Magnetic solid phase extraction of non-ionic surfactants from water

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Available online 5 March 2005

Abstract

Magnetic solid phase extraction was tested for the preconcentration of non-ionic surfactants based on oxyethylated nonylphenol, aliphatic alcohols and hydrogenated fatty acid methyl esters from water. Magnetic hydrophobic adsorbents exhibited the best extraction characteristics. Surfactants with the middle oxyethylation level were extracted efficiently while the extraction of surfactants with low and high oxyethylation levels was very low.
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Keywords: Solid phase extraction; Magnetic adsorbents; Non-ionic surfactants; Activated carbon; Magnetic PODMP; Surfactant extraction; Water purification

1. Introduction

Organic compounds with surface-active properties represent a very important group of industrially produced chemicals, the consumption of which has been increasing. Among them, products of oxyethylation of aliphatic alcohols, alkylphenols, carboxylic acid methylesters and amines are examples of non-ionic surfactants. The major part of the used non-ionic surfactants appears in waste water and consecutively also in surface water, which becomes contaminated. Waste water originating during various technological processes is treated before leaving the unit and entering the surface water, but even in treated water surfactant residues remain, causing possible environmental problems. For the determination of these compounds, different methods can be used including gas and liquid chromatography, gravimetric, spectrophotometric or enzymatic procedures, nuclear magnetic resonance, infrared spectroscopy or mass spectroscopy. The isolation and preconcentration of non-ionic surfactants and their residues is rather complicated. Liquid–liquid extraction, column chromatography, solid phase

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extraction (SPE), solid phase microextraction (SPME) and Wickbold [1] method have been used for this purpose.

Analysis of water samples containing suspended solids, microorganisms and salts is usually difficult. Solid particles cause the clogging of columns during the column chromatography and SPE and also during SPME particles sediment on the surface of the silica fiber. Because of these limitations the use of magnetic solid phase extraction (MSPE) [2], based on the batch adsorption of the target on a relatively small amount of magnetic specific adsorbent, for the preconcentration and isolation of surfactants from water samples was studied.

2. Experimental

Materials: Activated carbons Chezacarb B, S and SH were from Chemopetrol, Czech Republic. Poly(oxy-2,6-dimethyl-1,4-phenylene), ε-caprolactam and powdered iron(II, III) oxide were from Aldrich while DPA-6S (a polyamide derivative) was from Supelco. Non-ionic surfactant Tergitol (oxyethylated nonylphenol NP-9EO) was from Aldrich, Slovasol IS 455 and Slovasol IS 4510 (aliphatic alcohols C_{14} and C_{15} oxyethylated with 5 and 10 moles of ethylene oxide, respectively) were from Sloveca, Slovakia, and HROFAME 20 EO (methyl esters of rape oil hydrogenated fatty acids ethoxylated with 20 moles ethylene oxide) was from the Institute of Chemical Technology, Prague, Czech Republic. Other chemicals and materials were from Lachema, Czech Republic. A vortex mixer Heidolph Reax Top (Heidolph Instruments, Germany) and a Dynal Sample Mixer (Dynal, Norway) were used for the extraction experiments. Concentrations of surfactants were determined using UV–VIS spectrophotometer Cintra 20 (GBC, Australia).

Preparation of magnetic adsorbents: Activated carbon and Al_2O_3 were incorporated into magnetic iron oxides during precipitation of iron (II) and iron (III) chlorides with alkaline solution in a standard way [3]. Magnetic poly(oxy-2,6-dimethyl-1,4-phenylene) was molten with ε-caprolactam and powdered iron(II, III) oxide, milled and washed according to Safarik et al. [4]. Polyamide DPA-6S was post-magnetized with magnetic fluid stabilized with perchloric acid (prepared according to Massart [5]).

Extraction of surfactants: Solution of a tenside was added to 50 µl of settled adsorbent and the total volume was made up to 10.0 ml with distilled water. The sample was intensively stirred on a vortex mixer or rotated on a Dynal sample mixer. Magnetic particles were separated from the suspension using a magnetic separator or a strong permanent magnet. The adsorbed tenside was eluted 1–3 times with 1 ml methanol, each under thorough stirring on the vortex mixer. The time for both maximum adsorption and elution was determined from time dependence curves. Efficiency of elution was determined from the amount of adsorbed and subsequently released surfactant. Relative standard deviation (RSD) was calculated from 5 to 10 measurements.

Analytical methods: Concentration of Tergitol was directly determined spectrophotometrically at 276 nm. The concentration of Slovasol and HRO-FAME 20 EO was determined after reaction with a complex forming reagent (30 g $Co(NO_3)_2 \cdot 6H_2O$ and 200 g NH_4SCN in 1000 ml distilled water). Slovasol, which was present in the eluent (1–3 ml methanol), was pipetted into a flask with 15 ml methanol and evaporated on a rotary evaporator. Then 10 ml 1,2-dichloroethane was added to the evaporation residue, mixed and transferred into 150 ml separatory funnel with 5 ml of the complex forming reagent. After 60 s agitation, the bottom 1,2-dichloroethane fraction containing the dyed complex was filtered through porous glass and measured spectrophotometrically at 620 nm. Unbound Slovasol was determined in the same way after extraction of the supernatant with 1,2-dichloroethane [6].

Construction of adsorption isotherms: Solution of a tenside was added to 50 µl of settled adsorbent and the total volume was made up to 10.0 ml with distilled water. The suspension was mixed for 3–4 h at room temperature. Adsorption time was determined from a time dependence curve. After magnetic separation the concentration of free analyte (C_{eq}) was determined spectrophotometrically, and the amount of tenside bound to the unit

volume of the adsorbent (q_{eq}) was calculated. Maximum adsorption capacity Q (mg/ml) was calculated from the linearized form of the Langmuir isotherm.

3. Results and discussion

Magnetic solid phase extraction was tested for the preconcentration of non-ionic surfactants based on oxyethylated nonylphenol (NPEO), oxyethylated aliphatic alcohols (AEO) and oxyethylated hydrogenated fatty acid methyl esters originating in rape oil (HROFAME 20EO) from water. Tergitol (NP-9EO) and Slovasol IS 4510 (aliphatic alcohols C_{14} and C_{15} oxyethylated with 10 mol of ethylene oxide) were chosen as two representatives of surfactants with the same middle oxyethylation level and with nearly the same carbon atom number in the hydrophobic parts of the molecule. Slovasol IS 455 (aliphatic alcohols C_{14} and C_{15} oxyethylated with 5 mol of ethylene oxide) is a representative of surfactants with the low oxyethylation level, and HROFAME 20EO is a surfactant with a high oxyethylation level and longer aliphatic chains. Nowadays, surfactants with the middle oxyethylation level are preferred.

Different types of materials, e.g. activated carbon Chezacarb B (with highly porous structure), Chezacarb S (hydrophobic) and Chezacarb SH (hydrophilic), linear hydrophobic polymer PODMP (poly(oxy-2,6-dimethyl-1,4-phenylene)), polyamide DPA-6S (used for adsorption of polar compounds) and Al_2O_3 (common adsorbent) were magnetically modified and tested as magnetic adsorbents. The particle size of all adsorbents was about 100 μm. The dry weight of 1 ml settled suspension was 34.4 mg/ml (Chezacarb S), 33.6 mg/ml (Chezacarb B), 33.8 mg/ml (Chezacarb SH), 174 mg/ml DPA-6S, 149.6 mg/ml Al_2O_3 and 210.8 mg/ml (PODMP). According to preliminary experiments, only magnetic derivatives of Chezacarb S, PODMP and DPA-6S were selected for further experiments; nevertheless adsorption of Slovasol IS 455 on all mentioned adsorbents is also presented. Chezacarb SH was not used because the reproducibility of the extraction was

very low. Fig. 1 shows equilibrium adsorption isotherms of Tergitol. These isotherms follow the typical Langmuir adsorption pattern, and according to a classification system [5,7] belong to Class L2. After their linear transformation, maximum adsorption capacities were calculated (see Table 1).

Different parameters affecting both adsorption and desorption steps were studied. Surfactants were extracted by intensive stirring on the vortex mixer (shaking frequency 2400/min) or rotated on the Dynal sample mixer (40 rpm) and then eluted with 1 ml methanol on the vortex mixer (shaking frequency 2400/min). Time for both maximum adsorption and elution was determined from time dependence curves. The number of elution steps necessary to elute the maximum amount of
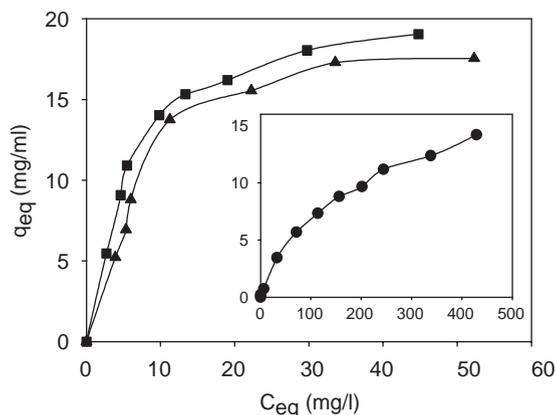

Fig. 1. Equilibrium sorption isotherms of tergitol on magnetic charcoal (▲), PODMP (■) and DPA-6S (●). C_{eq}—equilibrium liquid phase concentration of the non-adsorbed tergitol (mg/ml); q_{eq}—equilibrium solid phase concentration of the adsorbed tergitol (mg/l).

Table 1
Adsorption time and maximum adsorption capacities Q of Tergitol

	Chezacarb S	PODMP	DPA-6S
Time (h)	3	4	4
Q (mg/ml)	27.1	21.8	16.6
Q' (mg/g)	787.8	103.4	95.4

Q (mg/ml)—calculated using the settled volume of an adsorbent; Q' (mg/g)—calculated using the dry weight of an adsorbent.

Table 2
Extraction of Tergitol from a 10 ml sample on a vortex mixer using magnetic adsorbents

	Chezacarb S			PODMP			DPA-6S		
Sorption (min)	4	4	4	3	3	3	4	4	4
Elution (min)/(ml)	3/1	3/1	3/3	3/1	3/3	3/3	2/1	2/2	2/3
Tergitol (µg/ml)	10	20	50	5	30	50	10	30	50
Unbound (%)	0	0	21.5	12.2	10.1	11.9	66.7	75.74	60.8
Efficiency (%)	89.1	91.5	96.9	82.0	86.82	79.6	32.6	45.1	34.7
RSD (%)	8.7	7.1	8.3	22.5	7.2	4.9	23.9	14.7	18.1

Table 3
Extraction of Tergitol from a 10 ml sample on a Dynal sample mixer using magnetic adsorbents

	Chezacarb S			PODMP			DPA-6S		
Sorption (min)	20	20	20	5	5	5	30	30	30
Elution (min)/(ml)	3/1	3/1	3/2	3/1	3/1	3/3	2/1	2/1	2/2
Tergitol (µg/ml)	10	20	50	5	30	50	10	30	50
Unbound (%)	0	0	20	0	0	22	72.7	78.8	69.9
Efficiency (%)	87.3	95.4	86.6	89.5	92.6	98.6	27.7	23.0	23.0
RSD (%)	7.0	3.4	6.5	7.1	3.6	6.5	9.0	2.1	1.1

Table 4
Extraction of Slovasol IS 4510 from a 10 ml sample on a vortex mixer using magnetic adsorbents

	Chezacarb S		PODMP		DPA-6S	
Sorption (min)	4	4	3	3	3	3
Elution (min)/(ml)	2/3	2/3	3/1	3/1	2/3	2/3
Slovasol (µg/ml)	30	50	30	50	30	50
Unbound (%)	0	14.1	0	0	35.7	59.8
Efficiency (%)	69.6	68.3	91.4	93.4	45.5	51.7
RSD (%)	8.1	6.9	3.1	5.3	11.3	3.0

Table 5
Extraction of Slovasol IS 4510 from a 10 ml sample on a Dynal sample mixer using magnetic adsorbents

	Chezacarb S		PODMP		DPA-6S	
Sorption (min)	30	30	30	30	30	30
Elution (min)/(ml)	2/3	2/3	3/1	3/1	2/3	2/3
Slovasol (µg/ml)	30	50	30	50	30	50
Unbound (%)	0	0	0	0	38.9	46.5
Efficiency (%)	76.3	69.8	94.7	99.8	58.5	50.5
RSD (%)	4.8	3.2	5.5	4.1	5.1	6.2

adsorbed analyte was determined in preliminary experiments. The results obtained with three selected adsorbents are presented in Tables 2–5, while Table 6 shows the basic adsorption characteristics of Slovasol IS 455 on five of six magnetic adsorbents prepared. The time to reach the maximum adsorption under occasional mixing was between 30 and 120 min and under mild rotation on a Dynal sample mixer usually 20–30 min (except for adsorption of Tergitol on DPA-6S where the adsorption time was only 5 min). Intensive stirring on a vortex mixer enabled one to shorten this time to 1–6 min. Elution time was 0.5–3 min according to the type of tenside and adsorbent using a vortex mixer with maximum shaking frequency 2400/min. Extraction conditions (especially the intensity and time of stirring) can also influence the ratio of unbound/bound tenside, elution efficiency and reproducibility. The amount of adsorbents used did not substantially influence the elution recovery of the target compounds.

Adsorption was usually studied at three different concentrations of surfactants. Similar amounts of Tergitol were efficiently extracted on active carbon Chezacarb S and PODMP while polyamide

Table 6
Extraction of Slovasol IS 455 from a 10 ml sample on a vortex mixer using magnetic adsorbents

	Chezacarb S	Chezacarb B	PODMP	DPA-6S	Al_2O_3
Sorption (min)	10	5	6	1	5
Elution (min)	0.5	1	1	1	1
Slovasol (mg/ml)	0.28	0.28	0.28	0.28	0.28
Unbound (%)	75.8	67.7	44.4	67.2	67.9
Efficiency (%)	20.0	13.1	24.4	9.1	7.2

Elution was performed with 3×1 ml methanol.

DPA-6S exhibited very low adsorption and desorption. Slovasol IS 4510 was efficiently adsorbed on PODMP and slightly less on Chezacarb S. Slovasol IS 455 was both adsorbed and desorbed to a very limited extent on all adsorbents tested. The reason for the different behavior of Slovasol is probably connected to differences in the polarity of both surfactants. Slovasol IS 4510 differs from Slovasol IS 455 by its double oxylethylation level with a longer hydrophilic part of the molecule. The extraction efficiency values of HROFAME 20EO by all the studied magnetic adsorbents were lower than 10%, and therefore these results are not presented. The elution efficiency calculated from the amount of adsorbed and subsequently released tenside differed according to the type of the tenside and adsorbent used.

To summarize the results, it can be claimed that magnetic derivatives of hydrophobic charcoal Chezacarb S and PODMP exhibited the best adsorption and desorption characteristics. Surfactants with the middle oxyethylation level were extracted efficiently while the extraction of surfactants with low and high oxyethylation levels was very low. Both types of mixing (on a Dynal sample mixer and a vortex mixer) performed with similar efficiency. For extraction under thorough mixing, highly purified adsorbent is required in order to minimize release of impurities into a supernatant that can influence subsequent spectrophotometric measurements, especially in the UV region. The selection of the optimal mixing procedure will depend on the individual requirements (number of analyzed samples, total analysis time).

Standard solid-phase extraction was used several times for the preconcentration of non-ionic tensides from water samples. The reported recoveries [8,9] were similar (usually higher than 80%) to those obtained in our work. Magnetic solid phase extraction is thus an equivalent alternative of the column solid phase extraction; it is especially advantageous when the analysis should be performed in samples containing the particulate matter.

Acknowledgements

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