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Highly selective water-compatible molecularly imprinted polymers for benzophenone-4

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Abstract: Molecularly imprinting technology was applied for preparing selective sorbents for benzophenone-4 (BP4), an organic UV filter used in sunscreens and cosmetics. Several imprinted polymers were prepared by bulk polymerization, using BP4 as template. Combination of stability (mechanical and chemical), selectivity and robustness of the imprinted polymers with BP4 properties resulted in a successful imprinting process (imprinting factors in range 1.05–2.60). The prepared polymers were characterised by infrared spectroscopy, elemental analysis, conductometric titrations and nitrogen physisorption at 77 K. Adsorption capacities and selectivity towards 7 other organic UV filters (benzophenone-3, benzophenone-8, homosalate, butyl methoxydibenzoylmethane, ethyl hexyl salicylate, ethyl hexyl *p*-dimethylamino benzoate and ethyl hexyl *p*-methoxycinnamate) were determined, proving high adsorption capacity and high selectivity for BP4 binding. The highest adsorption capacity was observed for 4-vinylpyridine/ethylene glycol dimethacrylate co-polymer prepared in dimethyl sulfoxide (1.108 mmol g⁻¹). The imprinted polymer with the highest binding capacity was applied to solid phase extraction of BP4 from aqueous solutions with 98.5 % efficiency.

Keywords: UV filters; imprinting factor; binding selectivity.

INTRODUCTION

Molecularly imprinted polymers (MIPs) are smart synthetic materials which can be used for several applications:^{1–4} as sorbents for solid phase extraction (SPE),^{5–9} as stationary phase for chromatography,^{10–15} as sensors,^{16–18} artificial enzymes,^{19–21} as systems for controlled drug delivery and release,^{22–24} *etc.* Molecular imprinting technology (MIT) is based on interactions between template molecule and functional monomer in the presence of porogen. The chosen

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monomer should have at least one functional group which is likely to interact with the template. During the polymerization process monomer molecules, as present in excess, surround the template molecule, forming a pre-polymerization complex. Then, in the presence of a cross-linker, a rigid polymer network is formed usually by free radical polymerization. After the template is washed out, selective binding sites complementary to template molecules in size, shape and chemical characteristics remain in the polymer, enabling the template rebinding.¹ In some examples, only one monomer is used for the preparation of MIPs.^{25,26} The above-described approach is known as non-covalent imprinting and presents the most commonly used approach in MIT. Interactions like van der Waals, hydrogen and ionic bonding are involved in non-covalent imprinting process and, later on, in template rebinding. Thus, the higher the variety and strength of monomer-template interactions, the more selective polymer with higher binding capacity is obtained.¹

Imprinted polymers have good selectivity, chemical and mechanical stability; therefore, these materials can be universally applied in various fields of chemistry and biosciences.² Although extensive research is being done within the field, and many advances have been achieved in MIT in recent decades, MIPs are generally still lacking high binding efficiency. Most of the non-covalent MIPs described in the literature can bind only a small percent of the template amount initially used during polymerization.²⁵ Therefore, optimizing and fine tuning of polymerization conditions and the process itself to obtain highly selective polymers with high template binding efficiency is an on-going demand in MIT.²

The growing need for skin protection from the sun radiation has established UV filters as one of the emerging environmental contaminants.^{27,28} Regularly used sunscreen cosmetic products contain a high amount of UV filters (up to 15 %). UV filters can be divided into inorganic (zinc oxide and titanium oxide) and organic (benzophenones, cinnamates, dibenzoylmethanes, triazole derivatives, salicylates, *etc.*)²⁸

Benzophenone-type UV-filters are major ingredients of sunscreen products nowadays. According to EU regulations, BP4 or sulisobenzone (Fig. 1) and its sodium salt, BP5, can be used in sunscreens up to 5%.³⁰ When released in the environment, several adverse effects have been noticed such as coral bleaching, estrogenic activity in fish and even endocrine disrupting effects are suspected.^{27,31,32}

It is estimated that 40 % of coastal coral colonies worldwide are exposed to UV-filter pollution.^{28,33} BP3 can cause oxidative stress in zooxanthellae, organisms that live in symbiosis with corals. The decrease of zooxanthellae causes the lightening of the brown colour of the corals.^{27,32-34} BP4 was found in river, lake and sea water;³⁵ the EC_{50} value (half maximal effective concentration) of

BP4 is near 10 mg dm^{-3} in the *Isochrysis galbana*, *Scorpaenopsella armata*, *Paracentrotus lividus* and *Mytilus galloprovincialis*.^{27,36}

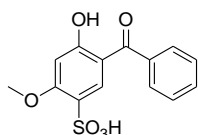


Fig. 1. Structure of benzophenone-4.

Although UV filters gained high attention with highly increased research interest in methods for pre-concentration and extractions from various samples with subsequent quantitation, only few papers describe MIT applied for development of UV filter imprinted polymers. Sun *et al.* described the application of MIP imprinted with BP2 for solid phase extraction (SPE) of four benzophenones from tap and river water. 4-vinylpyridine (4VP)/ethylene glycol dimetachrylate (EDMA) based polymer imprinted with benzophenone-2 (BP2) was successfully applied for the extraction of benzophenone-1 (BP1), BP2, benzophenone-4 (BP6) and benzophenone-8 (BP8).³⁷ Ayadi *et al.* described molecularly imprinted poly-aniline on silica support for the selective adsorption of BP4 from aqueous media.³⁸ To the best of our knowledge, no other examples of polymers imprinted using BP-type UV-filters as templates were published so far.

Within this study, we used BP4 as the template molecule to prepare several imprinted polymers by bulk polymerization.³⁹ Different polymer constituents were used: monomers (*N,N*-dimethylaminoethyl methacrylate-DMAEM and 4VP), cross-linkers (divinylbenzene-DVB and EDMA), porogenic solvents (ACN and DMSO). Polymers were characterized using FT-infrared spectroscopy (FTIR), nitrogen adsorption and adsorption isotherms. Binding capacity and selectivity towards other UV-filters was determined. Elemental analysis (EA) and conductometric titrations were used in order to estimate total and accessible binding places. The goal was to prepare selective sorbents for BP4 with high binding capacity, which can be used as potential sorbents for BP4 extraction and pre-concentration during sample preparation.

EXPERIMENTAL

Apparatus

Infrared spectra were recorded using Thermo Scientific Nicolet 6700 FT-IR Spectrometer, ATR technique. HPLC measurements were done using Agilent Technologies HPLC instrument Series 1260 with quaternary pump, on-line degasser, auto sampler and diode array detector. Conductometric titrations were done using WTWCond330i with TetraCon325 conductometric cell. Elemental analysis was performed by combustion analysis on a Vario EL III C,H,N,S/O elemental analyzer (Elementar Analysesysteme, GmbH, Hanau, Germany). Chromabond vacuum manifold (Macherey-Nagel) was used for SPE extraction. For nitrogen physisorption Sorptomatic 1990 Thermo Finnigan analyzer was used. MultiBio RS24 (BioSan) rotator and Microspin 12 centrifuge (BioSan) were used for conducting binding experiments.

Reagents

Benzophenone-4 (BP4), benzophenone-3 (BP3), ethyl hexyl salicylate (OS), ethyl hexyl *p*-dimethylamino benzoate (PABA-O), *N,N*-dimethylaminoethyl methacrylate (DMAEM), divinylbenzene (DVB), azobisisobutyronitrile (AIBN) were purchased from Sigma Aldrich. HPLC grade methanol and acetonitrile were purchased from Fisher Scientific. Benzophenone-8 (BP8) was purchased from the Tokyo Chemical Industry. 4-vinylpyridine (4VP) and ethylene glycol dimethacrylate (EDMA) were purchased from Acros Organics. Butyl methoxydi-benzoylmethane (AVB) and homosalate (HMS) were purchased from Merck.

Inhibitor remover (Sigma Aldrich) was used to remove polymerization inhibitors from 4VP, DMAEM and EDMA (5 mL of monomer/cross-linker was passed over 250 mg of inhibitor remover). DVB was purified using alumina, in the same way as EDMA. Commercially available BP4 is declared to have some percent of water bound. It was dried at 60 °C under vacuum, until no further change in mass was observed (color change from pale to clear lemon yellow was observed during drying). Other reagents were of analytical grade and used as received.

Preparation of imprinted and non-imprinted polymers

The imprinted polymers were prepared using bulk polymerization: template, monomer, cross-linker, porogen and polymerization initiator were placed in a glass vial. Upon dissolution, argon was purged through a pre-polymerization mixture for 5 min. AIBN was used as initiator (30 mg). Vials were tightly closed and left in an oil bath at 60 °C for 24 h. After polymerization was completed, the glass vials were broken and the polymer grounded in a mortar with pestle. The non-imprinted polymers were prepared as the imprinted ones, omitting the template presence. Composition of the prepared polymers is given in Table I.

TABLE I. Composition of prepared polymers

Polymer label	$m_{\text{BP4 template}} / \text{mg}$ (n / mmol)	$V_{\text{monomer}} / \mu\text{L}$ (n / mmol)	$V_{\text{cross linker}} / \text{mL}$	$V_{\text{porogen}} / \text{mL}$
NIP1	–	DMAEM 337 (2.0)	EDMA 1.888	ACN 2.730
MIP1	154.0 (0.5)	DMAEM 337 (2.0)	EDMA 1.888	ACN 2.730
NIP2	–	DMAEM 337 (2.0)	DVB 1.424	ACN 2.730
MIP2	154.0 (0.5)	DMAEM 337 (2.0)	DVB 1.424	ACN 2.730
NIP3	–	4VP 213 (2.0)	EDMA 1.888	DMSO 2.730
MIP3	154.0 (0.5)	4VP 213 (2.0)	EDMA 1.888	DMSO 2.730
NIP4	–	4VP 213 (2.0)	DVB 1.424	DMSO 2.130
MIP4	154.0 (0.5)	4VP 213 (2.0)	DVB 1.424	DMSO 2.130
NIP5	–	4VP 106.4 (1.0)	DVB 1.424	DMSO 2.000
MIP5	308.3 (1.0)	4VP 106.4 (1.0)	DVB 1.424	DMSO 2.000

Template was removed from the polymer by exhaustive washing using 2 % ammonia in methanol/water 1:1 volume ratio (process was monitored by HPLC supernatant analysis). The polymers were then washed several times with methanol and dried in an oven at 60 °C.

Binding experiments

Batch binding experiments were performed as follows: polymer 10.0±0.2 mg was weighed in a micro tube, and 2.000 mL of template solution in acetonitrile was added. The concentrations of template solution were 0.1–10 mmol dm⁻³ (0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 6.0,

8.0 and 10.0). Micro tubes were shaken using a rotator for 60 min, centrifuged (10 min, 14,500 rpm) and template concentration in supernatant was determined by HPLC.

The adsorption capacity was determined according to:

$$Q = \frac{(c_0 - c_f)V}{m} \quad (1)$$

where Q stands for adsorption capacity ($\mu\text{mol g}^{-1}$), c_0 for total concentration of template at the beginning (mM), c_f – free concentration of template after binding (mmol dm^{-3}), V – volume of template solution used for binding experiment (mL) and m – mass of the polymer used for binding experiment (g)²⁵.

The imprinting factors were determined according to:⁴⁰

$$IF = \frac{(n_{\text{bound}} / n_{\text{free}})_{\text{MIP}}}{(n_{\text{bound}} / n_{\text{free}})_{\text{NIP}}} \quad (2)$$

where IF stands for imprinting factor, $n_{\text{bound}} / \mu\text{mol}$ – amount of the template bound to NIP/MIP and $n_{\text{free}} / \mu\text{mol}$ – amount of the template free after binding.

Selectivity studies

10.0±0.2 mg of the imprinted polymer was weighed in a micro tube and 2.000 mL of 5.0 mmol dm^{-3} solution of selected UV filter was added. After 1 h of mixing, the polymer was removed by centrifugation, and UV filter concentration in supernatant was determined by HPLC according to procedure described in Section HPLC analysis.

HPLC analysis

BP4 was analyzed on Purospher Star RP18e 55-4 column, particle size was 3 μm , flow rate 1 mL min^{-1} , solvent A (1 % AcOH in water), solvent B (ACN), solvent volume ratio 80:20. Injection volume was 1.00 μL , column temperature 25 °C, detection wavelength 286 nm, retention time 3.30 min. Total method duration time was 4 min.

BP3 and BP8 were analyzed using Waters Symmetry C18 column, 3 mm×100 mm, 5 μm particle size. Flow rate was 0.6 mL/min , solvent A (water), solvent B (ACN), solvent volume ratio 30:70. Injection volume was 1.00 μL , column temperature 25 °C, total method duration time – 4 min. Retention times for BP3 and BP8 were: 2.27 and 1.46 min, respectively. For other UV filters, detection wavelengths were: 310 nm (OCT and PABA-O), 360 nm (AVB), 238 nm (OS and HMS). Retention times were OCT – 2.25 min, AVB – 2.09 min, OS – 2.64 min, HMS – 2.85 min and PABA-O – 2.32 min.

Solid phase extraction

100.0 mg of MIP4 was placed in an empty SPE cartridge with a frit on the bottom, PTFE filter (0.45 μm) was placed on the top of the polymer. Packed sorbent was washed with 1.000 mL of ACN, then 3 times with HPLC water (3×0.500 mL). 50 mL of BP4 solution (5.00 mg L^{-1}) was passed through the SPE cartridge at flow rate of approx. 1 mL min^{-1} . The sorption was repeated using the same solution (once already passed). BP4 concentration was determined in filtrate using HPLC.

Conductometric titrations

30–50 mg of polymer was placed in a titration cell, 20.0 mL of ACN added, suspension was stirred using a magnetic stirrer and titrated with 0.1024 M HCl solution at 25.0±0.5 °C. The amount of the N-containing group was calculated according to end-point HCl volume.

FTIR

FTIR spectra were recorded for NIPs, washed MIPs and MIPs that were washed and subsequently tested for template re-binding. Samples of polymers with bound template were obtained after binding experiments when a 10.0 mM template solution was used. After centrifugation, polymer was washed with a minimal volume of ACN, and dried in oven at 60 °C and atmospheric pressure for 24 h.

Nitrogen physisorption

Nitrogen physisorption was determined at 77 K. Samples were degassed for 1 h at room temperature and kept at 50 °C under vacuum for 24 h. The value of specific surface area of samples was determined using Braunauer, Emmet, Teller method (BET).

RESULTS AND DISCUSSION

Benzophenone 4 (Fig. 1) is a diprotic acid containing the sulfonic ($-\text{SO}_3\text{H}$) and the phenolic $-\text{OH}$ group. Acting as a strong acid, sulfonic group can form ionic pairs with basic monomers. Hydroxyl group in ortho position is forming a pseudo six-membered ring with benzophenone group and, as such, it most probably doesn't significantly contribute to the stability of the pre-polymerization complex. Methoxy ($-\text{OCH}_3$) group in the position 4 can act as H-bond acceptor (HBA). Two basic monomers were used in our study – DMAEM and 4VP. Both were expected to form ionic pairs and hydrogen bonds with template molecules, as well as to establish π - π stacking interactions (in case of 4VP). EDMA and DVB were used as cross-linkers, expecting that through π - π interactions DVB would contribute more to the binding capacity of the polymers than EDMA. If so, polymers prepared with DVB would have higher adsorption capacity than EDMA polymers. This was confirmed by binding experiments (Section *Binding isotherms*).

ACN is a commonly used solvent for MIP preparation because it favours non-covalent interactions.⁴⁰ Thus, ACN was our first choice for porogenic solvent, but was not applicable to all polymers preparation. When a combination of 4VP and EDMA/DVB was used, not all components were soluble in ACN. It seems that the ionic pair between 4VP and BP4 (or complex in general) is not soluble in EDMA/ACN or DVB/ACN. Monomer/template complex forms immediately upon mixing of these two components, which is easily observed by the colour change – mixture turns red (Fig. 2), 4VP is colourless to pale yellow liquid and BP4 is yellow solid.

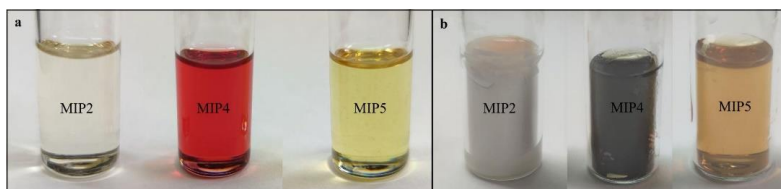


Fig. 2. MIP2, MIP4 and MIP5: a) pre-polymerization complexes and b) prepared polymers.

As this complex was not soluble in ACN, ACN/toluene mixtures, nor in acetone, other solvent had to be used. Therefore, dry DMSO was used even though it doesn't enable hydrogen bonding and is not the best choice for porogen. Pre-polymerization mixtures and obtained monolith polymers are shown in Fig. 2.

Binding isotherms

Binding of BP4 for NIPs and MIPs was conducted by batch binding experiments.²⁵ Binding isotherms were obtained as $Q = f(c_f)$ ⁴⁰ where Q stands for the adsorption capacity ($\mu\text{mol g}^{-1}$) and c_f for the free concentration of template after binding (mmol dm^{-3}), as defined in Eq. (1). Polymers showed very high capacities for binding BP4. As it can be seen on Fig. 3, BP4 binding capacity for each NIP is much lower than for the corresponding MIPs. Polymer MIP4 showed the highest binding capacity.

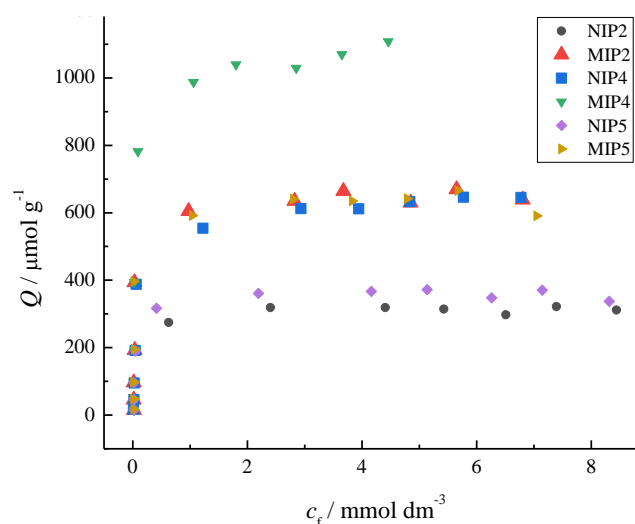


Fig. 3. Binding isotherms for selected polymers (Table I).

Obtained results imply that the imprinting process was successful. If template – monomer ionic pairs are formed, the formation of high-affinity binding sites is expected, as ionic interactions prevail as the dominant ones. Each available nitrogen-containing part of the polymer will bind the template. So, the only difference between the imprinted and the non-imprinted polymer is that MIP has more available monomer units than NIP because the template was present during polymerization.

Imprinting effect

Imprinting factor is calculated as ratio of the amount of template bound to imprinted vs. non-imprinted polymer. The imprinting factors for polymer pairs

MIP/NIP 2, 4 and 5, in ACN/water mixtures and ACN are shown in Table II. It is interesting that the presence of water in rebinding medium has a more prominent effect on imprinted polymers.

TABLE II. Imprinting factors (IF) for MIP/NIP pairs in ACN (IF_{ACN}) and in aqueous solutions containing 20 vol. % of ACN ($IF_{ACN-water}$)

Polymer	IF_{ACN}	$IF_{ACN-water}$ (20 vol. % ACN)	Improvement ($IF_{ACN-water}/IF_{ACN}$)
MIP1:NIP1	1.05	1.14	1.10
MIP2:NIP2	2.53	2.64	1.04
MIP3:NIP3	1.40	1.75	1.25
MIP4:NIP4	2.60	3.17	1.22
MIP5:NIP5	2.10	3.43	1.63

The imprinting factors in aqueous medium, for DVB polymers, are higher than in ACN, but the binding percentage (Table III) of the template to the polymer is lower. If water is present in porogen, some interactions between the template and the monomer, like hydrogen bonding, are disrupted. This leads to lower binding efficiency, but to higher imprinting factor. However, as the imprinted polymers have specific (imprinted) binding sites, the effect of water is lower than in non-imprinted ones. The improvement of imprinting factors in aqueous media compared to ACN is also shown in Table II (calculated as $IF_{ACN-water}/IF_{ACN}$). High imprinting factors in aqueous medium are of considerable importance when the application of these polymers in aqueous samples is considered.

TABLE III. Binding of BP4 to studied polymers calculated as the amount of bound BP4 relative to starting BP4 concentration (10 mmol dm⁻³)

Polymer	Binding of BP4 (ACN) / %	Binding of BP4 (20 % ACN, V/V) / %
NIP1	29.54	26.64
MIP1	30.52	29.38
NIP2	15.57	11.05
MIP2	31.94	24.69
NIP3	30.88	18.89
MIP3	38.61	28.96
NIP4	32.25	16.31
MIP4	55.41	38.22
NIP5	16.89	10.70
MIP5	29.54	29.10

Adsorption capacities

The measured adsorption capacities for imprinted polymers were in the range 0.591–1.108 mmol g⁻¹ of BP4. These capacities are much higher than those described in literature for “regular” MIPs for other templates. Ayadi *et al.*³⁹

described polymers for BP UV filters binding which had a capacity of 27.90 or 96.06 $\mu\text{mol g}^{-1}$.

The adsorption capacities obtained from binding experiments were compared to those calculated from the polymer composition (based on monomer composition), but also those obtained from elemental analysis and conductometric titrations (Fig. 4).

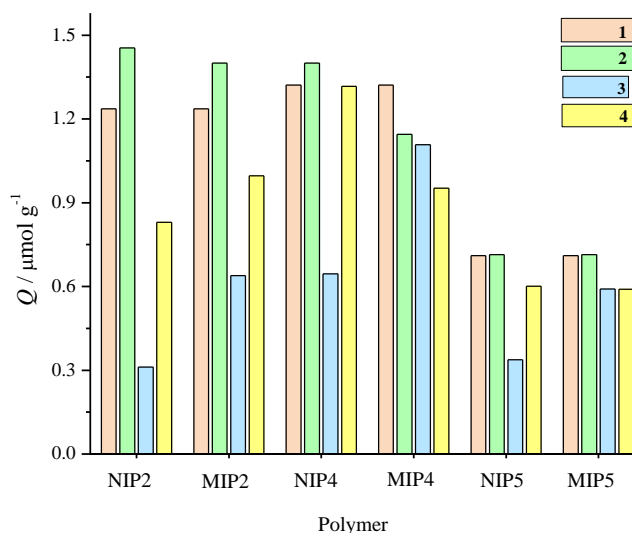


Fig. 4. 1: Calculated content of N – based on monomer composition, 2: N content determined by EA, 3: adsorption capacity – determined from adsorption isotherms, 4: monomer content determined by conductometric titration – HCl consumption.

According to the elemental analysis results (Supplementary material to this paper, Table S-V), polymers have adsorption capacity in the range 0.714 mmol g^{-1} (MIP5) up to 1.454 mmol g^{-1} (MIP4). Capacity was calculated according to the content of nitrogen (%) in the polymer, as all nitrogen in the polymer originates from the functional monomer. As can be seen in Fig. 4, all polymers have lower experimentally determined adsorption capacity than obtained from elemental analysis or based on the monomer and cross-linker composition. The only exception is polymer MIP4, where the adsorption capacity is very close to the determined content of N (EA data) and similar to the calculated nitrogen content, proving the most successful imprinting process for MIP4. To the best of our knowledge, this represents a unique example in the literature published so far.

Conductometric titrations were done to check the accessibility of monomer units in the polymer. Accessible binding sites were calculated according to 0.1 mol dm^{-3} HCl titration volume (titration graphs shown in Supplementary material, Figs. S-1 and S-2). The values obtained by conductometric titrations are

in between the calculated and the determined N , on one side, and the adsorption capacity on the other side. This can be explained as follows: not all monomer units are available for the template binding, but also, there are units not available for titration with HCl during the applied equilibration time. Again, there is one exception – MIP4.

BET surface (Supplementary material, Table S-VIII) areas are larger for MIPs compared to NIPs. However, it can be seen that binding capacity is not in direct correlation with specific surface area, *i.e.*, MIP4 ($663 \text{ m}^2 \text{ g}^{-1}$) and MIP5 ($634 \text{ m}^2 \text{ g}^{-1}$) have very similar BET areas, but the binding capacity for these two polymers differ almost twice ($1.108 \text{ mmol g}^{-1}$ for MIP4, $0.591 \text{ mmol g}^{-1}$ for MIP5). MIP2/NIP2 are found to be mesoporous materials, while MIP4/NIP4 and MIP5/NIP5 seem to be microporous.

Selectivity studies

Selectivity of the prepared polymers was studied by comparison of the binding of UV filters from few groups of organic UV filters. In Fig. 5, the adsorption capacities are shown for template and other studied UV filters when binding was done using 5 mM solutions.

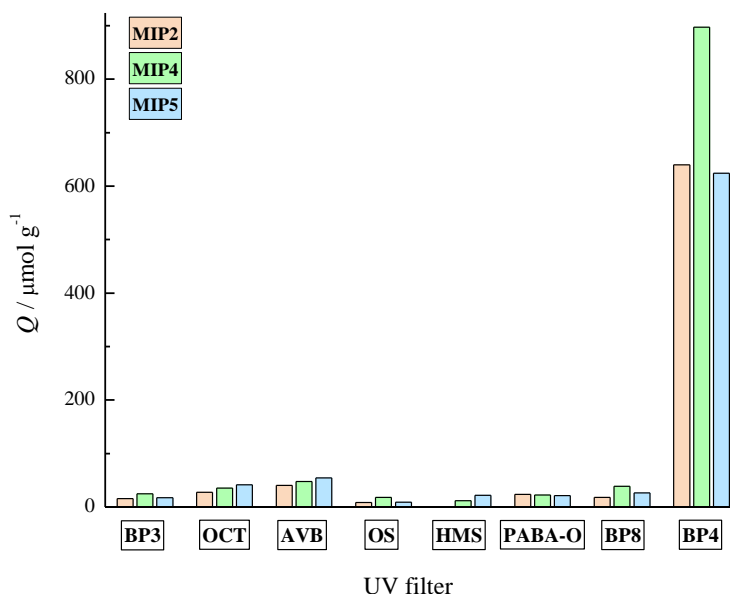


Fig. 5. Selectivity of imprinted polymers towards other UV filters.

As it can be seen, the binding of BP4 (55.4 %) compared to other UV filters (<5.5 %) is much higher due to different type of interactions between template and polymer: the template is bound to the polymer by strong ionic interactions between sulfonic group of the template and pyridine core (or amino group of

DMAEM) in the polymer. Stronger binding is also a consequence of hydrogen bonding between the –OH group of the template and pyridine core, even though the –OH group is at least partially bound in pseudo-six-membered ring with benzophenone oxygen. None of other UV filters have the acidic group as BP4 has, so the rest of the examined compounds bind to polymers mainly by hydrogen bonding.

Solid-phase extraction of BP4 from aqueous solutions

With MIP4 as a sorbent, 95.0 % of BP4 was adsorbed after the first elution. If the same BP4 solution was passed over MIP4 for the second time, the total of 98.5 % of BP4 adsorption was achieved. The obtained results indicate that the prepared imprinted polymer can be successfully applied for BP4 removal from aqueous solutions. The possibility of extraction from aqueous solutions is crucial for the application in real samples analysis as BP4 can be found in water ecosystems.³⁶

Infrared spectroscopy

There is no difference between MIP4 (Fig. 6a) and NIP4 (Fig. 6c) in FTIR spectra, indicating that the removal of the template molecule from the imprinted polymer was fully achieved by the applied washing procedure.

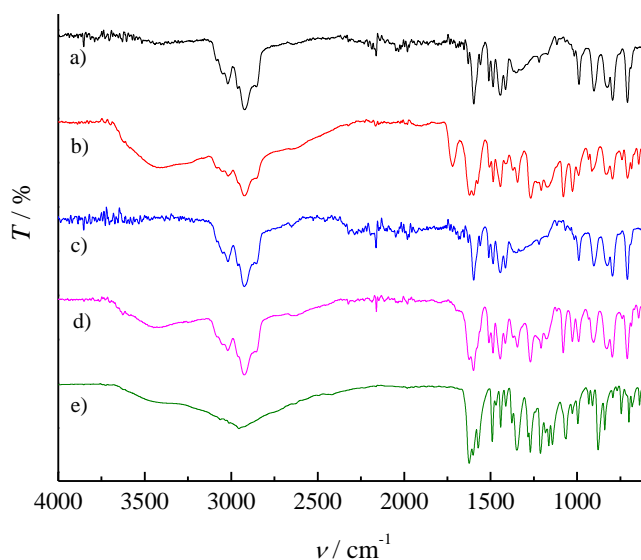


Fig. 6. Infrared spectra for selected polymers: a) MIP4; b) MIP4 with re-bound BP4; c) NIP4; d) NIP4 with bound BP4; e) BP4.

The difference within 1500–1700 cm^{-1} region between polymers with re-bound template (Fig. 6b and d) and unbound ones (Fig. 6a and c) confirms the

presence of the template when compared to the spectra of pure template (Fig. 6e). Furthermore, the presence of the re-bound template in spectra of Fig. 6b and d is visible within hydrogen bonds region ($3300\text{--}3500\text{ cm}^{-1}$). This is probably due to moisture traces present in BP4.

CONCLUSION

Benzophenone 4 (BP4) is one of the most commonly used organic UV filter in sunscreen lotions and other cosmetic products. As an emerging environmental contaminant, the need for quantitative determination upon environmental sample preconcentration has pointed out the need for BP4 selective sorbents development. Five polymer pairs of molecularly imprinted (MIPs) and nonimprinted polymers (NIPs) were prepared within this study. The polymers were characterized by template binding studies, infrared spectroscopy, elemental analysis, conductometric titrations and nitrogen adsorption analysis. All MIPs were successfully imprinted with BP4. However, the imprinting factor was higher in polymers containing DVB (2.10–2.60) compared to EDMA (1.05–1.40) polymers. The prepared polymers have high adsorption capacity for template binding – up to 1.108 mmol g^{-1} (MIP4). Binding of the template to prepared MIPs was compared to binding of 7 other organic UV filters, proving high BP4 MIPs selectivity. The nitrogen physisorption showed that differences in adsorption capacity are not the consequence of different specific surface areas. Finally, MIP4 was used as a sorbent for solid phase extraction of BP4 from aqueous solution, with 98.5 % sorption efficiency. The obtained results are promising for the application of MIPs as solid phase extraction sorbents for BP4 preconcentration from real samples, which is the subject of our ongoing study.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/11718>, or from the corresponding author on request.

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ИЗВОД

ВИСОКО СЕЛЕКТИВНИ ВОДОКОМПАТИБИЛНИ МОЛЕКУЛСКИ ОБЕЛЕЖЕНИ ПОЛИМЕРИ ЗА БЕНЗОФЕНОН-4

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Технологија молекулског обележавања примењена је у синтези селективних сорбента за бензофенон-4 (BP4), органски UV филтер који се користи у кремама за сунчање и другим козметичким производима. Полимери су добијени полимеризацијом у маси,

користећи (BP4) као матрицу. Комбинацијом стабилности (механичке и хемијске), селективности и робусности молекулски обележених полимера са својствима BP4 извршено је успешно обележавање (фактор обележавања 1,05–2,60). Карактеризација добијених полимера је извршена применом инфрацрвене спектроскопије, елементалне анализе, кондуктометријских титрација и физисорпције азота на 77 К. Адсорпциони капацитети и селективност испитани су за 7 других органских UV филтера (бензофенон-3, бензофенон-8, хомосалат, бутилметоксибензоилметан, етилхексил-салицилат, етилхексил-*p*-диметиламинобензоат и етилхексил-*p*-метоксицинамат), потврђујући велики адсорпциони капацитет и високу селективност за везивање BP4. Највећи адсорпциони капацитет показао је ко-полимер 4-винилпиридина и дивинилбензена добијен коришћењем диметил-сулфооксида као порогена (1,108 mmol/g). Полимер са највећим капацитетом за везивање BP4 примењен је као сорбент за екстракцију чврстом фазом BP4 из водених раствора са ефикасношћу од 98,5 %.

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REFERENCES

1. B. Sellergren, *Molecularly Imprinted Polymers: Man-Made Mimics of Antibodies and Their Applications in Analytical Chemistry*, Elsevier, Amsterdam, 2001. (ISBN: 978-0444547859)
2. *Handbook of Molecularly Imprinted Polymers*, C. Alvarez-Lorenzo, A. Concheiro (Eds.), Smithers Rapra, Shrewsbury, 2013 (ISBN: 978-1847359605)
3. *Molecularly Imprinted Materials: Science and Technology*, M. Yan, O. Ramström (Eds.), Marcel Dekker, New York, 2005 (ISBN: 978-0367578190)
4. *Molecular Imprinting of Polymers*, Landes Bioscience, S. Piletsky, A.P.F. Turner (Eds.), Georgetown, TX, 2006 (ISBN: 978-1587062193)
5. D. Sun, Z. Song, Y. Zhang, Y. Wang, M. Lv, H. Liu, L. Wang, W. Lu, J. Li, L. Chen, *Front. Environ. Chem.* **2** (2021) 703961 (<https://doi.org/10.3389/fenvc.2021.703961>)
6. F. Qiao, H. Sun, H. Yan, K. Row, *Chromatographia* **64** (2006) 625 (<https://doi.org/10.1365/s10337-006-0097-2>)
7. M. Sanagi, S. Salleh, W. Ibrahim, A. Naim, D. Hermawan, M. Miskam, I. Hussain, H. Aboul-Enein, *J. Food Compos. Anal.* **32** (2013) 155 (<https://doi.org/10.1016/j.jfca.2013.09.001>)
8. M. Lasakova, P. Jandera, *J. Sep. Sci.* **32** (2009) 799 (<https://doi.org/10.1002/jssc.200800506>)
9. F. Tamayo, E. Turiel, A. Martin-Esteban, *J. Chromatogr., A* **1152** (2007) 32 (<https://doi.org/10.1016/j.chroma.2006.08.095>)
10. Y. Huang, C. Zheng, Z. Liu, *Curr. Org. Chem.* **15** (2011) 1863 (<https://doi.org/10.2174/138527211795656651>)
11. W. Cheong, S. Yang, F. Ali, *J. Sep. Sci.* **36** (2013) 609 (<https://doi.org/10.1002/jssc.201200784>)
12. W. Cheong, F. Ali, J. Choi, J. Lee, K. Sung, *Talanta* **106** (2013) 45 (<https://doi.org/10.1016/j.talanta.2012.11.049>)
13. O. Baltrons, M. Lopez-Mesas, C. Palet, F. Derf, F. Porter-Koltalo, *Anal. Methods* **5** (2013) 6297 (<https://doi.org/10.1039/C3AY41227J>)
14. M. Malik, H. Shaikh, G. Mustafa, M. Bhangar, *Sep. Purif. Rev.* **48** (2019) 179 (<https://doi.org/10.1080/15422119.2018.1457541>)
15. T. Hishiya, H. Asunama, M. Komiyama, *Polym. J.* **35** (2003) 440 (<https://doi.org/10.1295/polymj.35.440>)
16. Y. Saylan, S. Akgonullu, H. Yavuz, S. Unal, *Sensors* **19** (2019) 1279 (<https://dx.doi.org/10.3390%2Fs19061279>)

17. K. Haupt, K. Mosbach, *Chem. Rev.* **100** (2000) 2495 (<https://doi.org/10.1021/cr990099w>)
18. N. Leibl, K. Haupt, C. Gonzato, L. Duma, *Chemosensors* **9** (2021) 123 (<https://doi.org/10.3390/chemosensors9060123>)
19. H. Lan, *PhD Thesis*, Iowa state University, 2018 (<https://dr.lib.iastate.edu/entities/publication/baf42fc0-5fec-465e-a78e-d8a0524c44f7>)
20. D. Mathew, B. Thomas, K. Devaky, *Artif. Cells Nanomed. Biotechnol.* **47** (2019) 1149 (<https://doi.org/10.1080/21691401.2019.1576703>)
21. X. li, M. Zangiabadi, Y. Zhao, *J. Am. Chem. Soc.* **143** (2021) 5172 (<https://doi.org/10.1021/jacs.1c01352>)
22. S. Zaidi, *Mater. Sci. Technol.* **3** (2020) 2589 (<https://doi.org/10.1016/j.mset.2019.10.012>)
23. S. He, L. Zhang, S. Bai, H. Yang, Z. Cui, X. Zhang, Y. Li, *Eur. Polym. J.* **143** (2021) (<https://doi.org/10.1016/j.eurpolymj.2020.110179>)
24. R. Liu, A. Poma, *Molecules* **26** (2021) 3589 (<https://doi.org/10.3390/molecules26123589>)
25. M. Pesic, M. Todorov, G. Becskereki, G. Horvai, T. Verbic, B. Tóth, *Talanta* **217** (2020) 121075 (<https://doi.org/10.1016/j.talanta.2020.121075>)
26. M. Sibrian-Vazquez, D. Spivak, *J. Am. Chem. Soc.* **126** (2004) 7827 (<https://doi.org/10.1021/ja038961b>)
27. L. L. R. de Miranda, K. E. Harvey, A. Ahmed, S. C. Harvey, *Environ. Monit. Assess.* **193** (2021) 1 (<https://doi.org/10.1007/s10661-021-09626-6>)
28. Y. Huang, P. Wang, J. C. F. Law, Y. Zhao, Q. Wei, Y. Zhou, Y. Zhang, H. Shi, K. S. Y. Leung, *Environ. Int.* **143** (2020) 105961 (<https://doi.org/10.1016/j.envint.2020.105961>)
29. Y. Huang, J. C. F. Law, T. K. Lam, K. S. Y. Leung, *Sci. Total Environ.* **755** (2021) 142486 (<https://doi.org/10.1016/j.scitotenv.2020.142486>)
30. *Regulation (EC) No. 1223/2009 of the European Parliament and of the Council of 30 November 2009*, Official Journal of the European Union (2009) L 342/59–L 342/209 (<http://data.europa.eu/eli/reg/2009/1223/oj>)
31. C. A. Downs, E. Kramarsky-Winter, J. E. Fauth, R. Segal, O. Bronstein, R. Jeger, Y. Lichtenfeld, C. M. Woodley, P. Pennington Y. Loya, *Ecotoxicol.* **23** (2014) 175 (<https://doi.org/10.1007/s10646-013-1161-y>)
32. C. Corinaldesi, F. Marcellini, E. Nepote, E. Damiani, R. Danovaro, *Sci. Total Environ.* **637** (2018) 1279 (<https://doi.org/10.1016/j.scitotenv.2018.05.108>)
33. C. A. Downs, E. Kramarsky-Winter, R. Segal, J. Fauth, S. Knutson, O. Bronstein, F. R. Ciner, R. Jeger, Y. Lichtenfeld, C. M. Woodley, P. Pennington, K. Cadenas, A. Kushmaro, Y. Loya, *Arch. Environ. Contam. Toxicol.* **70** (2016) 26 (<https://doi.org/10.1007/s00244-015-0227-7>)
34. O. Ben-Zvi, G. Eyal, Y. Loya, *Hydrobiologia* **759** (2015) 15 (<https://doi.org/10.1007/s10750-014-2063-6>)
35. B. Kasprzyk-Hordern, R. Dinsdale, A. Guwy, *Water Research* **43** (2009) 363 (<https://doi.org/10.1016/j.watres.2008.10.047>)
36. E. Paredes, S. Pérez, R. Rodil, J. B. Quintana, R. Beiras, *Chemosphere* **104** (2014) 44 (<https://doi.org/10.1016/j.chemosphere.2013.10.053>)
37. H. Sun, Y. Li, C. Huang, J. Peng, J. Yang, X. Sun, S. Zang, J. Chen, X. Zhang, *J. Sep. Sci.* **38** (2015) 3412 (<https://doi.org/10.1002/jssc.201500419>)
38. C. Ayadi, A. Anene, R. Kalfat, Y. Chevalier, S. Hbaieb, *Colloids Surfaces A* **567** (2019) 32 (<https://doi.org/10.1016/j.colsurfa.2019.01.042>)
39. Z. Dorko, A. Szakolczai, T. Verbic, G. Horvai, *J. Sep. Sci.* **38** (2015) 4240 (<https://doi.org/10.1002/jssc.201500874>)
40. *Molecularly Imprinted Polymers in Biotechnology*, B. Mattiasson, L. Ye (Eds.), Springer International Publishing, 2015 (ISBN: 978-3319207292).