

BIFUNCTIONAL ION EXCHANGE RESIN WITH THIOL AND QUATERNARY AMMONIUM GROUPS FOR THE SORPTION OF ARSENATE

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Received February 26, 2003

Accepted June 26, 2003

A bifunctional resin with thiol and quaternary ammonium groups was prepared from a macroporous strongly basic anion exchange resin of the styrene-divinylbenzene type. The key step of the synthesis is the reaction of the quaternary benzyltrimethylammonium group of the ion exchange resin with suitable sulfur-containing nucleophiles. Three synthetic routes are described: direct conversion to thiol with sodium sulfide, reaction with potassium *O*-ethyl dithiocarbonate followed by decomposition of the dithiocarbonate with ammonia or acid and conversion to polymeric isothiuronium salt by the reaction with thiourea and subsequent alkaline hydrolysis to thiol. Sorption of arsenate on thiol resin and its Fe(III) complex was studied.

Keywords: Ion exchangers; Functionalized resins; Polymers; Bifunctional sorbents; Thiols; Quaternary ammonium salts; Arsenate sorption; Iron complexes.

The pollution of water with heavy metals is still one of serious problems due to their toxicity for humans and other living organisms. This is the reason why much effort was devoted to the development of techniques for their removal mainly from drinking and also from waste water. One of the most dangerous, widely and intensively studied heavy metal contaminants, besides mercury and cadmium, is arsenic. It exists in water mainly in the form of oxoanions (of As(III) or As(V)), which are not selectively removed from an excess of "harmless" anions by classic weakly or strongly basic anion exchangers.

One of the functional groups with high affinity to heavy metals (including As) is the thiol (SH) group due to its soft Lewis base character. Compounds such as BAL (British AntiLewisite; 2,3-disulfanylpropan-1-ol) were

thus used for the treatment of the poisoning with As compounds such as war gas Lewisite (dichloro(2-chlorovinyl)arsane). Thiol resins prepared by different routes have been used for the removal of heavy metal cations from water^{1,2}, precious metal recovery from liquid wastes³, analysis of heavy metals (preconcentration and separation)⁴ and heavy metal intoxication treatment⁵. Sorption of arsenate and arsenite on thiol polymers was described⁶. Earlier, we have described a special macroporous polymer sorbent bearing thiol groups² for the removal of mercury from its aqueous solutions. It was prepared from a strongly basic anion exchange resin containing quaternary benzylammonium groups partly replaced by thiol groups, possessing high affinity to mercury. The remaining quaternary ammonium groups serve for the electrostatic binding of mercury complex anions (such as $[\text{HgCl}_4]^{2-}$) to the surface thiol groups and for hydrophilization of the matrix. They also keep the matrix swollen even after sorption of metal ions leading mostly to hydrophobic species. So the thiol groups are readily available for the sorption. A similar approach using a bifunctional resin with two types of anionic functional groups was described for the sorption of polyvalent cations⁷. Its phosphonic acid groups are responsible for the selectivity and sulfonic acid groups for electrostatic binding and hydrophilization of the matrix. The bifunctional anion exchange resin has two types of quaternary ammonium groups on the divinylbenzene-crosslinked polystyrene matrix: trihexylammonium exchange sites with bias forwards sorbing large, poorly hydrated anions, such as pertechnetate and perchlorate, for pertechnetate selectivity and triethylammonium exchange sites to improve sorption kinetics⁸.

The main aim of this study was to develop a new and effective method for the preparation of a thiol-type sorbent for the removal of anionic As from its aqueous solutions. The As anions can be removed by reaction with thiol or by ligand exchange on Fe(III) thiolate. Sorbents with Fe(III) attached ionically on a cation exchanger⁹ or in a complex on chelating sorbent bind arsenate by ligand exchange¹⁰.

An unusual preparation of thiol sorbents is based on alkylation of sulfur nucleophiles with quaternary benzylammonium groups on the styrene resin in analogy with low-molecular-weight benzyl(dimethyl)phenylammonium salts^{11,12} (Scheme 1). In order to prepare a thiol polymer, we used a two-step synthesis, (i) and (ii)². In the first step, a strongly basic anion exchanger **1** was reacted with potassium *O*-ethyl dithiocarbonate (i) giving *O,S*-dialkyl dithiocarbonate **2**. To obtain thiol **3** from **2**, ammonolysis with aqueous ammonia (ii-a) described previously or newly developed hy-

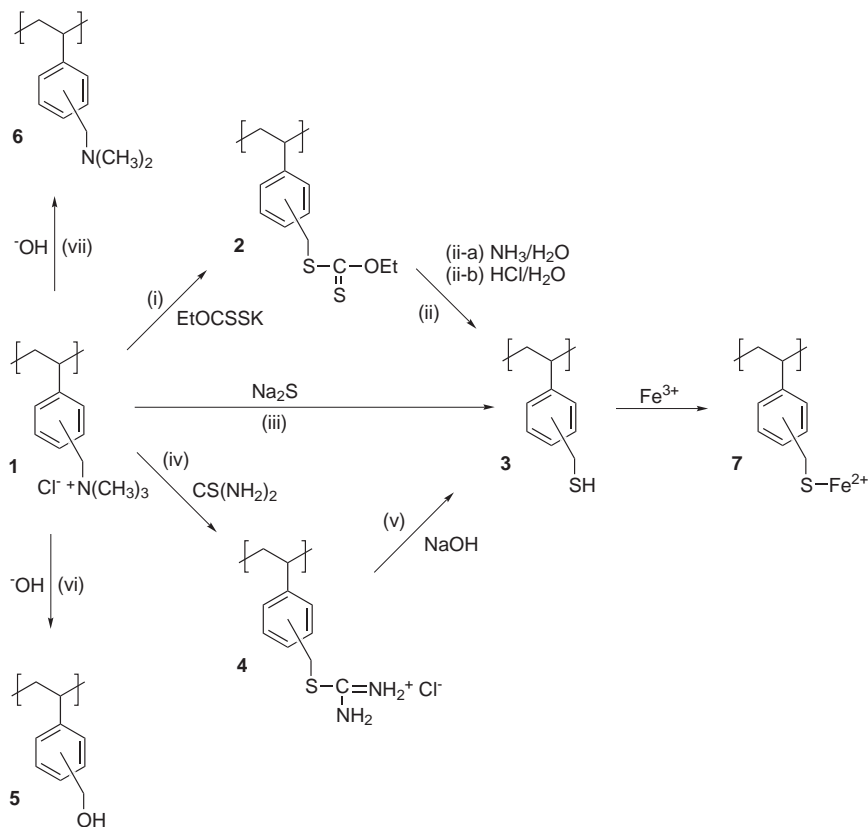
dolysis with hydrochloric acid (ii-b) was used in analogy with the low-molecular-weight compounds¹³.

The modified ligand-exchange sorbent for the removal of oxoanions from water is based on this thiol sorbent loaded with Fe^{3+} cations, which strongly complexes arsenate.

EXPERIMENTAL

Reagents and Instruments

Sodium sulfide nonahydrate (purissimum p.a.) and potassium ethyl xanthate (purum) were from Fluka, iron(III) nitrate nonahydrate, ammonium acetate, ethanol, methanol, hydrochloric acid, L-ascorbic acid, sulfuric acid, lead acetate trihydrate, silver nitrate, sodium ar-



SCHEME 1

Preparation of bifunctional thiol/quaternary ammonium polymer by modification of a strongly basic anion exchanger

senate, antimony(III) potassium tartrate and sodium hydroxide (all purissimum p.a.) were from Lachema (Czech Republic). Macroporous strongly basic anion exchanger Lewatit MP 500 in chloride form **1** (sucked dry contains 60% of water; dry resin contains 6.16% N (4.40 mmol/g), 15.60% Cl (4.40 mmol/g)) was obtained from Bayer (Germany). All the chemicals were used as supplied without additional purification.

Vacuum-dried samples of polymers were characterized by elemental analysis of S, N and Cl; IR spectra were recorded in KBr pellets (Perkin-Elmer Paragon 1000 PC FT-IR spectrometer) and solid-state ^{13}C NMR spectra were measured on a Bruker Avance MSL 200 MHz NMR spectrometer. ^{13}C NMR spectra simulations for the structure – NMR signal correlations were performed with the computer program ACD CNMR version 2.51.

Thiol sorbents were stored under 1% aqueous L-ascorbic acid to prevent oxidation, then washed with 0.1 M HCl and water before use.

Xanthate Route

The reaction with potassium O-ethyl dithiocarbonate ((i), **1** → **2**). Modified (i) was used². Polymer **1** (10 g sucked dry; 17.8 mmol N) was refluxed for 12 h with a solution of potassium O-ethyl dithiocarbonate (12.8 g, 80 mmol) in ethanol (128 ml), then the polymer was filtered off and washed successively with ethanol, methanol, water, 15% aqueous sodium chloride and water again until the eluent was chloride-free.

Polymer **2**: 3.30% N (2.36 mmol/g), 13.34% S (4.16 mmol/g); calculated: dithiocarbonate groups 2.08 mmol/g, quaternary ammonium groups 2.36 mmol/g; conversion of quaternary ammonium groups to dithiocarbonate 40.7%.

Ammonolysis of polymer 2 ((ii-a), **2** → **3a**). The dithiocarbonate polymer **2** was allowed to stand for 26 h at room temperature in aqueous ammonium hydroxide (7.5% NH_3), washed successively with water, 0.1 M aqueous hydrochloric acid and again water until the eluent was neutral.

Polymer **3a**: 3.66% N (2.61 mmol/g), 7.40% S (2.31 mmol/g); calculated: thiol groups 2.03 mmol/g, residual quaternary ammonium groups 2.61 mmol/g, residual dithiocarbonate groups 0.14 mmol/g (IR); hydrolysis conversion 94%, total conversion 37.4%.

Hydrolysis of polymer 2 with hydrochloric acid ((ii-b), **2** → **3b**). The dithiocarbonate polymer **2** was heated in 35% hydrochloric acid at 90 °C for 3 h and washed with water until the eluent was neutral.

Product **3b**: 3.54% N (2.53 mmol/g), 6.62% S (2.06 mmol/g); calculated: thiol groups 2.06 mmol/g, residual quaternary ammonium groups 2.53 mmol/g, dithiocarbonate groups 0 mmol/g (IR); hydrolysis conversion 100%, total conversion 47.8%.

Sodium sulfide route ((iii), **1** → **3c**, **3d**). Polymer **1** (10 g sucked dry; 17.8 mmol N) was heated for 5 or 12 h at 95 °C under stirring in a solution of sodium sulfide (38.44 g nonahydrate, 160 mmol) in water (80 ml). The product was washed with water, 1 M hydrochloric acid and again water until the eluate was sulfide-free.

Polymer **3c** (5 h reaction time): 3.86% N (2.75 mmol/g), 5.43% S (1.69 mmol/g); calculated: thiol groups 1.69 mmol/g, quaternary ammonium groups 2.75 mmol/g; conversion to thiol 30.9%, hydrolysis of ammonium groups 18.7%.

Polymer **3d** (12 h reaction time): 1.56% N (1.11 mmol/g), 8.22% S (2.56 mmol/g); calculated: thiol groups 2.56 mmol/g, quaternary ammonium groups 1.11 mmol/g; conversion to thiol 53.9%, hydrolysis of ammonium groups 22.6%.

Thiourea Route

Reaction of polymer 1 with thiourea ((iv), **1** → **4**). Lewatit MP 500 (10 g sucked dry; 17.8 mmol N) was heated in a solution of thiourea (12.16 g, 160 mmol) in ethanol (100 ml) under stirring for 24 h at 70 °C. The product was washed with water.

Polymer 4: 5.65% N (4.04 mmol/g), 1.00% S (0.31 mmol/g); calculated: isothiuronium groups 0.31 mmol/g, quaternary ammonium groups 3.42 mmol/g; conversion 8%.

Polymer 3e by alkaline hydrolysis of isothiuronium groups ((v), **4** → **3e**). Isothiuronium polymer **4** in 3.9 M aqueous sodium hydroxide (80 ml) was stirred with an anchor stirrer for 3 h at 95 °C and then washed successively with water, 1 M aqueous HCl and water until the eluent was neutral.

Polymer 3e: 5.51% N (3.94 mmol/g), 0.95% S (0.29 mmol/g); calculated: thiol groups 0.29 mmol/g, quaternary ammonium groups 3.94 mmol/g; total conversion 7%.

Fe(III)-Loaded Thiol Sorbent 7

Thiol resin **3d** (5.0 g sucked dry) was reacted with a 0.01 M buffered solution of iron(III) nitrate (200 ml) in 2.0 M ammonium acetate for 3 h under shaking and then washed with water until Fe³⁺ was absent in the eluate (KSCN test).

Polymer 7: 4.75% Fe (0.85 mmol/g); mole ratio SH/Fe = 3.

Acid-Base Properties

Sucked dry sorbent (ca 1 g) was added to a mixture of 0.2 M HCl (10.0 ml) and water (50 ml) and the suspension was titrated with 0.2 M NaOH while measuring pH with a Metrohm 691 pH meter. The dry matter content in sucked dry polymer was estimated gravimetrically.

Arsenate Sorption Experiments

Centrifuged polymer **3d** (0.3 g) was vigorously shaken with defined volumes of arsenate solutions of known concentrations for up to 4 h in tightly sealed vials at room temperature. The sorption capacity per g of dry polymer was calculated from the residual concentration of arsenate in solution measured by iodometric titration in strongly acidic medium¹⁴. Starting concentrations of arsenate were in the range 10–200 mmol/l. pH of stock arsenate solutions was adjusted by addition of 1 M hydrochloric acid. The sorption was measured as function of time, pH and starting concentration. Sorption capacity is given in mmol As per g of dry resin.

RESULTS AND DISCUSSION

Synthesis

Reaction of sulfur-containing nucleophiles with polymeric quaternary trialkylbenzyl ammonium salts proceeds in a slightly different manner from their low-molecular-weight analogs. The low-molecular-weight compounds give good yields only with benzyl(dimethyl)phenylammonium or benzylpyridinium salts but only negligible yields with benzyltrimethylammonium

salts¹². In contrast, polymer analogs give fair yields already with the trimethylammonium salt. In addition, thiol and not sulfide is formed by the reaction with sulfide due to steric hindrance.

The reaction of quaternary ammonium groups with potassium *O*-ethyl dithiocarbonate in ethanol (i) gave 47% yield (2.08 mmol/g of dithiocarbonate) after 12 h of reflux; prolonged reaction times had no effect. The dithiocarbonate content in polymer **2** could be easily followed by IR spectra using the strong band at 1015 cm⁻¹, corresponding with the C=S stretching vibration of the dithiocarbonate group.

The decomposition of dithiocarbonate in **2** with aqueous ammonia (ii-a) gave a 94% yield of thiol (some dithiocarbonate did not react). The total thiol content was 2.03 mmol/g.

The hydrolysis of dithiocarbonate groups in **2** with concentrated aqueous hydrochloric acid (ii-b) was quantitative (no C=S stretching band appears in IR spectra). The resulting polymer with 2.06 mmol/g of SH was almost without odor.

Acid hydrolysis of polymer dithiocarbonates was not accompanied by a significant degradation of residual quaternary ammonium groups to benzyl alcohol units **5** and trimethylamine as follows from elemental analysis.

Alkylation of sodium sulfide was a new procedure tested on a macroporous highly crosslinked ion exchanger (iii) in analogy to the low-molecular-weight trialkylbenzylammonium salts^{11,12}. With a low-molecular-weight alkylating reagent, both sodium sulfide and sodium hydrogensulfide, give predominantly sulfide rather than thiol. The reaction afforded a 38% conversion of quaternary ammonium groups to thiol (1.69 mmol thiol/g) after 5 h. The increase in the reaction time to 12 h increased the yield of thiol to 57% (2.56 mmol/g) while the hydrolysis of quaternary ammonium groups to alcohol **5** and trimethylamine was significantly enhanced ((vi), 17% of the quaternary ammonium base, calculated from N and S analyses) due to high pH of the sodium sulfide solution. The degradation is not significant after 5-h treatment. In contrast to low-molecular-weight analogs^{11,12}, no significant amounts of dialkyl sulfides are formed in the resin (as found from N and S analyses), probably for steric reasons. Longer reaction times caused no significant increase in the thiol group contents but led to hydrolysis of residual quaternary ammonium groups (vi).

This route involves a single-step process in water and affords high yields without the necessity of using the relatively expensive xanthogenate.

The reaction of polymeric trialkyl(benzyl)ammonium salt with sulfur nucleophiles is accompanied by side reactions. Especially in strongly alkaline sodium sulfide solutions, quaternary ammonium group is hydrolyzed

to alcohol and trimethylamine (vi). Titration curves did not show the presence of weakly basic tertiary amines which would be formed by splitting off methanol from the quaternary ammonium hydroxide (vii). The extent of this side reaction is calculated from N and S analyses taking into account weight changes caused by different molecular weights of the groups taking part in modifications. As a result, the conversion of ammonium groups to thiol (iii) is 40% and that of hydrolysis (vi) 19% in the reaction with sodium sulfide. In the first step of xanthate modification (i), the conversion is 41% for the reaction with xanthate and 13% for hydrolysis.

The reaction of an alkylating agent with thiourea and subsequent hydrolysis of the isothiuronium salt intermediate to thiol is another widely used method of thiol preparation known with low-molecular-weight compounds, quaternary ammonium salt being also considered as an alkylating agent¹⁵. Hydrolysis is usually performed under alkaline conditions¹⁶ (see steps (iv) and (v) in Scheme 1 for the polymer synthesis). This method, however, gives unsatisfactory results with polymers. The reaction of quaternary ammonium groups with thiourea (iv) gave only a poor yield (8%, 0.31 mmol/g), even after 24 h of the reaction. Subsequent hydrolysis of isothiuronium salt to thiol in alkaline medium (v) yielded the polymer containing 0.29 mmol thiol/g (7% overall yield). The hydrolysis of quaternary ammonium groups to benzyl alcohol did not significantly take place.

In all the cases, it was not possible to react more than 57% of the quaternary ammonium groups with a sulfur nucleophile even by a prolonged treatment (probably due to steric reasons in the resin). Such behavior is similar to that of another anion exchanger with quaternary ammonium groups, Ostion ATP 3011 where, after the reaction, 1.77 mmol SH/g, 0.94 mmol N/g and 65% conversion were found². Under drastic conditions, degradation of quaternary ammonium groups (vi) takes place instead. In Table I are summarized reaction yields of different routes used for introduction thiol groups. Polymer **3d** was only taken for more detailed sorption characterization because the conversion of quaternary to thiol (and thus capacity for selective binding of heavy metals) is the highest.

¹³C NMR Spectra

For the spectra and structure–signal correlation, see Fig. 1. The correlation with simulated spectra has proved the structure and gave an indirect proof of the presence of thiol groups (chemical shift of the thiol-bearing carbons).

Acid-Base Properties (Titration Curves)

No weakly basic or acid groups were found by titration of thiol sorbents **3a–3e**. This shows that the reaction proceeded without cleavage (vii) of the quaternary ammonium groups to polymeric tertiary amine and methanol. The pK of the thiol groups is probably too low to be titratable in aqueous medium.

TABLE I
Thiol polymers

Thiol polymer	Preparation route	N %	S %	Thiol mmol/g	Quaternary ammonium mmol/g	Total conversion %
3a	(i), (ii-a)	3.66	7.40	2.03	2.61	37.40
3b	(i), (ii-b)	3.54	6.62	2.06	2.53	47.80
3c	(iii) 5 h	3.86	5.43	1.69	2.75	30.90
3d	(iii) 12 h	1.56	8.22	2.56	1.11	53.90
3e	(iv), (v)	5.51	0.95	0.29	3.94	7.00

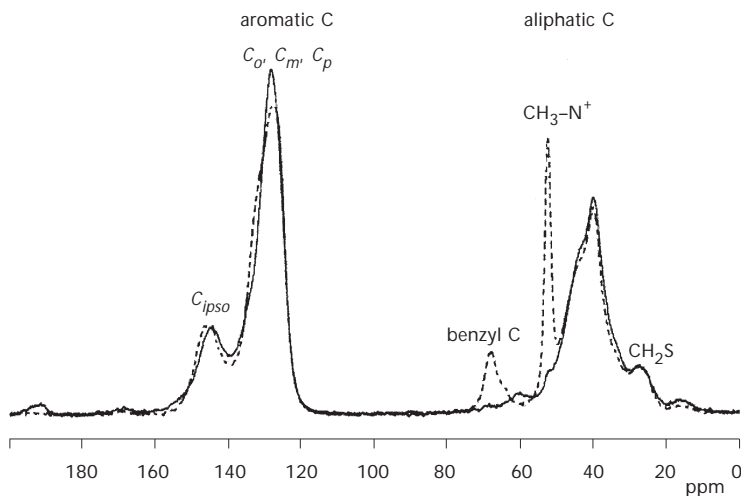


FIG. 1
 ^{13}C NMR spectra of starting quaternary ammonium polymer **1** (---) and thiol polymer **3d** (—)

Sorption Experiments

The sorption of arsenate on resins was measured as a function of time for different initial pH and concentrations of As(V). The results show that the sorption on the investigated resins is slow like all sorptions with a complexing reaction (Figs 2–4). The relative rate of equilibrium arsenate sorption is nearly independent of the starting concentration. The sorption

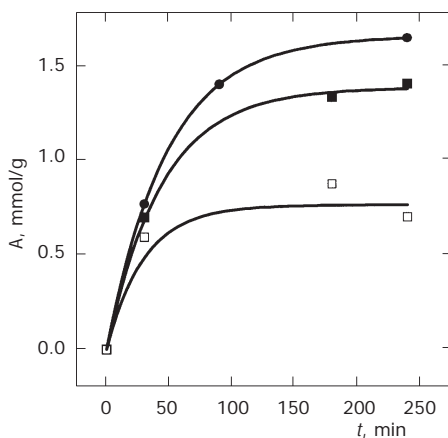


FIG. 2

Time dependence of arsenate sorption capacity A for $c_0 = 0.2$ mol/l on polymer **3d** at various pH: ● 2, ■ 6, □ 8

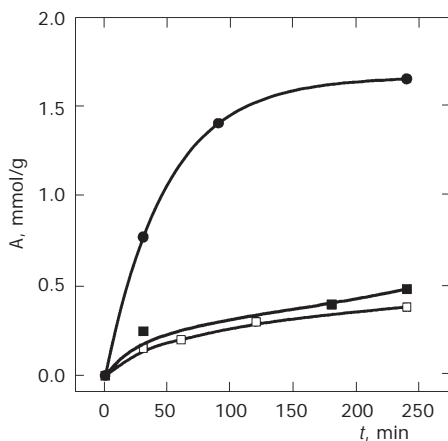


FIG. 3

Time dependence of arsenate sorption capacity A on polymer **3d** at pH 2 and various starting concentrations c_0 (in mol/l): □ 0.01, ■ 0.05, ● 0.2

rate on thiol resin **3d** slightly decreases with decreasing pH. The equilibrium capacity is higher at lower pH (Figs 2 and 5). The effect of pH on the equilibrium capacity of polymer **7** has the same trend but much more steep (Fig. 6). Despite that, the relative rate of sorption decreases only slightly with decreasing pH, similarly to **3d** resin. The maximum values of the equilibrium sorption are 1.65 and 3.78 mmol As per g of dry resin **3d** and **7**, respectively. The highest sorption occurs in a strongly acidic medium (pH 2)

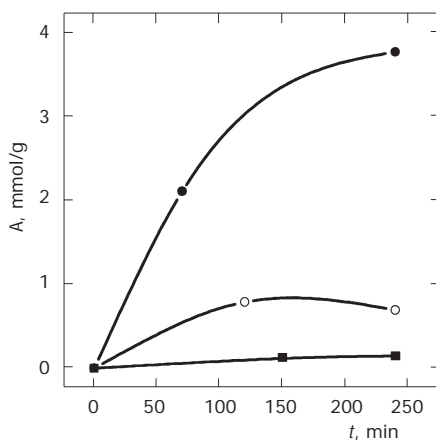


FIG. 4

Time dependence of arsenate sorption capacity A on polymer **7** at pH 2 and various starting concentrations c_0 (in mol/l): ■ 0.01, ○ 0.05, ● 0.2

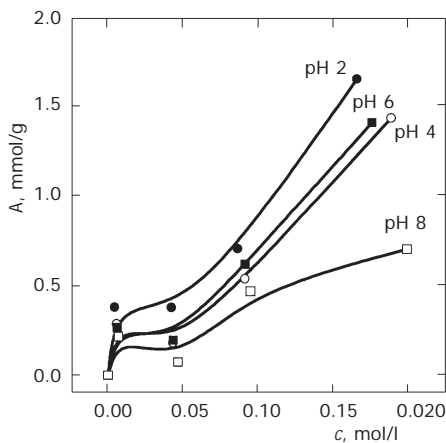


FIG. 5

Sorption isotherms (equilibrium sorption capacity vs equilibrium concentration) of arsenate on polymer **3d** at various pH: ● 2, ○ 4, ■ 6, □ 8

and then it rapidly decreases with increasing pH for resin 7. This decrease is much lower with **3d** resin being significant only at pH 8.8.

Neither the Freundlich nor Lagmuir isotherm fits well the data, which is probably caused by two different modes of arsenate sorption – specific (interaction with thiol or its Fe^{3+} complex at low concentrations) and non-specific (simple ion exchange with the remaining quaternary ammonium groups, significant mainly at higher concentrations).

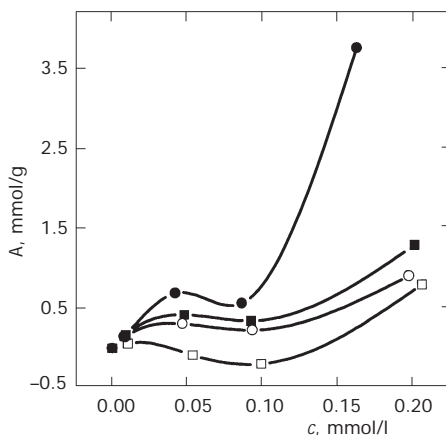


FIG. 6

Sorption isotherms (equilibrium sorption capacity vs equilibrium concentration) of arsenate on polymer 7 at various pH: ● 2, ○ 4, ■ 6, □ 8

CONCLUSIONS

Sorbents with thiol and quaternary ammonium groups were prepared from macroporous styrene-divinylbenzene strongly basic anion exchangers using four synthetic routes. The obtained thiol group contents were 2.56 mmol/g (reaction with sodium sulfide, (iii)), 2.06 mmol/g (reaction with potassium ethyl xanthate followed by acid hydrolysis, (i) and (ii-b)), 2.03 mmol/g (reaction with potassium *O*-ethyl dithiocarbonate followed by alkaline hydrolysis, (i) and (ii-b)) and 0.29 mmol/g (reaction with thiourea, (iv) and (v)). Thiol sorbent **3d** was loaded with Fe^{3+} ions for ligand-exchange experiments with arsenate. Sorption of As(V) from aqueous solutions with both these sorbents proved to be highly effective.

The authors thank the Grant Agency of the Czech Republic (Project No. 203/01/1310) for financial support.

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