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ORIGINAL PAPER

Organosilica composite for preconcentration of phenolic compounds from aqueous solutions

V. N. Zaitsev · V. A. Khalaf · G. N. Zaitseva

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Abstract A new adsorbent is proposed for the solid-phase extraction of phenol and 1-naphthol from polluted water. The adsorbent (TX-SiO_2) is an organosilica composite made from a bifunctional immobilized layer comprising a major fraction (91%) of hydrophilic diol groups and minor fraction (9%) of the amphiphilic long-chain nonionic surfactant Triton X-100 (polyoxyethylated isooctylphenol) (TX). Under static conditions phenol was quantitatively extracted onto TX-SiO_2 in the form of a 4-nitrophenylazophenolate ion associate with cetyltrimethylammonium bromide. The capacity of TX-SiO_2 for phenol is 2.4 mg g^{-1} with distribution coefficients up to 3.4×10^4 mL g^{-1}; corresponding data for 1-naphthol are 1.5 mg g^{-1} and 3×10^3 mL g^{-1}. The distribution coefficient does not change significantly for solution volumes of 0.025–0.5 L and adsorbent mass less than 0.03 g; 1–90 μg analyte can be easily eluted by 1–3 mL acetonitrile with an overall recovery of 98.2% and 78.3% for phenol and 1-naphthol, respectively. Linear correlation between acetonitrile solution absorbance (A_{540}) and phenol concentration (C) in water was found according to the equation $A_{540}=(6\pm1)\times10^{-2}+(0.9\pm0.1)C$ (μmol L^{-1}) with a detection range from 1×10^{-8} mol L^{-1} (0.9 μL g^{-1}) to 2×10^{-7} mol L^{-1} (19 μL g^{-1}), a limit of quantification of 1 μL g^{-1} (preconcentration factor 125), correlation coefficient of 0.936, and relative standard deviation of 2.5%. A solid-phase colorimetric method was developed for quantitative determination of 1-naphthol on adsorbent phase using scanner technology and RGB numerical analysis. The detection limit of 1-naphthol with this method is 6 μL g^{-1} while the quantification limit is 20 μL g^{-1}. A test system was developed for naked eye monitoring of 1-naphthol impurities in water. The proposed test kit allows one to observe changes in the adsorbent color when 1-naphthol concentration in water is 0.08–3.2 mL g^{-1}.

Keywords Organosilica composite · Solid-phase extraction · Phenol · 1-Naphthol · Ion associate · Naked eye test method

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Introduction

Phenolic compounds are common pollutants of environmental water due to their formation in natural processes and human activity. Whilst phenol itself is very toxic (maximum allowed concentration (MAC) in drinking water is 0.001 mL g^{-1}), some substituted phenols, e.g., nonylphenol, octylphenol, and pentachlorophenol, are even more hazardous, which is why European Union legislation stipulates a MAC for total phenolic content in drinking water of 0.5 μL g^{-1}. Due to this low MAC and the complicated composition of environmental samples, preconcentration of phenol traces is commonly required prior its quantitative determination. Solid-phase extraction (SPE) [1] or, more recently, microextraction (SPME) (e.g., see [2–4]) is widely used for this purpose. Copolymers [5–7], organosilicas [8, 9], and carbon derivatives [10] (including oxidized nanotubes [4]) are used as adsorbents in SPE cartridges. Gas chromatography is commonly used for determination of volatile phenolic compounds after SPE, but photometric analysis is also useful [11, 12], particularly for environmental objects [13–15], organic volatile media [16, 17], and for development of kits for naked eye monitoring.

For all known cases, the driving forces for SPE of phenolic compounds are hydrophobic; however, for the preconcentration of traces from water this type of interaction is ineffective for several reasons:

1. Hydrophobic interaction is not selective, e.g., silica with immobilized octadecylsilane groups (C_{18}-SiO_2) has been used for solid-phase extraction of phenols [18, 19], but C_{18}-SiO_2 is also commonly used for SPE of most organic compounds.
2. Affinity of phenol towards hydrophobic adsorbents is not high, which is why distribution coefficients for such adsorbents commonly are less than 100 mL g^{-1}.
3. Phenolic compounds are easily degraded in air. For this reason they are used as antioxidants [16]. After preconcentration on SPE, adsorbed phenol can undergo even more rapid chemical oxidation than in liquid media [20] due to the high dispersity of adsorbent resulting in better contact of adsorbed phenol with oxygen from air. Undesirable oxidation of phenol leads to garbling of analytical results, which is why the problem of sample conservation during phenol preconcentration is more critical with SPE than for liquid extraction [18].

Application of known adsorbents for SPE of phenol from natural and drinking water therefore needs further development, and problems relating to adsorbent selectivity and adsorbate stability should be solved. To stabilize adsorbate, phenolic compounds can be adsorbed from water in the form of their azo derivatives, which are much more stable. For example, phenol promptly reacts with 4-nitrophenyldiazonium (4-NPD) salts, giving intensely colored azo compounds, which in turn forms ion associates (IAs) with cationic surfactants [21]. The selectivity of this reaction, coupled with the stability of the IAs, provides the background for the development of our method for the determination of phenol in water, which includes sample conservation by the conversion of phenols into an oxidatively stable form, followed by appropriate SPE preconcentration. In this work a new chemically modified silica (CMS), containing polyoxyethylated isooctylphenol groups covalently linked to the surface (TX-SiO_2), is proposed as a sorbent, capable of the reversible and selective extraction of IAs from water solutions. The proposed SPE is amphiphilic as it contains both hydrophilic (oxyethyl and diol) and hydrophobic (isooctylphenol) groups on the surface. The amphiphilicity of the proposed SPE's surface may increase the selectivity of its interaction with IAs and reduce nonspecific sorption of hydrophobic organic compounds from matrix. The intensive color of IAs makes the proposed method promising for the development of a test method for visual monitoring of some phenolic compounds at trace levels found in water pollution.

Experimental

Chemicals and reagents

4-Nitrophenyldiazonium tetrafluoroborate was synthesized by a reported method [22]. 4-Nitrophenylazophenolate and its ion associate (IA) with cetyltrimethylammonium cation was synthesized according to [21].

4-Nitroaniline, sodium nitrite, ethyl alcohol, diethyl ether, concentrated HCl solution, 40% aqueous HBF_4, Triton X-100 (Fluka, Buchs, Switzerland), acetonitrile, and isopropyl alcohol were of analytical grade.

(3-(2,3-Epoxypropoxy)-propyl)-trimethoxysilan (Merck, Darmstadt, Germany) was distilled under vacuum directly before use, and toluene was dried as described in [23].

The starting phenol solution, 1 mg mL^{-1}, and purified by sublimation before use, was prepared according to [24]. Solutions of lower concentrations were prepared by dilution of starting solution immediately before use.

Solutions of 1 M sodium carbonate (analytical grade), 10^{-3} M cetyltrimethylammonium bromide (CTABr) (Merck, Darmstadt, Germany), and 0.02 M 4-nitrophenyldiazonium tetrafluoroborate (4-NPD) were prepared by dissolving their exact masses in water. Doubly distilled water was used for the preparation of all aqueous solutions.

Instrumentation

UV–Vis electronic absorption spectra of the solutions were recorded on a Specord M-40 spectrophotometer (Carl Zeiss Jena) in the visible region (400–700 nm) in quartz cells (l=1 cm). Diffuse reflectance UV–Vis spectra of colored sorbents were measured on a Densitometer CS-9301PC (Shimadzu) relative to Al_2O_3 in the range 200–700 nm. FTIR spectra were measured as selfsupporting wafers on a Nexus-470 spectrometer, manufactured by Termo-Nicolet. The pH of the solutions was controlled by using an I-130 pH meter. Thermogravimetric studies were performed on a Q-1500 D derivatograph of a Paulic-Paulic-Erdey system (Hungary) at atmospheric pressure, with open platinum crucibles and Al_2O_3 as standard for comparison. Heating rate was 10 °C min^{-1} in the range 20–800 °C, sorbent mass was 100–300 mg. The concentration of functional groups on the surface of epoxypropoxypropyl silica (epoxy-SiO_2) was calculated from thermogravimetric data using Eq. (1):

$$C_{\mathrm{L}}\left(\mathrm{mol\,g^{-1}}\right) = \frac{\Delta m}{M_{\mathrm{r}} \cdot g} \tag{1}$$

where Δm is mass loss (g) of CMS in the temperature range 200–700 °C, corresponding to thermal decomposition of organic fragments; M_{r} is the formula weight of the 2, 3-epoxypropoxypropyl group; g is sorbent mass (g). Concentration of polyoxyethylated isooctylphenolic groups, cova-

lently linked to the surface of TX-SiO_2, was calculated using the same equation, where Δm is the difference between mass loss of TX-SiO_2 and epoxy-SiO_2, and M_r is average formula weight of Triton X-100 (for n=10). Synthesis of silica with covalently linked groups of polyoxyethylated isooctylphenol macroporous silica (Silochrome C-120, from Stavropol, Russia) (fraction 300–500 μm) was calcined in a furnace at 450 °C for 6 h. After this 4.53 mmol (1 mL) of (3-(2,3-epoxypropoxy)-propyl)-trimethoxysilane was added to 10 g silica in 50 mL toluene. The resulting suspension was stirred at reflux for 10 h under argon (to prevent possible hydrolysis of epoxy groups). The solid phase was separated by filtration and washed with toluene under argon (15 h in a Soxhlet apparatus). The epoxy-SiO_2 thus prepared was dried at 100 °C under vacuum. Triton X-100 (5 mL) was added to 2 g epoxy-SiO_2 in 20 mL toluene and the mixture was heated at 110 °C for 10 h. The solid phase was filtered and washed with isopropanol in a Soxhlet apparatus for 15 h. Drying in an oven at 110 °C gave TX-SiO_2.

Adsorption procedure

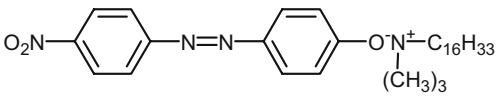
Sorption characteristics of TX-SiO_2 were studied in the static mode. For this purpose, the solution of IA was added to 0.02–0.06 g TX-SiO_2 and it was stirred for sufficient time to reach sorption equilibrium. Extraction level (%) of IA for TX-SiO_2 was studied as a function of: (a) the time of phases contact (τ=0–40 min), (b) the volume of reaction mixture (V=25–1,000 mL), (c) concentration of analyzed compound (4.2×10^{-4}–2.5×10^{-6} M).

Detection procedure

The concentration of phenol in the solution was determined photometrically after coupling with 4-nitrophenyldiazonium salts, as described in [21]. The level of phenol extraction and the sorption capacity of TX-SiO_2 for phenol were calculated by measurement of the residual phenol concentration in water or by its content in acetonitrile eluate. IA was eluted from TX-SiO_2 with acetonitrile in the dynamic mode. For this 0.03 g TX-SiO_2 was put into a glass column (h=2 mm, d=5 mm) and eluent was passed with a flow rate of 1 mL min^{-1}. Absorbance of the acetonitrile solution was measured at λ=540 nm. For the development of a kit for naked eye monitoring of 1-naphthol, after contacting of TX-SiO_2 with polluted water, adsorbent was separated by filtration, dried at room temperature, and photographed.

Results and discussion

Many aromatic compounds (e.g., phenols and aromatic amines) irreversibly react with 4-nitrophenyldiazonium salts to give azo compounds. However, only some of them, particularly the products of azo coupling with phenols, give stable ion associates with cationic surfactants, similar to the IA, e.g., 4-nitrophenylazophenolate cetyltrimethylammonium:



Due to the presence of the chromophoric center in such associates, they are used for the photometric determination of phenols [21]. The simultaneous presence of the long-chain alkyl fragment and the charged center in the IA molecule gives rise to its specific properties, which distinguish it from the majority of accompanying compounds. In particular, such IAs may have high affinity towards sorbents with amphiphilic surface, which is why a new CMS, containing covalently linked groups of polyoxyethylated isooctylphenol on the surface (TX-SiO_2), was proposed as the sorbent for IA.

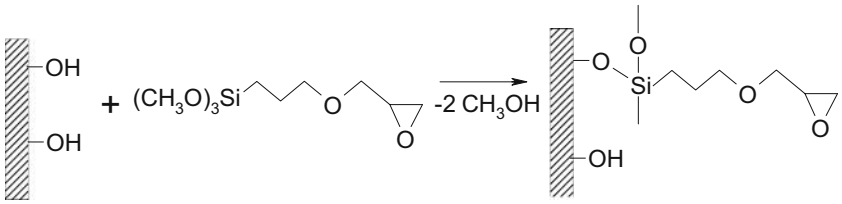
Immobilization of polyoxyethylated isooctylphenol

Immobilization of polyoxyethylated isooctylphenol on the silica surface was performed by a two-step method. Silica containing covalently linked epoxy groups on the surface was prepared by treating silica with (3-(2,3-epoxypropoxy)-propyl)-trimethoxysilane (Scheme 1).

Silicas with surface epoxides react with amines and alcohols, resulting in the immobilization of the latter on the surface [25]. We supposed that polyoxyethylated isooctylphenol may also react with epoxy-silica, forming the CMS according to Scheme 2.

Triton X-100 immobilization was monitored by IR spectroscopy and thermogravimetrically. The IR spectroscopy data provide evidence for the immobilization of (3-(2,3-epoxypropoxy)-propyl)-trimethoxysilane according to Scheme 1. Absorption bands occur in the IR spectrum of epoxy-SiO_2 that are characteristic of the stretching and deformation vibrations of alkyl fragments: ν(C–H) at 2,850–2,950 and δ(C–H) at 1,460 cm^{-1}, respectively (Fig. 1). The intensity of vibrations of alkyl fragments (ν(C–H)) increases in the IR spectrum of TX-SiO_2. Bands in the spectrum at 1,612–1,510 cm^{-1} are characteristic of stretching vibrations of aromatic rings ν(–C=C–), which confirms that the TX-SiO_2 synthesis proceeded according to Scheme 2. A significant increase in the intensity of $\nu(CH_3)$ absorption bands is observed in the IR spectrum of TX-SiO_2 after IA sorption (Fig. 1). The ratio of intensities of absorption bands of stretching vibrations of $-CH_3$ group (2,962 and 2,872 cm^{-1}) and $-CH_2$ group (2,926 and 2,853 cm^{-1}) characterize carbon chain branching in the surface compound [26]. A significant increase of the intensity of $\nu(CH_3)$ bands

Scheme 1 Preparation of the intermediate epoxy-silica surface



indicates IA adsorption. The bands of $-NO_2$ groups (at 1,570 and 1,300 cm^{-1}), which come from the 4-nitrophenylazophenolate fragment (Structure 1) are also present in the IR spectrum of TX-SiO_2 after IA sorption (Fig. 1).

Under thermal treatment at 200–700 °C, 1 g epoxy-SiO_2 lost 32 mg of its initial mass. Under the same conditions TX-SiO_2 lost 51 mg. These data were used to determine concentration of the immobilized groups on both CMSs. From Eq. (1) concentration of epoxy groups on epoxy-SiO_2 was determined as 275 μmoL g^{-1}. One gram of TX-SiO_2 lost 19 mg more than epoxy-SiO_2 due to immobilization of Trtiton X-100. Thus the concentration of immobilized polyoxyethylated isooctylphenolic groups was found from Eq. (1) to be 25 μmoL g^{-1} (molecular mass of Triton X-100 was attributed to M_r), which accounts for 9% of total surface coverage with organic layer. The rest of the immobilized layer (250 μmoL g^{-1}) comprises hydrophilic alkyldiol groups, formed from hydrolysis of epoxy groups, as shown in Scheme 2.

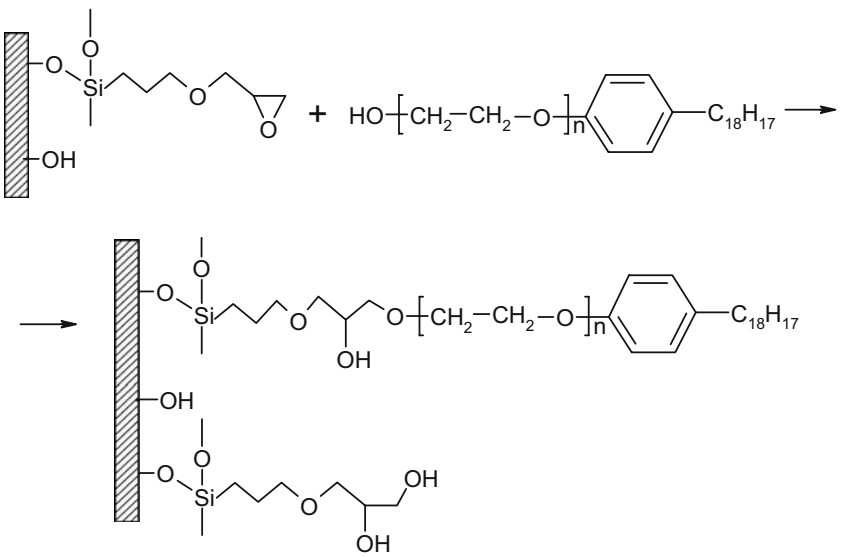
Diffuse reflectance spectra

TX-SiO_2 has no adsorption band in the visible region of the diffuse reflectance spectrum (DRS). The adsorbent becomes red after it was immersed into aqueous solution containing the phenolic compounds 4-NPD and CTABr. An intense absorption band with maximum at 530 nm (Fig. 2) is observed in the DRS for TX-SiO_2 isolated from this solution. The position of the band is overlaps with the adsorption maximum of ion associate between 4-nitrophenylazophenolate and CTABr, while 4-nitrophenylazophenolate itself has an adsorption maximum at 490 nm (Fig. 2). Thus DRS data confirm the results of IR spectroscopic studies and provide evidence for phenol adsorption in the form of an IA between 4-nitrophenylazophenolate and CTABr.

Sample preconcentration

Even 2 M aqueous HCl does not cause analyte desorption. IA is easily desorbed from the surface of TX-SiO_2 with acetonitrile, so this solvent was used as an eluent. By measurement of the eluate absorbance at 540 nm it was shown that the time required for sorption equilibrium in the TX-SiO_2/IA system depends on the concentration of phenolic compounds in the solution. We investigated this phenomenon for phenol and 1-naphthol (Fig. 3). For the solutions with phenol concentration higher than 10 μmol L^{-1}, the equilibrium is set after 10 min, whereas for 1-naphthol solutions with the same concentrations it is set after 20 min. For the phenol concentration less than 2.5 μmol L^{-1} this time increases to 15 min (Fig. 3). Obtained data were considered for further adsorption

Scheme 2 Preparation of TX-SiO_2 by immolization of Triton X-100



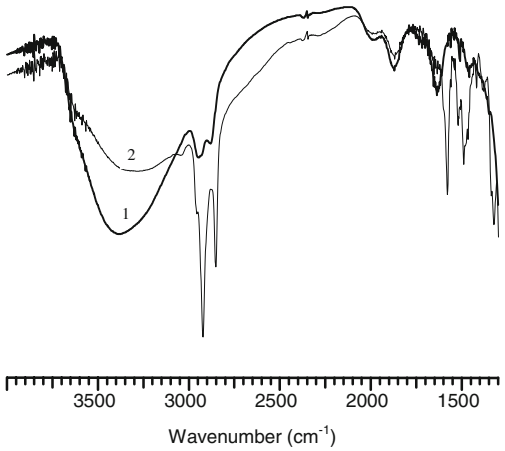


Fig. 1 Normalized FTIR spectra of *1* epoxy-SiO_2, *2* TX-SiO_2 after sorption of phenol IA

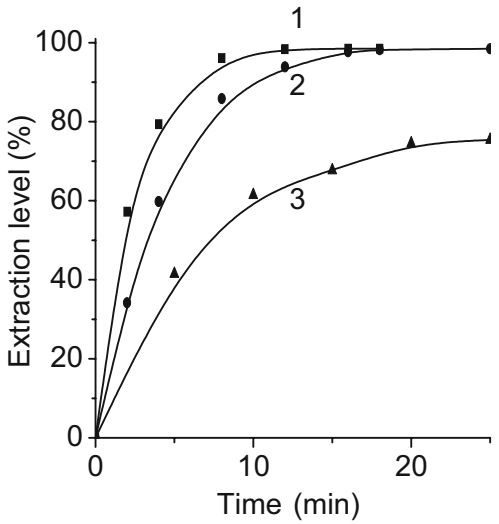


Fig. 3 Dependency of extraction level (*R*, %) of phenol (*1*, *2*) and 1-naphthol (*3*) on the time of phase contact (τ, min): 1.3–25 mL, 2–100 mL

experiments with water samples containing phenol in representative environmental conditions. Adsorbent was allowed to be in contact with phenol-containing solution for 40 min. As expected, phenol, 1-naphthol, and 4-nitrophenylazophenolates have no visible adsorption on TX-SiO_2 (Fig. 4). In contrast, the IA has high affinity towards TX-SiO_2. The IA adsorption isotherm can be attributed to a Langmuir L-type isotherm, where linear correlation between concentration of phenolic compounds in solution and the adsorbent capacity is observed (Fig. 4). By approximation of isotherm data it was found that adsorbent capacity for phenol in the Henry region is up to 2.1 mg g^{-1}, whereas its total capacity is slightly higher: 2.4 mg g^{-1}. Extraction of phenol in the Henry region is quantitative with a distribution coefficient up to 3.4×10^4 mL g^{-1}. The total capacity of TX-SiO_2 for 1-naphthol is lower than for phenol and it reached 1.5 mg g^{-1}. The Henry region for 1-naphthol is also narrower (up to 1.3 mg g^{-1}) with a weaker affinity and with a distribution coefficient of about 3×10^3 mL g^{-1} (Fig. 4).

The recovery of phenol and 1-naphthol after preconcentration on TX-SiO_2 was studied as a function of solution volume and the adsorbent mass. The degree of extraction of phenolic compounds ($\lg D_g$) in the form of IA is high (up to 4.9) and does not changed significantly in the range of solution volume 0.025–0.5 L (Table 1). At the same time desorption of IA from TX-SiO_2 to acetonitrile is complete. It was found that 1–90 μg of phenol in the form of its IA can be easily eluted from SPEs to the solution with 1–3 mL acetonitrile. Final recovery factors for phenol and 1-naphthol are as high as 98.2% and 78.3%, respectively (Table 1).

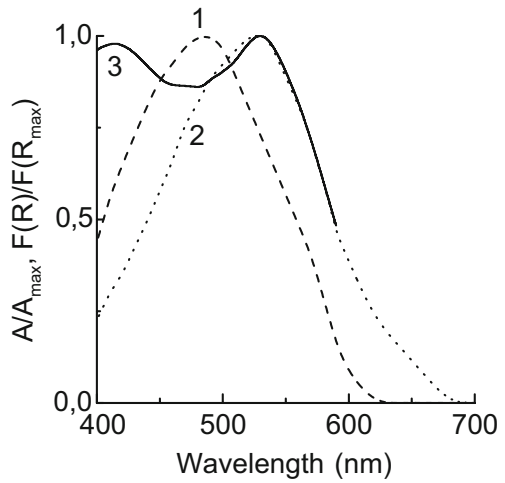


Fig. 2 Normalized absorption spectra of aqueous solutions of 4-nitrophenylazophenolate (*1*), IA (*2*), and diffuse reflectance spectra of TX-SiO_2 with adsorbed IA (*3*)

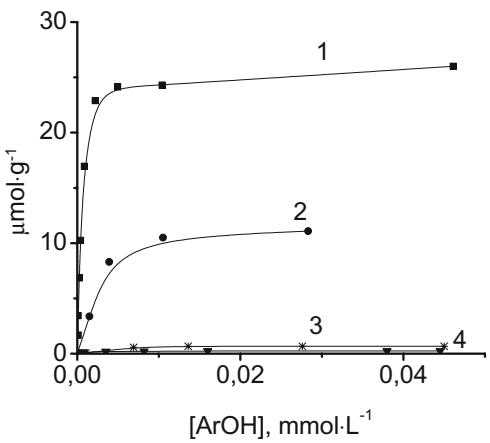


Fig. 4 Sorption isotherms for phenol IA (*1*) and 1-naphthol IA (*2*), 4-nitrophenylazophenolate (*3*), and phenol (*4*) on TX-SiO_2: $V_{phenols}$= 25 mL, $C(Na_2CO_3)$=0.04 M; C(4-NPD)=4.8×10^{-4} M, C(CTABr)= 1.3×10^{-4} M; τ=40 min, m=0.03 g

Table 1 Recovery of phenol (and 1-naphthol) from model solution

m(TX-SiO_2) (g)	V (L)	Obtained content (μg)	RSD (%)	Recovery (%)	lgD_g	Concentration factor
0.03	0.025	9.7±0.6	3	97.6	4.5	12.5
	0.05	9.6±0.4	3	96.2	4.6	25
	0.1	9.4±0.7	3	94.3	4.7	50
	0.25	8.9±0.3	2	89.5	4.9	125
	0.5	4.8±1.1	10	47.6	4.2	250
	1.0	1.6±1.4	30	15.7	3.8	500
0.06	0.025	9.8±0.8	3	98.2	4.4	12.5
0.05		9.8±0.5	2	98.2	4.4	
0.04		9.8±0.6	3	98.0	4.5	
0.03		9.8±0.6	3	97.8	4.6	
0.02		6.7±0.7	4	67.5	3.4	
0.03[a]	0.025	11.3±0.5	2	78.3	3.5	12.5
	0.05	9.4±0.7	3	65.2	3.5	25

m_{phenol}=9.9 μg, $m_{1\text{-naphthol}}$=14.4 μg, $t(p=0.95, n=3)$=4.30, τ=40 min, $V(CH_3CN)$=2 mL
[a] Recovery is reported for 1-naphthol

As can be seen from Table 1, by increasing of the adsorbent mass for the same volume of solution we can slightly increase the distribution coefficient, but this is not efficient. In contrast, for experiments with 0.02 g TX-SiO_2 as SPE, both D_g and recovery of phenolic compounds decrease sharply (Table 1). We therefore concluded that for effective adsorption of phenol on TX-SiO_2 under static conditions, the maximum ratio of solution volume to adsorbent mass should not be higher than 8,000 mL g^{-1} and adsorbent mass should be more than 0.02 g. These data allowed for development of our method for the photometric determination of phenol at MAC levels. The calibration graph was constructed with three replicates per standard at nine concentration levels varying from 1×10^{-8} mol L^{-1} (0.9 μL g^{-1}) to 4×10^{-7} mol L^{-1} (38 μL g^{-1}). For this, 250 mL of phenol-containing water in the range of solution treated with 4.8 mL of 0.02 M 4-NPD, 8 mL of 1 M Na_2CO_3, and 25 mL of 10^{-3} M CTABr was mixed with 0.03 g of TX-SiO_2. The resultant suspension was stirred for 20 min, after which the solid phase was filtered, washed with water, and dried at 40 °C. Adsorbed IA was eluted from TX-SiO_2 with 1 mL acetonitrile and its content was determined photometrically as described above.

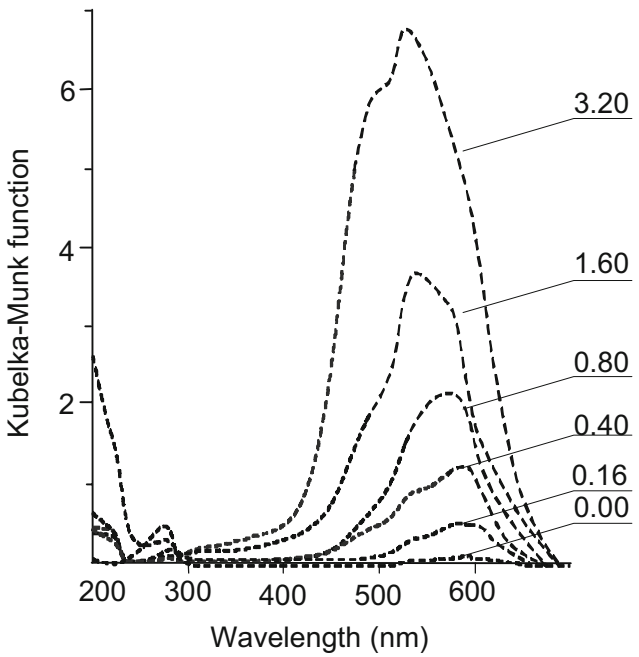


Fig. 5 Diffuse reflectance spectra of TX-SiO_2 after interaction with solution of 1-naphthol IA (mL g^{-1})

The limit of detection (LOD) and the limit of quantification (LOQ) of the method were calculated from the data in the linear range of the calibration plot using Eq. (2):

$$\mathrm{LOD(LOQ)} = \frac{kS_b}{S} \quad (2)$$

Here k is a factor that equals 3 for the LOD and 10 for the LOQ, S_b is the standard deviation of the blank, and S is the slope of the calibration graph in the linear range. Linear correlation between acetonitrile solution absorbance and phenol concentration in water was found according to the equation $A_{540}=(6\pm1)\times10^{-2}+(0.9\pm0.1)C$ (μmol L^{-1}) with a detection range from 1×10^{-8} mol L^{-1} (0.9 μL g^{-1}) to 2×10^{-7} mol L^{-1} (19 μL g^{-1}), a limit of quantification of 1 μL g^{-1} (preconcentration factor 125), correlation coefficient 0.936, and relative standard deviation of 2.5%.

Since IA has an intense blue (for 1-naphthol) or red (for phenol) color, it was used for development of the solid-phase colorimetric method and test systems for naked eye monitoring of 1-naphthol impurities in water. As can be seen from Fig. 5, DRS of TX-SiO_2 with adsorbed IA of 1-naphthol has an absorption band with maximum at 540 nm.

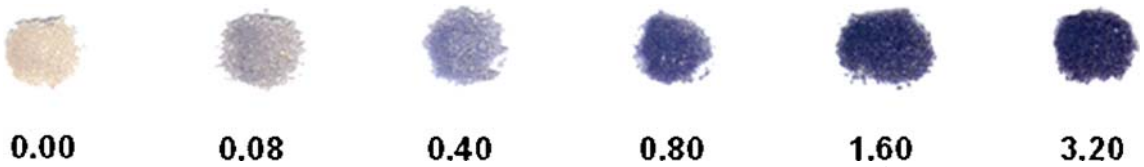


Fig. 6 Color scale for TX-SiO_2 after its interaction with various concentrations of 1-naphthol IA (mL g^{-1})

Intensity of the band correlates with concentration of 1-naphthol in solution (Fig. 5). This feature was exploited to develop kits for water impurity monitoring. In a typical experiment the colorimetric detection of 1-naphthol was tested in the concentration range from zero to 3.2 mL g^{-1} for 30 mg TX-SiO_2. The results show increasing adsorbent color intensity with increasing 1-naphthol content in solution. Thus 1-naphthol can be detected at concentrations as small as 0.08 mL g^{-1} (MAC for drinking water is 0.1 mL g^{-1}) from a change of adsorbent color from white–yellow to light blue (Fig. 6). The increase of blue color intensity can be observed in all studied regions. The color of the adsorbent was stable for more than 10 days.

The solid-phase colorimetric method for 1-naphthol determination was developed by using scanner technology (densitometer) with further numerical data analysis in Photoshop 6.0 by using the RGB color model. Intensity of all color channels correlates with the 1-naphthol concentration in water according to the following equation: $Y = Y_0 + A \times \exp(-C/t)$ using Y_0, A, and t-equation coefficients listed in Table 2. The detection limit of the method was calculated as described elsewhere [27].

The most efficient approach was to use the R-channel, since better correlation was observed together the lowest absolute value of Y_0 and highest pre-exponential factor (Table 2). For this technology the detection limit of 1-naphthol in water solution is 6 μL g^{-1} (which is 15 times lower than the MAC) and the quantification limit is 20 μL g^{-1}.

Application

The proposed TX-SiO_2 was successfully applied as SPE adsorbent in the determination of phenol in environmental water samples with unknown contents of phenolic compounds. Water samples (water from the river Lybid, Kiev) were examined directly using the procedure proposed for phenol preconcentration with subsequent photometric determination in acetonitrile eluate in the form of its ion associate. To examine the reliability of the proposed system, certain amounts of standard phenol solution were added to the sample solutions and analyzed according to the proposed method. Phenol content was calculated by comparing the results obtained before and after addition of the standard solutions of phenol. The amounts of phenol in the samples taken are summarized in Table 3. As can be seen, the samples taken from the river in Kiev contain about 3.5±0.3 μL g^{-1} phenol.

Conclusions

Our proposed organosilica adsorbent for SPE of phenolic compounds from aqueous solutions demonstrated high affinity towards ion associates of azophenolates with cationic surfactants. Owing to this affinity 0.03 g of the adsorbent can completely (>98.2%) remove phenol (up to 2.4 mg g^{-1}) and 1-naphthol (1.5 mg g^{-1}) from up to 250 mL of polluted water under static conditions. Adsorbed analyte can be easy eluted with acetonitrile for further analysis or quantitative determination on the phase of adsorbent by solid-phase colorimetry. This new procedure allows the simple determination of phenol and 1-naphthol in polluted water at MAC levels. The stability and high intensity of the color of adsorbate allows monitoring of 1-naphthol by the naked eye test method.

Table 2 Metrological data of solid-phase colorimetric determination of 1-naphthol

Color components	Equation coefficients $Y = Y_0 + A \times \exp(-C/t)$		R^2	Detection range (mL g^{-1})	Detection limit, (mL g^{-1})
	Y_0	A			
R	18.9	232.5	0.990	0.02–1.2	0.006
G	31.7	215.6	0.974	0.02–2.0	0.007
B	97.2	123.8	0.976	0.02–3.1	0.008

Table 3 Analysis of phenols in the Lybid river (Kiev, Ukraine)

Amount of phenol added (μL g^{-1})	Amount of phenol found (μL g^{-1})	RSD (%)
0	3.5±0.3	2.9
2.0	5.4±0.4	2.8
4.0	7.4±0.5	2.7
6.0	9.3±0.5	2.2

$t(p=0.95, n=3)=4.3$, m(TX-SiO_2)=0.03 g, V(sample)=250 mL, τ=40 min

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