



## Oxidation of As(III) in aqueous solutions by means of macroporous redox copolymers with *N*-chlorosulfonamide pendant groups

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### ABSTRACT

The possibility of oxidizing As(III) to As(V) in aqueous solutions by means of heterogeneous oxidants, i.e. synthetic macromolecular redox compounds, was studied. The materials contain *N*-chlorosulfonamide functional groups in the sodium form: [P]–SO<sub>2</sub>NCINa (R/ClNa, 2.1 mmol/g) or in the hydrogen form: [P]–SO<sub>2</sub>NClH (R/ClH, 2.4 mmol/g), attached to a cross-linked macroporous poly(styrene-divinylbenzene) matrix. They were obtained through the transformation of *Amberlyst 15* (Rohm and Haas) commercial cation exchanger's sulfonic functional groups. The experiments were conducted in the H<sub>2</sub>O and 0.01 M NaOH environment (R/ClNa) and in the H<sub>2</sub>O and 0.01 M H<sub>2</sub>SO<sub>4</sub> environment (R/ClH), using the batch process and the column process and NaAsO<sub>2</sub> solutions (93–375 mg As(III)/dm<sup>3</sup>). The experiments showed that the two copolymers' capacity to oxidize As(III) is high and depends on the process conditions. In the column process experiments, conducted using NaAsO<sub>2</sub> solutions with a concentration of ~93 mg As(III)/dm<sup>3</sup> at a flow rate of 4 BV/h (R/ClH) and 6 BV/h (R/ClNa), a breakthrough (defined as the exceedance of 0.05 mg As(III)/dm<sup>3</sup> in the effluent) would occur after the solutions amounting to about 400 bed volumes had been passed through the column.

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### 1. Introduction

Inorganic arsenic compounds are toxic to living organisms, and those present in natural waters pose a major environmental problem today. Since 1987 they have been listed by the International Agency for Research on Cancer (IARC) as compounds proven to be carcinogenic to humans [1].

The threats posed by arsenic are connected with its high concentrations in natural waters (mainly ground waters) used as a source of drinking water. At the beginning of the 21st century the allowable arsenic content in drinking water was reduced from 0.05 to 0.01 mg/dm<sup>3</sup>, but the water drawn from natural intakes often does not meet this standard, particularly in Asia, South America and also in many European countries (Slovakia, Hungary, Croatia, the UK, France) [2–8].

Currently intensive research aimed at developing effective technologies to bring the arsenic concentration in water down to the standard level is being conducted all over the world. The research covers adsorption, ion exchange, precipitation and biological processes [9–13]. The oxidation of As(III) to As(V) receives much attention due to the fact that most of the technologies used to remove arsenic compounds from water, including the Best

Available Technologies (BAT), are rather ineffective towards As(III) [14–17]. This applies particularly to processes, such as ion exchange or adsorption, used in the removal of impurities from dilute solutions.

The principal factor taken into consideration in the design of a technology for removing arsenic from water is the oxidation state in which the arsenic occurs. In the water environment this element occurs (in the form of arsenites and arsenates) in the +3 and +5 oxidation state. However, in the most often affected ground waters mainly As(III) compounds, characterized by a much higher toxicity than arsenates, are present. It is characteristic of arsenites that they occur in the undissociated form in the pH range typical for natural waters (pK<sub>a1</sub> = 9.2, pK<sub>a2</sub> = 12.1, pK<sub>a3</sub> = 13.4; H<sub>3</sub>AsO<sub>3</sub>, H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>, HAsO<sub>3</sub><sup>2-</sup>), whereas As(V) compounds occur in the dissociated form (pK<sub>a1</sub> = 2.2, pK<sub>a2</sub> = 7.1, pK<sub>a3</sub> = 11.5; H<sub>3</sub>AsO<sub>4</sub>, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup>) in natural waters. Since most methods of removing arsenic from water are ineffective towards undissociated molecules, the presence of As(III) compounds makes it difficult to reduce the total arsenic content to the permissible level.

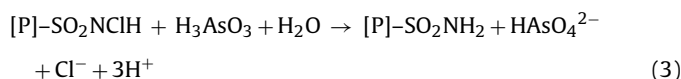
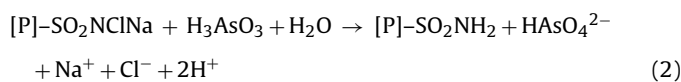
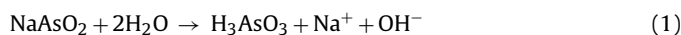
The oxidation of As(III) to As(V) is critical to any technology of arsenic removal from water. One could use micromolecular, homogeneous oxidants (e.g. chlorine and its derivatives) for this purpose. However, due to the fact that in waters arsenic occurs in a relatively small concentration (which needs to be reduced to below 0.01 mg/dm<sup>3</sup>), the adverse effect of the homogeneous oxidant (the excess of which lowers the quality of the treated water) poses a problem. Research is underway on the use of inorganic heteroge-

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neous oxidants (manganese or iron oxides). Natural and synthetic manganese minerals, e.g. birnessite, form the main group of such materials. Also (hydrated) iron oxides, used mainly as adsorbents of arsenic compounds, show some capacity to oxidize As(III) in certain conditions. The drawback of these materials is their physical form, making it difficult to run the processes in column conditions due to the high hydraulic resistance of the beds, and the fact that impurities may get into the cleaned water [18–23]. Intensive research into the synthesis and use of hybrid materials containing iron or manganese oxides permanently dispersed in the structure of micro- or macroporous cross-linked organic polymers has been underway for several years now. Such materials combine the very good oxidizing and/or adsorptive properties of manganese and iron oxides with the excellent hydraulic properties of organic ion exchangers usually used as the feedstock for the synthesis of hybrid polymers [24–29].

In the present study, heterogeneous synthetic redox polymers–copolymers of styrene and divinylbenzene, with *N*-chlorosulfonamide groups in the sodium form (R/ClNa) and in the hydrogen form (R/ClH) – have been used for the first time to oxidize As(III) contained in aqueous solutions. The macroporous structure of the polymer matrix makes for excellent column process hydraulic conditions and active chlorine (oxidation degree +1) endows the materials with strongly oxidizing character. The aim of the study was to examine the possibilities of oxidizing As(III) to As(V) in accordance with the following reactions:



[P] stands for the copolymer styrene/divinylbenzene macroporous structure.

The experiments were conducted in a water environment with different pH values, in both batch and column conditions.

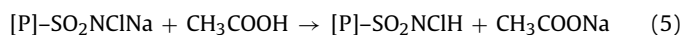
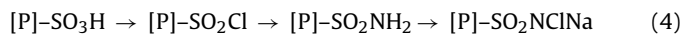
The R/ClNa copolymer is a macromolecular analogue of Chloramine-T (*N*-chloro-*p*-toluenesulfonamide sodium salt) – a well-known water-soluble micromolecular oxidizing and disinfecting agent. The copolymer's hydrogen form has no equivalent among micromolecular compounds since the *N*-chloro-*p*-toluenesulfonamide acid forming after Chloramine-T aqueous solution is treated with mineral acid, quickly undergoes disproportionation producing *N,N*-dichloro-*p*-toluenesulfonamide and *p*-toluenesulfonamide. The R/ClH copolymer was obtained and tested in the course of research on the oxidation of nitrites by means of the R/ClNa copolymer. By replacing the sodium atoms with hydrogen atoms in the functional groups of the *N*-chlorosulfonamide copolymer a new heterogeneous oxidant highly effective in oxidizing nitrites contained in aqueous solutions was obtained [30]. In contrast, the copolymer with its functional groups in the sodium form was inactive towards nitrites.

## 2. Experimental

### 2.1. Reagents

Copolymers having *N*-chlorosulfonamide groups in the sodium or hydrogen form were prepared in accordance with the methods

described previously [30–32]:



*Amberlyst 15* (Rohm and Haas) – a commercially available sulfonate cation exchanger – was used as the starting material. It is a macroporous poly(S/20%DVB) resin containing 4.7 mmol  $-\text{SO}_3\text{H/g}$  in the dry state (surface area 45 m<sup>2</sup>/g, average pore diameter 25 nm). The end product contained 2.1 mmol/g  $-\text{SO}_2\text{NCINa}$  groups (i.e. 4.20 mequiv of active chlorine/g) and 0.70 mmol/g  $-\text{SO}_3\text{Na}$  groups. The *N*-chlorosulfonamide groups were transformed from the sodium form into the hydrogen form by treating the R/ClNa product with an excess of 0.05 M CH<sub>3</sub>COOH. The R/ClNa resin was placed in a glass column and was washed first with 0.05 M CH<sub>3</sub>COOH and then with distilled water. For a sample containing 50 mequiv of active chlorine (~12.5 g of resin), 1.0 dm<sup>3</sup> of the acid was used. The product was analysed after drying to a constant weight at normal conditions. The active chlorine content of the hydrogen form resin was 4.80 mequiv/g.

All the reagents were of analytical grade. The arsenite stock solution (1 mg As(III)/cm<sup>3</sup>) was prepared from sodium (meta)arsenite NaAsO<sub>2</sub> (Fluka, purity > 99%). The solutions used in the investigations contained arsenic alone or in a mixture with sulphuric acid or with sodium hydroxide. The solutions used in the batch regime experiments were: NaAsO<sub>2</sub> (375 mg As(III)/dm<sup>3</sup>) in (a) water, (b) 0.01 M H<sub>2</sub>SO<sub>4</sub> and (c) 0.01 M NaOH. The solutions used in the experiments in the dynamic regime were: NaAsO<sub>2</sub> (93 mg As(III)/dm<sup>3</sup>) in (a) water, (b) 0.01 M H<sub>2</sub>SO<sub>4</sub> and (c) 0.01 M NaOH.

### 2.2. Analytical methods

The active chlorine content in the heterogeneous oxidants (R/ClNa, R/ClH) was determined by the iodometric method modified by the longer interaction of the reagents.

Arsenic determinations (for concentrations > 0.05 mg/dm<sup>3</sup>) were carried out using the spectrophotometric molybdenum blue method (Spekol 1200, Specord 210, Analytical Jena, Germany). Arsenate ions formed a colourless antimonyl–arsenomolybdate complex, which was reduced with ascorbic acid, producing a blue species. The absorbance measurement was taken at 730 or 880 nm, depending on the desired sensitivity [33]. Since arsenite does not form the molybdenum complex, the obtained absorbance value was for arsenate only. In order to determine the total arsenic concentration, prior to the analysis an oxidizing agent (potassium iodate) was used to convert As(III) into As(V). The arsenite concentration was calculated as the difference between the total arsenic concentration and the arsenate concentration [34]. For arsenic concentrations lower than 0.05 mg/dm<sup>3</sup>, hydride generation atomic absorption spectrometry HG AAS with a graphite tube (AAS Avanta) was used. As(III) and As(V) were first separated using a strong-base anion exchange resin (Amberlite IRA 402Cl), after adjusting the pH to 4.0–4.2 [35]. This technique was validated by using solutions with known arsenite and arsenate concentrations.

Chloride ions were estimated by argentometric titration, using 0.01 M AgNO<sub>3</sub> with a system of Ag/AgCl/calomel electrodes.

### 2.3. Batch oxidation studies

In all the experiments carried out in the batch regime at room temperature, a measured amount of the resin (ca. 0.24 g R/ClNa or 0.21 g R/ClH) placed in a flask was shaken mechanically with 50 cm<sup>3</sup> (100% excess of active chlorine) or 200 cm<sup>3</sup> (100% excess of arsenite) of NaAsO<sub>2</sub> solution (375 mg As(III)/dm<sup>3</sup>). Time-dependent measurements of the As(III) and As(V) content in the solution were performed. After the reaction the polymeric reagent was separated

**Table 1**  
Analytical data of the reaction in the batch regime between R/CINa resin and arsenite solution (an 100% excess of NaAsO<sub>2</sub> in relation to stoichiometry).

	0.24 g R/CINa + 200 cm <sup>3</sup> NaAsO <sub>2</sub> solution (375 mg As(III)/dm <sup>3</sup> )	
	In water	In 0.01 M NaOH
<i>Concentration of arsenite, mg/L</i>		
Before reaction	375	375
After reaction (24 h)	226	267
<i>pH value</i>		
Before reaction	10.6	12.3
After reaction	9.3	12.2
<i>Active chlorine in a sample of R/CINa, mmol</i>		
Before reaction	0.5	0.5
After reaction	0.10	0.16

**Table 2**  
Analytical data of the reaction in the batch regime between R/CIH resin and arsenite solution (an 100% excess of NaAsO<sub>2</sub> in relation to stoichiometry).

	0.21 g R/CIH + 200 cm <sup>3</sup> NaAsO <sub>2</sub> solution (375 mg As(III)/dm <sup>3</sup> )	
	In water	In 0.01 M H <sub>2</sub> SO <sub>4</sub>
<i>Concentration of arsenite, mg/L</i>		
Before reaction	375	375
After reaction (24 h)	193	190
<i>pH value</i>		
Before reaction	10.6	2.0
After reaction	3.5	1.9
<i>Active chlorine in a sample of R/CIH, mmol</i>		
Before reaction	0.50	0.50
After reaction	0.01	0.01

from the reaction medium by filtration and was analysed for active chlorine content.

Initially in the batch oxidation studies a double excess of As(III) relative to the reaction (reactions 2 and 3) stoichiometry was used. The aim was to determine the capacity of the R/CINa and R/CIH copolymers to oxidize As(III) in various environments. The experiments were conducted in water alone (for both redox polymers) as well as in 0.01 M NaOH (R/CINa) and in 0.01 M H<sub>2</sub>SO<sub>4</sub> (R/CIH).

#### 2.4. Column tests

Column experiments were carried out using glass columns (1.0 cm diameter and 250 mm length) and pumps (GILSON Minipuls 3, KNAUER K 500) to ensure a constant flow rate. A sample of R/CINa ((a) 4.35 g in the dry state, ~8.7 cm<sup>3</sup> after swelling in water, (b) 7.75 g in the dry state, ~15.7 cm<sup>3</sup> after swelling in water) or R/CIH resin ((a) 4.2 g in the dry state, ~8.3 cm<sup>3</sup> after swelling in water, (b) 7.75 g in the dry state, ~15.3 cm<sup>3</sup> after swelling in water) was packed into the column. Then NaAsO<sub>2</sub> solutions (93 mg As(III)/dm<sup>3</sup>, in water and 0.01 M NaOH for R/CINa, in water and 0.01 M H<sub>2</sub>SO<sub>4</sub> for R/CIH) were passed through the copolymer beds. The examined flow rates ranged from 4 to 18 bed volumes/h. Fractions (100, 250 cm<sup>3</sup>) were collected to estimate their composition in terms of pH, arsenate, arsenite and chloride ion concentrations.

### 3. Results and discussion

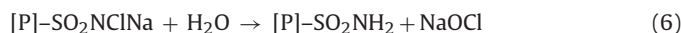
Because of the high active chlorine content in the redox copolymers, As(III) solutions with very high concentrations (93–375 mg As/dm<sup>3</sup>), many times exceeding the As(III) concentrations in natural waters, were used in the experiments. Thanks to this choice of reagents both the stationary and column experiments could be carried out efficiently in a relatively short time. The experimental results provided a good basis for planning further experiments using dilute As(III) solutions with concentrations close to those found in practice.

It should be added that aqueous solutions of NaAsO<sub>2</sub>, i.e. reagents with the simplest chemical composition, have a pH of about 10.6 (according to reaction (1), which is rather far from neutral pH).

#### 3.1. Batch oxidation studies

The results indicate that the *N*-chlorosulfonamide polymer in the sodium form shows a particularly high efficiency with which it oxidizes As(III) to As(V) in a weakly alkaline environment. In this environment its oxidizing capacity amounted to 1.81 mmol As(III)/g (Table 1). After 24 h of the reaction the concentration of As(III) in the aqueous solution decreased by 39.8% (78.8% of the redox polymer's oxidizing capacity used) and the unused amount

of active chlorine (calculated per 0.1 mmol) was almost identical to the amount in the polymer, determined after the reaction. In the strongly alkaline medium (0.01 M NaOH) the redox polymer's oxidizing capacity was 1.3 mmol As(III)/g and the As(III) concentration decreased by 28.7% (56.8% of the polymer's oxidizing power used) in the course of the reaction. The amount of active chlorine determined in the copolymer when the processes ended was found to be ca. 25% smaller than the one calculated from the change in the As(III) concentration. This was due to the release of some of the active chlorine from the copolymer's functional groups in accordance with the reaction:



The NaOCl present in the solution was not fully used in the oxidation of As(III) because of the unfavourable alkaline environment.

The *N*-chlorosulfonamide copolymer in the hydrogen form was found to be a very effective oxidant of As(III) in both water alone and in 0.01 M H<sub>2</sub>SO<sub>4</sub>. It appears from Table 2 that thanks to the use of the R/CIH, the As(III) concentration in the two solutions decreased almost by half. In the experimental conditions, in which it is theoretically possible to oxidize 50% of the As(III) present in the solution, its concentration decreased by 48.6% in water (96.5% of the active chlorine used) and by 49.6% in 0.01 M H<sub>2</sub>SO<sub>4</sub> (98.5% of the active chlorine used). The calculated oxidizing capacity of the R/CIH amounted to respectively 2.32 mmol As(III)/g and 2.36 mmol As(III)/g, which is evidence of the nearly total use of the redox polymer's oxidizing capacity. The active chlorine present in the copolymer's functional groups was practically used up whereby chlorides (in the amount of 0.5 mmol) appeared in the solution.

According to Table 2, the oxidation of As(III) by means of R/CIH was accompanied by a marked decrease in the pH from 10.6 to 3.5. It was found, that the presence of 0.01 M H<sub>2</sub>SO<sub>4</sub> in the environment was not necessary to aid reaction (3), which without the acid practically ran its full course.

The almost identical efficiency of the reaction in the two environments is due to the fact that the R/CIH polymer considerably reduces the pH of the reaction medium, and consequently the oxidation process in both cases proceeded at a similarly low pH. This is confirmed by results obtained in studies on the oxidizing power of this redox copolymer. The formal redox potential of the reaction system with R/CINa copolymer was high and similar in water alone and in the 0.01 M H<sub>2</sub>SO<sub>4</sub> environment [36]. The increased acidity of the solution is mainly due the oxidation of As(III) to As(V) (reactions (2) and (3)), but the hydrogen ions introduced into the solution are not neutralized as in the case of the functional groups in the sodium form.

In order to examine the suitability of the redox copolymers for the so-called deep oxidation of arsenic, which is vital for the removal of minute quantities of this element from water, further experiments were carried out using a double excess of oxidant

**Table 3**

Analytical data of the reaction in the batch regime between R/CINa resin and arsenite solution (an 100% excess of active chlorine in relation to stoichiometry).

	0.24 g R/CINa + 50 cm <sup>3</sup> NaAsO <sub>2</sub> solution (375 mg As(III)/dm <sup>3</sup> )	
	In water	In 0.01 M NaOH
<i>Concentration of arsenite, mg/L</i>		
Before reaction	375	375
After reaction (24 h)	7.7	43
<i>pH value</i>		
Before reaction	10.6	12.2
After reaction	6.8	11.5
<i>Active chlorine in a sample of R/CINa, mmol</i>		
Before reaction	0.50	0.50
After reaction	0.205	0.215

(active chlorine in the functional groups of the polymer) relative to the stoichiometric amount. The obtained results confirmed the very high oxidizing efficiency of the synthesized heterogeneous redox polymers with regard to As(III). After the 24-h-long reaction the As(III) concentration in the solutions decreased from 375 mg/dm<sup>3</sup> to as low as 8 mg/dm<sup>3</sup> (Tables 3 and 4).

A poorer result was obtained only for the reaction carried out using R/CINa copolymer in the 0.01 M NaOH environment. This is in accordance with previous studies on the oxidation of cyanides, thiocyanates and sulfides by means of R/CINa copolymer [37–39]. Despite the unfavourable (for oxidation) strongly alkaline environment, the process efficiency amounted to 88% (Table 3). An analysis of the amount of active chlorine remaining in the copolymer's functional groups after the oxidation process showed that it quite closely corresponded to the theoretical amount calculated from reactions (2) and (3). This indicates that the functional groups are stable in the water environment and that the redox polymer can precisely “dose” the oxidant proportionally to the amount of the reductant in the solution. Figs. 1 and 2 additionally show changes in the As(III) concentration in the first 8 h of the reaction for the two copolymers. Besides the clearly lower efficiency in the 0.01 M NaOH environment one can notice that the oxidation of As(III) by the R/CIH copolymer is slower than that by the R/CINa copolymer. Hence it appears that the R/CIH copolymer, even though it shows a higher oxidizing capacity and is capable of oxidizing practically the total amount of As(III) present in the solution, requires a longer contact time, which may be of significance for column processes.

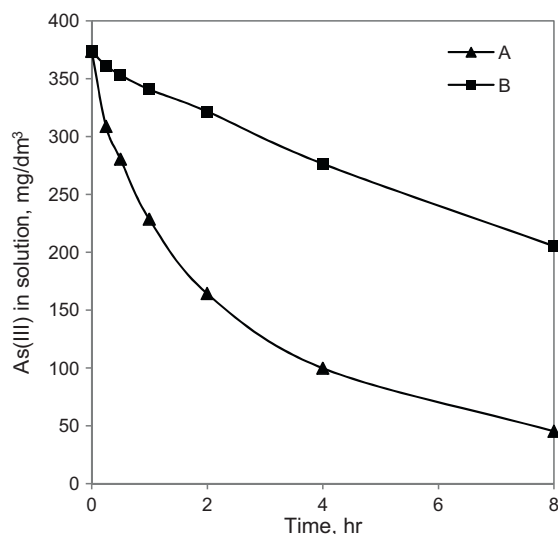
### 3.2. Column tests

In the first stage of the column tests, the NaAsO<sub>2</sub> solutions (93 mg As(III)/dm<sup>3</sup>) with different acidity were passed at a flow rate of 18 BV/h through R/CINa and R/CIH beds, each containing 10 mmol (20 mequiv) of active chlorine. First the R/CINa bed and an aqueous solution of NaAsO<sub>2</sub> with pH = 10.6 were used as the

**Table 4**

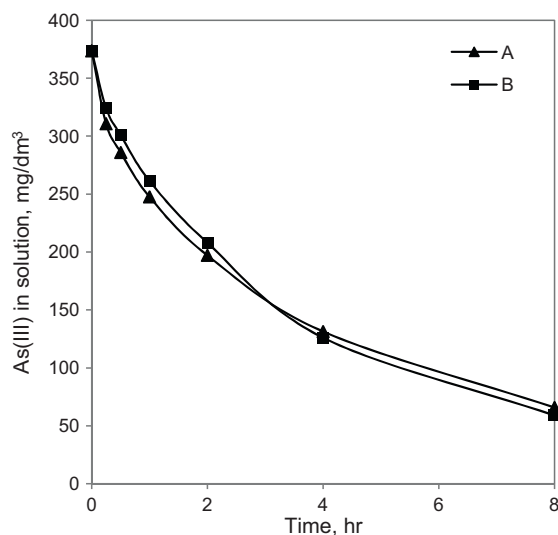
Analytical data of the reaction in the batch regime between R/CIH resin and arsenite solution (an 100% excess of active chlorine in relation to stoichiometry).

	0.21 g R/CIH + 50 cm <sup>3</sup> NaAsO <sub>2</sub> solution (375 mg As(III)/dm <sup>3</sup> )	
	In water	In 0.01 M H <sub>2</sub> SO <sub>4</sub>
<i>Concentration of arsenite, mg/L</i>		
Before reaction	375	375
After reaction (24 h)	16	24
<i>pH value</i>		
Before reaction	10.6	2.0
After reaction	2.3	1.7
<i>Active chlorine in a sample of R/CIH, mmol</i>		
Before reaction	0.50	0.50
After reaction	0.23	0.24

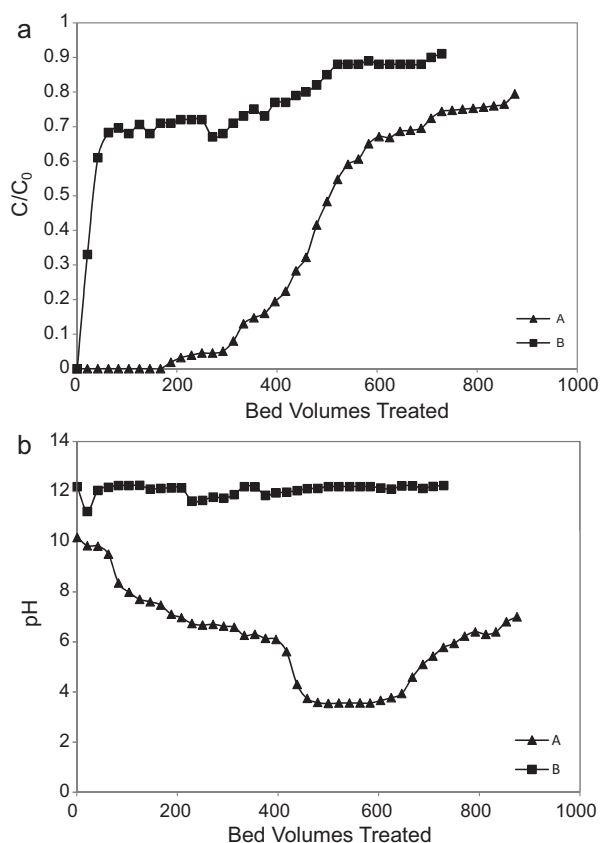


**Fig. 1.** Decrease of As(III) concentration in a batchwise reaction: (A) in water, (B) in 0.01 M NaOH. 0.24 g of R/CINa + 50 cm<sup>3</sup> NaAsO<sub>2</sub> solution (375 mg As(III)/dm<sup>3</sup>).

reagents. Fig. 3 shows the breakthrough curve (Fig. 3a, curve A). The obtained results confirm the copolymer's capacity to oxidize As(III) in a close to neutral environment. Despite the high flow rate of the solution through the bed and the relatively high concentration of As(III) (~93 mg/dm<sup>3</sup>), a breakthrough (at this stage defined as the exceedance of  $c/c_0 = 0.05$ ) occurred at BV = ~170, after 1200 cm<sup>3</sup> of the solution had passed through the bed. The operating capacity of R/CINa to oxidize As(III) amounted to 0.34 mmol As(III)/g of the copolymer (25.5 mg As(III)/g). After the breakthrough the oxidation process continued and the As(III) concentration in the column effluent reached half the initial concentration value after 3620 cm<sup>3</sup> of the As(III) solution (BV = 510) had passed through the column. The calculated total oxidizing capacity of the copolymer in those conditions amounted to 1.03 mmol As(III)/g (77.2 mg As(III)/g). This value is much lower than what appears from the active chlorine content in the copolymer. This is due to the high flow rate of the NaAsO<sub>2</sub> solution, making it difficult to fully use the copolymer's oxidizing power. It should be noted that the redox reactions proceed much slower than the ion exchange reactions and in addition, the reagents here occur in different phases.



**Fig. 2.** Decrease of As(III) concentration in a batchwise reaction: (A) in water, (B) in 0.01 M H<sub>2</sub>SO<sub>4</sub>. 0.21 g of R/CIH + 50 cm<sup>3</sup> NaAsO<sub>2</sub> solution (375 mg As(III)/dm<sup>3</sup>).



**Fig. 3.** (a) Arsenite breakthrough curve for R/CINa resin in the column; influx  $\text{NaAsO}_2$  ( $93 \text{ mg As(III)/dm}^3$ ) in: (A) water, (B) 0.01 M NaOH, flow rate 18 BV/h. (b) pH value of effluent.

The shape of the pH–effluent volume curve (Fig. 3b, curve A) requires a comment. In accordance with reaction (2), the reaction medium is acidified in the course of oxidation. Hydrogen ions are partially neutralized as a result of the ion exchange in the sodium-form *N*-chlorosulfonamide groups (whose  $\text{pK}_a$  is  $\sim 7.2$ ) [32]:

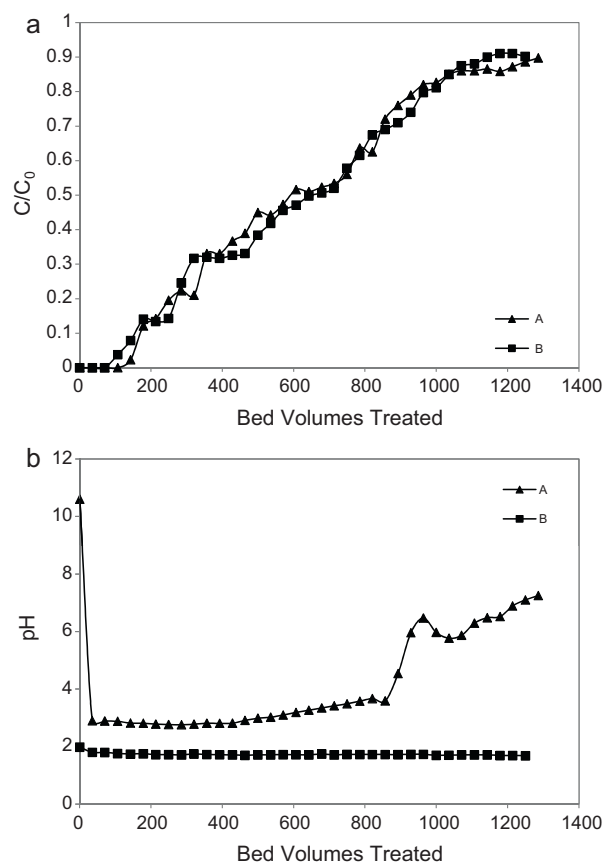


Once the ion-exchange capacity of the functional groups still present in the copolymer is exhausted, the neutralization stops and the oxidation reaction proceeds using the *N*-chlorosulfonamide transformed into the hydrogen form (consistently with reaction (3)). As a result, the pH of the effluent decreases to below 4. As the bed's oxidizing capacity is being exhausted, the reaction advancement slows down and even smaller amounts of hydrogen ions are introduced into the solution whereby the effluent's pH returns to its initial value.

Similar column tests were carried out for an identical R/CINa bed and an effluent in the form of a solution of  $\text{NaAsO}_2$  ( $93 \text{ mg As(III)/dm}^3$ ) in the 0.01 M NaOH environment. In this case, the results were not satisfactory: the R/CINa copolymer turned out to be ineffective as an As(III) oxidant since a breakthrough occurred already in the first fraction (Fig. 3a, curve B). It was found that at a pH of about 12 the reaction practically did not proceed.

The breakthrough curve for the R/CIH copolymer and  $\text{NaAsO}_2$  solution (Fig. 4a, curve A) and the one for an identical bed and a solution of  $\text{NaAsO}_2$  in 0.01 M  $\text{H}_2\text{SO}_4$  (Fig. 4a, curve B) show that the effectiveness of R/CIH is much lower than that of R/CINa.

In the case of the solution in the 0.01 M  $\text{H}_2\text{SO}_4$  environment, a bed breakthrough occurred after the oxidation of the As(III) (in the amount equivalent to 66 bed volumes) present in the solution (up to the breakthrough merely  $450 \text{ cm}^3$  of the solution had



**Fig. 4.** (a) Arsenite breakthrough curve for R/CIH resin in the column; influx  $\text{NaAsO}_2$  ( $93 \text{ mg As(III)/dm}^3$ ) in: (A) water, (B) 0.01 M  $\text{H}_2\text{SO}_4$ , flow rate 18 BV/h. (b) pH value of effluent.

been passed through the bed). The operating capacity of R/CIH to oxidize As(III) was  $0.13 \text{ mmol As(III)/g}$  of the copolymer ( $9.7 \text{ mg As(III)/g}$ ). In the case of the reaction in the aqueous solution, a bed breakthrough occurred after As(III) in the amount equivalent to 89 bed volumes had been oxidized (up to the breakthrough  $600 \text{ cm}^3$  of the solution had passed through the column) and the copolymer's operating oxidizing capacity amounted to  $0.18 \text{ mmol As(III)/g}$  ( $13.5 \text{ mg As(III)/g}$ ). Since in the acidic environment R/CIH shows a high oxidizing capacity, the oxidation process continued after the breakthrough. The As(III) concentration in the effluent reached half of the initial concentration after  $4080 \text{ cm}^3$  (BV = 600) and  $4454 \text{ cm}^3$  (BV = 655) of respectively water alone and 0.01 M  $\text{H}_2\text{SO}_4$  had been passed through the column. In those conditions the calculated total oxidizing capacity amounted to respectively  $1.21 \text{ mmol As(III)/g}$  ( $90.65 \text{ mg As(III)/g}$ ) and  $1.33 \text{ mmol As(III)/g}$  ( $99.6 \text{ mg As(III)/g}$ ). In the case of the reaction in the aqueous solution, the degree of use of the active chlorine present in the copolymer's functional groups amounted to 50%. A similar result (45%) was obtained for the R/CINa copolymer and an identical solution, but the oxidizing capacity was used differently. In the case of the R/CIH copolymer a bed breakthrough would occur early and subsequently the arsenic concentration in the effluent would slowly and uniformly increase. In the case of R/CINa copolymer a breakthrough would occur much later and was followed by a rapid increase in As(III) concentration. The previous observations (made in the batch process studies) concerning the poorer kinetics of As(III) oxidation by means of R/CIH in comparison with that of the As(III) oxidation by means of R/CINa were confirmed.

In the second stage of the column tests, the flow rate of the  $\text{NaAsO}_2$  solution through the copolymer beds was reduced to

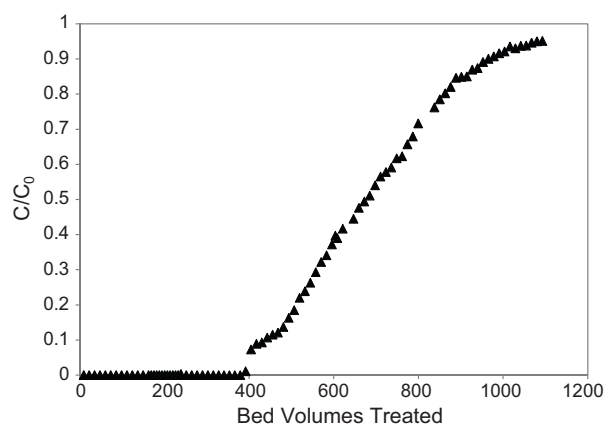


Fig. 5. Arsenite breakthrough curve for R/ClNa resin in the column; influent  $\text{NaAsO}_2$  ( $93 \text{ mg As(III)/dm}^3$ ) in water, flow rate 6 BV/h.

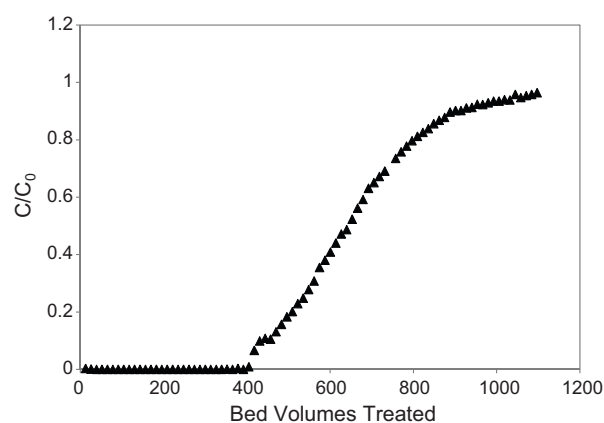


Fig. 6. Arsenite breakthrough curve for R/ClH resin in the column; influent  $\text{NaAsO}_2$  ( $93 \text{ mg As(III)/dm}^3$ ) in water, flow rate 4 BV/h.

6 BV/h (for R/ClNa) and to 4 BV/h (for R/ClH). The tests were carried out only for aqueous solutions of  $\text{NaAsO}_2$  without pH adjustment. As(III) and As(V) in collected fractions were separated using a strongly alkaline anion exchanger bed and As(III) was determined using HG AAS. Thanks to the deliberate variation of the flow rate of the  $\text{NaAsO}_2$  solution through the copolymer beds, the effectiveness of copolymer oxidizing capacity utilization markedly improved. The similar shape of the curves shown in Figs. 5 and 6 proves that the flow rates of the solutions through the beds were correctly matched to the oxidizing properties of the two redox polymers. The operating and total oxidizing capacities of the copolymers, determined from the breakthrough curves, amount to respectively  $0.96 \text{ mmol As(III)/g}$  and  $1.72 \text{ mmol As(III)/g}$  (R/ClNa) and  $0.968 \text{ mmol As(III)/g}$  and  $1.6 \text{ mmol As(III)/g}$  (R/ClH). It should be highlighted that the As(III) concentration in the collected fractions until the moment of bed breakthrough amounted to from a few to between  $10$  and  $20 \mu\text{g/dm}^3$ , while the initial concentration amounted to  $93 \text{ mg As(III)/dm}^3$  (the final concentration of As(III) constituted  $1/5000$  of the initial concentration).

#### 4. Conclusions

Thanks to the use of the synthetic macroporous redox copolymers with *N*-chlorosulfonamide pendant groups in the sodium ([P]– $\text{SO}_2\text{NCINa}$ ) and hydrogen form ([P]– $\text{SO}_2\text{NClH}$ ), the As(III) present in the water solutions was successfully oxidized to As(V) with a very high efficiency in various reaction conditions.

In the batch experiments the capacity of the two copolymers to oxidize As(III) was determined and it was found to be commensurate with the active chlorine content in them, amounting to  $1.81 \text{ mmol As(III)/g}$  for R/ClNa and  $2.32 \text{ mmol As(III)/g}$  for R/ClH. The acidity of the reaction medium was found to affect the course of oxidation of As(III) to As(V) by means of the heterogeneous oxidants – the reaction proceeded efficiently in the environment of  $\text{pH} < 10$ , whereas a strongly alkaline environment was not favourable to it. By conducting the experiments with an excess of the oxidant the As(III) concentration in the equilibrium solutions was reduced from  $375 \text{ mg/dm}^3$  to between  $10$  and  $20 \text{ mg/dm}^3$ , which indicates that the two polymeric reagents can be used in column conditions.

In the column experiments with the [P]– $\text{SO}_2\text{NCINa}$  bed, despite the use of a very high As(III) concentration ( $93 \text{ mg/dm}^3$ ) in the influent, the arsenic present in the solution was practically totally reduced. It was found that in the case of the [P]– $\text{SO}_2\text{NClH}$  bed a similar reaction requires a longer contact time. It should be noted that in both copolymer cases the As(III) concentration in the effluent from the column was reduced from a few to between  $10$  and  $20 \mu\text{g As(III)/dm}^3$ .

The obtained results show that beds made of the two copolymers can be successfully used for the removal of arsenic compounds from water. The use of an oxidizing bed (oxidation of As(III) to As(V)) before an adsorption bed or an ion-exchange bed (for removing As(V)) seems to be a good solution.

#### References

- [1] US Department of Health and Human Services, Toxicological Profile for Arsenic, Agency for Toxic Substances and Disease Registry, 2007, Retrieved: 11.07.2010, from: <http://www.atsdr.cdc.gov/toxprofiles/tp2.pdf>.
- [2] I. Villaescusa, J.-C. Bollinger, Arsenic in drinking water: sources, occurrence and health effects (a review), *Rev. Environ. Sci. Biotechnol.* 7 (2008) 307–323.
- [3] I. Celik, L. Gallicchio, K. Boyd, T.K. Lam, G. Matanoski, X. Tao, M. Shiels, E. Hammond, L. Chen, K.A. Robinson, L.E. Caulfield, J.G. Herman, E. Guallar, A.J. Alberg, Arsenic in drinking water and lung cancer: a systematic review, *Environ. Res.* 108 (2008) 48–55.
- [4] M. Bissen, F.H. Frimmel, Arsenic—a review. Part I: occurrence, toxicity, speciation, mobility, *Acta Hydrochim. Hydrobiol.* 31 (2003) 9–18.
- [5] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, *Talanta* 58 (2002) 201–235.
- [6] M. Clara, F. Magalhaes, Arsenic. An environmental problem limited by solubility, *Pure Appl. Chem.* 74 (2002) 1843–1850.
- [7] A.E. Schulman (Ed.), Arsenic Occurrence in Public Drinking Water Supplies, US Environmental Protection Agency, EPA-815-R-00-023, Washington, 2000.
- [8] Arsenic poisoning in Bangladesh/India, Retrieved: 14.12.2010, <http://www.sos-arsenic.net>.
- [9] K.-S. Ng, Z. Ujang, P. Le-Clech, Arsenic removal technologies for drinking water treatment, *Rev. Environ. Sci. Biotechnol.* 3 (2004) 43–53.
- [10] J.-Q. Jiang, Removing arsenic from groundwater for the developing world—a review, *Water Sci. Technol.* 44 (2001) 89–98.
- [11] P. Mondal, C.B. Majumder, B. Mohanty, Laboratory based approach for arsenic remediation from contaminated water: recent developments, *J. Hazard. Mater.* B137 (2006) 464–479.
- [12] T.S.Y. Choong, T.G. Chuah, Y. Robiah, F.L.G. Koay, I. Azni, Arsenic toxicity, health hazards and removal techniques from water: an overview, *Desalination* 217 (2007) 139–166.
- [13] D. Mohan, Ch. U. Pittman Jr., Arsenic removal from water/wastewater using adsorbents—a critical review, *J. Hazard. Mater.* 142 (2007) 1–53.
- [14] G. Ghurye, D. Clifford, As(III) oxidation using chemical and solid phase oxidants, *J. AWWA* 96 (2004) 84–96.
- [15] M. Bissen, F.H. Frimmel, Arsenic—a review. Part II: oxidation of arsenic and its removal in water treatment, *Acta Hydrochim. Hydrobiol.* 31 (2003) 97–107.
- [16] E. Kociotek-Balawejder, D. Ociński, Oxidation of As(III) to As(V) as a process aiding the removal of arsenic from water, *Przem. Chem.* 85 (2006) 1027–1030 (in polish).
- [17] G. Ghurye, D. Clifford, Laboratory Study on the Oxidation of Arsenic(III) to Arsenic(V), US Environmental Protection Agency, EPA-600-R-01-021, Houston, 2001.
- [18] A. Amirbahman, D.B. Kent, G.P. Curtis, J.A. Davis, Kinetics of sorption and abiotic oxidation of arsenic(III) by aquifer materials, *Geochim. Cosmochim. Acta* 70 (2006) 533–547.
- [19] O.X. Leupin, S.J. Hug, Oxidation and removal of arsenic(III) from aerated groundwater by filtration through sand and zero-valent iron, *Water Res.* 39 (2005) 1729–1740.

- [20] Ch. Tournassat, L. Charlet, D. Bosbach, A. Manceau, Arsenic(III) oxidation by birnessite and precipitation of manganese(II) arsenate, *Environ. Sci. Technol.* 36 (2002) 493–500.
- [21] B.A. Manning, S.E. Fendorf, B. Bostick, D.L. Suarez, Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite, *Environ. Sci. Technol.* 36 (2002) 976–981.
- [22] J.E. Greenleaf, L. Cumbal, I. Staina, A.K. SenGupta, Abiotic As(III) oxidation by hydrated Fe(III) oxide (HFO) microparticles in a plug flow columnar configuration, *Trans. IChemE* 81 (2003) 87–98.
- [23] P. Lakshminatharaj, B.R.V. Narasimhan, S. Prabhakar, G. Bhaskar Raju, Adsorption studies of arsenic on Mn-substituted iron oxyhydroxide, *J. Colloid Interface Sci.* 304 (2006) 317–322.
- [24] M.J. DeMarco, A.K. SenGupta, J.E. Greenleaf, Arsenic removal using a polymeric/inorganic hybrid sorbent, *Water Res.* 37 (2003) 164–176.
- [25] P. Sylvester, P. Westerhoff, T. Moller, M. Badruzzaman, O. Boyd, A hybrid sorbent utilizing nanoparticles of hydrous iron oxide for arsenic removal from drinking water, *Environ. Eng. Sci.* 24 (2007) 104–112.
- [26] C.M. Iesan, C. Capat, F. Ruta, I. Udrea, Evaluation of a novel hybrid inorganic/organic polymer type material in the arsenic removal process from drinking water, *Water Res.* 42 (2008) 4327–4333.
- [27] V. Lenoble, Ch. Chabroulet, R. al Shukry, B. Serpaud, V. Deluchat, J.-C. Bollinger, Dynamic arsenic removal on a MnO<sub>2</sub>-loaded resin, *J. Colloid. Interface Sci.* 280 (2004) 62–67.
- [28] V. Lenoble, Ch. Laclautre, B. Serpaud, V. Deluchat, J.-C. Bollinger, As(V) retention and As(III) simultaneous oxidation and removal on a MnO<sub>2</sub>-loaded polystyrene resin, *Sci. Total Environ.* 326 (2004) 197–207.
- [29] E. Kociołek-Balawejder, A. Ciechanowska, D. Ociński, E. Stanisławska, Method for producing of manganese dioxide containing hybrid copolymer, *Zgł. Pat. Pol.* (2009) 388431 (in polish).
- [30] R. Bogoczek, E. Kociołek-Balawejder, E. Stanisławska, Macromolecular *N*-chlorosulfonamide as an oxidant for residual nitrites in aqueous media, *Ind. Eng. Chem. Res.* 44 (2005) 8530–8534.
- [31] R. Bogoczek, E. Kociołek-Balawejder, *N*-monohalogeno- and *N,N*-dihalogeno-poly(styrene-co-divinylbenzene)/sulfonamides, *Polym. Commun.* 27 (1986) 286–288.
- [32] (a) R. Bogoczek, E. Kociołek-Balawejder, Kationity s chlorirujuscimi, oksidnielnymi i baktericidnymi svojstvami, *Vysokomol. Soyedin* 29 (A) (1987) 2346–2352; (b) R. Bogoczek, E. Kociołek-Balawejder, *Polym. Sci. U.S.S.R.* 29 (1987) 2580, Engl. edition.
- [33] V. Lenoble, V. Deluchat, B. Serpaud, J.-C. Bollinger, Arsenite oxidation and arsenate determination by the molybdenum blue method, *Talanta* 61 (2003) 267–276.
- [34] D.L. Johnson, M.E.Q. Pilon, Spectrophotometric determination of arsenite, arsenate, and phosphate in natural waters, *Anal. Chim. Acta* 58 (1972) 289–299.
- [35] M.-J. Kim, Separation of inorganic arsenic species in groundwater using ion exchange method, *Bull. Environ. Contam. Toxicol.* 67 (2001) 46–51.
- [36] R. Bogoczek, E. Kociołek-Balawejder, E. Stanisławska, Potentiometric studies of oxidation–reduction reactions with redox copolymers, *J. Appl. Polym. Sci.* 107 (2008) 2190–2195.
- [37] E. Kociołek-Balawejder, A redox copolymer having *N*-chlorosulfonamide groups for cyanide ion decomposition in dilute aqueous solutions, *React. Polym.* 33 (1997) 159–165.
- [38] E. Kociołek-Balawejder, A macromolecular *N*-chlorosulfonamide as oxidant for thiocyanates, *React. Polym.* 41 (1999) 227–233.
- [39] E. Kociołek-Balawejder, A copolymer with *N*-chlorosulfonamide pendant groups as oxidant for residual sulfides, *React. Funct. Polym.* 52 (2002) 89–97.