Journal of Hazardous Materials 170 (2009) 722–728

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Development of sulfamethoxazole-imprinted polymers for the selective extraction from waters

Martin Valtchev[a,b], Barbara S. Palm[a,*], Marion Schiller[a], Ute Steinfeld[a]

[a] Korea Institute of Science and Technology (KIST) Europe, Universität des Saarlandes, Campus E7 1, Stuhlsatzenhausweg 97, D-66123 Saarbrücken, Germany
[b] Technische Chemie, Fachrichtung 8.1, Naturwissenschaftlich-Technische Fakultät III, Universität des Saarlandes, Campus C4 2, Postfach 15 11 50, D-66041 Saarbrücken, Germany

ARTICLE INFO

Article history:
Received 22 October 2008
Received in revised form 29 March 2009
Accepted 6 May 2009
Available online 14 May 2009

Keywords:
Molecularly imprinted polymer (MIP)
Pollutant removal
Sulfamethoxazole
Solid phase extraction
Wastewater

ABSTRACT

Sulfamethoxazole (SMX) is an antibiotic of growing environmental concern. As specific filter material for the extraction of SMX from waters, a series of SMX-imprinted polymers have been synthesised varying their composition parameters, and their efficiency to selectively remove the contaminant SMX from complex polluted water was tested. Most of the developed materials exhibited an excellent uptake of the target pollutant SMX of more than 80% or even 90% and effective separation from selected easily degradable accompanying substances even in complex wastewater mixtures. All the results for SMX uptake and release were compared to the commonly used adsorbent activated carbon (AC).

1. Introduction

In recent years, there has been growing concern about the occurrence of pharmaceuticals in the aquatic system [1]. Antibiotics are of special relevancy by regarding the amounts that are used and their ecotoxicological effects by possible enhancement of resistance formation in bacteria [2–4]. Sulfamethoxazole (SMX) is a sulfonamide antibiotic which is largely applied in human and veterinary medicine. Traces of SMX and other hardly degradable antibiotics can be detected in sewage drainages and surface waters [5].

Actually, the activated carbon (AC) adsorption method is widely used for pollutant removal from municipal and other waste sources. These conventional adsorbents, however, suffer from insufficient regeneration and poor selectivity towards the target pollutant because they differentiate only by some generic property like hydrophobicity [6].

Polymers are actively used in wastewater treatment in the form of flocculants or resins [7,8]. In order to enhance selectivity, the use of molecularly imprinted polymers (MIPs) as selective sorbents is becoming increasingly popular [6–10].

Molecular imprinting technique as enzyme analogy was first described in 1973 by Wulff et al. [11]. Significant progress in the field of non-covalent imprinting could be achieved by Mosbach [12]. MIPs are highly cross-linked polymers which can be synthesised in the presence of target molecules named templates. A high level cross-link is necessary to obtain a stable three-dimensional frame, where specific binding sites and cavities complementary to the template are imprinted. MIPs are largely applied as selective adsorbents in solid phase extraction (SPE) [9,13–16] and as stationary phase in liquid chromatography [17–20], but also in catalysis. They are successfully used as selective membranes in sensor technology [21–24] as well as in membrane separation [25,26]. However, their applicability as selective polymeric filter material for water treatment has only been rarely examined.

In this study, polymers imprinted with SMX were developed and tested as specific adsorbent material for the removal of SMX from aqueous medium. Because multiple variables affect the characteristics of the produced MIPs [27], a series of different polymers were prepared using different kinds of functional monomers, cross-linkers and porogens.

2. Materials and methods

2.1. Materials

All fine chemicals were purchased from Aldrich, Merck or Fluka. The unsaturated compounds methacrylic acid (MAA), N-vinylpyrrolidone (NVP), ethylenglycoldimethacrylate (EGDMA) and divinylbenzene (DVB) were purified prior to use via standard procedures and distilled under reduced pressure in order to remove stabilizers.

* Corresponding author. Tel.: +49 681 9382 226; fax: +49 681 9382 249.
E-mail address: barbara.palm@kist-europe.de (B.S. Palm).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.05.007

2.2. General polymer synthesis

In a 50 mL Duran glass test tube, the template SMX was dissolved in the selected solvent (porogen) in an ice bath and mixed with the respective amount of functional monomers and cross-linkers for each polymer, summarized in Table 1. Synthesis of the associated non-imprinted control polymers (NIPs) took place analogously, omitting the template sulfamethoxazole. The mixture was put in a Vortex shaker and degassed with nitrogen for 5 min. After adding the starter azoisobutyronitrile (AIBN) it was put again in the shaker until the starter had completely dissolved and the solution was purged with nitrogen for another 5 min to remove traces of oxygen. The tube was immediately sealed with a silicon septum, immersed into an oil bath and heated in nitrogen for 24 h at 60 °C.

2.3. General cleaning step

After synthesis the tube was carefully shattered and the hard polymer was removed, ground and pulverized by a centrifugal mill. The powder was extracted with ethyl acetate for 24 h by using a Soxhlet system. The polymer was subsequently put into centrifuge vials and washed three times with 30 mL of the below-mentioned solution. It was centrifuged after each washing step and the supernatant was removed:

1. 0.01 M phosphoric acid (H_3PO_4) solution in acetone/water (1:1) at 50 °C;
2. deionised water at room temperature;
3. acetone at room temperature.

After the last cleaning the polymer was put for 12 h at 60 °C in the drying chamber and stored in a vacuum desiccator.

2.4. Sample preparation

Stock solutions were prepared by dissolving the pharmaceuticals in bidistilled water. The stock solutions were stored in a refrigerator. The concentrations of SMX were in the range of 0.1–10,000 μM; the concentrations of caffeine and salicylic acid 100 μM each.

Standardized synthetic wastewater[1] was prepared dissolving 16 g peptone, 11 g meat extract, 0.7 g sodium chloride, 0.4 g calcium chloride, 0.2 g magnesium sulfate and 2.8 g potassium hydrogen phosphate in 1 L bidistilled water, the pH was adjusted to 7.0 ± 0.1.

Pre-experiments showed no adsorption of the monitored organic species onto flasks or HPLC-vials.

2.5. Selective binding experiments

2.5.1. Effect of time

The rate of SMX adsorption by the polymer sorbents was studied (10 mL, 10 μM) with 100 mg of the sorbent over a series of varying contact time (5–240 min). The percentage extraction of SMX was already constant after 5–10 min, but 15 min was used in all subsequent experiments to ensure setting of equilibrium and to limit the screening time.

2.5.2. Binding experiments

In the following, the sorption, washing and desorption step was performed in the same way. To 100 mg of polymer in a 50 mL centrifuge vial, 10 mL of the respective solution (aqueous solution of the target compounds for uptake experiment or deionised water for the washing step or desorption solution) was pipetted. Desorption with a 0.01 M H_3PO_4 solution in acetone/water (1:1) was performed at 50 °C. The suspension was shaken for 15 min and subsequently centrifuged for 10 min at 4000 rpm. A sample was pipetted from the supernatant and centrifuged for another 10 min at 16,000 rpm in a micro-centrifuge. A final sample was taken from the supernatant to determine concentration of remaining compounds in solution by HPLC. Concentrations after sorption and washing were determined with the second HPLC method and with the first HPLC method after desorption. Solutions of SMX at 50 μM, 1 μM, 0.1 μM were used. The difference of concentration before ($c(\mathrm{SMX})_{init}$) and after sorption ($c(\mathrm{SMX})_{eq}$) is used to calculate the adsorbed amount of SMX ($n(\mathrm{SMX})_{sorb}$) or sorption in percent (Eqs. (1) and (2)):

$$\text{sorption}\,(\%) = n(\mathrm{SMX})_{sorb}/n(\mathrm{SMX})_{total} \times 100 \quad (1)$$

$$\text{sorption}\,(\%) = (c(\mathrm{SMX})_{init} - c(\mathrm{SMX})_{eq})/c(SMX)_{init} \times 100 \quad (2)$$

The sorption or uptake of caffeine (CAF) and salicylic acid (SAL) was determined analogously. All values were measured in triplicate. Unless otherwise noted, the error in sorption (%) was ±4%.

To examine the effect of solution pH value on sorption, 100 mg of the sorbent was equilibrated with SMX solutions (10 mL, 10 μM) with various pH 1–9 for 15 min. SMX concentration in the supernatant was determined by HPLC. To investigate the influence of ionic strength, the experiments were performed analogously with added I = 0–0.5 M which was adjusted by using NaCl.

2.6. Sorption isotherm study

100 mg of the respective polymer was mixed with 10 mL SMX solution with various concentrations of SMX (10–10,000 μM) and equilibrated for 15 min at room temperature. 1 mL of the sample was taken and centrifuged, the SMX concentration in supernatant was analyzed using HPLC. The sorption capacity (a_{eq}, mol g^{-1}) was calculated as

$$a_{eq} = (c_{init} - c_{eq})V\ \mathrm{m}^{-1} \quad (3)$$

where c_{init} and c_{eq} are the initial and equilibrium concentrations (mol/l) of SMX in the solution, respectively, m is the weight of the sorbent in g and V is the volume of the aqueous solution in L.

2.7. Column experiments

The syringe column (55.0 mm × 6.0 mm) was packed with ca. 300 mg of the respective polymer. A solution containing SMX (10 μM) and CAF and SAL (100 μM each) was continuously passed through the column at a flow rate of 1–2 mL min^{-1} at room temperature by means of a vacuum pump. Fractions of 10–50 mL were taken and the concentrations of the compounds determined by HPLC. The breakthrough volumes were determined at an effluent concentration of 1% of the influent concentration of the respective substance.

2.8. HPLC analysis

The concentrations were determined using the Agilent 1100 HPLC system and the HPLC column Reprosil Pur C18-AQ-3 μm with a flow rate of 0.2 mL min^{-1} and temperature at 25 °C. SMX was detected at 265 nm, CAF at 275 nm and SAL at 242 nm.

Eluent A: methanol and
Eluent B: water/acetic acid (80:1).

Two HPLC methods (gradient elution) were used. Method 1 (injection volume 10 μL) started with 10% A which increased to 70% A within 25 min, remained 70% A for 10 min and returned to

[1] According to: RL67/548/EWG, appendix V: C.11.1.6.1.3.

Table 1
Ratios of template to monomer to cross-linker (T:M:C), porogen type and volume and amount of initiator used in the synthesis of the imprinted polymers.

MIP	Template	Monomers			Cross-linkers		Porogen		Initiator
	SMO	MAA	ITA	NVP	EGDMA	DVB	*V*	Type	AIBN
	(mmol)	(mmol)			(mmol)		(mL)		(mg)
P1	1		2		10		12	DMF	50
P2	1		3		10		12	DMF	50
P3	1		4		10		12	DMF	50
P4	1		4		20		12	DMF	50
P5	1		2		10		16	Ethanol/H_2O (5:3)	50
P6	1		2		10		16	Acetone/H_2O (5:3)	50
P7	1		2		10		12	Dioxan	50
P8	1		4			20	12	DMF	50
P9	1	2	1		20	20	12	DMF	50
P10	10	2	1		20	20	12	DMF	200
P11	1		2	2	20	20	5	DMF	200
P12	1	4		2	20	20	5	DMF	200
P13	1	2		2	20	20	5	DMF	200
P14	1	2		2	40		5	DMF	200
P15	1		2	2	40		5	DMF	200

10% A within 5 min Method 2 (injection volume 500 μL) started with 20% A, which increased to 70% A within 17 min, remained 70% A for 8 min, and returned to 20% A within 5 min. The first method was used for relatively concentrated solutions (about 100–1 μM) and the second for diluted solutions (about 1–0.1 μM).

3. Results and discussion

3.1. Extraction experiments: binding experiments (aqueous SMX solutions)

MIPs as HPLC stationary phases to detect SMX have been reported previously [28–32], using the functional monomers methacrylic acid (MAA) and 4-vinylpyridine or a mixture of them. In order to optimise the MIP fabrication procedure to achieve optimum selectivity and affinity for extraction purposes, MAA was completely or partly replaced by itaconic acid (ITA), a dicarboxylic acid, and N-vinylpyrrolidone (NVP) (Table 1), both able to form hydrogen bonds. Moreover, the ratio of template to monomer to cross-linker (T:M:C) was varied systematically and four different porogens were used.

In order to study the template recognition of the polymers, binding experiments with SMX solutions were carried out for screening. In the polymer series P1, P2, P3 and P4, with ITA as sole functional monomer, the overall high sorption values for the target pollutant SMX from water were hardly affected with variation of the (T:M:C)-ratio (Table 2), pointing at four carboxylic acid functions per template (P1) being sufficient for excellent uptake. The increase of ITA content in the series P1, P2 and P3 led to smoother polymers which highly expanded their volume in water and other polar solvents (solvatation of carboxylic acids).

Table 2
Extraction of SMO with polymers P1–P7[a].

MIP	% adsorbed SMO[b]	
	Sorption step (S)	Desorption step (D)
P1	97	23
P2	95	20
P3	96	23
P4	94	14
P5	39	5
P6	69	23
P7	92	2

[a] c_0(SMO) = 50 μM; *m*(polymer) = 100 mg.
[b] Error in %sorption: for values >80: ±7; for values 80 ≥ *x* ≥ 20: ±6; for values <20: ±4.

Polymers P1, P5, P6 and P7 were prepared at a constant (T:M:C)-ratio of 1:2:10 (Table 1). They differed in the solvents used for their preparation to evaluate the influence of these porogens on the accessibility of the polymer binding sites [27] and the binding strength. The choice of porogen is however limited to the solubility of all compounds (template, functional monomer and cross-linker). In order to dissolve the template SMX and the functional monomer ITA which was used throughout this study, a polar solvent was necessary (alcohols, acetone, dimethyl form amide (DMF), dioxane).

MIPs P5 and P6 were synthesised in ethanol/water or acetone/water. They showed low affinity towards the target molecule SMX compared to their respective analogues P1 and P7, which were synthesised in DMF or dioxane (Table 2). The reason for that are the water molecules acting as competing ligands for the hydrogen bonding sites, resulting in a destabilisation of the interactions between the functional groups of the monomer and the template molecule in the pre-polymerisation complex [32].

With polymer P7, template bleeding (continuous loss of template not completely removed during work-up) could be observed which has been discussed in several references [33,34] and can be attributed to unfavourable polymer morphology and porosity created by dioxane as porogen. Within this series of SMX-imprinted polymers, DMF was found to be the best porogen.

Within the series of the polymers P8–P15, the cross-linker ethylene glycol dimethacrylate (EGDMA) was partly or completely substituted by divinylbenzene (DVB) (Table 1) to benefit from additional hydrophobic interactions and aromatic stacking of the latter [35]. Furthermore, combinations of two different functional monomers were checked for possible cooperative effects on SMX binding and the amount of cross-linker was doubled from P9 onwards to obtain more rigid polymer particles.

Because the first polymer series P1–P4 showed very high SMX uptake at 50 μM, the initial SMX concentration for the testing of P8–P15 was lowered to 1 μM and finally to 0.1 μM. Even at this low concentration range, MIPs P8, P9 and P10 provided the best sorption results (Figs. 1 and 2). Mixtures of EGDMA, DVB, MAA and ITA produced superb sorbents with sorption being well above 90%. The introduction of NVP to MIPs P11–P15 also led to excellent sorbents, apparently not affected by the decrease in pore volume due to the decrease in porogen volume from 12 mL to 5 mL (Figs. 1 and 2). Only P14 and P15 with EGDMA as the sole cross-linker showed slightly decreased SMX uptake pointing at only a small additional contribution of the hydrophobic and stacking interactions of DVB in P8–P13 (Fig. 1).

P10 was produced with a 10 times higher amount of template, however, no significant improvements in the extraction

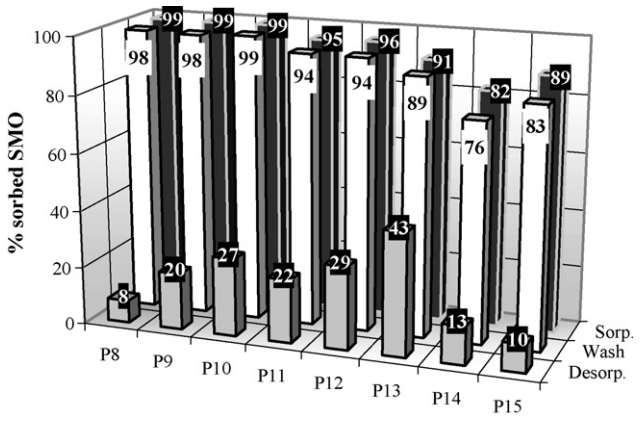

Fig. 1. Extraction of SMX from a 1 μM solution with the polymers P8–P15.

of SMX compared to its analogue P9 (Figs. 1 and 2) could be achieved.

For all polymers P8–P15, a washing step with water did not affect the adsorbed pollutant significantly. This step could be applied in uptake processes from real wastewater, in order to separate the target biorefractory compound from other biodegradable accompanying substances which could subsequently be treated by conventional biological methods.

Concentration decrease in sorption solution to 0.1 μM allowed differentiation between MIP P1 and MIP P7 (Fig. 2), which showed similar sorption in higher concentrations (Table 2). MIP P7, prepared in dioxane, showed a much lower affinity to SMX as MIP P1 (prepared in DMF) and compared to all other measured MIPs (Fig. 2).

In order to release the bound molecules and to regenerate the polymeric sorbents for further reuse, the experimental conditions for effective desorption were developed. Mixtures of methanol and acetic acid reported by several authors [28–32] for on-line elution were not successful under equilibrium conditions, nor were pure organic solvents like methanol or ethanol, ethyl acetate and acetone. To increase effectiveness, the strength of the acidic component was increased by choosing phosphoric acid which was, at the other hand, not too strong to hydrolyse, e.g. the ester bonds of EGDMA within the polymer. An acetone/water mixture (1:1), for good solubility, with a low concentration of phosphoric acid of $c(H_3PO_4) = 0.01$ M seems suitable to elute at least two-third of the adsorbed target molecule SMX in almost all cases (Fig. 1 and Table 2).

In order to examine the effect of solution pH value and the ionic strength on sorption, binding experiments were carried out within the range of pH 1–9 and $I = 0$–0.5 M.

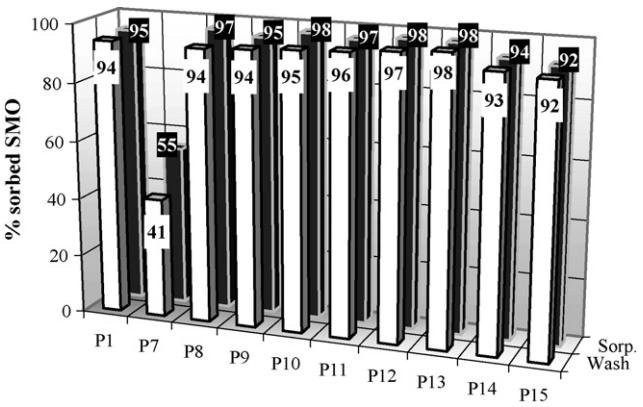

Fig. 2. Extraction of SMX from a 0.1 μM solution with the polymers P1 and P7–P15.

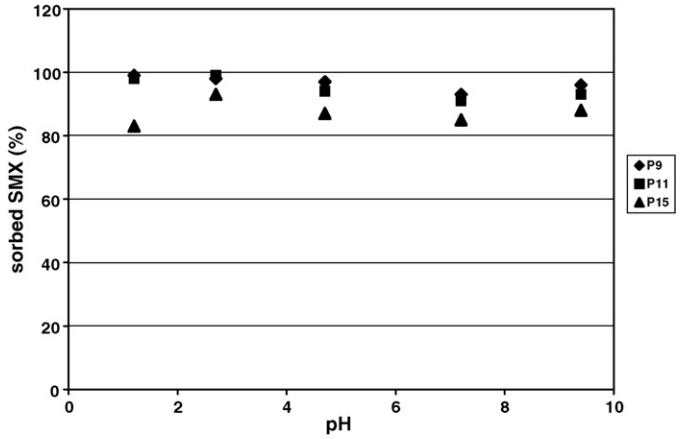

Fig. 3. Influence of solution pH on SMX uptake by polymers P9, P11 and P15 (experimental conditions: 10 mL of 10 μM SMX, 100 mg sorbent, 15 min).

The surface charge of the synthesised polymers is changed by deprotonation and protonation reactions of their functional groups like the carboxyl moieties. Under acidic condition (pH < 2–3), they are supposed to be protonated and neutral, whereas at pH > 7–8, surface charge becomes more negative because of deprotonation, which provides more adsorption sites for ionic interactions. The charge of SMX is also affected by solution pH due to the ability of the sulfonamide group to be deprotonated ($pK_a = 5.6$ [36]).

Surprisingly, there is only a negligible effect of pH on the high SMX sorption of three selected representative polymers in the range of pH 1–9 (Fig. 3). It seems as if the protonation status and the charge of the sorbents or the target compound SMX play almost no role for their interaction with each other, an indication of the predominantly hydrophobic nature of the binding of SMX to the polymers. This can be confirmed by the lack of influence of increasing ionic strength ($I = 0$–0.5 M) on the sorption behaviour of the three polymers (Fig. 4), a fact that points to a rather small contribution of ionic interactions to the binding.

3.2. Sorption isotherm study

To evaluate the adsorption capacity of the polymers for SMX and the equilibrium constants and to understand the characteristics of the adsorption, it was important to study the equilibrium adsorption isotherms. The Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of homogeneous

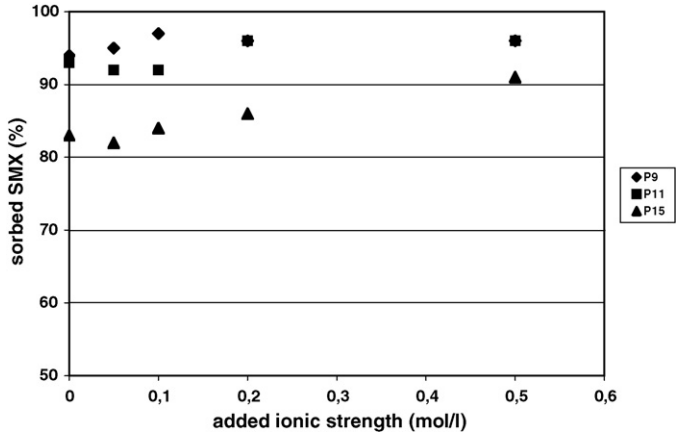

Fig. 4. Influence of ionic strength on SMX uptake by polymers P9, P11 and P15 (experimental conditions: 10 mL of 10 μM SMX, 100 mg sorbent, 15 min; NaCl was used to adjust ionic strength).

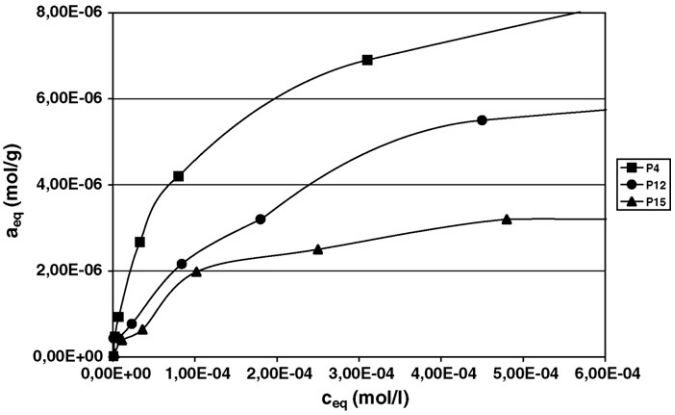

Fig. 5. Adsorption isotherm of SMX from aqueous solution on P4, P12 and P15 (experimental conditions: 10 mL solution, 100 mg sorbent, 15 min).

sites [37]. The Langmuir isotherm is represented by the equation:

$$a_{eq} = \frac{A_{max} K_a c_{eq}}{1 + K_a c_{eq}} \quad (4)$$

a_{eq} (mol g^{-1}) is the adsorbed amount of SMX per gram of polymer sorbent, A_{max} is the maximum SMX sorption capacity, K_a is the Langmuir isotherm constant, and c_{eq} is the equilibrium concentration.

The adsorption isotherms of some of the examined MIP are shown in Fig. 5. The plots of $1/a_{eq}$ versus $1/c_{eq}$ gave straight lines according to the linear form of the Langmuir isotherm equation:

$$\frac{1}{a_{eq}} = \frac{1}{A_{max}} + \frac{1}{A_{max} K_a c_{eq}} \quad (5)$$

The maximum sorption capacities (A_{max}) and binding constants (K_a) were calculated from the intercept ($1/A_{max}$) and slope ($1/A_{max}K_a$) and are given in Table 3.

The binding constants K_a of the five examined polymers appear in the same order of magnitude (about $1–3 \times 10^{-4}$ M), with a slightly smaller constant for P12. However, a weaker affinity of P12 to the target compound cannot be suggested, because for certain values in the plots of $1/a_{eq}$ versus $1/c_{eq}$, small changes in the adsorbed amount of compound which are within the error range might result in large changes in intercept and slope of the plot and thus in the Langmuir parameters. Nevertheless, the binding constants K_a and the comparable maximum sorption capacities A_{max} point to similar sorption behaviour of the five examined polymers, only P15 reaches saturation already at about 2×10^{-5} mol g^{-1}.

3.3. Extraction experiments: competitive binding experiments (wastewater)

To evaluate the influence of the polymer composition on SMX sorption and selectivity in real samples and to simultaneously maintain the reproducible conditions for the polymer screening, extraction experiments were conducted in standardized wastewater spiked with the biodegradable substances caffeine (CAF), an often accompanying product in pharmaceuticals, and salicylic acid (SAL), a hydrolysis product of the widely used analgetic acetyl salicylic acid. In this complex mixture of organic matter and salts, the complementary interactions between the target compound and the polymer binding sites are expected to decrease compared to pure water due to the competitive polymer binding of the wastewater ingredients and their tendency to interact with each other and the target compound.

Table 3
Langmuir isotherm parameters and regression coefficients for adsorption of SMX on selected polymers[a].

MIP	Maximum sorption capacity	Binding constant	Regression coefficient
	A_{max} (mol g^{-1})	K_a (M^{-1})	R^2
P4	6.4×10^{-5}	30,100	0.99
P9	6.5×10^{-5}	18,700	0.96
P11	5.3×10^{-5}	26,000	0.95
P12	6.5×10^{-5}	5,800	0.98
P15	2.3×10^{-5}	20,400	0.99

[a] c_0(SMX) = 10 μM; m(polymer) = 100 mg.

Table 4
Extraction of SMO, CAF and SAL from standardized wastewater with the polymers P4, P8, P11, P12, P15 (MIP) and their corresponding non-imprinted polymers (NIP)[a].

MIP		% adsorbed substance[b]			NIP		% adsorbed substance[b]		
		SMO	CAF	SAL			SMO	CAF	SAL
P4	S[c]	86	19	5	N4	S	88	29	4
	D[c]	27	5	5		D	20	18	5
P8	S	93	51	3	N8	S	87	55	6
	D	42	39	3		D	39	43	8
P11	S	85	45	12	N11	S	87	39	13
	D	28	34	10		D	30	28	11
P12	S	76	37	9	N12	S	87	42	16
	D	23	23	3		D	40	28	17
P15	S	85	38	16	N15	S	88	30	11
	D	29	17	6		D	29	22	6

[a] c_0(SMO; CAF; SAL) = 10 μM each; m(polymer) = 100 mg.
[b] Error in %sorption: for values >80: ±7; for values 80 ≥ x ≥ 20: ±6; for values <20: ±4.
[c] S: sorption step, D: desorption step.

Nevertheless, almost all of the selected polymers showed an uptake of the target substance SMX of more than 80%, with slightly enhanced values for P8 and P9 and a slightly lowered one for P12 (Table 4). Rather independently from their composition, they exhibit a pronounced selectivity towards SAL which is only absorbed by less than 20% of its initial concentration as well as towards CAF whose uptake is only less than half of that of SMX. Thus, effective SMX absorption and separation from the chosen easily degradable accompanying substances are provided even in complex mixtures.

For a following advanced effluent treatment, the target substance should be able to be released from the polymer sorbent. The selected polymers were subjected to one desorption step which resulted in the removal of at least two-third of the adsorbed SMX from almost all the MIPs (Table 4). Thus, only 2–3 desorption steps or continuous elution will be necessary to recover the whole amount of adsorbed SMX.

However, no substantial difference in uptake of the target compound and separation from the accompanying substances could be observed under the present experimental conditions between MIPs and their analogous non-imprinted references NIP (Table 4).

This could be due to the fact that both types of polymers exhibit a large amount of sites for predominant unspecific binding, maybe caused by possible destruction of specific binding sites during polymer grinding at work-up, by a template-monomer prepolymerisation complex which is too dynamic and flexible [38] at the required polymerisation temperature (60 °C) to create cavities of specific SMX shape, or by a pronounced influence of unspecific interactions on binding.

Another possible reason could be that both imprinted and non-imprinted polymers exhibit such large binding constants that, although actually differing in their binding affinities, a comparable extraction behaviour for both polymers even in complex wastewater mixtures can be observed, under the given experimental concentrations for screening and the presumption that the

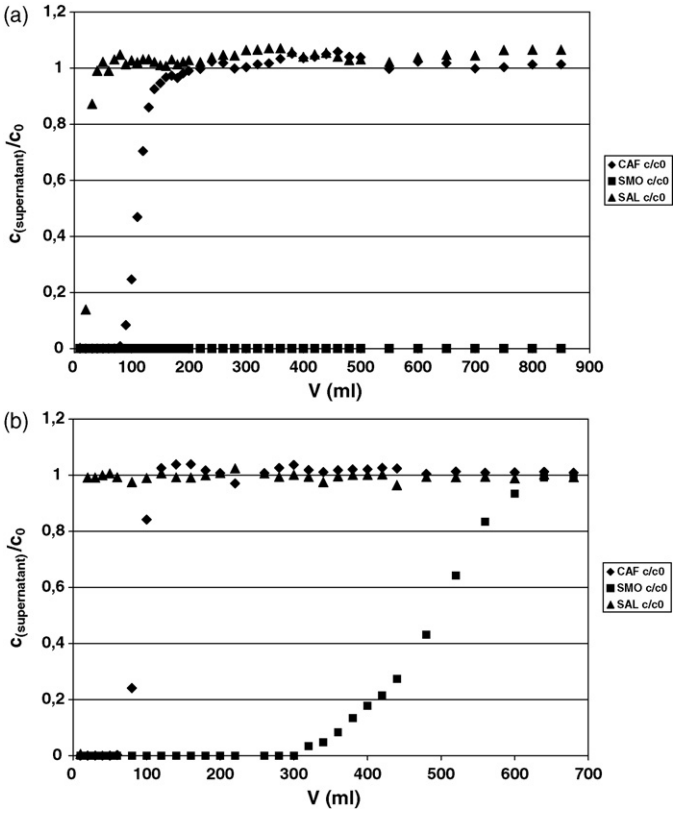

Fig. 6. (a) Column experimental result of SMX, CAF and SAL sorption by polymer P9 (experimental conditions: solution of 10 μM SMX, 100 μM CAF and 100 μM SAL at different volumes, 300 mg polymer sorbent; flow rate of 1–2 mL min^{-1}). (b) Column experimental result of SMX, CAF and SAL sorption by polymer N9 (experimental conditions: solution of 10 μM SMX, 100 μM CAF and 100 μM SAL at different volumes, 300 mg polymer sorbent; flow rate of 1–2 mL min^{-1}).

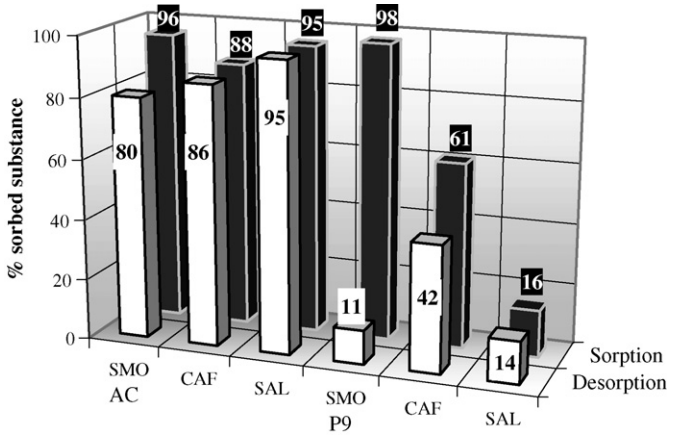

Fig. 7. Extraction of SMX, CAF and SAL from a 10 μM solution with P9 and activated carbon.

amount of the available adsorption sites in the polymers is larger compared to the provided amount of the sorbat. Thus, remarkable differences might only be observed in more diluted conditions for batch experiments.

In other conditions than those in the screening experiments, an indication of a difference between MIP and NIP can indeed be observed. Next step after the screening procedure is the application of the most promising candidates in filtration columns. Fig. 6 shows the adsorption of the three compounds onto P9 respectively N9 in a column. Maximum sample volume up to which quantitative sorption occurred was determined by passing the influent continuously through the column. In the case of both polymers (Fig. 6(a) and (b)), effluent concentration of SAL reached the influent concentration immediately, because of poor adsorption of SAL by the polymers in general. Breakthrough of CAF occurred at about 60 mL for the NIP and 80 mL for the MIP. However, almost 100% removal of SMX from the influent until more than 850 mL was obtained for the imprinted P9, while the breakthrough for SMX concentration of 0.1 μM in the effluent occurred at about 320 mL with the respective non-imprinted polymer, pointing to a stronger interaction of the target compound with the imprinted polymer in the column experiments.

Compared to the widely spread adsorbent activated carbon (AC), the developed imprinted polymers indeed show a different adsorption and desorption behaviour, as seen in Fig. 7 with MIP P9 as example. Although both materials equally extract the target substance SMX almost completely, AC also absorbs the easily degradable CAF and SAL in high yields which might lead, together with the apparent poor regeneration ability, to a rapid saturation of the filter. On contrary, the MIP shows a selective separation from the accompanying compounds which could be treated by conventional biological methods as well, and a more effective recovery of the adsorbed substances for an intended subsequent reuse of the filter material.

The direct comparison, however, of the polymers in this study and their extraction experiment results for recognition and separation with the previously synthesised SMX-MIPs for HPLC stationary phases [28–32] is only little significant, because the experimental setup (batch experiments and chromatography) and the equilibrium conditions were different in each case, resulting in different obtained values for the different purposes.

4. Conclusions

The goal of this study was to develop and optimise SMX-specific polymer material for the selective extraction of SMX from complex aqueous medium. For this screening purpose, a series of SMX-imprinted polymers was synthesised, varying systematically the nature and ratio of functional monomers and cross-linkers, and the nature of porogens. DMF was found to be the best porogen, resulting in very stable polymers with overall high recognition abilities for the target pollutant SMX.

MIPs made from ITA (P1–P4 and P8) or from mixtures of MAA, ITA and NVP as functional monomers and EGDMA and DVB as cross-linkers (P9–P15) produced excellent sorbents with an uptake of SMX well above 90% even at low concentrations <1 μM.

Even in complex aqueous mixtures as standards for real wastewater, most of the examined polymers showed an effective absorption of the target substance SMX of more than 80% and pronounced selectivity in relation to the two chosen biodegradable substances CAF and SAL which were only absorbed by less than 50% respectively 20% of their initial concentration, in contrast to the widely used unselective adsorbent AC.

In a sole desorption step for recovery and further treatment of SMX, slightly acidic mild conditions were sufficient to effectively release the bulk of the adsorbed target molecule from all polymers, which might be completed by repetition of the desorption step or continuous elution in principle. Thus, reusability of the filter material is feasible, but still has to be tested in several repeating uptake-release-cycles. Further experiments have to be done in order to optimise and reduce the elution volume to achieve effective enrichment for subsequent treatment.

Also, further optimization of synthesis conditions like, e.g. polymerisation at low temperature or suspension/emulsion poly-

merisation might lead to smaller polymer particles and to an improvement of selectivity.

Acknowledgement

The authors thank the Water Environment and Remediation Center (Korea Institute of Science and Technology (KIST) Seoul, Korea) for financial support.

References

[1] K. Kümmerer, Pharmaceuticals in the Environment. Sources, Fate, Effects and Risks, Springer-Verlag, Berlin, Heidelberg/New York, 2001.
[2] R. Hirsch, T. Ternes, K. Haberer, K.-L. Kratz, Occurrence of antibiotics in the aquatic environment, Sci. Total Environ. 225 (1999) 109–118.
[3] K. Kümmerer, A. Henninger, Promoting resistance by the emission of antibiotics from hospitals and households into effluents, Clin. Microbiol. Infect. 9 (2003) 1203–1214.
[4] A.K. Sarmah, M.T. Meyer, A.B.A. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere 65 (2006) 725–759.
[5] B. Halling-Sørensen, S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lützhøft, S.E. Jorgensen, Occurrence, fate and effects of pharmaceutical substances in the environment—a review, Chemosphere 36 (1998) 357–393.
[6] A. Bereczki, A. Tolokan, G. Horvai, V. Horvath, F. Lanza, A.J. Hall, B. Sellergren, Determination of phenytoin in plasma by molecularly imprinted solid-phase extraction, J. Chromatogr. A 930 (2001) 31–38.
[7] M.C. Annesini, F. Gironi, B. Monticelli, Removal of oxygenated pollutants from wastewater by polymeric resins: data on adsorption equilibrium and kinetics in fixed beds, Water Res. 34 (2000) 2989–2996.
[8] Y. Liu, S. Wang, J.J. Hua, Synthesis of complex polymeric flocculant and its application in purifying water, Appl. Polym. Sci. 76 (2000) 2093–2097.
[9] B. Sellergren, Direct drug determination by selective sample enrichment on an imprinted polymer, Anal. Chem. 66 (1994) 1578–1582.
[10] G. Wulff, Enzyme-like catalysis by molecularly imprinted polymers, Chem. Rev. 102 (2002) 1–28.
[11] G. Wulff, A. Sarhan, K. Zabrocki, Enzyme-analogue built polymers and their use for the resolution of racemates, Tetrahedron Lett. 14 (1973) 4329–4332.
[12] K. Mosbach, Molecular imprinting, Trends Biochem. Sci. 19 (1994) 9–14.
[13] N. Masqué, R.M. Marcé, F. Borrull, New polymeric and other types of sorbents for solid-phase extraction of polar organic micropollutants from environmental water, Trends Anal. Chem. 17 (1998) 384–394.
[14] D. Stevenson, Molecular imprinted polymers for solid-phase extraction, Trends Anal. Chem. 18 (1999) 154–158.
[15] N. Masqué, R.M. Marcé, F. Borrull, Molecularly imprinted polymers: new tailor-made materials for selective solid-phase extraction, Trends Anal. Chem. 20 (2001) 477–486.
[16] C. Poole, New trends in solid-phase extraction, Trends Anal. Chem. 22 (2003) 362–373.
[17] A.G. Mayes, K. Mosbach, Molecularly imprinted polymers: useful materials for analytical chemistry? Trends Anal. Chem. 16 (1997) 321–332.
[18] P. Sajonz, M. Kele, G. Zhong, B. Sellergren, G. Guiochon, Study of the thermodynamics and mass transfer kinetics of two enantiomers on a polymeric imprinted stationary phase, J. Chromatogr. A 810 (1998) 1–17.
[19] M.-C. Hennion, Solid-phase extraction: method development, sorbents, and coupling with liquid chromatography, J. Chromatogr. A 856 (1999) 3–54.
[20] L.I. Andersson, Molecular imprinting: developments and applications in the analytical chemistry field, J. Chromatogr. B 745 (2000) 3–13.
[21] B. Sellergren, Noncovalent molecular imprinting: antibody-like molecular recognition in polymeric network materials, Trends Anal. Chem. 16 (1997) 310–320.
[22] K. Yano, I. Karube, Molecularly imprinted polymers for biosensor applications, Trends Anal. Chem. 18 (1999) 199–204.
[23] P. Metilda, K. Prasad, R. Kala, J.M. Gladis, T. Prasada Rao, G.R.K. Naidu, Ion imprinted polymer based sensor for monitoring toxic uranium in environmental samples, Anal. Chim. Acta 582 (2007) 147–153.
[24] V. Vishnuvardhan, K.P. Prathish, G.R.K. Naidu, T. Prasada Rao, Fabrication and topographical analysis of non-covalently imprinted polymer inclusion membranes for the selective sensing of pinacolyl methylphosphonate—a simulant of Soman, Electrochim. Acta 52 (2007) 6922–6928.
[25] M. Yoshikawa, T. Fujisawa, J. Izumi, T. Kitao, S. Sakamoto, Molecularly imprinted polymeric membranes involving tetrapeptide EQKL derivatives as chiral-recognition sites toward amino acids, Anal. Chim. Acta 365 (1998) 59–67.
[26] C.D. Lang, H. Peng, X.Y. Bao, L.H. Nie, S.Z. Yao, Study of a molecular imprinting polymer coated BAW bio-mimic sensor and its application to the determination of caffeine in human serum and urine, Analyst 124 (1999) 1781–1785.
[27] D. Batra, K.J. Shea, Combinatorial methods in molecular imprinting, Curr. Opin. Chem. Biol. 7 (2003) 434–442.
[28] N. Zheng, Q. Fu, Y. Li, W. Chang, Z. Wang, T. Li, Chromatographic characterization of sulphonamide imprinted polymers, Microchem. J. 69 (2001) 55–60.
[29] N. Zheng, Y. Li, W. Chang, Z. Wang, T. Li, Sulfonamide imprinted polymers using co-functional monomers, Anal. Chim. Acta 452 (2002) 277–283.
[30] M. Davies, V. De Biasi, D. Perrett, Approaches to the rational design of molecularly imprinted polymers, Anal. Chim. Acta 504 (2004) 7–14.
[31] N. Zheng, Y.-Z. Li, M.-J. Wen, Sulfamethoxazole-imprinted polymer for selective determination of sulfamethoxazole in tablets, J. Chromatogr. A 1033 (2004) 179–182.
[32] X. Liu, C. Ouyang, R. Zhao, D. Shangguan, Y. Chen, G. Liu, Monolithic molecularly imprinted polymer for sulfamethoxazole and molecular recognition properties in aqueous mobile phase, Anal. Chim. Acta 571 (2006) 235–241.
[33] C. Baggiani, L. Anfossi, C. Giovannoli, Solid phase extraction of food contaminants using molecular imprinted polymers, Anal. Chim. Acta 591 (2007) 29–39.
[34] P. Dzygiel, E. O'Donnell, D. Fraier, C. Chassaing, P.A.G. Cormack, Evaluation of water-compatible molecularly imprinted polymers as solid-phase extraction sorbents for the selective extraction of sildenafil and its desmethyl metabolite from plasma samples, J. Chromatogr. B 853 (2007) 346–353.
[35] P. Villar, M.J. Whitcombe, E.N. Vulfson, Matrix effects on the selectivity of a cholesterol-imprinted polymer, Polymer 48 (2007) 1483–1489.
[36] C.-E. Lin, W.-C. Lin, Y.-C. Chen, S.-W. Wang, Migration behavior and selectivity of sulfonamides in capillary electrophoresis, J. Chromatogr. A 792 (1997) 37–47.
[37] I.J. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[38] A.G. Mayes, M.J. Whitcombe, Synthetic strategies for the generation of molecularly imprinted organic polymers, Adv. Drug Deliv. Rev. 57 (2005) 1742–1778.