MIR were eluted with ethanol-water mixture (4:1, v/v) in the Soxhlet extractor for 36 h to remove the template. The MIR were characterized by FTIR-spectroscopy, laser diffraction spectroscopy and differential thermal analysis. The maximum recovery and sorption capacity of MIR synthesized in the presence of a porogen with M_w 10000 were 47% and 4.7 μmol Qu/g, respectively. The maximum imprinting factor was 1.41. The sorption kinetics of quercetin by a non-imprinted resin (NIR) is best described by a pseudo-second-order model, while MIR has a mixed pseudo-first-second-order mechanism.

Keywords

molecular imprinting
hydrophilic resins
sorption
rebinding
quercetin

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Key findings

- We obtained a molecularly imprinted hydrophilic phloroglucinol-melamine-formaldehyde resin for the sorption concentration of quercetin.
- The sorption capacity for quercetin by the molecularly-imprinted sample was ~5 μmol/g, and the imprinting factor was 1.41.
- The quercetin rebinding process was in compliance with the pseudo-second-order model and the Freundlich model.

1. Introduction

Molecularly imprinted polymers (MIP) are widely used in analytical chemistry and other fields for selective extraction, separation and preconcentration of target molecules. One of the significant disadvantages of traditional organic solvent synthesized MIP is the insufficiently selective binding of organic analytes from aqueous matrices. This is caused by the structural changes of the MIP and, consequently, its binding sites due to the swelling of the polymer in polar solvents.

Hydrophilic molecularly imprinted resins (MIR), which are produced using hydrophilic monomers such as phenols, aldehydes, melamine or urea, have recently attracted increasing attention of researchers [1–16]. The high density of hydrophilic functional groups in MIR

(hydroxyl, amino and imino groups, as well as ether bonds) promotes the formation of complexes with template molecules through multiple hydrogen bonds, π–π– and electrostatic interactions, which makes molecular imprinting more effective. MIR have been widely used in separation and preconcentration [17, 18]. Resorcinol-formaldehyde resins were used to extract sulfonamide antibiotics [19] and aminophenol-formaldehyde resins were used to determine perphluorocarboxylic acids, chlorophenols, benzoic acids, dyes, plant growth regulators and for selective absorption of tetramethylpyrazine (ligustrazine) in traditional Chinese herb [20–23], etc. Among the obvious advantages of MIR are good adsorption capacity, high recovery and selectivity, as well as their reusability in aqueous solutions.

In this work, the molecular imprinting method was used to produce quercetin-imprinted phloroglucinol-melamine-formaldehyde resins [24]. Polyethylene glycol of varied average molecular mass was used as a porogen to increase adsorption capacity of MIR.

Quercetin has numerous biological and pharmacological activities, including antiviral, anti-inflammatory, antiallergic and antitumor properties [25]. Quercetin is introduced into the composition of some pharmaceutical drugs and dietary supplements; however, its recovery from plant extracts is extremely difficult. So, it is important to develop selective, fast and simple methods for separation and determination of quercetin in plant extracts.

2. Materials and Methods

2.1. Chemicals and materials

We used phloroglucinol (≥99.0%, Sigma-Aldrich, China); melamine (99%, Acros Organics, United Kingdom); formaldehyde (37.6%, Merck, Germany); polyethylene glycol (average molecular mass, M_w: 4000, 6000, and 10000 Da, Panreac); quercetin (99.3%, Sigma-Aldrich); acetic acid (99.9%, ECROS, Russia); acetonitrile for HPLC (>99.9%, Cryochrome, Russia); ethanol (95%, RFC, Russia), etc.

A standard solution of $5.00 \cdot 10^{-4}$ mol/L of quercetin was prepared by dissolving it in 95% ethanol; calibration solutions of $1.00 \cdot 10^{-6}$–$7.50 \cdot 10^{-5}$ mol/L were prepared by diluting the standard solution with ultrapure water (18 MΩ·cm, Aqualab UVOI-"MF"-1812 water purification system, Mediana-Filter, Russia).

2.2. Instrumentation

The resin particle size distribution was studied by laser diffraction (SALD-2300 particle size analyzer with a SALD-BC23 batch cell unit, Shimadzu, Japan). A Spectrum 100 FTIR spectrometer (Perkin Elmer, USA) with a Quest ATR accessory (Specac, UK) was used to record IR spectra in the attenuated total reflection (ATR) mode. The differential thermal analysis (TGA/DSC) was performed with a Mettler Toledo TGA/DSC 3+ Star System at a heating rate of 10 °C/min under nitrogen atmosphere with a flow rate of 50 mL/min. The total specific surface area was determined by thermal desorption of gas-adsorbate (BET) using an analyzer of specific surface area of dispersed and porous materials ThermoSorb TPD 1200 (Catakon, Russia). The concentration of quercetin in solutions was measured by UV-vis spectroscopy (UV-2600, Shimadzu, Japan).

2.3. Synthesis of phloroglucinol-melamine-formaldehyde resins (PMFR)

Molecularly imprinted resins (MIR) were prepared by polycondensation of monomers in an ethanol-water mixture (ethanol:water ratio 5:4, v/v) [24]. For this purpose, phloroglucinol (3 mmol) and formaldehyde (12 mmol) were dissolved in 4.5 ml of ethanol-water mixture at room temperature under ultrasound and magnetically stirred for 30 min (solution A). Melamine (1 mmol) and formaldehyde (2 mmol) were dissolved in 1.5 mL of ethanol-water mixture under heating to 80 °C and stirred continuously until complete dissolution (solution B). After cooling solution B to room temperature, it was mixed with solution A. Polyethylene glycol (0.025 mmol) as a porogen and quercetin (0.16 mmol) as a template were added to the obtained prepolymerization mixture. The mixture was stirred under heat (40 °C) for 30 min and incubated in an air thermostat at 60 °C for 2 h, then at 80 °C for 24 h. Quercetin was not added to the non-imprinted resin (NIR) sample. After drying, the PMFR samples were ground for 1 min either in a laboratory ball mill ML-1 (EcON, Russia) or in an agate mortar.

To remove the template after synthesis, the samples were eluted with an ethanol:water mixture (9:1, v/v) by Soxhlet extraction (500 mg, 125 mL, 36 h) and then dried at 60 °C. The concentration of quercetin was monitored by spectrophotometry (λ 373.6 nm), and the apparent degree of template removal was calculated as the proportion of quercetin eluted from the PMFR MIR samples relative to the amount added during the MIR synthesis.

2.4. Adsorption experiments

The kinetics of quercetin (template) rebinding were studied under static adsorption conditions using 10 μmol/L aqueous solution of quercetin. 50 mg of MIR or NIR sample was placed in the studied quercetin solution (~50 mL), then aliquots (3.0 mL) of this solution were taken every 5–15 min to determine quercetin by spectrophotometry at 367.6 nm wavelength. To study rebinding isotherms, an adsorption experiment was carried out with 5–70 μmol/L quercetin solutions at 27 °C (TS-1/80 SPU dry-air thermostat, Russia): 10 mg of MIR or NIR sample was placed in 10 ml of quercetin solution and incubated for 1 day with periodic stirring until equilibrium was reached.

The adsorption properties of MIR and NIR and the efficiency of molecular imprinting were characterized by calculating the recovery (R, %), sorption capacity (q, μmol/g) and imprinting factor (IF) as the ratio of the MIR sorption capacity to the NIR sorption capacity at the current time t.

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The kinetics of quercetin rebinding by MIR and NIR samples was studied using pseudo-first and pseudo-second order models [6, 21, 26]. The Langmuir and Freundlich models [9, 21, 26–28] were applied to describe the mechanism of the rebinding. Linearized equations were used to test model compliance: the Scatchard equation and the logarithmic form of the Freundlich equation. In the first case, the adsorption process was characterized by calculating the effective binding constant K_a and the maximum sorption capacity q_{max}. In the second case, the adsorption coefficient β and the empirical constant n were used as a measure of heterogeneity of binding sites.

3. Results and Discussion

In this work, three samples of quercetin-imprinted phenol-amino-formaldehyde resins (MIR) were obtained by polycondensation of melamine and phloroglucinol (phloroglucinol:melamine ratio 3:1) in the presence of formaldehyde, varying the average molecular mass of polyethylene glycol (porogen) 4000, 6000 and 10000 Da: PMF 3-1-4K, PMF 3-1-6K and PMF 3-1-10K respectively. Non-imprinted samples (NIR) were obtained in the absence of quercetin. Extraction with an ethanol-water mixture (ethanol:water ratio 4:1, v/v) by the Soxhlet method for 36 h was chosen to remove the template from the obtained MIR samples as a method providing the maximum apparent degree of template removal (Table 1).

Laser diffraction, FTIR-spectroscopy, and differential thermal analysis were used to characterize the obtained PMFR samples. It was shown (Figure 1) that the median particle diameter of PMF MIR increases with the average molecular mass of the porogen from 21.8 (M_w 4000) to 67.9 μm (M_w 10000).

In the FTIR spectra (Figure 2) out-of-plane deformation bands (δ_{oop}) of N–H bonds in the region 811–814 cm^{-1}, C–O–C stretching region 1000–1111 cm^{-1}, NH deformation vibrations in aromatic amines 1272–1370 cm^{-1}, stretch vibrations (ν) of C=C of aromatic ring (1614, 1450 cm^{-1}) and C=N of triazine (1550, 1350 cm^{-1}) and stretching region 3200–3400 cm^{-1} of O–H and N–H groups were identified.

The results of the differential thermal analysis in an inert medium (N_2) showed that the resins are thermally stable up to 200 °C, and in the temperature range 250–450 °C (Figure 3, TGA and DTA-curves of thermogravimetric and differential thermal analysis, respectively) they are thermally decomposed, accompanied by an exothermic effect (Figure 3, DSC-curve of differential scanning calorimetry).

The recovery and sorption capacity of PMFR during the rebinding of quercetin increase with increasing the average molecular mass of polyethylene glycol (Table 2). Thus, the maximum recovery and sorption capacity of PMF 3-1-10K MIR synthesized in the presence of a porogen with an average molecular mass of 10000 Da reached ~43% and 4.71 μmol/g of quercetin, respectively. The maximum IF was 1.41 (in 90 min).

The MIR obtained in this work are stable after removal of the template in a Soxhlet apparatus using various elution solvents (Table 2) and subsequent drying at 60 °C. Using 3-1-6K MIR as an example, it was shown that they can be reused after 2–3 elutions with ethanol-water mixture (2–3 cycles). In this case, the decrease in the sorption capacity during the rebinding of quercetin was no more than 8%.

The kinetics of quercetin rebinding under static sorption conditions are better described by the pseudo-second-order model for most MIR samples (Table 3, Figure 4a), while for PMF 3-1-10K MIR a mixed mechanism was observed (Table 4, Figure 4b). It should be noted that kinetic models of rebinding for the samples with the highest M_w of the porogen (PMF 3-1-10K MIR) confirmed (Tables 3, 4) the efficiency of molecular imprinting, as q_e(MIR) > q_e(NIR).

Table 1 Optimization of elution solvent.

PMFR	Eluent	*K* (%)[a]
PMF 3-1-6K	EtOH:H_2O (4:1, v/v)	22
	MeOH:H_2O (4:1, v/v)	18
	EtOH:HAc[b] (9:1, v/v)	17
	MeOH:HAc (9:1, v/v)	16
	ACN:H_2O (1:1, v/v)	10

[a] Apparent degree of template removal;
[b] HAc – acetic acid.

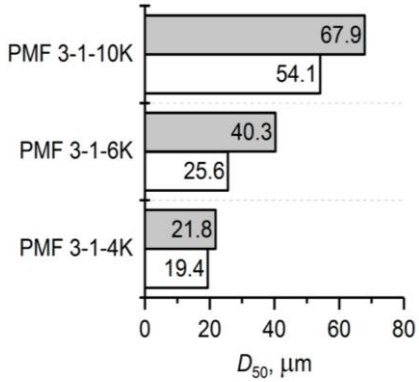

Figure 1 Median diameter (D_{50}) of PMFR (white bars – NIR, gray bars – MIR).

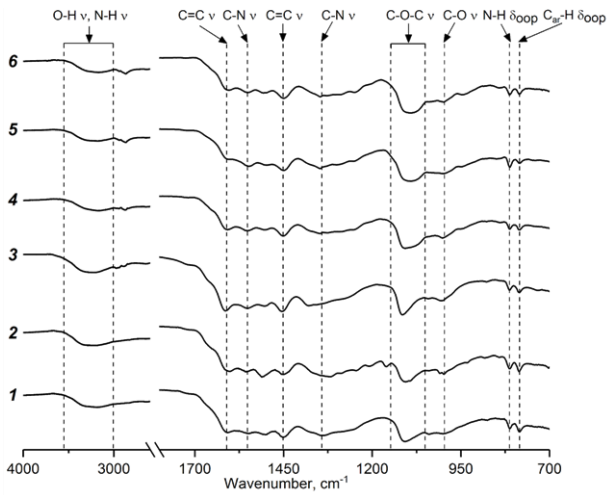

Figure 2 ATR FTIR-spectra of PMFR: PMF 3-1-4K MIR (1) and PMF 3-1-4K NIR (2), PMF 3-1-6K MIR (3) and PMF 3-1-6K NIR (4), PMF 3-1-10K MIR (5) и PMF 3-1-10K NIR (6).

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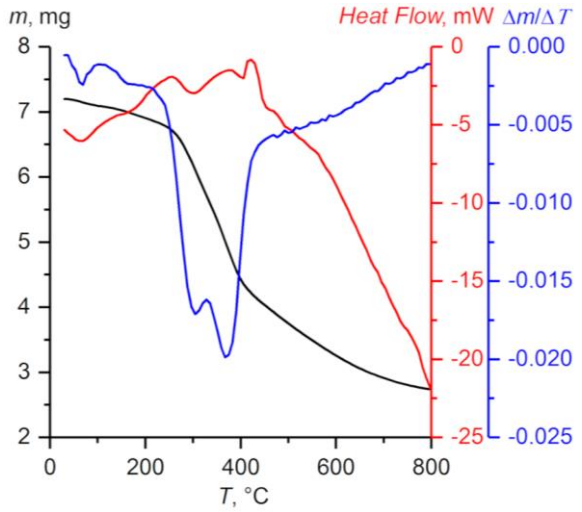

Figure 3 TGA (black), DSC (red) and DTA (blue) curves of PMF 3-1-10K MIR (N_2, 10 °C/min).

The isotherms of quercetin rebinding by PMFR samples are better described by the Freundlich model (Table 5), which confirms the heterogeneity of the surface and different types of binding centers (the empirical coefficient n is 0.5–0.6). At the same time, the empirical coefficient β, which characterizes the adsorption of quercetin, is 1.5–3.0 times higher for MIR samples than for NIR samples. This can be explained by the formation of molecular imprints that are complementary to the template molecules. The compliance with the Freundlich model correlates well with the results of the specific surface area obtained by BET (Table 6).

The relevant task of this work is to apply the advantages of the prepared MIR for selective adsorption of target biomolecules from biological matrix (plant extract). In this experiment, it takes quercetin (template) and rutin as the target flavonols, their diluted solutions as a sample matrix to simulate the selective adsorption of flavonols from the biological matrix (ethanol:water extract). The effect of concentration was studied by adding quercetin or rutin in the range of $7.5{\cdot}10^{-6}$–$7.0{\cdot}10^{-5}$ mol/L (Table 7). No significant change in the imprinting factor of quercetine was observed as the concentration further increased from $7.5{\cdot}10^{-6}$ to $7.0{\cdot}10^{-5}$ mol/L. So, it can be concluded that MIR can selectively adsorb target flavonol quercetin in diluted ethanol:water extract without the matrix interference of the biological matrix. It was noted (Table 7) that PMF 3-1-4K MIR selectively adsorbs quercetin, but PMF 3-1-10K MIR adsorbs rutin more selectively than quercetin as a template. Thus, quercetin can be considered as a dummy template for the selective recovery of rutin. The results proved the specific selectivity of obtained PMF MIR, and are expected to be further applied to the imprinting and selective recognition of more flavonoids so as to play an important role in plant analysis.

4. Limitations

In this work, samples of quercetin-imprinted phloroglucinol-melamine-formaldehyde resins with an insufficiently high recovery (~43%) were obtained, which is probably due to the small pore size and low permeability. Therefore, the following studies will be aimed at increasing the sorption capacity of MIR samples by optimizing the amount of porogen. At the same time, it is important to control the efficiency of molecular imprinting (IF at least 1.5).

Table 2 Sorption parameters of PMFR (50 mL of 10 μmol·L^{-1} quercetin solution, 50 mg of PMFR).

PMFR	R_{max} (%)		q_{max} (μmol/g)		IF_{max}
	MIR	NIR	MIR	NIR	
PMF 3-1-4K	21.6	21.7	2.50	2.58	1.13[a]
PMF 3-1-6K	41.4	48.1	4.63	5.42	1.13[b]
PMF 3-1-10K	42.6	41.1	4.71	4.69	1.41[c]

[a] 15 min; [b] 35 min; [c] 90 min.

Table 3 Pseudo-second-order kinetics parameters of PMFR.

PMFR		q_{24h} (μmol/g)	k_2 (g·μmol^{-1}·min^{-1})	q_e (μmol/g)	R^2
PMF 3-1-4K	MIR	2.50	$7.9{\cdot}10^4$	1.47	0.9290
	NIR	2.58	$4.2{\cdot}10^5$	1.60	0.9616
PMF 3-1-6K	MIR	4.63	$2.2{\cdot}10^4$	1.92	0.8664
	NIR	5.42	$6.3{\cdot}10^3$	3.87	0.8167
PMF 3-1-10K	MIR	4.71	$4.1{\cdot}10^3$	3.15	0.7729
	NIR	4.69	$2.2{\cdot}10^4$	1.72	0.8604

Table 4 Pseudo-first-order kinetics parameters of PMFR.

PMFR		q_{24h} (μmol/g)	k_1 (min^{-1})	q_e (μmol/g)	R^2
PMF 3-1-6K	MIR	4.63	$3.2{\cdot}10^{-3}$	4.17	0.9406
	NIR	5.42	$6.7{\cdot}10^{-3}$	4.86	0.5760
PMF 3-1-10K	MIR	4.71	$5.5{\cdot}10^{-3}$	4.62	0.9432
	NIR	4.69	$2.5{\cdot}10^{-3}$	4.16	0.7472

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5. Conclusions

Therefore, the molecular imprinting methodology allowed obtaining a hydrophilic phloroglucinol-melamine-formaldehyde resin for the sorption concentration of quercetin. It was shown that in the presence of polyethylene glycol (porogen) with an average molecular mass of 10000 Da, the sorption capacity of quercetin by the molecularly-imprinted sample was ~5 μmol/g, the specific surface area was 288.1 m²/g, and the imprinting factor was 1.41. It was shown that recovery of quercetin (21–43%) is slightly lower, but the imprinting factor (1.4) is not inferior to that of the similar methods for extracting phenolic compounds [26] and dyes [29] with resorcinol-melamine-formaldehyde and phenol-formaldehyde resins, as well as quercetin with surface-imprinted polymers [30, 31]. Modeling of the kinetics and isotherms of quercetin rebinding by the samples, obtained in the presence of polyethylene glycol of different average molecular mass, showed compliance with the pseudo-second-order model and the Freundlich model describing an inhomogeneous surface.

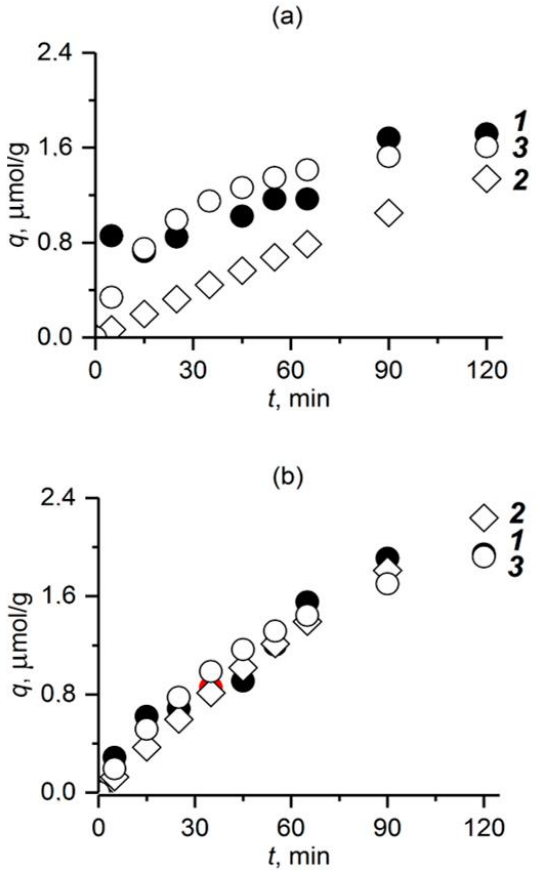

Figure 4 Kinetic adsorption curves of PMF 3-1-6K MIR (a) and PMF 3-1-10K MIR (b) for quercetin rebinding: experimental curve (1), pseudo-first-order model (2), pseudo-second-order model (3).

Table 5 Modeling of quercetin sorption isotherms by Freundlich.

PMFR		β	n	R^2
PMF 3-1-6K	MIR	$4.5 \cdot 10^{-3}$	0.5	0.9462
	NIR	$2.7 \cdot 10^{-3}$	0.5	0.9759
PMF 3-1-10K	MIR	$1.1 \cdot 10^{-2}$	0.6	0.9179
	NIR	$3.7 \cdot 10^{-3}$	0.5	0.9008

Table 6 Surface characteristics of the PMFR.

PMFR	S_{BET} (m²/g)		V (cm³/g)		Pore size (nm)	
	MIR	NIR	MIR	NIR	MIR	NIR
PMF 3-1-6K	288.1	285.9	0.17	0.15	2.44	2.08

Table 7 Effect of the concentration of quercetin (Qu) and rutin (Rut) at the range of $7.5 \cdot 10^{-6}$–$7.0 \cdot 10^{-5}$ mol/L on the imprinting factor (IF).

MIR	IF (n = 8, P = 0.95[a])	
	Qu	Rut
PMF 3-1-4K	1.16±0.06	0.78±0.09
PMF 3-1-6K	1.18±0.08	1.20±0.04
PMF 3-1-10K	1.42±0.05	1.68±0.05

[a] confidence interval

• Supplementary materials

No supplementary materials are available.

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• Conflict of interest

The authors declare no conflict of interest.

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