Using macroporous *N*-chlorosulfonamide S/DVB copolymer as an aid to iron removal from water*

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Abstract: The de-ironing of water is a basic stage in water-treating technology. Consequently, the oxidation of easily soluble Fe(II) to poorly soluble Fe(III) compounds is indispensible. In order to oxidize Fe(II) ions to Fe(III), a macromolecular and macroporous product in bead form was used: polystyrene cross-linked by divinylbenzene, which contains pendant *N*-chlorosulfonamide groups in both the sodium and hydrogen forms. To assist the process of removing residual iron from water, this polymer—a macromolecular analog of Chloramine T, containing more than 4.0 mequiv of active chlorine/g—was prepared, starting from the sulfonate cation exchanger Amberlyst 15 by a three-step transformation of its functional groups. The investigations were carried out using both the batchwise and column methods, and 0.0025 M as well as 0.02 M $FeSO_4$ solutions with different acidity were used. We found that the oxidation of ferrous ions to ferric by *N*-chlorosulfonamide copolymer was effective and was favored by a low pH. The oxidative ability of the copolymer was 225 mg Fe(II)/g. We established that the oxidation reaction could be operated in two directions. In acidic media (pH < 2.5), Fe(III) ions remained in the solution as products of the reaction. The higher the pH, the more the poorly soluble ferric compounds sedimented in the inner structure of the copolymer beads. In this way, new hybrid materials were obtained, i.e., by ferrous/ferric oxides and hydroxides, by nanoparticles, modified materials which can serve as specific reacting sorbents and catalysts.

Keywords: water-treating; iron; macroporous; *N*-chlorosulfonamide; de-ironing of water; hybrid polymer.

INTRODUCTION

The first person to synthesis macromolecular *N*-chlorosulfonamide, a linear polymer, was Y. Nakamura [1]. Cross-linked copolymers were synthesized and investigated by D. W. Emerson [2]. We have synthesized and investigated cross-linked and macroporous sodium and hydrogen form halogene sulfonamide copolymers [3,4]. The polymeric or copolymeric derivatives of *N*-chlorosulfonamide compounds are known to be efficient oxidants. They disinfect water, inactivating undesirable microorganisms by oxidizing them [2,5–7]; they oxidize low-molecular organic compounds (alcohols to aldehydes) [8,9]; they oxidize a number of low-molecular-weight toxic anions [10–13]. Recently, we studied the oxidative properties of the *N*-chlorosulfonamide copolymer in relation to nitrites, which are undesirable
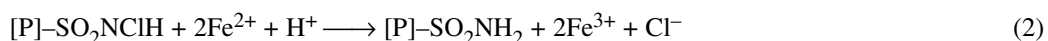

(toxic pollutants) in natural as well as industrial waters [14]. The well-known sodium salt of this macro-molecular oxidant was inactive in the said conditions; however, its hydrogen form was very reactive and enabled us to complete the nitrite elimination.

In this paper, for the first time macromolecular *N*-chlorosulfonamide was utilized to eliminate cations from aqueous solutions—Fe(II) ions were oxidized, to aid the process of residual iron removal from waters.

The ferrous/ferric compounds that appear in natural waters are characterized by low toxicity, but they show a significant negative influence on the water's quality. Even at a concentration level as low as 1.0 mg/L, they cause a deterioration of the color, taste, and flavor of water. They are responsible for precipitation of deposits in heat exchangers as well as in water-sewage installations. The ferrous/ferric cations originate from natural processes, corrosion, as well as from wastewater, sewage, and industrial waters. The presence of ferrous/ferric compounds in municipal utility water should not exceed 0.5 mg/L. These cations are undesirable in the production of cellulose and paper and in the textile, pharmaceutical, dairy, and fermentative industries. Similarly, some pigment production and dye-stuff synthesis requires ferrous/ferric-free water, i.e., below 0.1 mg Fe/L. In water used for the manufacture of white pigments and some sorts of paper, the concentration of iron cannot exceed 0.001 mg Fe/L.

In underground waters, iron compounds occur mainly in the form of second-stage oxidation ions. In well-oxygenated surface waters, iron occurs mainly in the third degree of oxidation. These conditions favor the generation and precipitation of poorly soluble Fe(III) deposits. The classical methods for the removal of iron compounds depend on the oxidation of Fe(II) to Fe(III) by means of various water-soluble oxidation agents (e.g., chlorine), followed by the coagulation, sedimentation, and filtration of the deposits [15]. A nearly neutral reaction of the aqueous solution is observed. The yield of the Fe(II)/Fe(III) oxidation reaction depends inter alia on the oxidants' concentration and proportion in the water, and on the reagents' contact time. The removal of iron from water is still an open problem, although cost-effective treatment methods are known [16].

In this investigation, we tried to obtain the Fe(II) oxidation reaction by means of water-insoluble, heterogeneous reagents. The solid oxidant was a *N*-chlorosulfonamide copolymer in both sodium and hydrogen forms:

$$[P]-SO_2NClNa + 2Fe^{2+} + 2H^+ \longrightarrow [P]-SO_2NH_2 + 2Fe^{3+} + NaCl \qquad (1)$$

$$[P]-SO_2NClH + 2Fe^{2+} + H^+ \longrightarrow [P]-SO_2NH_2 + 2Fe^{3+} + Cl^- \qquad (2)$$
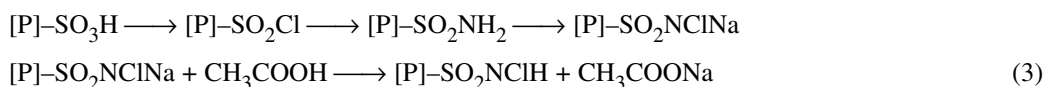
[P] stands for the copolymer styrene/divinylbenzene, macroporous structure in bead form (ca. 1 mm in diameter). The *N*-chlorosulfonamide groups contain the appropriate oxidizing agent—chlorine with the oxidation number +1 covalently bound to the macromolecular solid carrier. It was possible to achieve the projected reaction in an effective and quantitative manner through both the batchwise and column methods. If there is a large concentration and proportion of the oxidant in the solid phase, and all the liquid parts have direct contact with it, the velocity and direction of the Fe(II)/Fe(III) reaction are very favorably affected.

The sodium derivative of the *N*-chlorosulfonamide copolymer used here is a high-molecular-weight equivalent of the known micromolecular oxidant, Chloramine T, which is used in analytical chemistry for the quantitative, titrimetric determination of ferrous ions [17,18].

EXPERIMENTAL

Reagents

Copolymers with *N*-chlorosulfonamide groups in sodium or hydrogen form (R/Na stands for [P]–SO_2NClNa and R/H stands for [P]–SO_2NClH) were prepared according to methods published in detail elsewhere [3,4,14]:

$$[P]–SO_3H \longrightarrow [P]–SO_2Cl \longrightarrow [P]–SO_2NH_2 \longrightarrow [P]–SO_2NClNa$$

$$[P]–SO_2NClNa + CH_3COOH \longrightarrow [P]–SO_2NClH + CH_3COONa \qquad (3)$$

As the starting material, we used Amberlyst 15 (produced by Rohm and Haas Co.), a commercially available sulfonate cation exchanger. This is a macroporous poly (S/20 % DVB) resin, which contained 4.7 mmol/g $–SO_3^-$ groups in the dry state (the surface area 45 m^2/g, average pore diameter 25 nm). The product contained 2.15 mmol/g $–SO_2NClNa$ groups (i.e., 4.30 mequiv of active chlorine/g) and additionally 0.70 mmol/g $–SO_3Na$ groups. The transformation of the *N*-chlorosulfonamide groups from sodium to hydrogen form was achieved by treating the R/Na product with an excess of acetic acid. In stationary experiments, a sample of the R/Na was shaken with an excess of 0.1 M CH_3COOH. After 2 h of shaking, the resin beads were separated from the solution by filtration and were washed with distilled water. In dynamic experiments, the R/Na resin was placed in a glass column and was washed first with 0.05 M CH_3COOH and then with distilled water. For a sample which contained 100 mequiv of active chlorine (~25 g of resin), 2.0 L of the said acid was used. The product was analyzed after drying to constant weight at normal conditions. The active chlorine content of the hydrogen form resin was 4.80 mequiv/g.

Analytical-grade ferrous sulfate was used for the preparation of the aqueous solutions, containing $FeSO_4$ both alone and in a mixture with sulfuric acid. The solutions used in the batch regime experiments were: 0.02 M $FeSO_4$ (ca. 1120 mg Fe^{2+}/L) in: (1) water, (2) 0.001, (3) 0.01, or (4) 0.1 M H_2SO_4. The solutions used in the experiments carried out in the dynamic regime were: 0.0025 M $FeSO_4$ (140 mg Fe^{2+}/L) in: (1) water, (2) 0.01 M H_2SO_4.

Analysis

The active chlorine content in the resin (R/Na, R/H) was determined by the iodometric method. Additionally, *N*-chlorosulfonamide groups in the H form were determined by alkalimetric pH titration.

The ferrous/ferric ion concentrations were determined by standard spectrophotometric methods (Spekol 1200, Analytic Jena, Germany). The Fe(II) concentration was determined using the formation of an orange complex compound with 1.10 phenanthroline monohydrate. The absorbancy measurement was taken at 510 nm wavelength [19]. Fe(III) concentration was determined by the use of the red-colored complexes which were formed by the reaction of Fe(III) with thiocyanates. The absorbency was determined at 480 nm wavelength.

Chloride ions were estimated by argentometric titration, using 0.01 M $AgNO_3$ with the Ag/AgCl/calomel electrodes system.

Redox potentials of R/Na and R/H

Into 11 separate samples of R/Na (0.48 g, ~2.0 mequiv of active chlorine), or 11 separate samples of R/H (0.42 g, ~2.0 mequiv of active chlorine), we introduced the following increasing solution volumes of 0.02 M $FeSO_4$ (in water or 0.01 M H_2SO_4): (1) 0.0 mL, (2) 12.5 mL, (3) 25 mL, (4) 37.5 mL, (5) 50 mL, (6) 62.5 mL, (7) 75 mL, (8) 87.5 mL, (9) 100 mL, (10) 125 mL, and (11) 150 mL. To the first (1) sample of the copolymers only distilled water (or 0.01 M H_2SO_4) was added. The increasing solution volumes of $FeSO_4$ were required to bring about a reduction of (1) 0 %, (3) 25 %, (5) 50 %, (7) 75 %, and (9) 100 % of the functional group active chlorine. However, the last two samples for each copolymer contained (10) 125 % and (11) 150 % of the ferrous ion relative to stoichiometry. All these samples, in closed vessels, were shaken at room temperature. After 24 h, the electric potential of the reaction media in the vessels (protected from air contact) was measured by means of a platinum/calomel electrode pair.

Ferrous solution treatment

In all studies involving the batch regime at room temperature, a measured amount of the resin (ca. 0.50 g R/Na or R/H), placed in a flask, was shaken mechanically with a ferrous solution, employing different acidity media: (a) 200 mL of 0.02 M $FeSO_4$ (100 % excess of ferrous ions) or (b) 50 mL (100 % excess of active chlorine). Time-dependant measurements were made of the Fe(II) and Fe(III) contents in solution. After the reaction, the polymeric reagent was separated from the reaction medium by filtration; it was water-washed and then washed with 50 mL of 1 M H_2SO_4. The concentration of Fe(II) and Fe(III) ions in the effluent was determined. Finally, the spent resin was analyzed for active chlorine content.

In the experiments involving the dynamic regime, a sample of R/Na (9.5 g in the dry state, ~17.5 mL after swelling in water, 40 mequiv active chlorine content) was packed into a glass column (inner diameter ~1.15 cm; height of packing ~17.5 cm). The resin bed of R/Na was transformed into hydrogen form by allowing first 1 L of 0.05 M CH_3COOH to pass through the bed, and then distilled water, until neutral reaction of the outflow was achieved. Next, 0.0025 M $FeSO_4$ solutions of diverse acidity were passed through the bed of R/Na or R/H. The examined flow rate was ~15 bed volumes/h. Fractions (250 mL) were collected to estimate their composition in terms of pH and ferrous, ferric, and chloride ions. When the copolymer lost its oxidizing capacity, the resin bed was washed with distilled water. Next, 1 M H_2SO_4 was passed through the column and fractions of ca. 25 mL were collected. They were analyzed for the content of Fe(II) and Fe(III) ions. Finally, the exhausted copolymer was removed from the column, then water-washed, air-dried, and subjected to an analysis of active chlorine content.

RESULTS AND DISCUSSION

In our previous investigations, we utilized the *N*-chlorosulfonamide copolymer as a heterogenic oxidant for toxic admixtures, which may occur in waters in the form of anions; the admixtures were thereby transformed by oxidation to less harmful products (e.g., the sulfides to sulfates, the nitrites to nitrates). Now, for the first time, we investigate the *N*-chlorosulfonamide copolymer reaction with metal cations. This type of reaction, with the participation of micromolecular organic chloramines (inter alia Chloramine T) is described in the literature and is utilized in redoximetry. We have foreseen that the utilization of a heterogenic oxidant would be advantageous for the processes of natural and industrial water treatment in many respects. One example is the formation of cations of some metals, in particular those which deposit more easily after oxidizing to a higher oxidation degree. The de-ironing of waters is one of the more important processes in which these kinds of oxidants (the copolymers) could be of value, in particular when the problem is the removal of residual amounts of these ions.

In the Experimental Section, we observe that the *N*-chlorosulfonamide copolymer contains a small quantity of sulfonic groups with cation exchange properties, besides containing the fundamental functional groups with their oxidative properties. The sulfonic groups arise as a result of the hydrolysis which occurs as a side reaction during copolymer sulfonamide preparation. These groups are able to bind the Fe(II)/Fe(III) cations, and they show a higher affinity to the Fe(III) ions than to the Fe(II) ions. It is worth adding that the theoretic oxidation capacity of the *N*-chlorosulfonamide copolymer, in relation to Fe(II), is several times greater than its ion exchange capacity coming from the sulfonic groups.

In the preliminary examination, we used the batchwise method. Fe(II) ions were oxidized by means of the R/Na copolymer. A solution of 0.02 M $FeSO_4$ with increasing acidity was added to samples of the copolymeric oxidant, whereby the influence of the pH on the reaction progression was examined (Fig. 1a, Table 1, where the reductor is in 100 % excess in relation to the stoichiometry of the oxidant). Favorable progress of the process was noted in all media under examination. Distinct progress of the Fe(II) to Fe(III) oxidation process was noted, as well as the favorable influence of the low pH. The oxidation capacity of the copolymer, determined after 24 h, was highest in the 0.1 M H_2SO_4 solu-
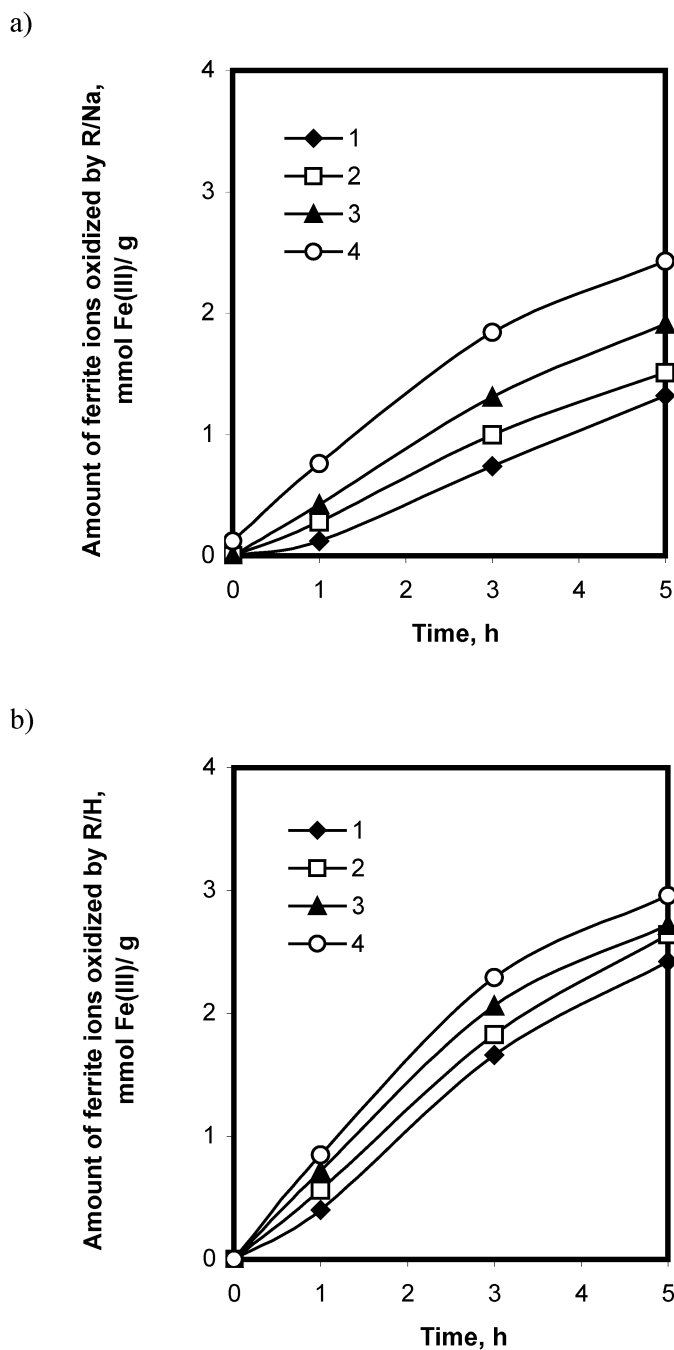
a)

b)

Fig. 1 Amount of ferric ions oxidized by copolymers in a batchwise reaction: (a) 0.48 g R/Na + 200 mL 0.02 M $FeSO_4$ in (1) water, (2) 0.001 M H_2SO_4, (3) 0.01 M H_2SO_4, (4) 0.1 M H_2SO_4; (b) 0.42 g R/H + 200 mL 0.02 M $FeSO_4$ in (1) water, (2) 0.001 M H_2SO_4, (3) 0.01 M H_2SO_4, (4) 0.1 M H_2SO_4.

tion; this was 2.96 mmol Fe(II)/g [i.e., 69 % of the theoretic oxidation capacity which, calculated from eq. 1, was 4.3 mmol Fe(II)/g]. Incidentally, some of the copolymers' samples changed their color from cream to reddish-brown. The solution with $FeSO_4$ alone (without any sulfuric acid addition) caused the greatest change in color. The copolymer color change resulted from iron deposited inside the bead inner space. Of particular significance here is the deposition of sparingly soluble Fe(III) compounds at relatively high pH (although this may be still lower than pH 7.0). It should be added that the quantity of deposited ferrous/ferric compounds was considerably higher than that caused by the ion exchange reaction of the $-SO_3H$ groups. The ferrous/ferric compounds deposited inside the copolymer beads could be easily washed out with 1 M H_2SO_4.

Table 1 Results of a 24 h batchwise reaction between R/Na and ferrous ions in media of different acidity, i.e., a 100 % excess of ferrous ions in relation to stoichiometry.

| | 0.48 g R/Na + 200 mL 0.02 M $FeSO_4$ | | | |
	H_2O	in 0.001 M H_2SO_4	in 0.01 M H_2SO_4	in 0.1 M H_2SO_4
Fe(II) in solution, mmol				
Before reaction	4.0	4.0	4.0	4.0
After reaction	3.06	2.92	2.81	2.58
Fe(III) in solution, mmol				
After reaction	0.34	0.60	1.11	1.36
Iron eluted from resin				
Fe(II), mmol	<0.01	<0.01	<0.01	<0.01
Fe(III), mmol	0.60	0.48	0.07	0.05
pH				
Before reaction	3.65	3.11	2.53	1.78
After reaction	2.87	2.75	2.47	1.75
Cl^- in solution after reaction, mmol	0.6	0.68	0.72	0.77
Active chlorine in sample of resin, mequiv				
Before reaction	2.0	2.0	2.0	2.0
After reaction	0.64	0.58	0.44	0.36
Operating oxidizing capacity, mmol Fe(II)/g R/Na	1.96	2.25	2.48	2.96

In the next stage of the investigation, the reagents were used in a reciprocal proportion, whereby a 100 % stoichiometric excess of the active chlorine was provided. These conditions were chosen in order to investigate the activity of the copolymer with respect to a very small concentration of ferrous ions, and in order to drive the reaction to completion (Table 2). As with the previous stage of the investigation, the most substantial conversion of Fe(II) to Fe(III) took place in the most acidic medium: the concentration of ferrous ions fell from 1117 to 55 mg/L after 24 h. This means that 95 % Fe(II) decreased from the solution. Samples of the copolymer were tested for active chlorine content after the end of the process. This established that nearly 50 % of the initial value remained.

Table 2 Results of a 24 h batchwise reaction between R/Na and ferrous ions in media of different acidity, i.e., a 100 % excess of active chlorine in relation to stoichiometry.

Time, h	0.48 g R/Na + 50 mL 0.02 M $FeSO_4$			
	H_2O	0.001 M H_2SO_4	0.01 M H_2SO_4	0.1 M H_2SO_4
	Concentration of ferrous ions in solution, mg Fe(II)/L			
0	1117	1117	1117	1117
1	880	850	690	580
3	570	495	325	255
5	430	375	185	130
24	188	158	79	55
	Concentration of ferric ions in solution after 24 h, mg Fe(III)/L			
24	363	456	914	1010
	Iron eluted from copolymer, mg Fe(III)			
24	29.1	25.65	6.15	2.70
	pH after reaction			
24	3.14	2.95	2.41	1.68
	Active chlorine in a sample of R/Na, mequiv			
Before reaction	2.0	2.0	2.0	2.0
After reaction	0.9	0.90	0.88	0.87

As has been established, the Fe(II) oxidation process benefits from the low pH of the reactive medium, so in the next investigation stage the *N*-chlorosulfonamide copolymer was used in hydrogen form. In all the R/H samples under investigation, higher progress in the Fe(II) to Fe(III) oxidation reaction was detected, compared to the parallel R/Na samples (Fig. 1b, Tables 3 and 4). As shown by Table 3, the oxidation capacity of the copolymer was highest in the medium of 0.1 M H_2SO_4: 4.21 mmol Fe(II)/g (i.e., 88 % of the theoretic oxidation capacity). In the course of the oxidation process, the R/H samples changed color differently than previously—from cream to clear gray. The essential difference was the smaller quantity of iron compounds deposited inside the copolymer beads. This was the effect of the lower pH in comparison with the former process media. Attention should be paid to the Fe(II) concentration change after 24 h in the process, with an excess of R/H (Table 4, 0.1 M H_2SO_4 medium). This fell ca. 150-fold—from 1117 to 8 mg Fe(II)//L.

Table 3 Results of a 24-h batchwise reaction between R/H and ferrous ions in media of different acidity, i.e., a 100 % excess of ferrous ions in relation to stoichiometry.

	0.42 g R/H + 200 mL 0.02 M FeSO$_4$			
	H$_2$O	in 0.001 M H$_2$SO$_4$	in 0.01 M H$_2$SO$_4$	in 0.1 M H$_2$SO$_4$
Fe(II) in solution, mmol				
Before reaction	4.0	4.0	4.0	4.0
After reaction	2.68	2.51	2.42	2.23
Fe(III) in solution, mmol				
After reaction	0.92	1.28	1.49	1.73
Iron eluted from resin				
Fe(II), mmol	<0.01	<0.01	<0.01	<0.01
Fe(III), mmol	0.39	0.22	0.09	0.04
pH				
Before reaction	3.65	3.11	2.53	1.78
After reaction	2.79	2.75	2.34	1.73
Cl$^-$ in solution after reaction, mmol	0.70	0.75	0.82	0.937
Active chlorine in sample of resin, mequiv				
Before reaction	2.0	2.0	2.0	2.0
After reaction	0.50	0.38	0.28	0.11
Operating oxidizing capacity, mmol Fe(II)/g R/H	3.14	3.55	3.76	4.21

Table 4 Results of a 24 h batchwise reaction between R/H and ferrous ions in media of different acidity, i.e., a 100 % excess of active chlorine in relation to stoichiometry.

Time, h	0.42 g R/H + 50 mL 0.02 M FeSO$_4$			
	H$_2$O	0.001 M H$_2$SO$_4$	0.01 M H$_2$SO$_4$	0.1 M H$_2$SO$_4$
	Concentration of ferrous ions in solution, mg Fe(II)/L			
0	1117	1117	1117	1117
1	940	760	760	550
3	570	265	285	285
5	430	190	135	130
24	117	55	11	8
	Concentration of ferric ions in solution after 24 h, mg Fe(III)/L			
24	863	948	1010	1087
	Iron eluted from copolymer, mg Fe(III)			
24	6.81	5.68	4.60	1.10
	pH after reaction			
24	2.76	2.61	2.32	1.66
	Active chlorine in a sample of R/H, mequiv			
Before reaction	2.0	2.0	2.0	2.0
After reaction	0.88	0.87	0.85	0.83

To establish why the *N*-chlorosulfonamide copolymer oxidizes Fe(II) ions faster in the hydrogen form than in the sodium form, reductometric titration of R/Na and R/H by 0.02 M FeSO$_4$ was conducted. To mark the significant points on the potentiometric curve, separate samples of the oxidant and the reducer were used. This procedure was applied because of the low reaction velocity, due to the fact that the reagents formed different states of aggregation.

A comparison of the titration curves establishes that as well as the ionic form of the functional group (Fig. 2a, curves 2 and 3), the process medium pH (Fig. 2a, curves 1 and 2) controls the oxidation process. The highest oxidation potential (+650 mV) was found in the medium of 0.01 M H$_2$SO$_4$. This high potential corresponded with the quantitative oxidation of the Fe(II) ions (Fig. 2b, curve 1). It was observed that the lower the redox potential in the given measured point, the more unreacted Fe(II) remained in the post-reaction solution. This has several causes: the molar proportion of the reagents, the ionic form of the heterogenic oxidant (i.e., the applied copolymer), and the process medium pH.

In the column investigation, the first step was to pass a solution of 0.0025 M FeSO$_4$ (pH = 3.5) over the glass column of the R/Na resin bed. The solution had a fairly high Fe(II) concentration. This was to take advantage efficiently of the total active chlorine combined with the resin, and indicate the operating oxidation capacity. As calculated, the R/Na resin bed which contained 40 mequiv active chlorine can oxidize the Fe(II) ions present in between 10 and 20 L of the said solution. Since the Fe(II) solution is not very persistent, this was prepared immediately before passing to the column, and protected against contact with the air. Given an applied flow rate of ca. 15 bed volumes/h, fractions of 250 mL were collected within 1 h.

The first fractions of the effluent (3.4 L, $V/V_o = 200$) showed a pH > 10 and no Fe(II) or Fe(III) ions (Figs. 3a,b, curve 1). The change of the resin bed color from cream to reddish, which came down from the head of the column, marked the deposition of Fe(II)/Fe(III) compounds inside the copolymer bead structure. In the following fractions, we found a progressive rise in the Fe(II) ions concentration, as well as a much lower than anticipated presence of Fe(III) ions (the pH of the effluent was 2.8–3.0). After passing through a 7.5 L solution ($V/V_o = 440$) the Fe deposits were very distinctly apparent in the resin bed. This was so disadvantageous that the process was stopped when the deposit retarded the flow of the solution (at 14.5 L, $V/V_o = 850$).

Afterwards, the resin bed was water-washed, poured out from the column, and air-dried. It was 9.35 g. This copolymer was contacted with 1 M H$_2$SO$_4$, and the iron compounds were transferred to the aqueous, acidic solution. The chemical analysis showed that the copolymer's structure contained ca. 0.95 g of iron, almost exclusively as the derivatives of Fe(III). The balance of Fe(III) showed that the result of the analyzed process was the oxidation of ca. 1.15 g Fe(II) to Fe(III); however, only 15 % Fe(III) was in the effluent, and as much as 85 % remained in the resin bed. We calculated that the amount of iron separated from the resin bed considerably exceeded the resin's cation exchange capacity. The operating oxidation capacity of the resin bed in column R/Na ($C/C_o = 0.5$, $V/V_o = 480$) was calculated on the basis of the breakthrough curve—this was 20.3 mmol Fe(II), only 47 % of the theoretic oxidation capacity.

In the second column process, the influent concentration was as before, but the resin bed was R/H (Figs. 3a,b, curve 2). The first fractions (1 L $V/V_o = 60$) did not contain any Fe(II) or Fe(III) ions, the pH was 2.75, and the copolymers bed changed color from cream to light green. This showed that the Fe ions were combined by the resin via ion exchange. Subsequently, a fairly high concentration of Fe(III) ions was observed in the effluent, and then their concentration gradually decreased. The pH of the effluent maintained a level of 2.8–2.9. The process was concluded after passing through 17 L FeSO$_4$ ($V/V_o = 970$) of the influent. During the flow, there were fewer small deposits; these were substantially less than before and they did not retard the column process.

At the end of the column process, the treatment of the spent column resin bed followed the previous pattern. As analysis showed, the resin contained ca. 0.75 g Fe in its inner structure, and as before was formed almost exclusively of derivatives of Fe(III). The balance of Fe(III) showed that the result was the oxidation of ca. 1.55 g Fe(II) to Fe(III). Of this amount, one-half of the Fe(III) was in the so-
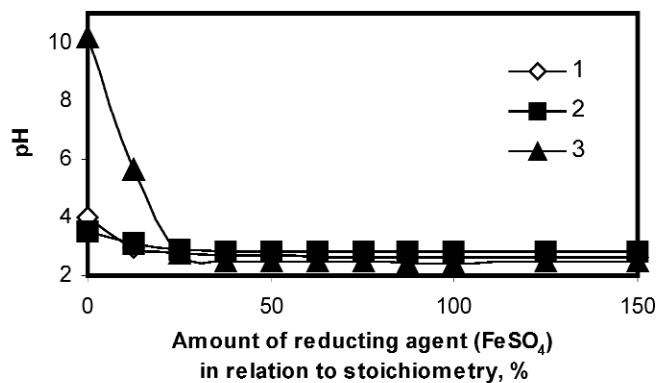
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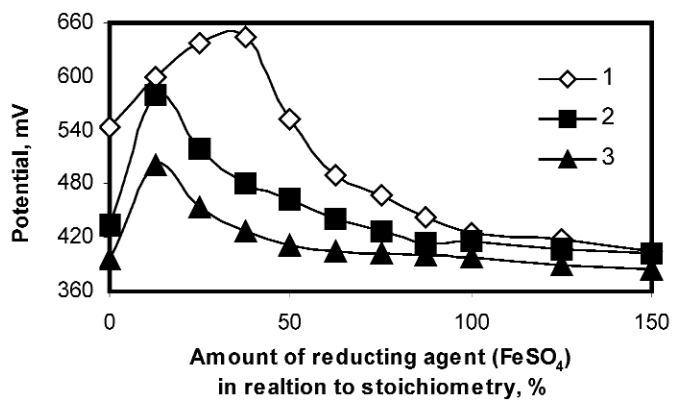
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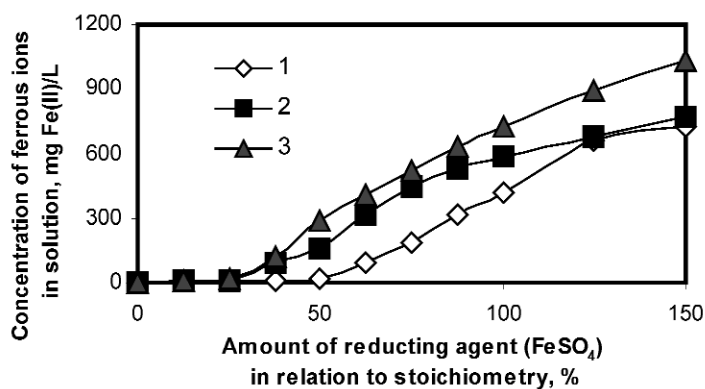
c)

Fig. 2 (a) Redox titration curve of R/Na by 0.02 M $FeSO_4$ in water (3) and the redox titration curve of R/H by 0.02 M $FeSO_4$ in (2) water, in (1) 0.01 M H_2SO_4; (b) concentration of ferrous ions in solution; (c) pH value.
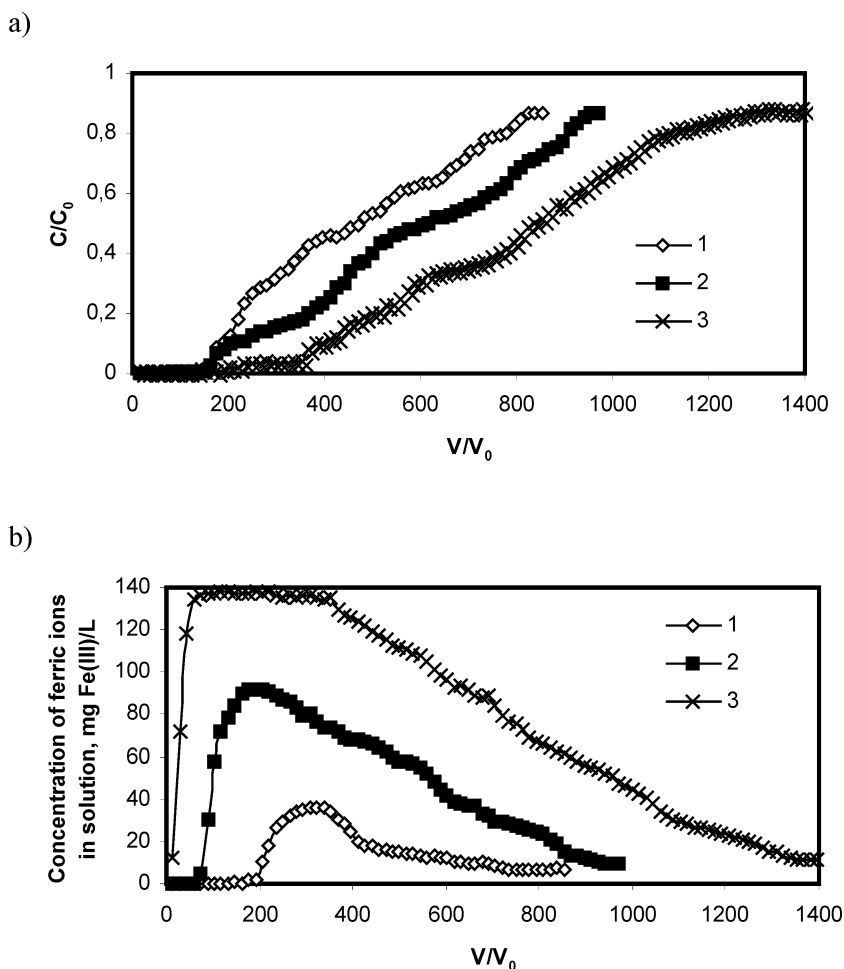
a)

b)

Fig. 3 (a) Ferrous ions breakthrough curve for copolymers in the column process: (1) R/Na, influx 0.0025 M FeSO$_4$ in water, (2) R/H, influx 0.0025 M FeSO$_4$ in water, (3) R/H, influx 0.0025 M FeSO$_4$ in 0.01 M H$_2$SO$_4$; (b) concentration of ferric ions in effluent.

lution; the other half remained in the resin bed. The operating oxidation capacity (calculated on the basis of the breakthrough curve) of the resin bed R/H (C/C$_0$ = 0.5, V/V$_0$ = 620) was 26.4 mmol Fe(II); this was 66 % of the theoretic value. The remainder of the active chlorine may have been unattainable for the influent because of the deposit which blocked the functional groups.

In the last column process (Figs. 3a,b, curve 3), the R/H resin bed was applied, but the influent was 0.0025 M FeSO$_4$ in 0.01 M H$_2$SO$_4$ (pH = 2.40). Although the first three fractions were free of Fe(II), they did not contain the anticipated amount of Fe(III) ions—the ions were bound in the column by way of ion exchange. The following fractions (6.0 L, V/V$_0$ = 350, pH = 2.30) did not contain Fe(II) ions; instead, they contained Fe(III) ions, well into the anticipated high concentration of 140 mg Fe(III)/L. Afterwards, the concentration of Fe(III) gradually decreased; the process concluded after passing through a 24 L solution (V/V$_0$ = 1400). This time, we detected neither the deposition of precipitates nor any impediments in the column function. The analysis of the spent copolymer resin bed showed a trace amount of iron: 44.0 mg Fe(III), which is only 0.082 mmol Fe/g of the copolymer. The operating oxidation capacity of the copolymer in the said conditions was the greatest and was 35.7 mmol Fe(II) (C/C$_0$ = 0.5, V/V$_0$ = 860): i.e., almost 90 % of the theoretic value.

CONCLUSION

The copolymer S/DVB with a macroporous structure which contains *N*-chlorosulfonamide functional groups effectively oxidizes Fe(II) to Fe(III) ions in an aqueous solution. The oxidation capacity of the copolymer is high. It is over 200 mg Fe(II)/g of the resin. It has been established that it is possible to conduct the oxidation process columnwise, in two directions. If the process is at pH < 2.5, then the Fe(III) ions remain in the solution (the effluent) as chemical reaction products. They can be precipitated after neutralization in the form of poorly soluble derivatives. This makes a "deep" de-ironing of waters possible. If the oxidation is carried out at pH > 2.5, the oxidation products Fe(III) only partly remain in the solution (the effluent). They become partly deposited in the copolymer's inner bead structure as oxides and/or hydroxides. These proportions depend on the medium's pH as well as on the ionic form of the copolymer's functional group. The products obtained in this investigation contained ca. 0.1 g Fe(III) within 1.0 g of the copolymer. These products are modern "nanomaterials", that is, hybrid materials whose inner structure contains nanoparticles of ferrous/ferric compounds. These products may be utilized inter alia as specific reagents, sorbents, and catalysts [20–26]. Hybrid polymers which contain in their structure iron compounds can be obtained using a *N,N*-dichloro derivative of the copolymeric sulfonamide ([P]-SO_2NCl_2) as the starting material [27], whereas the method described in this paper, utilizing the R/Na as the raw material, is more effective.

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