

Redox Polymer with *N,N*-Dichlorosulfonamide Functional Groups as Arsenite Oxidant in Aqueous Solutions

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ABSTRACT: A macroporous, styrene-divinylbenzene polymer with *N,N*-dichlorosulfonamide functional groups ($-\text{SO}_2\text{NCl}_2$), containing two chlorine atoms with oxidation number +1, have been prepared through the chemical modification of a commercial sulfonic cation exchanger (Amberlyst 15, Rohm and Haas). Obtained product was used as the heterogeneous oxidant of As(III) in aqueous solutions. The polymer's oxidizing capacity, determined as part of the batch studies, amounted to 193.29 mg As(III) g^{-1} (pH = 7.7) and 206.03 mg As(III) g^{-1} (pH = 2.0). The suitability of the redox polymer for long-lasting operation in the aqueous environment was confirmed in the column study conducted using a solution with a concentration of 10 mg As(III) dm^{-3} at a flow rate of 6 bed volumes (BV) h^{-1} . The concentration of As(III) in the effluent reached the value of 0.01 mg As(III) dm^{-3} only after 8 weeks of continuous operation when 7930 BV of the solution had passed through the bed. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41552.

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INTRODUCTION

This study is a continuation of the research on the oxidation of arsenite in aqueous solutions, using as heterogeneous oxidants reactive polymers which include active chlorine (the +1 degree of oxidation) covalently bound to a nitrogen atom in their functional groups.¹ Porous heterogeneous oxidants, in the form of spherical beads characterized by excellent hydraulic properties and applied in column processes, are especially effective for removing residual contaminants (i.e., toxic reducers) from aqueous media. Most of the traditional oxidation techniques, using low molecular reagents, do not achieve the removal of undesirable contaminants from solutions to a level regarded as safe for disposal, unless an oxidant excess is used (but this results in the deterioration in the quality of the treated water).

Arsenites, as highly harmful compounds, pose various environmental hazards. The long-term ingestion of water containing even small quantities of inorganic arsenic species causes liver, lung, kidney, bladder, and skin cancer.^{2,3} The effective removal of arsenites from surface and municipal waters often requires a pre-oxidation step to convert As(III) to As(V). This is due to the chemical properties of arsenites which are present in the waters as undissociated molecules ($pK_{a1} = 9.2$, $pK_{a2} = 12.1$, $pK_{a3} = 13.4$), being more mobile in the aqueous environment than arsenate ions ($pK_{a1} = 2.2$, $pK_{a2} = 7.1$, $pK_{a3} = 11.5$). The oxidation state of arsenic is then the main factor influencing the effectiveness of most of the technologies used for arsenic

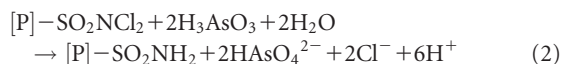
removal from water. Hence, intensive research is underway to find new methods for arsenic oxidation, based on heterogeneous^{1,4–9} or, to a lesser degree, homogeneous oxidants.^{10–13} Attention is also given to the development of photochemical oxidation processes conducted in the presence of TiO_2 or combining hydrogen peroxide/ozone with ultraviolet radiation.^{14–18} Because adsorption is the most suitable technique for the treatment of diluted solutions, a special effort is devoted to methods based on heterogeneous oxidants.

The present authors have already reported the results of their successful studies on the oxidation of arsenite to arsenate by macroporous poly(styrene-co-divinylbenzene) (S/DVB) containing *N*-chlorosulfonamide functional groups (in sodium as well as in hydrogen forms).¹ The results obtained in the column tests were very promising—the final concentration of As(III) in the effluent amounted to 1/5000 of its initial concentration in it. In this way the oxidation of As(III) to As(V) can be carried out before adsorption or ion-exchange processes which are effective toward As(V).

In the method proposed in the present article the oxidation of As(III) has been extended to the use of a polymer having *N,N*-dichlorosulfonamide groups (abbreviated as R/Cl₂), which consists of a styrene-divinylbenzene macroporous matrix with attached functional groups containing two chlorine atoms with oxidation number +1. Owing to its oxidative properties the polymer has been used as a biocide for water disinfection, in

some organic synthesis applications and as a decontaminant of chemical warfare agents.^{19–25} Our investigations have been devoted to the synthesis of this polymer and its application in the removal of some toxic inorganic admixtures (cyanide, thiocyanate, sulfide, nitrite), through their transformation into environmentally safe substances (i.e., oxidation of sulfide to sulfate), from waters.^{26–29}

The present study focuses on the possible use of R/Cl₂ for arsenite oxidation in aqueous solutions according to the eqs. (1) and (2)^{10,30}:



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

The R/Cl₂ polymer is a macromolecular analogue of dichloramine-T (*N,N*-dichloro-*p*-toluenesulfonamide)—a well-known micromolecular oxidizing agent. It should be noted that dichloramine-T as a water-insoluble compound can be used only in waterless environments, while R/Cl₂, being a water-insoluble, but porous oxidant, shows excellent properties in water treatment processes. The most important advantage of solid phase oxidation conducted in the column process is the possibility of using a large excess of the oxidant without introducing some micromolecular compounds (oxidants) into the treated water which lower its quality [the concentration of active chlorine in the polymer (R/Cl₂) bead swollen in water reaches ca. 2.5M]. Moreover, the synthetic, macroporous polymer used as the feedstock for the synthesis of R/Cl₂ redox polymer exhibits excellent hydraulic and mechanical properties. Thus, owing to the high active chlorine content in R/Cl₂, it can be expected that this polymer will be an effective and efficient heterogeneous oxidant for arsenites.

EXPERIMENTAL

Materials

All the reagents used were of analytical grade. Solutions were prepared with deionized water (18.3 MΩ cm⁻¹; Barnstead, EASYpure RF). The arsenite stock solution (1.0 mg As(III) cm⁻³) was prepared from sodium (meta)arsenite NaAsO₂ (Sigma-Aldrich, >99% purity). The composition of the working solutions is given in Table I.

Sulfonic cation exchanger *Amberlyst 15* produced by Rohm and Haas Co. (presently Dow Chemical Company) was used as the starting material for the synthesis of the redox polymer. *Amberlyst 15* is a macroporous S/DVB resin containing 4.7 mmol —SO₃H g⁻¹, characterized by a surface area of 45 m² g⁻¹, an average pore diameter of 25 nm, a uniformity coefficient of less than 1.70 and a harmonic mean size of 600–850 μm.

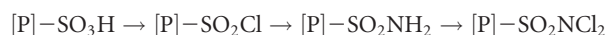
Synthesis of Redox Polymer

The redox polymer having *N,N*-dichlorosulfonamide groups was prepared in accordance with the method described previously.^{30,31} The following procedure was used:

Table I. Composition of Working Solutions Used in Experiments

Studies	Environment	As(III) concentration	
		mg dm ⁻³	mmol dm ⁻³
Batch	Water	375.0	5.0
	Water	5.0 ^a	0.067 ^a
	0.01M H ₂ SO ₄	375.0	5.0
Redox	Water	375.0	5.0
	0.01M H ₂ SO ₄	375.0	5.0
Column	Water	10.0	0.135
	Water	93.0	1.25
	0.01M H ₂ SO ₄	93.0	1.25

^aThe solution additionally contained 1.0 or 5.0 mmol dm⁻³ of the particular ions (chlorides, sulfates, bicarbonates, or phosphates).



The obtained product, in the dry state, contained 2.05 mmol —SO₂NCl₂ g⁻¹ (~8.0 meq of active chlorine g⁻¹) and a small amount (0.60 mmol g⁻¹) of sulfonic groups formed as a result of a side reaction during the conversion of sulfochloride into sulfonamide groups.

Analytical Methods

The active chlorine content in the R/Cl₂ redox polymer was determined by the iodometric method modified with the longer interaction of the reagents. The concentration of chlorides in the solutions was estimated by argentometric titration, using 0.01M AgNO₃ with a system of Ag/AgCl/calomel electrodes.

Arsenic concentration was determined using the spectrophotometric molybdenum blue method (Specord 210, Analytical Jena, Germany) with absorbance measurement at 880 nm.⁸ Prior to the analysis an oxidizing agent (potassium iodate) was used to convert As(III) into As(V) (arsenite does not form a molybdenum complex). The arsenite concentration was calculated as the difference between the total arsenic concentration and the arsenate concentration. Arsenic solutions containing less than 0.05 mg As dm⁻³ were analyzed by means of hydride generation atomic absorption spectrometry with a graphite tube (AAS Avanta). Since this method enables one to determine only the total arsenic concentration, As(III) and As(V) were first separated using a strong base anion exchanger (Amberlite IRA 402Cl), after adjusting the pH to 4.0.³²

Oxidation Studies

Oxidation experiments were performed in both batch (the kinetics, the influence of co-existing ions, redox studies) and column regimes, using an IKA KS-260 control shaker and the Gilson MiniPuls3 peristaltic pump with the FC204 Fraction Collector, respectively.

Batch Experiments. In order to determine the oxidative capacity of R/Cl₂ and to examine its suitability for the oxidation of residual amounts of As(III) (deep oxidation), kinetic studies were carried out for both an oxidant (R/Cl₂) and reductant (arsenite) excess. A measured amount of the redox polymer (0.125 g) placed in a flask was shaken for 24 h with 50 cm³ (an

excess of chlorine) or 200 cm³ (an excess of arsenite) of 5.0 mM NaAsO₂ solution in water or 0.01M H₂SO₄. The concentration of As(V) was analyzed in appropriate time intervals. After 24 h the redox polymer was separated from the reaction medium by filtration and was analyzed for active chlorine content. The effect of various competing anions, such as sulfates, phosphates, chlorides, and bicarbonates was assessed using 1 and 5 mM solutions of the particular ions in 0.067 mM NaAsO₂. A sample of the hybrid polymer (0.1 g) was shaken for 24 h in an Erlenmeyer flask with 50 cm³ of the appropriate solutions.

Redox Studies. In order to determine of the standard redox potential of the heterogeneous system (the polymer with the active chlorine/aqueous solution of NaAsO₂) special potentiometric titration³³ was performed using 5.0 mM NaAsO₂ solutions in water or in 0.01M H₂SO₄. The following increasing solution volumes of the titrant: (1) 0.0 cm³, (2) 25 cm³, (3) 50 cm³, (4) 75 cm³, (5) 100 cm³, (6) 125 cm³, and (7) 150 cm³ were loaded into seven separate samples of the heterogeneous oxidant (0.125 g, ~1.0 meq of active chlorine). The reaction medium (25 cm³ of water) was exclusively added to the first sample (1) of the polymer. The increasing solution volumes of NaAsO₂ were required to obtain (1) 0 : 1, (2) 0.25 : 1, (3) 0.5 : 1, (4) 0.75 : 1, (5) 1 : 1, (6) 1.25 : 1, and (7) 1.5 : 1 of the stoichiometric ratio of the reductant [As(III)] to the oxidant (Cl⁺). The samples were placed in separate, tightly closed, light-proof glass cells, and shaken at room temperature for 24 h. Then pH and redox potential values were measured using a platinum/calomel electrode pair (Millivoltmeter CPI-501, Zabrze, Poland). The vessels were protected from contact with air during the measurements. Additionally, the As(III) and As(V) concentration in each sample was determined by the methods described above.

Column Tests. Column studies were carried out using glass columns (6 or 10 mm in diameter). A sample of R/Cl₂ [(a) 2.4 g in the dry state, ~4.0 cm³ after swelling in water, (b) 4.0 g in

the dry state, ~7.5 cm³ after swelling in water] was packed into the column. Then NaAsO₂ solutions [(a) 1.25 mM, (b) 0.135 mM, in water] were passed once through the polymer beds. The flow rate was 6 or 18 bed volumes/h. Fractions (30, 250 cm³) were collected to estimate their composition in terms of pH and arsenate, arsenite and chloride ion concentrations.

RESULTS AND DISCUSSION

Because of the exceptionally high active chlorine content in the redox polymer [1.0 g of R/Cl₂ theoretically can oxidize as much as 300 mg of As(III)], solutions with a relatively high reductant concentration [many times exceeding the As(III) concentrations in natural waters] were used in the preliminary studies. The studies were conducted in neutral and acidic conditions (0.01M H₂SO₄) because of the highest stability of the polymer in such an environment. In strong alkaline conditions R/Cl₂ undergoes dechlorination and loses one of the two active chlorine atoms attached to the functional group.²⁷ Incidentally, all the processes (coagulation, adsorption) used to remove arsenic from waters are usually conducted in neutral or weak acidic conditions.

Batch Studies

In the first stage of batch studies a double (relative to the stoichiometric demand) excess of the NaAsO₂ reductant (Reaction 2) was used. The obtained results are presented in Table II.

The results indicate that a substantial part of the arsenites present in the solution have been oxidized to arsenates. In the course of 24 h the concentration of As(III) decreased from 375 to 254.2 mg dm⁻³ in distilled water and to 246 mg dm⁻³ in 0.01M H₂SO₄. In the case of an As(III) excess relative to the active chlorine content in the redox polymer sample, at which theoretically 50% of the As(III) present in the solution can be oxidized, the As(III) concentration decreased by 32.2% in distilled water (a 62.9% use of the active chlorine) and by 34.4% in 0.01M H₂SO₄ (a 67.2% use of the active chlorine). The calculated oxidizing capacity of the polymer amounted to 193.3 and 206.0 mg As(III) g⁻¹ in distilled water and 0.01M H₂SO₄, respectively.

Due to the high active chlorine content in the redox polymer, its oxidation capacity toward arsenites was larger than other *N*-halogenosulfonamide polymers, especially under neutral environment (Table III). Only in acidic conditions the copolymer with -SO₂NCIH functional groups exhibited almost equal effectiveness as an arsenite oxidant, which was the result of its higher redox potential (0.56 V) in comparison to R/Cl₂ polymer (0.49 V).¹ However, it should be mentioned that despite the highest redox potential of the polymers with *N*-chlorosulfonamide functional groups in the acidic conditions, the decrease of pH causes the drop in the reaction rate.³⁶ This can be explained by a decreased degree of dissociation of arsenites in acidic conditions, which involve a longer reaction time to reach a new equilibrium between dissociated and undissociated arsenite molecules. The optimal pH conditions should therefore ensure a proper balance between redox potential (favorable low pH) and the reaction rate (favorable higher pH). The disadvantage of the studied redox polymer is its instability in strong alkaline conditions. At high pH values the functional groups of the polymer

Table II. Analytical Data on Reaction Between R/Cl₂ Resin and Arsenite Solution in Batch Regime (100% Excess of NaAsO₂ in Relation to Stoichiometry)

	0.125 g R/Cl ₂ + 200 cm ³ 5.0 mM NaAsO ₂ solution	
	In water	In 0.01M H ₂ SO ₄
Concentration of arsenite mg dm ⁻³	0	0
Before reaction	375	375
After reaction (24 h)	254	245
pH value	0	0
Before reaction	10.6	2.04
After reaction	7.66	2.01
Active chlorine in sample of R/Cl ₂ , mmol	0	0
Before reaction	0.5	0.5
After reaction	0.15	0.14

Table III. Oxidation Capacity Toward As(III) for Various Macromolecular Oxidants

Heterogeneous oxidant	Oxidation capacity, mg As(III) g ⁻¹		
	Batch studies	Column studies	Lit.
[P]-SO ₂ NCINa	135.6 (pH 9.3) 97.4 (pH 12.2)	71.92 (6 BV/h)	1
[P]-SO ₂ NClH	176.8 (pH 3.5) 173.81 (pH 1.9)	72.5 (4 BV/h)	1
[P]-SO ₂ NBrNa	103.4 (pH 6.6) 86.9 (pH 11.3)	31.03 (6 BV/h)	34
[P]-SO ₂ NCl ₂	206.03 (pH 1.9) 193.29 (pH 7.7)	147.83 (6 BV/h)	This study
R/S/Mn	~ 80 (pH 6.5)	18.8 ^a	9

^aThe value was calculated before reaching the breakthrough point.

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

undergo dechlorination and lose one of the two active chlorine atoms, leading to the conversion of dichlorosulfonamide groups (–SO₂NCl₂) into monochlorosulfonamide groups (–SO₂NClNa).²⁷ Because alkaline environment is usually unfavorable for oxidation reactions this inconvenience does not reduce the usability of the R/Cl₂ polymer. Satisfactory oxidation properties in the wide pH range exhibit hybrid polymers consisting of manganese dioxide deposited within the polymeric skeleton.^{7–9,35} In the case of such materials the oxidation rate is the highest under acidic and neutral environment, whereas under alkaline conditions this type of heterogeneous oxidants required multiple longer reaction time to ensure adequate effectiveness.⁹ However, at neutral pH the hybrid polymer coated with manganese dioxide exhibited the oxidation capacity over twice lower than of the studied R/Cl₂ redox polymer (Table III).

In the next stage of batch studies the oxidation reaction was conducted at a double excess of the oxidizer relative to the stoichiometric demand. The aim was to determine whether the copolymer was suitable for the thorough oxidation of As(III)—a precondition for its use in the column process. Figure 1 shows the oxidation kinetics in the course of the first 8 h while the reagents before and after the reactions are characterized in Table IV.

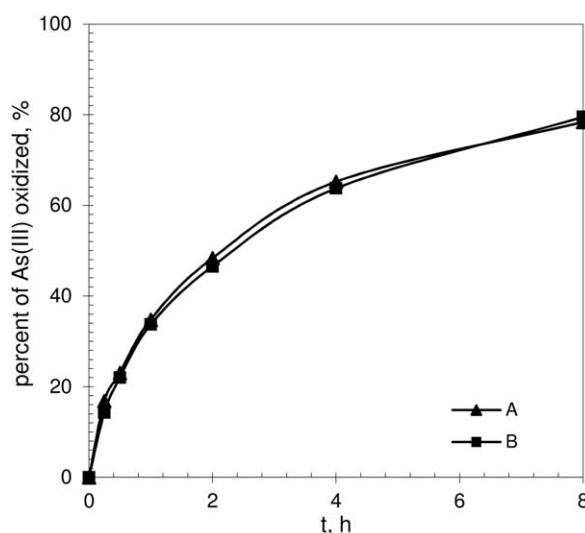


Figure 1. Kinetics of As(III) oxidation in batchwise reaction: (A) in water, (B) in 0.01M H₂SO₄; 0.125 g of R/Cl₂, 50 cm³ 5.0 mM NaAsO₂ solution.

The obtained results show that also in the above conditions the yield of the oxidation of As(III) to As(V) was very high. After 24 h the concentration of As(III) in the solution decreased from 375 to 29.8 mg dm⁻³ and 20.2 mg dm⁻³ in, respectively, distilled water and 0.01M H₂SO₄, which is indicative of favorable conditions for As(III) oxidation in the acidic environment. This is in agreement with the results obtained for other heterogeneous oxidants presented in the Table III. The marked reduction in the pH in distilled water was due to the fact that the As(III) oxidation reaction was accompanied by the introduction of hydrogen ions into the solution (Reaction 2). It should also be noted that the amount of active chlorine remaining in the polymer functional groups after the oxidation process was close to the theoretical one, for both the reaction environments. This is indicative of the precise stoichiometric release of active chlorine from the functional groups in the presence of the reductant in the adopted experimental conditions.

If R/Cl₂ was to be used to oxidize As(III) in natural waters, it was necessary to determine the influence of foreign ions on the course and efficiency of this process. For this purpose further experiments were conducted in the presence of sulfates, chlorides, bicarbonates, and phosphates. Considering that the

Table IV. Analytical Data on Batch Regime Reaction Between R/Cl₂ Resin and Arsenite Solution (100% Excess of Active Chlorine in Relation to Stoichiometry)

	0.125 g R/Cl ₂ + 50 cm ³ 5.0 mM NaAsO ₂ solution	
	In water	In 0.01M H ₂ SO ₄
Concentration of arsenite, mg dm ⁻³		
Before reaction	375	375
After reaction (24 h)	29.8	20.2
pH value		
Before reaction	10.7	2.02
After reaction	2.44	1.76
Active chlorine in sample of R/Cl ₂ , mmol		
Before reaction	0.5	0.5
After reaction	0.31	0.24

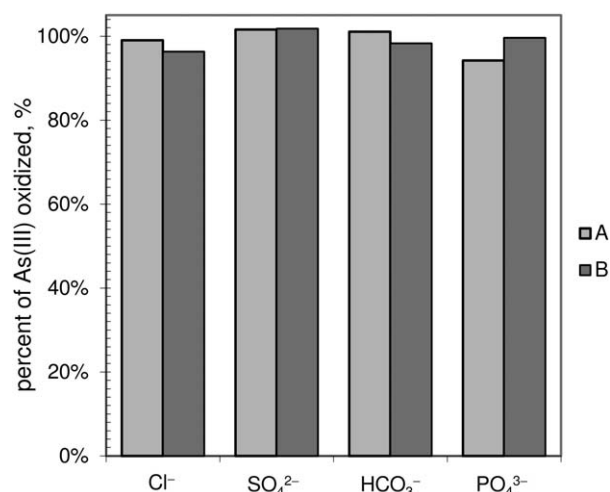


Figure 2. Efficiency of As(III) oxidation by means of R/Cl₂ in presence of co-existing ions in various concentrations: (A) 1.0 mM, (B) 5.0 mM; 0.1 g R/Cl₂, 50 cm³ 0.067 mM NaAsO₂ solution.

concentrations of the anions commonly occurring in natural waters usually considerably exceed the concentrations of As(III), the influence of their presence on As(III) oxidation efficiency was studied in 1 and 5 mM solutions of the particular anions. The studies showed that despite the high concentrations, the anions had practically no influence on the efficiency of As(III) oxidation by means of the R/Cl₂ copolymer (Figure 2).

Redox Studies

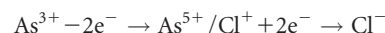
Figure 3(a) shows the redox titration curves for the reduction of R/Cl₂ with increasing doses of the reductant (an arsenite solution). Curve A represents the reaction between R/Cl₂ and NaAsO₂ in distilled water. In this case, the shape of the curve is characteristic of the redox titration of the oxidizer with the reductant. The formal redox potential of the polymer (i.e., the potential read for the middle point of the redox titration curve, at which the reductant-to-oxidizer ratio is 0.5 : 1), determined by titration, amounted to 0.45 V [Figure 3(a), point 3 on curve A, pH = 2.6]. The marked reduction in the redox potential, observed toward the end of titration, was caused by an increase in the pH of the solution [Figure 3(c), curve A], resulting in the deterioration in the reaction conditions. Curve B in Figure 3(a) illustrates the course of the reaction between R/Cl₂ and NaAsO₂ in the acidic environment. In these conditions the curve is flat—after an initial slight decrease the system redox potential stabilizes at a constant level of approximately 0.50 V. The formal redox potential of the polymer in these conditions amounted to 0.49 V (point 3 on curve B, pH = 1.87).

It emerges from this stage of the investigations that: (a) R/Cl₂ is a medium-power oxidizer, which is advantageous (too strong oxidizers may enter into undesirable reactions with the constituents of the treated water), (b) the acidic environment favors the oxidation of arsenites by means of the investigated polymer, (c) the curves do not show any inflexion, which could be due to the presence of two chlorine atoms in the function groups of the polymer, (d) after half of the active chlorine is reduced the heterogeneous oxidizer still shows high oxidizing power (the

N-chlorosulfonamide polymer exhibited a very high redox potential in the acidic environment).¹

Fixed-Bed Column Study

Preliminary fixed-bed column studies were conducted using high concentration (1.25 mM) arsenic solutions in distilled water and in 0.01M H₂SO₄, which would be passed through a fixed R/Cl₂ bed (2.4 g, *h* = 14 cm) in a glass column 6 mm in diameter at a flow rate of 18 BV h⁻¹. The aim of the studies was to test the capacity of the heterogeneous oxidizer to release active chlorine from the functional groups, but only in the amount corresponding to the concentration of the reductant [As(III)] present in the solution. Theoretically, according to the reaction stoichiometry, the molar concentration of arsenates and that of chlorides in the solution leaving the column should be identical:



The obtained bed breakthrough curves with marked chloride anion concentrations [Figure 4(a,b)], confirmed the high stability of the redox polymer functional groups and their capacity to

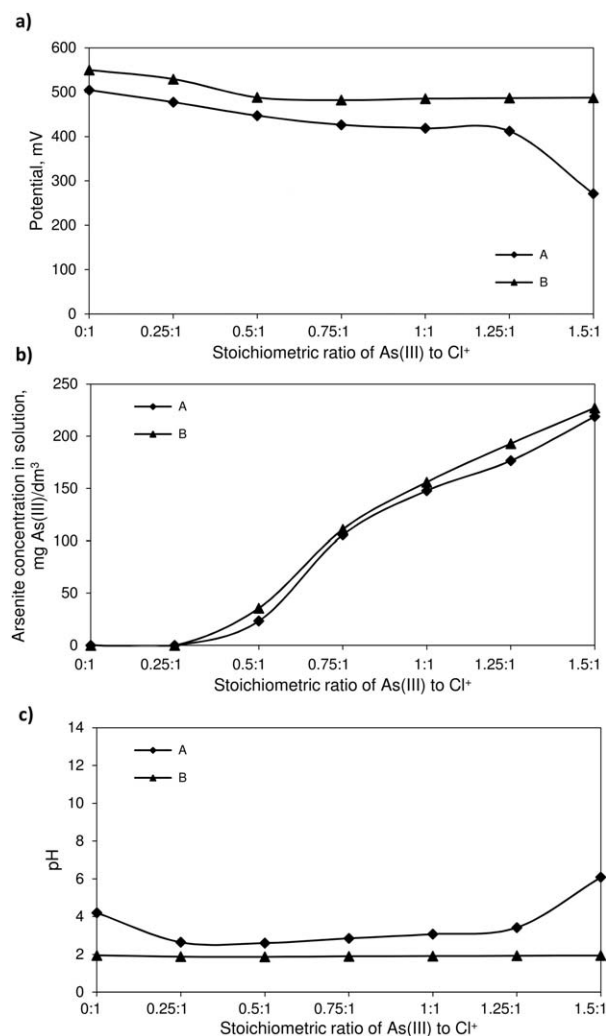


Figure 3. (a) Redox titration curves of R/Cl₂ by 0.005M NaAsO₂ in: (A) water, (B) 0.01M H₂SO₄ (reaction time = 24 h), (b) concentration of arsenites in solution, (c) pH value; 0.125 g R/Cl₂.

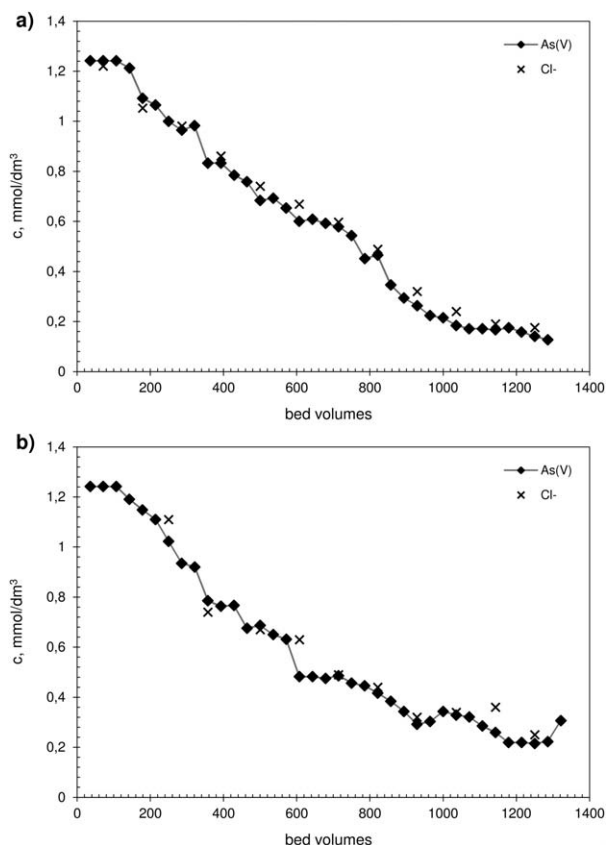


Figure 4. As(V) and chloride ion concentration in effluent from column containing R/Cl₂ polymer bed; influx 1.25 mM NaAsO₂ in (a) water alone, (b) 0.01M H₂SO₄; flow rate 18 BV h⁻¹.

precisely “dose” the oxidizer into the solution, in both distilled water and 0.01M H₂SO₄.

However, due to the very high rate of flow of the solution through the polymer bed a breakthrough (defined as an exceedance of $c/c_0 = 0.05$) occurred very quickly and the working oxidizing capacity was found to amount to merely 16.9 mg As(III) g⁻¹ (this value was similar for the two studied environments), which constituted 5.6% of the theoretical capacity.

The most important stage in the column studies consisted in passing the solution with a low arsenic content (0.135 mM) through an R/Cl₂ bed (4.0 g, $d = 1$ cm, $h = 9.5$ cm) at a flow rate of merely 6 BV h⁻¹ (redox reactions proceed much slower than ionic reactions in ion exchange processes). The aim of this stage was to test the polymer’s capacity for long-lasting operation, and the full exploitation of its theoretical oxidizing capacity. The As(III) concentration in the effluent from the column did not exceed 0.004–0.006 mg dm⁻³ throughout the experiment, whereas the maximum allowable arsenic concentration in potable water amounts to 0.01 mg dm⁻³ (Figure 5). A bed breakthrough occurred after passing 59,133 cm³ of the solution (7930 BV) and the working oxidizing capacity of the polymer was found to amount to 147.83 mg As(III) g⁻¹ (49.4% of the total capacity). This value is the highest from among other *N*-halogenosulfonamide redox polymers (Table III), which confirmed the suitability of R/Cl₂ polymer

for long lasting column processes. The working oxidation capacity of the hybrid polymer coated with manganese dioxide was much smaller (18.8 mg As g⁻¹), but this value was calculated before the breakthrough point of the bed was reached. It is worth mentioning that due to some adsorptive properties of manganese dioxide, the hybrid polymers with MnO₂ deposit can simultaneously play the role of As(III) oxidant and adsorbent.^{7,9,35} Introduction into such materials both manganese and iron oxides significantly improves their adsorptive properties toward arsenites [13.5 mg As(III) g⁻¹, 14.5 mg As(V) g⁻¹] but simultaneously diminishes the oxidative capacity of the hybrid polymer due to the lower content of manganese oxide.³⁷ Hybrid polymers exhibiting both oxidative and sorptive properties toward arsenite species, may be useful in drinking water purification, where the As concentration typically does not exceed 1.0 mg dm⁻³. In contrast the studied R/Cl₂ redox polymer exhibiting distinctively better oxidative properties, can be used in wastewater treatment with high arsenite concentration, ranging from several to tens mg dm⁻³, for example, as the pretreatment fixed oxidizing bed.

It appears from the graph shown in Figure 5(b) that the pH of the effluent stabilized at a level of approximately 4.0 and after the breakthrough it increased to about seven as a result of the inhibition of the As(III) oxidation reaction (Reaction 2) causing the acidification of the reaction medium. The reduction of the

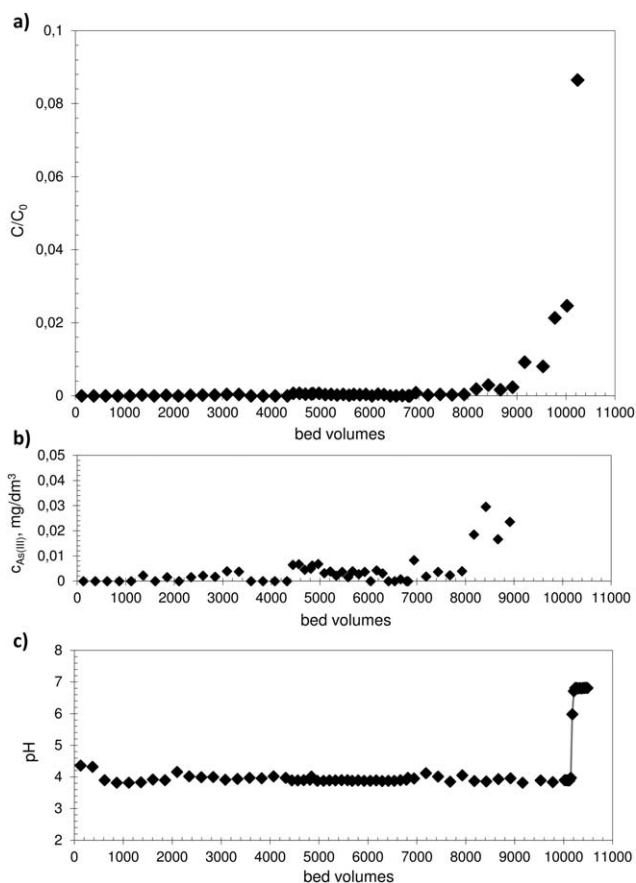


Figure 5. (a) Arsenite breakthrough curve for R/Cl₂ resin in column; influx 0.135 mM NaAsO₂ in water, flow rate 6 BV h⁻¹, (b) As(III) concentration in effluent, (c) pH value of effluent.

rate of flow of the solution through the bed to 6 BV h^{-1} in this experiment ensured a sufficiently long reagent contact time whereby the theoretical oxidizing capacity of R/Cl_2 could be more fully exploited. It should be noted that the used concentration of $10 \text{ mg As(III) dm}^{-3}$ is still many times higher than the arsenite concentrations in natural waters.

CONCLUSIONS

The redox polymer with *N,N*-dichlorosulfonamide functional groups has been found to be an effective oxidizer of As(III). The polymer's oxidizing capacity determined as part of the batch studies amounted to $193.29 \text{ mg As(III) g}^{-1}$ ($\text{pH} = 7.7$) and $206.03 \text{ mg As(III) g}^{-1}$ ($\text{pH} = 2.0$), constituting, respectively, 64.5% and 68.7% of the oxidizing capacity which follows from the active chlorine content. Thanks to the use of a double oxidizer excess relative to the amount of As(III) in the solution in the batch studies over 90% of the arsenic present in the solution was oxidized.

The normal oxidizing potential of the R/Cl_2 polymer, determined in the redox studies amounted to 0.45 V ($\text{pH} = 2.6$) and 0.49 V ($\text{pH} = 1.87$), confirming the polymer's high effectiveness as an oxidizer of As(III).

The effectiveness of the R/Cl_2 polymer was further confirmed in the column studies in which a solution with a $10 \text{ mg As(III) dm}^{-3}$ concentration, that is, much higher than in natural waters usually subjected to treatment, would be passed through a bed of the heterogeneous oxidizer. The As(III) concentration in the effluent reached 1% of the initial value only after 8 weeks of continuous operation when 60 dm^3 of the solution, corresponding to 7930 BV, had passed through the bed. The suitability of the polymer for long-lasting operation in the aqueous environment stems from the stability of its functional groups (confirmed in the batch studies and in the preliminary column studies), manifesting itself in the capacity for the precise release of active chlorine only in the amount corresponding to the reductant concentration in the solution.

It has also been found that the presence of sulfates, chlorides and bicarbonates, as well as phosphates, in concentrations considerably higher than in natural waters has no significant effect on the effectiveness of As(III) oxidation by means of the R/Cl_2 polymer.

The obtained results confirmed that the studied redox polymer, among other heterogeneous, polymeric based oxidants, exhibits the highest effectiveness in the arsenite oxidation processes provided both in batch and column regime. Along with the excellent hydraulic and mechanical properties of the spherical polymeric beads, high stability of functional groups in neutral and acidic conditions, the ability for precise release of active chlorine only in the amount corresponding to the reductant concentration in treated solution, the studied redox polymer seems to be suitable for long-lasting operations realized industrially in water and wastewaters treatment.

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REFERENCES

1. Kociołek-Balawejder, E.; Ociński, D.; Stanisławska, E. *J. Hazard. Mater.* **2011**, *189*, 794.
2. Yunus, M.; Sohel, N.; Hore, S. K.; Rahman, M. *Kaohsiung J. Med. Sci.* **2011**, *27*, 371.
3. Celik, I.; Gallicchio, L.; Boyd, K.; Lam, T. K.; Matanoski, M.; Tao, X.; Shiels, M.; Hammond, E.; Chen, L.; Robinson, K. A.; Caulfield, L. E.; Herman, J. G.; Guallar, E.; Alberg, A. *J. Environ. Res.* **2008**, *108*, 48.
4. Lafferty, B. J.; Ginder-Vogel, M.; Sparks, D. L. *Environ. Sci. Technol.* **2010**, *44*, 8460.
5. Saleh, T. A.; Agarwal, S.; Gupta, V. K. *Appl. Catal. B-Environ.* **2011**, *106*, 46.
6. Li, X.; Liu, C.; Li, F.; Li, Y.; Zhang, L.; Liu, C.; Zhou, Y. *J. Hazard. Mater.* **2010**, *173*, 675.
7. Lenoble, V.; Chabroulet, C.; Al-Shukry, R.; Serpaud, B.; Deluchat, V.; Bollinger, J.-C. *J. Colloid Interface Sci.* **2004**, *280*, 62.
8. Lenoble, V.; Deluchat, V.; Serpaud, B.; Bollinger, J.-C. *Talanta* **2003**, *61*, 267.
9. Ociński, D.; Jacukowicz-Sobala, I.; Kociołek-Balawejder, E. *J. Appl. Polym. Sci.* **2014**, *131*, 39489.
10. Sorlini, S.; Gialdini, F. *Water Res.* **2010**, *44*, 5653.
11. Ghurye, G.; Clifford, D. Laboratory Study on the Oxidation of Arsenic(III) to Arsenic(V), US Environmental Protection Agency: Houston, USA, 2001, EPA-600-R-01-021.
12. Ghurye, G.; Clifford, D. *J. AWWA* **2004**, *96*, 84.
13. Lee, G.; Song, K.; Bae, J. *Geochim. Cosmochim. Acta* **2011**, *75*, 4713.
14. Bissen, M.; Frimmel, F. H. *Acta Hydrochim. Hydrobiol.* **2003**, *31*, 97.
15. Bissen, M.; Vieillard-Baron, M.; Schindelin, A. J.; Frimmel, F. H. *Chemospheres* **2001**, *44*, 751.
16. Zhang, F.-S.; Hideaki, I. *Chemospheres* **2006**, *65*, 125.
17. Lee, H.; Choi, W. *Environ. Sci. Technol.* **2002**, *36*, 3872.
18. Lescano, M. R.; Zalazar, C. S.; Cassano, A. E.; Brandi, R. *J. Photochem. Photobiol. Sci.* **2011**, *10*, 1797.
19. Emerson, D. W. *Ind. Eng. Chem. Res.* **1990**, *29*, 448.
20. Beldar, A. G.; Sharma, M. E.-J. *Chem.* **2011**, *8*, 288.
21. Gupta, H. K.; Mazumder, A.; Garg, P.; Gutch, P. K.; Dubey, D. K. *Tetrahedron Lett.* **2008**, *49*, 6704.
22. Gutch, P. K.; Shrivastava, R. K.; Dubey, D. K. *J. Appl. Polym. Sci.* **2007**, *105*, 2203.
23. Gutch, P. K.; Srivastava, R. K.; Sekhar, K. *J. Appl. Polym. Sci.* **2008**, *107*, 4109.
24. Gutch, P. K.; Singh, R.; Acharya, J. *J. Appl. Polym. Sci.* **2011**, *121*, 2250.
25. Gutch, P. K.; Singh, R. *J. Polym. Mater.* **2011**, *28*, 431.
26. Kociołek-Balawejder, E. *Eur. Polym. J.* **2000**, *36*, 1137.
27. Kociołek-Balawejder, E. *Eur. Polym. J.* **2000**, *36*, 295.
28. Kociołek-Balawejder, E. *Eur. Polym. J.* **2002**, *38*, 953.

29. Bogoczek, R.; Kociołek-Balawejder, E.; Stanisławska, E. *React. Funct. Polym.* **2006**, *66*, 609.
30. Bogoczek, R.; Kociołek-Balawejder, E. *Angew. Makromol. Chem.* **1989**, *169*, 119.
31. Bogoczek, R.; Kociołek-Balawejder, E. *Polym. Commun.* **1986**, *27*, 286.
32. Kim, M.-J. *Bull. Environ. Contam. Toxicol.* **2001**, *67*, 46.
33. Bogoczek, R.; Kociołek-Balawejder, E.; Stanisławska, E. *J. Appl. Polym. Sci.* **2008**, *107*, 2190.
34. Ociński, D.; Stanisławska, E.; Kociołek-Balawejder, E. *React. Funct. Polym.* **2013**, *73*, 108.
35. Lenoble, V.; Laclautre, Ch.; Serpaud, B.; Deluchat, V.; Bollinger, J.-C. *Sci. Total Environ.* **2004**, *326*, 197.
36. Kociołek-Balawejder, E.; Ociński, D.; Stanisławska, E. *Polimery (in English)* **2012**, *57*, 101.
37. Jacukowicz-Sobala, I.; Ociński, D.; Kociołek-Balawejder, E. *Ind. Eng. Chem. Res.* **2013**, *52*, 6453.