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Molecularly Imprinted "Bulk" Copolymers as Selective Sorbents for Gallic Acid

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ABSTRACT: We report the synthesis of molecularly imprinted sorbents, selective for gallic acid. The particles were prepared by using acrylic acid, acrylonitrile, and hydroxyethyl methacrylate as functional monomers, whereas ethyleneglycol dimethacrylate and 1,4-buthanediol dimethacrylate were used as crosslinkers. Preparation and manipulation protocols were adjusted considering template's nature. To highlight the influence of monomer/crosslinker nature upon imprinted particles, the adsorption capacity, the imprinting factor, and the distribution and selectivity coefficients were calculated. An imprinting factor of 3.53 and a selectivity coefficient of 6.86 were found for hydroxyethyl methacrylate/ethylene glycol methacrylate system. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: crosslinking; molecular imprinting; molecular recognition; sorbent; selectivity

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INTRODUCTION

Molecularly imprinted polymers (MIPs) are synthetic polymeric materials, with specific recognition sites, complementary in shape, size, and functional groups to the template molecule, involving an interaction mechanism based on molecular recognition. Their stability, ease of preparation, and low cost for most of the target analytes make this imprinting method attractive for numerous applications. Over 1450 references related to the use of MIPs in a large range of application areas have been recently collected.[1]

Research into novel MIPs and their application for drugs and pollutants determination, in biological and environmental samples have been the base activity of molecular imprint-based solid-phase extraction (MISPE) domain.[2–7] MISPE has been used to determine drugs in biological fluids,[8–12] water,[13,14] apple extracts, and urine.[15] It was also used to separate and detect nicotine in chewing gum and tobacco,[16] bentazone in water,[17] triazine herbicides in beef liver,[18] and diosgenine in complex mixtures of steroids.[19] Separation on most current SPE sorbents is based on the physicochemical retention on the functionalized surface.[20]

Owing to a low affinity of the sorbent toward the template, other components of the mixture are also adsorbed in small amount in the polymer matrix. Noncovalent imprinting generates active binding sites with a relatively high specificity if a proper monomer is used. Therefore, a considerable amount of work is spent on optimizing a complete analytical method.

Optimization of the MISPE method should be based on understanding how the strength and nature of imprint–analyte and polymer surface–analyte interactions, respectively, vary with the type of solvent or buffer employed.

An MIP is synthesized by polymerization of functional monomers and crosslinkers in the presence of a high concentration of template. An advanced extraction is necessary to gain a higher amount of free high-affinity sites. Exhaustive washing of the MIPs leads to a material with greater ability to absorb the analyte from highly diluted samples throughout molecular recognition. The "bulk" polymerization,[21–24] suspension polymerization,[25,26] precipitation,[27] and dispersion polymerization[28] are the most well-known techniques for MIP preparation. Among them, the "bulk" polymerization is considered as the most reliable one.

The gallic acid (GA) or 3,4,5-trihydroxybenzoic acid is a biologically active compound widely present in plants.[29–32] According to the literature, GA is also a strong natural antioxidant[33,34] used in pharmaceutical industry (in synthesis of trimethoprim), in food and feed industry for antioxidant making, in ink dyes and photography, and in paper manufacturing.

Table I. Monomer and Crosslinker Quantities Used for the Synthesis of Imprinted and Nonimprinted Polymers

	Monomer			Crosslinker	
Sorbent code[a]	AA (g/mmol)	AN (g/mmol)	HEMA (g/mmol)	EDMA (g/mmol)	BDMA (g/mmol)
MIP 1	0.216/3	–	–	2.973/15	–
MIP 2	–	0.195/3	–	2.973/15	–
MIP 3	–	–	0.39/3	2.973/15	–
NIP 1	0.216/3	–	–	2.973/15	–
NIP 2	–	0.195/3	–	2.973/15	–
NIP 3	–	–	0.39/3	2.973/15	–
MIP 11	0.216/3	–	–	–	3.395/15
MIP 22	–	0.195/3	–	–	3.395/15
MIP 33	–	–	0.39/3	–	3.395/15
NIP 11	0.216/3	–	–	–	3.395/15
NIP 22	–	0.195/3	–	–	3.395/15
NIP 33	–	–	0.39/3	–	3.395/15

[a]Polymer notations are as follows: MIP molecularly imprinted polymers containing GA and NIP nonimprinted polymers without GA; the numbers following the notation correlate imprinted/nonimprinted polymer pairs, for example MIP 1 with NIP 1 points out the components of the system, for example MIP 2 is an AN/EDMA system and MIP 22 is an AN/BDMA system.

This article describes the synthesis and characterization of various polymerization systems for MIP particle preparation, selective for GA. Some important parameters of MIPs—the adsorption capacity, the imprinting factor, and the distribution and selectivity coefficients—were compared to establish which system is the most favorable one for molecular recognition of GA.

EXPERIMENTAL

Materials

Ethylene glycol dimethacrylate (EDMA, 98%), 1,4-butanediol dimethacrylate (BDMA, 98%), acrylic acid (AA, 99%), acrylonitrile (AN, 98%), 2-hydroxyethyl methacrylate (HEMA, 98%), *N,N*-dimethylformamide (DMF, reagent grade and high-pressure liquid chromatography [HPLC] grade), ethanol absolute (99.6%), acetonitrile (reagent grade), and 2,2′-azobis(2-isobutyronitrile) were purchased from Merck (Bucharest, Romania). GA (98% purity and 10% crystallization water) and resorcinol (R, 98% purity) were purchased from Fluka (Bucharest; Romania). All monomers and solvents used were purified before use, according to the standard procedures.

Characterization

Both adsorption and extraction processes were assessed using HPLC (1200 Series with RID detector from Agilent Technologies (Waldbronn, Germany)). A scanning electron microscope, Quanta 200, was used for microstructure analyses. The infrared spectra were acquired on FTIR-Tensor 30 BRUCKER spectrometer, on ATR and thermogravimetric analyses were performed on a Q5000IR from TA Instruments. Extraction of the template was accomplished using an ultrasonication water bath Elmasonic S10 from Elma.

Preparation of Imprinted Polymer Particles

In a typical run, the functional monomer (Table I) was first premixed with 0.085 g (0.5 mmol) of GA, to establish physical bonding, and 4 mL (52 mmol) of dimethylformamide as porogen, in 10 mL polymerization vials. Over the monomer/template complex, ethylene glycol dimethacrylate or 1,4-buthanediol dimethacrylate was added as crosslinker (Table I) and 0.3 g of 2,2′-azobis(2-isobutyronitrile) as radical initiator. After 10 min of degassing by ultrasonication and 5 min of purging with nitrogen, the vials were sealed off and immersed in a heated water bath at 65°C for 21 h of polymerization. Afterward, the vials were broken and the polymers were mechanically grounded and sieved (70 μm fraction was further used). In parallel with imprinted polymers, a series of nonimprinted (blank) polymers, without GA, were prepared in the same conditions as control.

The template removal was accomplished by 3-h ultrasonication with ethanol (5 mL of ethanol per 1 g of MIP). The removal of GA from the imprinted polymers was verified using two methods. The first method consisted in an identification reaction of GA from residual washing solutions, using a 1% ferric chloride aqueous solution and, the second consisted in FTIR characterization of imprinted polymers before and after extraction and nonimprinted polymers.

Tests Description and Calculation Method

Adsorption Tests. To achieve an optimal adsorption and imprinting factor, the rebinding capacity was tested at three different volumetric ratios of the feed solvent, ethanol : acetonitrile, 85 : 15, 75 : 25, and 65 : 35. Acetonitrile is a nonsolvent for GA and is supposed to enhance the uptake of GA in the specific sites by increasing the affinity toward the polymer. Adsorption tests consisted in placing 50 mg of polymer particles in 5 mL of an ethanol : acetonitrile solution with a 7.73 g/L concentration of GA. After 20 h of contact at 25°C, residual solutions were analyzed by HPLC and compared with the initial solution.

Selectivity Tests. To be relevant, selectivity was highlighted by a competitive uptake of GA [Figure 1(a)] and another compound,

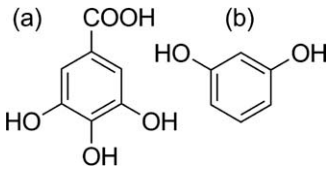

Figure 1. Chemical structure of GA (a) and resorcinol (b).

resorcinol [Figure 1(b)], with a similar structure. The polymer particles were contacted with an equimolecular mixture of GA and resorcinol (12.84 g/L concentration of solids) solubilized in ethanol : acetonitrile. The procedure is similar to the one described for adsorption: 50 mg of polymer particles was contacted with 5 mL of an ethanol : acetonitrile solution (volumetric ratio, 85 : 15) for 20 h at 25°C. The residual solutions were analyzed by HPLC and compared with the initial solution.

Calculation Method. All samples were tested under the same conditions: 25°C, 54 Barr, 20 μL injection volume, 1 mL/min elution flow, and DMF as elution solvent. After adsorption, residual solutions were tested by HPLC. The area under the component's characteristic peak, from elution diagram, is proportional to the concentration in the analyzed mixture. The uptake of GA, by the polymer, was calculated as a difference between initial concentration and residual concentration of GA in the solution, best described by eqs. (1)–(3).

$$c_{ads} = c_R - c_{res} \tag{1}$$

$$c_{res} = \frac{A_{res} \cdot c_R}{A_R} \tag{2}$$

$$c_{ads} = \frac{m_{GA}}{V_S} \Rightarrow m_{GA} = c_{ads} \cdot V_S \Rightarrow Q = \frac{m_{GA}}{m_{Polymer}} * 1000 \tag{3}$$

$$F = \frac{m_{MIP}}{m_{NIP}} \tag{4}$$

$$K_d = \frac{(c_R - c_{res}) * V_S}{m_{Polymer} * c_R} \tag{5}$$

$$k = \frac{K_{d,1}}{K_{d,2}} \tag{6}$$

The notations in eqs. (1)–(3), are as follows: c_R—the concentration of GA from the reference solution (7.73 g/L); c_{res}—the concentration of GA from the residual solution (g/L); A_{res}—the peak area of GA from the residual solution; A_R—the peak area of GA from the reference solution; c_{ads}—the concentration of GA (g/L) adsorbed by 50 mg of polymer; V_S—the volume of the initial solution (5 mL); m_{GA}—the quantity of GA (g) adsorbed by 50 mg of polymer; and $m_{Polymer}$—the amount of polymer (50 mg) taken into account. The adsorption capacities for GA, Q, Eq. (3), were given as grams of GA per 1 g of polymer.

The physical significance of the imprinting factor (F) refers to the number of times the imprinted polymer adsorbs specifically the analyte, relative to the blank polymer. Imprinting factor, F, was best appreciated with relation (4), where the m_{MIP} is the quantity of GA adsorbed by the imprinted polymer, whereas the m_{NIP} represents the quantity of GA adsorbed by the blank (non-imprinted) polymer.

Equations (1)–(3) were also used for the calculation of the adsorbed resorcinol and GA quantities in selectivity tests (initial concentrations of GA and resorcinol, c_R, were 7.8 and 5.04 g/L, respectively). Distribution coefficients, K_d, were calculated for each component of the mixture, as the concentration of adsorbed specie, per gram of sorbent, relative to the concentration of the remaining specie in the solution, using Eq. (5).[35] The selectivity coefficient, k, indicates the affinity with which the template is adsorbed relative to another competitor specie, and is given by Eq. (6) in which $K_{d,1}$ and $K_{d,2}$ represented the distribution coefficients of GA and resorcinol, respectively.

RESULTS AND DISCUSION

Interaction Structures of the Monomer–Template Complex

The monomer must possess in its structure, functional groups to interact quite strongly with the functional groups of the template and form a stable complex. The choice of functional monomer depends on the nature of the template. In this case, the template is GA which possess both hydroxyl and carboxyl groups. Selecting the monomers and crosslinkers was very difficult as the method is based on molecular imprinting and not on ionic imprinting. Therefore, the synthesis of molecularly imprinted particles with GA was performed using various polymerization systems, based on AA, AN, or hydroxyethyl methacrylate as functional monomer and EDMA or BDMA as crosslinker. The functional monomers were chosen to interact with both hydroxyl and carboxyl groups of GA. AN is known to be a very polar molecule which forms strong and numerously hydrogen bonding. For compatibility reasons, the crosslinkers were both acrylates. Coordination of one molecule of GA is hypothetically completed using a maximum of four monofunctional monomer molecules. To ensure a complete coordination and a high conversion, an excess of functional monomer (GA : monomer = 1 : 6 molar ratio) was added to each polymer sample. However, the —OH substituents from the aromatic nucleus of GA enhance the acidity of the carboxylic group owing to their withdrawing inductive effect ($-I$). Thus, the carboxylic group is the most reactive, followed by meta-hydroxyl groups. Because of their high reactivity, AA and AN will first coordinate with the carboxyl group and then one meta-hydroxyl group followed by a random order for the other two groups [Figure 2(a,b)]. HEMA has lower reactivity; therefore, it should only coordinate with the carboxyl group [Figure 2(c)].

Infrared Spectroscopy

The FTIR spectra of imprinted polymers MIP 3 [Figure 3(a)] and MIP 33 [Figure 3(b)] before and after extraction compared to their blank homologues NIP 3 and NIP 33 showed that an efficient removal of GA from the particles was performed. This assumption was made based on the disappearance of GA characteristic peaks, in the extracted polymer spectra from 3491, 3350, and 1694 cm^{-1} assigned to —OH (from crystallization water), —OH (phenolic), and —COOH, respectively, and from 1539 and 1453 cm^{-1} assigned for —C=C— (aromatic) stretching vibration. The polymer characteristic bands showed up stretching vibrations at 2951, 1724, 1448, 1252, and 1144 cm^{-1} owing to —CH_2—, —C=O, —CH_3, —C—O—C—, and —C—O—, respectively. No other

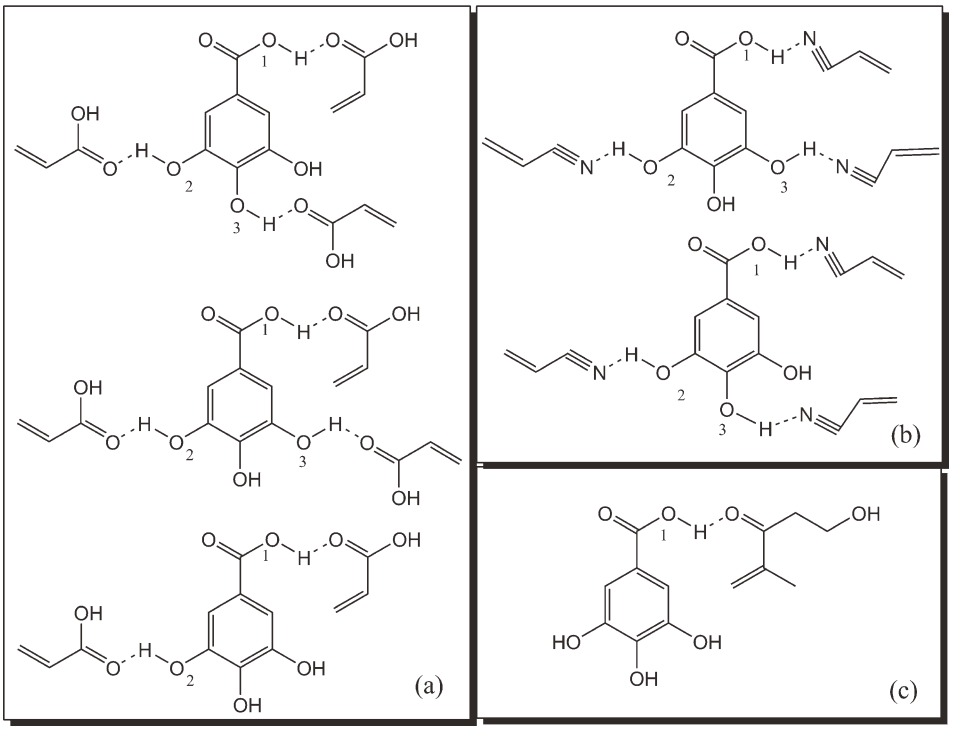

Figure 2. Possible interaction structures of AA–GA (a), AN–GA (b), and HEMA–GA (c) complexes.

bands were present in the spectra of imprinted polymers as compared with the blank ones, indicating that imprinting implied noncovalent bonding only. The infrared spectra of MIP 1, MIP 11, MIP 2, and MIP 22 compared with their nonimprinted polymers, NIP 1, NIP 11, NIP 2, and NIP 22 led to the same conclusions. These FTIR results show that GA was successfully extracted from the solid-imprinted polymer samples using the method described in **Preparation of imprinted polymer particles** section.

Microstructure of Polymers

The microstructure of all polymer particles, investigated by SEM, was found to be similar. Representative micrographs of MIP 3 and MIP 33 are shown in Figure 4. The particles were irregular in shape and size and the surface morphology of polymers was homogeneous with low porosity (Figure 4(a,b), medallion), suggesting that rebinding of the analyte was probably limited to surface processes. Micrographs of MIP 1, MIP 11, MIP 2, and MIP 22 did not present significant changes in

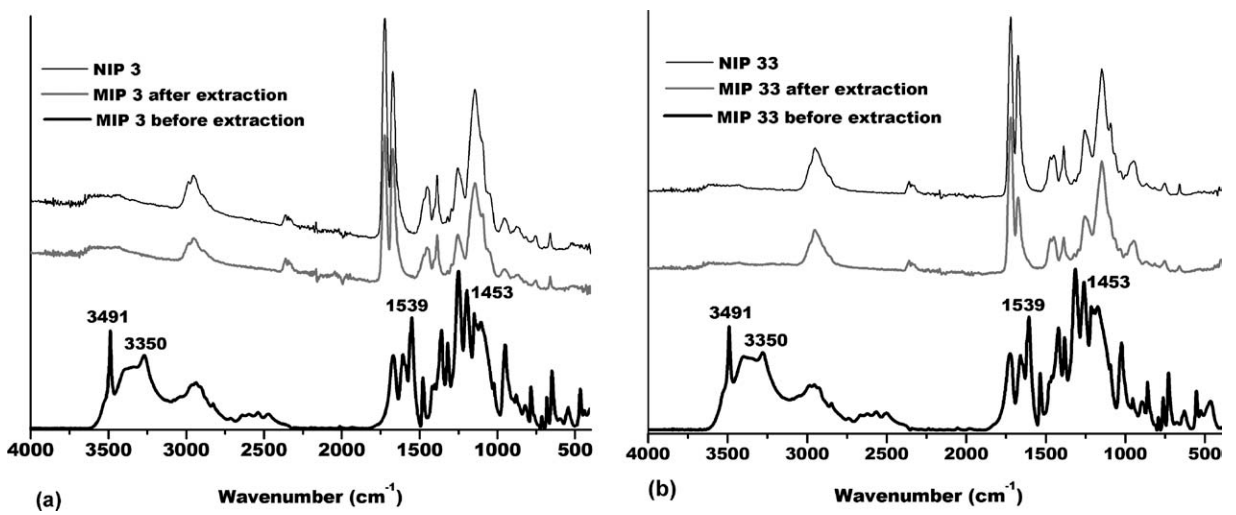

Figure 3. FTIR spectra of HEMA-based sorbents: MIP 3 (HEMA/EDMA-imprinted polymer) before and after extraction and nonimprinted polymer NIP 3 (a), MIP 33 (HEMA/BDMA-imprinted polymers) before and after extraction and nonimprinted polymer NIP 33 (b).

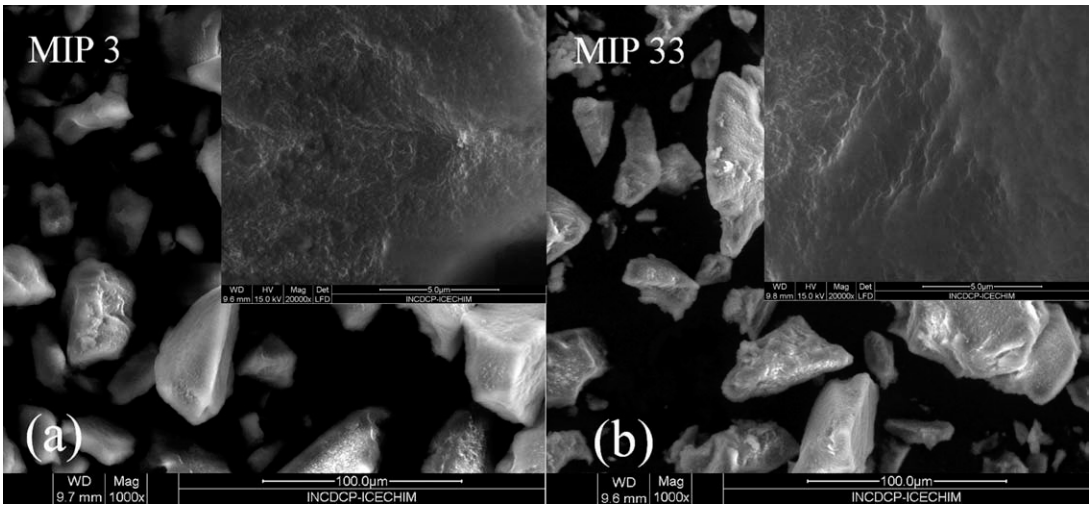

Figure 4. Surface morphology of HEMA-imprinted sorbent particles at 100 and 5 μm, in medallion, for MIP 3 (HEMA/EDMA-based polymer), (a) and MIP 33 (HEMA/BDMA-based polymer), (b).

morphology either. Therefore, monomer/crosslinker nature did not influence the porosity, in any of these cases, apparently.

Thermal Stability

Thermal analyses were carried out in nitrogen atmosphere at a 10°C/min heating rate. Some differences between decomposition features, owing to crosslinking degree and reactivity variations, were observed. The weight loss of all imprinted polymers was over 98% at 600°C.

EDMA has a higher reactivity compared with HEMA,[36] and tends to homopolymerize, leading to a nonhomogeneous copolymer. Therefore, a visible hump on the derivative weight curve of MIP 3 [Figure 5(a)] appeared. A maximum decomposition temperature was registered at 395.85°C. Decomposition curve of MIP 33 [Figure 5(b)] presented one important decomposition maximum as well, at 383.56°C, attributed to polymer degradation. Similar behaviors were observed for MIP 2, MIP 22 [Figure 6(b)] and MIP 1, MIP 11 [Figure 6(a)]. It can be noted that the heterogeneity of polymers can also be caused by the fact that no stirring was used along the polymerization process and the crosslinking points started and spread randomly. Although phenols are well known for their polymerization inhibiting effect, GA does not affect the stability of the sorbents as proven in the previous studies.[37]

Adsorption Capacity and Imprinting Factor

As described in **Tests Description and Calculation Method** section, the influence of monomer/crosslinking nature upon imprinted particles performance—adsorption capacity, imprinting factor, and selectivity—was studied. The adsorption capacities, Q, for both imprinted and nonimprinted polymers, at 85 : 15, 75 : 25, and 65 : 35 volumetric ratios, of the feed solution, are given together in Table II.

The systems with EDMA registered high values for GA uptake, at 75 : 25 ethanol/acetonitrile volumetric ratios, whereas the systems with BDMA presented adsorption maximums at various volumetric ratios. Comparing the systems from the point of view of the monomer, it can be noticed that MIP 2 and MIP

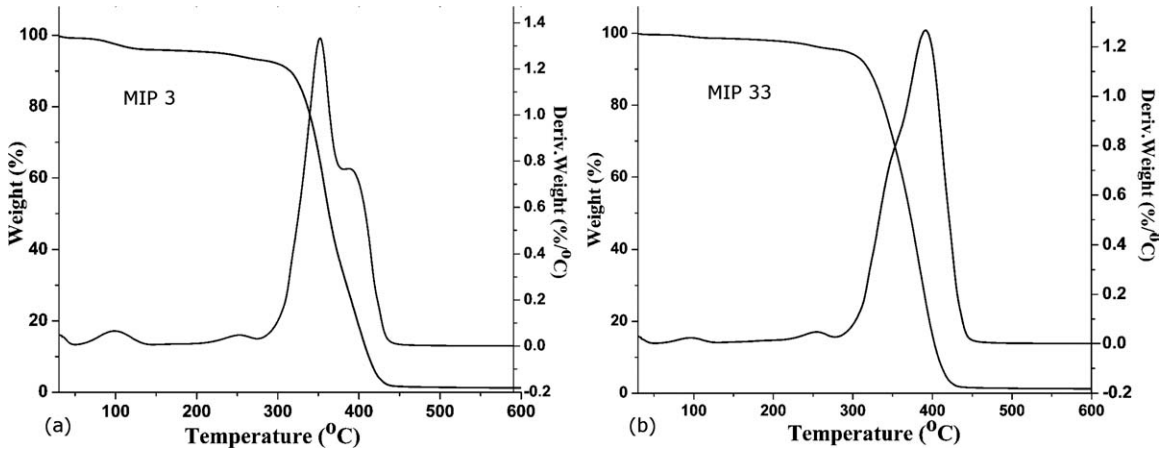

Figure 5. Thermal degradation of MIP 3 (HEMA/EDMA-imprinted polymer) (a) and MIP 33 (HEMA/BDMA-imprinted polymer) (b) after removal of GA.

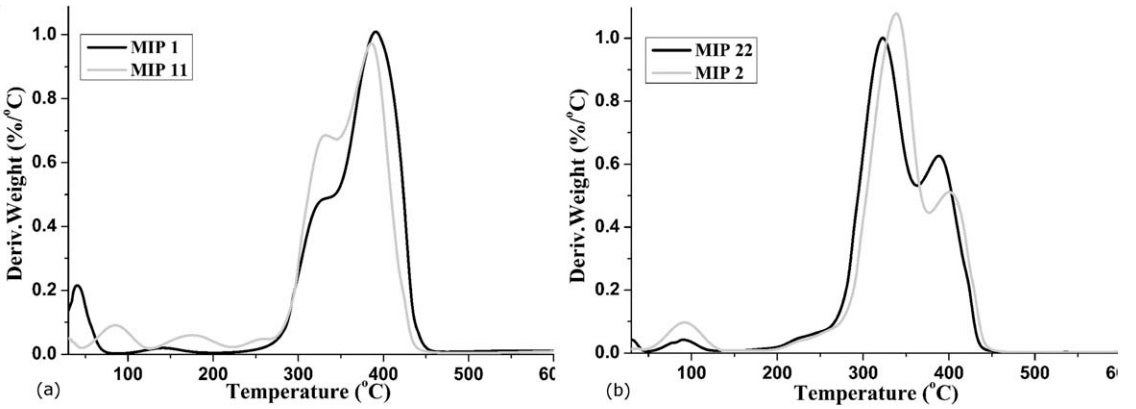

Figure 6. Derivative weight variation with temperature for MIP 1 and MIP 11 (AA/EDMA and AA/BDMA-imprinted polymers, respectively). (a) MIP 2 and MIP 22 (AN/EDMA and AN/BDMA-imprinted polymers, respectively). (b) After GA removal.

22, based on AN, registered the highest sorption capacities toward GA, at 75 : 25 and 65 : 35 volumetric ratios, respectively. Nonimprinted polymers NIP 2 and NIP 22, based on AN as well, registered higher uptake values compared with the other NIPs, at the same volumetric ratios mentioned for the imprinted ones.

Calculation of imprinting factor for all six polymers, using Eq. (4), led to important results that allowed optimization of the adsorption method. The highest imprinting factor, 3.58, was attributed to MIP 3 [Figure 7(a)]. At 85 : 15 volumetric ratio, the difference between MIP 3 imprinting factor and MIP 1 or MIP 2 (2.47 and 2.51, respectively) was significant. For MIP 11, MIP 22, and MIP 33 [Figure 7(b)], the variations are similar. A imprinting factor of 2.37 was obtained for MIP 33 at 85 : 15 volumetric ratio. This value was superior to all BDMA-based polymers.

By increasing the ethanol percent, the polymers gain specificity, but with a significant loss in uptake capacity. Although all polymers registered relative low adsorption capacity at 85 : 15 volumetric ratio, high imprinting factors were obtained.

The polarity of the feed solutions influenced differently the adsorption capacities and the imprinting factors for each polymer. The nonsolvent, acetonitrile, added in the feed solution should have increased the migration of GA molecules from the solution toward the polymer surface. Judging from the maximums registered for the uptake capacity, the adsorption was higher as the acetonitrile volume increased. However, acetonitrile's high polarity (acetonitrile > ethanol) weakens the bonding between the analyte and the substrate. Thus, a further increase of acetonitrile led to a decrease of imprinting factor as tests results showed.

The adsorption capacities of imprinted bulk polymers, attained in the present study, are similar to PVA-imprinted polymer membranes, prepared by a direct crosslinking of the PVA/GA solutions.[38] Adsorption capacities of imprinted membranes were nearly 65 mg/g of xerogel. However, comparing the value recorded for the nonimprinted polymers, that is 35 g/g xerogel, the imprinting factor did not even reach the value of 2. Imprinted polymer with GA, obtained by bulk polymerization of 4-vinylpyridine, was a first approach of ionic imprinted

Table II. Variation of Polymer Adsorption Capacities for GA with the Ethanol : Acetonitrile Volumetric Ratio

Ethanol : acetonitrile ratio[a] (vol/vol)	$Q_{MIP\ 1}$ (g GA/g MIP 1)[b]	$Q_{MIP\ 2}$ (g GA/g MIP 2)[b]	$Q_{MIP\ 3}$ (g GA/g MIP 3)[b]	$Q_{NIP\ 1}$ (g GA/g NIP 1)[b]	$Q_{NIP\ 2}$ (g GA/g NIP 2)[b]	$Q_{NIP\ 3}$ (g GA/g NIP 3)[b]
85/15	0.036	0.05	0.036	0.014	0.020	0.010
75/25	0.059	0.078	0.068	0.032	0.041	0.036
65/35	0.035	0.044	0.039	0.020	0.028	0.021

	$Q_{MIP\ 11}$ (g GA/g MIP 11)[b]	$Q_{MIP\ 22}$ (g GA/g MIP 22)[b]	$Q_{MIP\ 33}$ (g GA/g MIP 33)[b]	$Q_{NIP\ 11}$ (g GA/g NIP 11)[b]	$Q_{NIP\ 22}$ (g GA/g NIP 22)[b]	$Q_{NIP\ 33}$ (g GA/g NIP 33)[b]
85/15	0.043	0.045	0.026	0.021	0.022	0.011
75/25	0.052	0.057	0.055	0.036	0.039	0.034
65/35	0.052	0.061	0.048	0.036	0.044	0.033

[a]The volumetric ratio of the feed solvent mixture; the concentration of the feed solution was 7.73 g L^{-1} GA., [b]The subscript after *Q* designates the code of the polymer sorbent for which the values below are attributed.

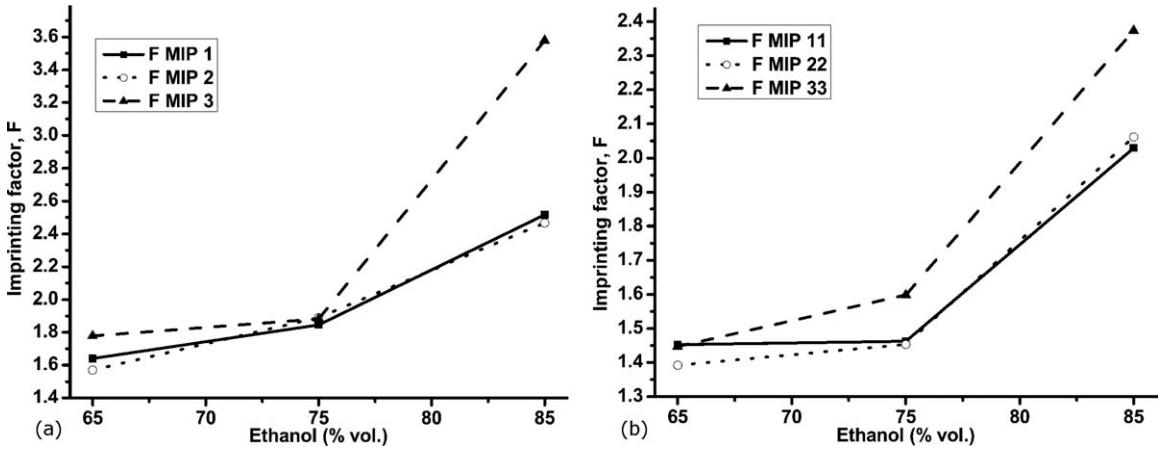

Figure 7. Variation of imprinting factors, F MIP, with the ethanol volumetric ratio, for EDMA systems, MIP 1, MIP 2, and MIP 3 (AA/EDMA, AN/EDMA, and HEMA/EDMA-imprinted polymers) (a) and BDMA systems, MIP 11, MIP 22, and MIP 33 (AA/BDMA, AN/BDMA, and HEMA/BDMA-imprinted polymers) (b).

polymer with GA.[39] According to this study, a 4 : 1 = 4VP : GA (molar ratio), led to a 2.19 imprinting factor and a 6 : 1 = 4VP : GA (molar ratio) to an uptake of 78 mg GA/g MIP. A higher adsorption capacity was obtained but the specificity of polymers was also low.

In both the approaches, a significant parameter was neglected—the polarity of the feed solvent. Aqueous solution and methanol/water solutions, respectively, used as feed solvents in this comparative research, are very polar (dielectric constants: 80.4 for water and 33.6 for methanol) relative to ethanol (dielectric constant, 25). As shown in this study, the polarity of the media has a great influence upon recognition and binding ability of MIPs. When enhancing the ratio of acetonitrile, (dielectric constant 37.5), higher uptake capacities and low imprinting factors were obtained; similar behavior to the one mentioned previously. This behavior takes into account that in polar solvent migration of ions is enhanced by interactions between surrounding polar species, leading to a high unspecific adsorption of all compatible species.

The selectivity tests on PVP-imprinted particles showed that the proportion between adsorbed GA and other related species was little (approx. 60 mg/g of MIP gallic and approx. 45 mg/g of MIP for 3,4-dihydroxybenzoic acid).

For HEMA–EDMA-based MIPs, lowering the polarity of the media led to stronger interactions between the analyte and the imprinted sites. Migration of analyte is slowed down by the absence of polar molecules and fewer molecules reach the surface of the polymer. Therefore, adsorption capacity was lower but specific.

Distribution and selectivity coefficients

The adsorption study also underlines that the most favorable volumetric ratio for achieving high selectivity, that is good imprinting factor was 85 : 15. Accordingly, the selectivity tests were performed at the optimum ethanol/acetonitrile volumetric ratio 85 : 15. The competitive uptake of GA and resorcinol, *R*, was quantified by calculating the distribution coefficients, K_d and selectivity coefficients, *k* (Table III).

Binding selectivity refers to the difference of affinity with which distinct ligands bind to a substrate, forming a complex. Distribution coefficients quantified the repartition of the two species between solid and liquid phase. The selectivity coefficient, *k* is a measure for the equilibrium displacement reaction of one ligand by another ligand in a complex with the polymer substrate. In this case, ligand 1 is represented by GA and ligand 2 by resorcinol. The greater the selectivity coefficient, *k*, the more GA will displace resorcinol from the complex formed with the substrate.

All polymers adsorbed very specific GA molecules compared with resorcinol. High specificity of MIP 3 was confirmed by the selectivity coefficient, *k*. The maximum indicated a 6.86 times higher affinity of MIP 3 for GA than for resorcinol. Polymer MIP 2 also showed a relatively high imprinting effect compared with NIP 2. However, this homologue, MIP 22, presented a close value for the selectivity coefficient with that of the

Table III. Distribution and Selectivity Coefficients, for Imprinted Polymers and Their Nonimprinted Pairs, Resulted from the Competitive Binding Data

Sorbent code	$K_{d,1}$[a] (mL/g)	$K_{d,2}$[a] (mL/g)	k[b]
MIP 1	4.194	3.431	1.22
MIP 2	5.068	2.747	1.84
MIP 3	5.026	0.732	6.86
NIP 1	1.799	2.383	0.754
NIP 2	2.390	2.004	1.19
NIP 3	1.133	0.362	3.13
MIP 11	2.914	1.509	1.93
MIP 22	3.439	1.230	2.80
MIP 33	3.684	1.369	2.70
NIP 11	1.30	0.770	1.70
NIP 22	1.791	0.600	2.99
NIP 33	1.979	1.029	1.92

[a]Distribution coefficients of GA and resorcinol, respectively., [b]Selectivity coefficient shows the affinity of the sorbent for GA relative to resorcinol.

nonimprinted polymer, NIP 22, indicating a small difference in affinity between GA and resorcinol. MIP 1 and MIP 11, as well as their nonimprinted pairs, NIP 1 and NIP 11, reveal similar variations for the two coefficients, as the HEMA-based polymers, but having significant lower values.

The more conformations monomer–template complex will adopt, the lower the selectivity will be. AN–GA or AA–GA complex will produce multiple imprinted cavities but there are not alike and the selectivity process is not controlled. This is the reason why the uptake on MIP 2, MIP 22, MIP 1, and MIP 11 sorbents was high but not very selective. In the case of HEMA–GA complex, the number of possible structures is limited by the low reactivity of the monomer which theoretically interacts only with the carboxylic group of GA. This explains the significant increase in selectivity of the imprinted cavities but also the low adsorption capacity of HEMA-based sorbents.

CONCLUSIONS

The 70-μm particle dimension allowed an efficient removal of the template from imprinted polymers by a simple and nonthermal method: extraction with ultrasonication. FTIR spectra of imprinted polymers (after extraction) and nonimprinted polymers showed that GA was removed quantitatively from the samples using one portion of ethanol. Noncovalent interaction between polar groups of GA and polar groups of functional monomer during the imprinting is presumed, because of the absence of other bands in the FTIR spectra of imprinted extracted polymers compared with the blank nonimprinted ones. The analyte recognition was achieved by a similar noncovalent mechanism.

The adsorption tests, at different ethanol : acetonitrile volumetric feed ratios, allowed optimization of the conditions for selective adsorption processes. According to the adsorption results, the uptake capacity and imprinting factors registered maximums at different ratios of the feed solution. However, the optimal volumetric ratio of ethanol : acetonitrile, chosen for future tests, was 85 : 15. The decrease in adsorption at the optimal ratio varied between 30 and 50% but the imprinting factors were the highest.

The imprinting factor of 3.53 and selectivity coefficient 6.86 were attributed to MIP 3 (HEMA/EDMA-imprinted polymer) which was considered as the most adequate system for molecularly imprinting with GA.

All investigated parameters—adsorption capacity, imprinting factor, distribution, and selectivity coefficient—led to global lower values for BDMA-based sorbents, indicating that a longer chain crosslinker was not able to maintain the shape of the cavities during manipulation or that the hydrophobic chain induced a decrease in polymer affinity for GA.

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