

## The Conditions of Cationic Exchange with the Use of Recycling Polystyrene Derivative, the Product of Sulfonation by Silica Sulfuric Acid

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**ABSTRACT:** Growing amount of waste plastics has become an environmental problem on a global scale. This study presents an investigation of the conditions of cleaning water from heavy metal ions using chemically recycled polystyrene. To get effective ion exchangers, the sulfonation of virgin polystyrene and expanded polystyrene wastes were obtained using silica sulfuric acid. As it turned out, the use of this solid sulfonating agent simplifies the separation of the polymeric product from the acid and the solvent in comparison to conventional sulfonation methods. The ion exchange behavior of copper and zinc cations in the yielded sulfonated derivatives of polystyrene was studied. Batch shaking adsorption experiments depending on contact time, pH, temperature, and dosage of adsorbate were carried out. The stability of resin to cyclical adsorption and regeneration (column experiment) was also investigated. We report that resins have a high adsorption efficiency with total ion exchange capacity (IEC) about 2.6 meq g<sup>-1</sup>, which drops with decreasing pH owing to competition between protons H<sup>+</sup> and metal cations, whereas with the increasing resin doses the removal of cations rises for a constant initial metal concentration. The speed of cation exchange for yielded adsorbents was even better than for commercial resins. After 360 cyclical adsorption and regeneration in column, resin had working IEC of about 2.3 meq g<sup>-1</sup>. The study shows that cation exchange resin from polystyrene wastes can be used as an efficient adsorbent for the removal of heavy metal ions from water. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

The presence of heavy metal ions such as cadmium, lead, chromium, copper, and zinc in water often indicates anthropogenic environmental pollution. These metals are of special concern because they are nondegradable and can be bioaccumulated. In industrial wastewater streams and urban runoff samples, copper and zinc are detected in more than 90% of cases, whereas the percentage of cadmium, lead, and chromium was smaller.<sup>1,2</sup> Industrial wastewaters usually contain copper in a concentration range from about 5 to 250 mg L<sup>-1</sup> and zinc in concentration range from 10 to 400 mg L<sup>-1</sup>.<sup>1</sup> Such amounts of harmful metals discharged without treatment are a hazard to the public health and the environment. The World Health Organization recommended a maximum acceptable concentration 1.5 mg L<sup>-1</sup> of copper and 3 mg L<sup>-1</sup> of zinc in drinking water.<sup>3,4</sup>

Copper is not considered very harmful to human health but high accumulation of copper can be the cause of Parkinson's disease,

anemia, allergies, hair loss, appetite disturbance, hyperactivity, low thyroid activity, headaches, skin conditions, constipation, learning disabilities, and/or depression. Zinc in its ionic form, Zn<sup>2+</sup>, is necessary for proper body function, but an excess is toxic. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause considerable health problems, such as stomach cramps, skin irritations, vomiting, nausea, and anemia. Very high levels of zinc can damage the pancreas, disturb the protein metabolism, and cause arteriosclerosis.<sup>5</sup>

To remove metal ions effectively from metal-laden wastewater, the most common techniques such as reduction, precipitation, and ion exchange are used. Recovery of metal value, selectivity, less sludge volume produced, and the meeting of strict discharge specification is the main advantage of ion exchange over chemical precipitation.<sup>6</sup>

The cation exchanger contains permanently bound negatively charged functional groups like the sulfonic ones and less

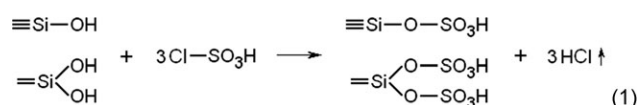
commonly the carboxylic, phosphonic, and phosphinic groups. In cation exchange, ions of positive charge from aqueous solution replace dissimilar cations in the solid resin. It is noteworthy that cation exchanger prefers ions of high charge, small hydrated volume and those which interact strongly with its functional groups.<sup>7–16</sup>

In the present study, adsorption of zinc and copper ions from water using synthesized resins was performed. The cation exchange behavior of chosen metals depending on pH, temperature, agitation time, and the adsorbate amount was studied. Resins were obtained by sulfonation of virgin polystyrene (VPSS) and expanded polystyrene (EPSS) waste using solid silica sulfuric acid as the sulfonating agent. By using silica sulfuric acid as the sulfonating agent for polystyrene modification, it is possible to obtain a product which can be used for purification of water.<sup>17</sup> The synthesized resins caused a decrease in concentration of the solved impurities. Moreover, silica sulfuric acid simplifies the reaction in comparison to the conventional sulfonation methods. These experiments were conducted to confirm the usefulness of the obtained resins in different conditions and to determine the best ones for cation exchange.

## EXPERIMENTAL

### Polystyrene Sulfonation Procedure and Characteristic of the Resins

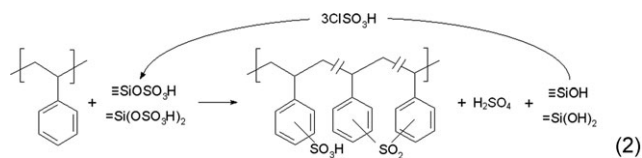
Preparation of silica sulfuric acid: a 500-mL suction flask equipped with a constant pressure-dropping funnel and a gas inlet tube for conducting the HCl gas over the adsorbing solution (i.e., water) was used. It was filled with silica gel dried at 160°C (2–7 mm particle size, from POCh, Gliwice, Poland). Chlorosulfonic acid from Sigma-Aldrich, Saint Louis, USA was added dropwise over a period of 30 min at room temperature. The substrates were mixed with a constant quantity of silica gel: 4.5 g–1 mL of chlorosulfonic acid.<sup>18</sup> Thus, the HCl gas was immediately released from the reaction vessel. After completing the addition of the silica gel, the mixture was shaken for at least 3 h. The chlorosulfonic acid probably reacts with silanol [tbond]Si–OH and silanodiol =Si(OH)<sub>2</sub> groups from the silica gel surface and in consequence silica sulfuric acid is formed:



Samples consisting of 5 g of (Chemical Company Dwory, Oświęcim, Poland,  $M_{r,VPSS} = 170,000$ ) and EPSS waste ( $M_{r,EPSS} = 110,000$ ) were dissolved in 100 mL of 1,2-dichloroethane each. These substrates were then mixed with an appropriate amount of silica sulfuric acid in a thermostated reaction vessel. As 2 mol of ClSO<sub>3</sub>H was used per 1 mol of monomeric unit of polystyrene to synthesize silica sulfuric acid, the polystyrene to sulfonating agent molar ratio was 1 : 2. The experiments were performed for 7 h at a temperature of 60°C.

The suspended small particles of sulfonated derivatives of VPSS and sulfonated derivatives of EPSS waste were separated from

much bigger particles of silica sulfuric acid by filtration and from solvent by decantation and evaporation on the watch glass-making membrane. Polystyrene derivative was then flushed using water and dried to get rid of the presence of H<sub>2</sub>SO<sub>4</sub>, the by-product of sulfone formation. The great advantage of the method was that sulfonated derivatives of polystyrene were easily separated from silica sulfuric acid by filtration and from solvent by decantation. The polystyrene sulfonation with the use of silica sulfuric acid probably proceeds as it is shown in eq. (2).



The resins were washed with 10% (w/w) HCl solution for full protonation. Then, the hydrogen form of the resins was washed with distilled water to remove the excess acid. The dried membrane was crushed with the use of porcelain mortar to get small crumbs.

The total exchange capacity (with unit of meq g<sup>-1</sup> of dry polymer) of sulfonated polystyrene (VPSS and EPSS) was determined by measuring the concentration of H<sup>+</sup> that was exchanged with sodium cation for 24 h at constant temperatures of 20 and 25°C, whereas acid-form resin samples were equilibrated with 0.2 mol L<sup>-1</sup> NaCl solution.

Before the exchange experiments, weighted appropriate amounts of resins were separately conditioned in deionized water for 24 h.

The Fourier transform infrared spectroscopy (FTIR) spectra for the selected products were obtained on the Perkin-Elmer Spectrum One FTIR spectrometer. Samples were prepared in the form of KBr disks.

The contents of sulfur and carbon in obtained products were determined by using a Perkin-Elmer CHNS/O elemental analyzer. The contents of sulfur and carbon were then used for the calculations of the number of sulfonic groups per monomer unit.

Water absorption of sulfonated products was determined by weight from mass differences between wet and dry polymers after a 24-h contact with deionized water.

### Cation Exchange and Batch Experiments

Solutions of heavy metal sulfates (ZnSO<sub>4</sub>, CuSO<sub>4</sub> reagent grade, POCh) were prepared in distilled water. To characterize metal adsorption, stock solutions of 2500 mg L<sup>-1</sup> of each metal ion were diluted in water with conditioned resin to obtain samples containing 100 mg L<sup>-1</sup> of metal ion. Under these experimental conditions, it was confirmed that no chemical precipitation occurred. The solutions were shaken (180 rpm) in 250-mL closed flasks with appropriate amounts of resins in an incubator at 20–60°C for a period of 5–120 min. The initial water pH was adjusted with diluted 0.1 M HCl at the range of 2.7–5.2. Then, the resins were separated by decantation and the water was analyzed by a Thermo E.C. Solaar M AAS spectrometer. The metal ion concentration in the original solutions was also determined.

The percentage removal of the metal ions %A and their uptake on the VPSS and EPSS resins were calculated using the following equations:

$$\%A = (c_i - c_f) \cdot 100 / c_i (\%) \quad (3)$$

$$Uptake = [(c_i - c_f)V] / (m \cdot M) \text{ (mmol g}^{-1}\text{)} \quad (4)$$

$$\text{Competitive uptake} = \left\{ [(c_{i1} - c_{f1}) / M_1] + [(c_{i2} - c_{f2}) / M_2] \right\} V / m \text{ (mmol g}^{-1}\text{)} \quad (5)$$

where  $c_i$  and  $c_f$  are the concentrations of the metal ion ( $\text{mg L}^{-1}$ ) in initial and final solutions, respectively,  $V$  is the volume of the solution (L),  $m$  is the mass of the adsorbent (g),  $M$  is the molar mass of metal ( $\text{g mol}^{-1}$ ), 1 is zinc, and 2 is copper.

The pH of solution at equilibrium with metal ions was predicted with the assumption that zinc or copper metal ion reveals one (eq. (6)) and two (eq. (7)) protons from the exchanger. The calculated pH was then compared with the measured pH.

$$\text{pH}_{1\text{H}} = -\log \left( 10^{-\text{pH}_i} + \frac{c_i - c_f}{M \cdot 1000} \right) \quad (6)$$

$$\text{pH}_{2\text{H}} = -\log \left( 10^{-\text{pH}_i} + \frac{(c_i - c_f) \cdot 2}{M \cdot 1000} \right) \quad (7)$$

where  $\text{pH}_i$  is the initial pH of the metal solution.

### Stability of the Resin and Column Experiments

Stability of the resin during adsorption of copper ions and EPSS resin regeneration were studied in column. About 1.5 g of dry resin was overloaded by 10 mL 36 g  $\text{L}^{-1}$  copper sulfate, washed with deionized water, then regenerated by introducing 10 mL 3% (v/v) sulfuric acid, and once again washed with deionized water, all cyclically 360 times. After every 20 cycles, resin was fully protonated with 30 mL 3% (v/v) sulfuric acid and washed with deionized water. Working capacity of the resin was determined titrimetrically by measuring amounts of protons revealed by 10 mL sodium chloride 30% (w/v) solution and 100 mL of deionized water.

## RESULTS AND DISCUSSION

### Characterization of the Obtained Resins VPSS and EPSS

Analysis of FTIR spectra of obtained resins confirmed polystyrene sulfonation (Figure 1). The appearance of a band at  $1175 \text{ cm}^{-1}$  from stretching vibration of  $\text{O}=\text{S}=\text{O}$  was used to confirm the sulfonation of polystyrene. Further evidence of sulfonation was the presence of the peaks at  $1097$  and  $1128 \text{ cm}^{-1}$ . These bands have been attributed to the in-plane skeletal vibrations of the disubstituted benzene rings.<sup>19</sup> Changes in the intensities of the band at  $698$  and  $756 \text{ cm}^{-1}$  were also observed. These two bands are characteristic for out-of-plane skeleton binding vibrations of the benzene ring and the out-of-plane binding vibration of the five  $-\text{CH}-$  groups in the benzene ring characteristic for the monosubstituted benzene ring, that is without the sulfo-group.<sup>20</sup> Depending on the sulfonation conditions, the formation of sulfone and the crosslinking of the product is possible. The FTIR spectra of different polysulfones<sup>21</sup>

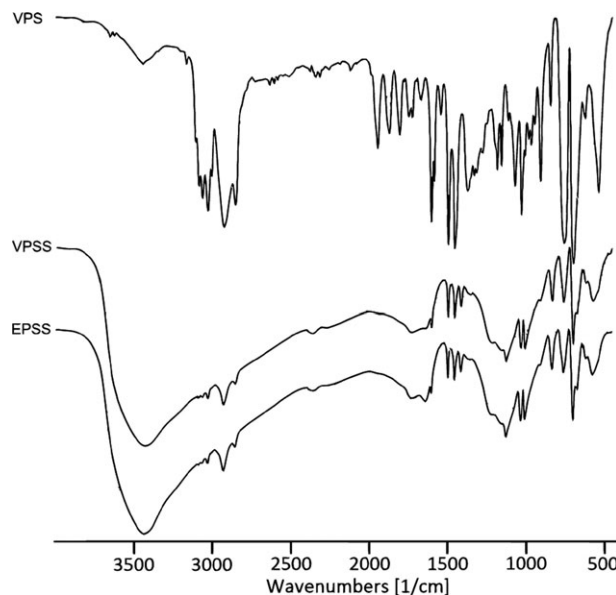


Figure 1. FT-IR spectra of polystyrene VPS and resins: VPSS, EPSS.

have characteristic bands for the  $\text{C}-\text{SO}_2-\text{C}$  group. We observed a band at  $770 \text{ cm}^{-1}$  that corresponds to the symmetric stretching of  $\text{C}-\text{S}-\text{C}$ . Probably, the obtained sulfonated derivatives of polystyrene are crosslinked via intermolecular and intramolecular sulfone bridges. The  $-\text{OH}$  groups' (probably from  $-\text{S}(=\text{O})_2(\text{OH})$  groups) stretching vibration at frequency  $3.4 \cdot 10^2 \text{ cm}^{-1}$  was observed in VPSS and EPSS FTIR spectra.<sup>22</sup>

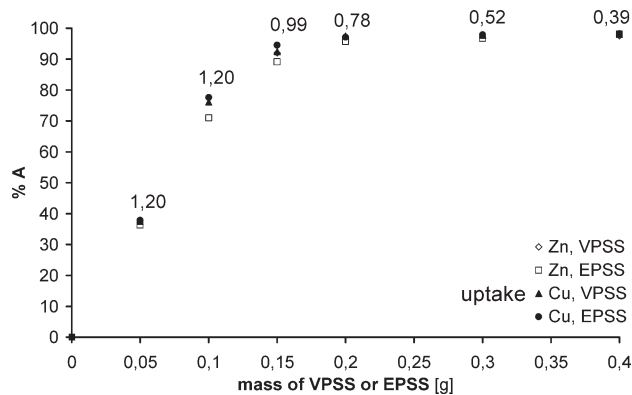
Both VPSS and EPSS resins were insoluble in water but absorbed their enlarging mass about eight times.

Elemental analysis showed that VPSS and EPSS resins had approximately 62 and 61% (weight) of carbon and about 9.2 and 8.9% (weight) of sulfur which means that statistically there were together about 0.44 and 0.43 of  $-\text{S}(=\text{O})_2(\text{OH})$  and  $-\text{C}-\text{S}(=\text{O})_2-\text{C}-$  groups per monomer unit of polymer, respectively.

### Effect of Resin Dose on Adsorption

The effect of resin dosage on the removal of zinc and copper ions by VPSS and EPSS cation exchange resins is shown in Figure 2. The amount of resin was tested in the range of 0.05–0.4 g and equilibrated for 2 h at  $20^\circ\text{C}$  at an initial metal concentration of  $100 \text{ mg L}^{-1}$  in 100 mL solutions separately.

It was found that the adsorption percentage of metal ions increased with higher resin dosages for a given initial concentration, and the percent adsorption approached 100% for 0.2 g of resin for both separately adsorbed metal ions (Figure 2). This can be explained by the fact that the increasing amount of the adsorbent provides a greater number of adsorption sites for a fixed initial solute concentration. Consequently, the optimum dosage of resin for adsorption experiments was determined to be 0.2 g and it was subsequently used in all the following batch experiments. It is worth noting that for the same concentration of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions, as in our experiment, Pehlivan and Altun<sup>23</sup> have used 0.1 g of the commercial Dowex 50 W resin to remove ions from only 20-mL solutions ( $25^\circ\text{C}$ , 180 rpm).



**Figure 2.** Effect of VPSS dosage on uptake ( $\text{mmol g}^{-1}$ ) of copper(II) ions and the effect of VPSS and EPSS dosage on the adsorption (%A) of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions from water (initial concentration of each metal  $100 \text{ mg L}^{-1}$ ; volume of sorption medium,  $100 \text{ mL}$ ; time of adsorption,  $2 \text{ h}$ ; stirring rate,  $180 \text{ rpm}$ ; temperature,  $20 \pm 1^\circ\text{C}$ ; initial pH,  $5.2$ ).

### Effect of Agitation Time on Adsorption

Adsorption of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  by two different resins VPSS and EPSS was studied by mixing samples for a predetermined time interval in a temperature-controlled shaker. Figure 3 shows that the adsorption of heavy metal ions is rapid at the initial step up to  $15 \text{ min}$ , then continues at a much slower rate to reach a maximum value at about  $30 \text{ min}$  for both metal ions. The results show similarities of physical properties and valence of the metals. This can be reasonably explained by considering the diffusion of the metal ions through the ionic membrane. These processes depend on the ionic radius of the metals and the stability of the metal–ligand complex.

The optimal amount  $0.2 \text{ g}$  of VPSS and EPSS per  $100 \text{ mL}$  of  $100 \text{ mg L}^{-1}$  of metal ions solutions corresponds with the optimal amount of commercial Amberlite IRN77 resin which was used by Rengaraj et al.<sup>6</sup> to remove  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Ni}^{2+}$  from water. Amberlite IRN77 resin effectively removed heavy metal ions after no  $<150\text{-min}$  batch experiments. The Dowex 50 W resin,  $0.1 \text{ g}$  per  $20 \text{ mL}$  of metal ions solution cleaned water from zinc and copper ions after  $60 \text{ min}$ .<sup>23</sup>

A looser structure of the resins and its high-moisture holding capacity in water (Table I) is the consequence of low crosslinking of VPSS and EPSS and the presence of sulfone bridges (besides sulfo-groups) with high affinity of water. Functional sulfo-groups in these ion exchangers are easily available to cations. Probably, this is the reason for the fast removal of heavy metal ions from water by VPSS and EPSS. On the contrary, commercial resins Dowex 50 W and Amberlite IRN77 consist of polystyrene and divinylbenzene as the crosslinking agent. In spite of the fact that commercial resins have more sulfo-groups in the same mass (total exchange capacity, Table I) as VPSS and EPSS, they are slower exchangers owing to their consistency.

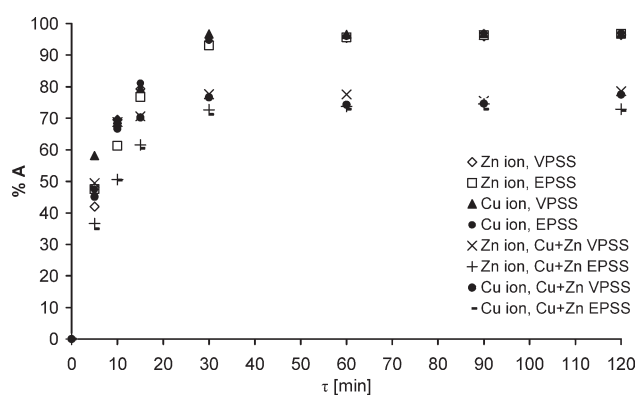
### Effect of pH on Adsorption

Owing to the formation of metal hydroxides and their precipitation at high pH, the initial pH of the metal ion solutions was below 6. These results (Figure 4) suggest that the metal ion adsorption decreases under highly acidic condition for the obtained resins. At

low pH, the adsorption of copper was found to be lower owing to the high concentration of very mobile hydrogen ions.

Owing to the electron-donating nature of  $-\text{S}(=\text{O})_2(\text{O}^-)$  group and the electron-accepting nature of zinc and copper metal cations, the ion exchange mechanism could be preferentially considered. The  $\text{Zn}^{2+}$  as well as  $\text{Cu}^{2+}$  may be attached to two hydroxyl groups from two adjacent sulfo-groups which can donate two pairs of electrons to the metal ion and release two hydrogen ions into solution. At low pH owing to the numerical dominance of  $\text{H}^+$  over metal cations, the sulfo-groups are protonated and the surface charge diminishes. At pH 2.7, before exchange starts there are slightly (about 1.3 times) more protons than zinc or copper cations in the solution. A removal of metal ions from water is correlated with the release of  $\text{H}^+$  which makes their dominance much bigger. On the basis of pH values and %A experimental data at equilibrium, it can be calculated that the dominance of protons over copper and zinc is 30 and 39 times greater, respectively. The value of pH calculated with the assumption that one  $\text{Cu}^{2+}$  reveals two protons is close to pH measured (Figure 4). The data for zinc (data not shown) are similar and indicate that, in general, metal ions tend to attach to the number of sulfo-groups that equal their oxidation number.

The Zn and Cu metal cations are present as hexaqua complex ions with six surrounding water molecules in the solution and they probably pass through resin in this form.<sup>24</sup> As the adsorption phenomena depend on the charge density of cations, the diameter of hydrate cations is very important. The charges of the metal cation are therefore the same at higher pH,  $\text{Zn}^{2+}$  ions with a greater diameter and are less adsorbed than  $\text{Cu}^{2+}$  ions with a smaller diameter. The situation is different when pH is very acidic. As electronegativities of zinc and copper are 1.66 and 1.75, respectively, in the Allred and Rochow scale, the zinc ions are less pH sensitive than the copper ions probably owing to its higher affinity to  $-\text{O}^-$  group of the sulfo-group. As the pH value is significant for the performance of the resin, the differences in binding



**Figure 3.** Effect of contact time on the separate and competitive adsorption (%A) of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions from water by VPSS and EPSS resins (initial concentration of each metal,  $100 \text{ mg L}^{-1}$ ; volume of sorption medium,  $100 \text{ mL}$ ; amount of resin,  $0.2 \text{ g}$ ; stirring rate,  $180 \text{ rpm}$ ; temperature,  $20 \pm 1^\circ\text{C}$ ; initial pH,  $5.2$ ).

**Table I.** Characteristic Data of Tested VPSS and EPSS Compared With Selected Commercial Cation Exchangers

Characteristic	VPSS	EPSS	Dowex 50 W-X8 <sup>a</sup>	Amberlite IRN77 <sup>a</sup>
Active group	Sulfonic acid	Sulfonic acid	Sulfonic acid	Sulfonic acid
Matrix	Sulfone crosslinked PS	Sulfone crosslinked PS	PS-DVB gel	PS-DVB gel
Ionic form	H <sup>+</sup>	H <sup>+</sup>	H <sup>+</sup>	H <sup>+</sup>
Physical form	Irregular crumbs	Irregular crumbs	Spherical beads	Spherical beads
Mean particle size (mm)	1	1	0.56	0.65
Total exchange capacity (meq g <sup>-1</sup> ), dry resin	2.65	2.59	4.8	≥4.8
	2.64 <sup>b</sup>	2.58 <sup>b</sup>		
Moisture holding capacity (%)	680	530	55	49-55

<sup>a</sup>Manufacturer data, <sup>b</sup>Total exchange capacity determined at 20°C. Abbreviation: PS-DVB, poly(styrene-co-divinylbenzene).

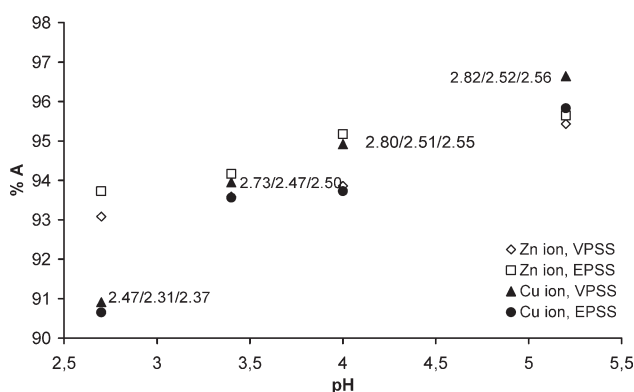
affinity of heavy metal ions can be used as the way for their separation from the exchanger.

### Effect of Temperature on Adsorption

The effect of temperature on the adsorption of zinc and copper ions was investigated in a batch-type reaction. The percentage adsorption vs. temperature curves is shown in Figure 5. The adsorption of zinc cations is very high and generally does not change with temperature. The experimental results suggest that binding of copper ions is slightly more temperature dependent than that of zinc ions. The maximum adsorption of copper rises at the temperature range from 20 to 40°C. At 40°C, the maximum adsorption of this metal reaches its maximum. Above 40°C, desorption of copper ions prevails over adsorption.

### Competitive Adsorption Behavior on Adsorption

Competitive adsorption of zinc and copper ions by VPSS and EPSS resins was studied. In the control experiment, zinc and copper are used separately. Then, the removal of zinc and copper ions after 60 min reached more than 95% for both metals

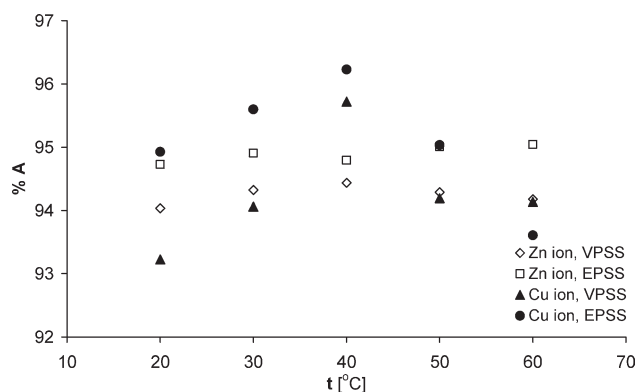


**Figure 4.** Effect of pH on the adsorption (%A) of Zn<sup>2+</sup> and Cu<sup>2+</sup> ions from water by VPSS and EPSS resins (initial concentration of each metal 100 mg L<sup>-1</sup>; volume of sorption medium, 100 mL; amount of resin, 0.2 g; stirring rate, 180 rpm; temperature, 20 ± 1°C; agitation time, 1 h); p<sub>H1H</sub>/p<sub>H2H</sub>/p<sub>Hm</sub>—pH of samples with VPSS and Cu<sup>2+</sup> at equilibrium; p<sub>H1H</sub>—pH predicted with assumption that metal ion replaces one H<sup>+</sup> from resin; p<sub>H2H</sub>—pH predicted with assumption that metal ion replaces two H<sup>+</sup> from resin; p<sub>Hm</sub>—pH measured.

and for both VPSS and EPSS resins (Figure 3). When Zn<sup>2+</sup> and Cu<sup>2+</sup> as competing ions were present together in 100-mL solution at the same concentration of 100 mg L<sup>-1</sup> each, a reduction of their removal to about 70% was observed (Figure 3). Metal ions even if attached to two adjacent sulfo-groups do not use all possible active sites in the resin. The total exchange capacities of both VPSS and EPSS resins, (Table I) are much higher than the double value of the uptake ions removed separately after reaching the equilibrium (30 min or more, Table II). Therefore, in VPSS and EPSS, a lot of free changing sites which could remove cations from water still remain. According to the data summarized in Table II, uptakes of cations removed separately are minor than *uptakes* of cations removed simultaneously by the same amounts of resins. The reason for this phenomenon is probably owing to the presence of many metal ions with high affinity to sulfo-groups which can compete with hydrogen cations. A faster adsorption of metal ions by VPSS resin than by EPSS shows that a higher total ion exchange value of VPSS should be taken into account.

### Stability of EPSS Resin to Adsorption and Regeneration

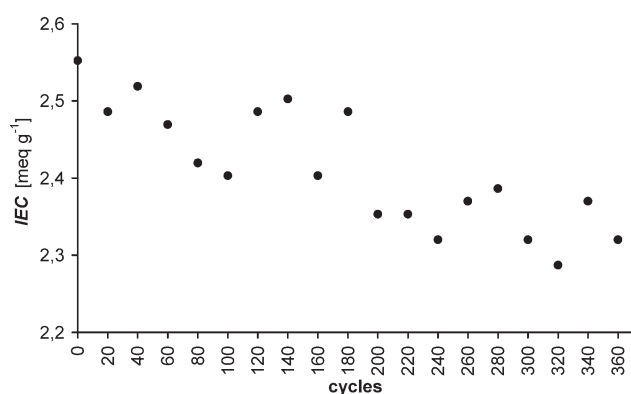
Stability of the EPSS resin during adsorption of copper ions and resin regeneration was studied in column. Resin was overloaded by copper sulfate, washed with deionized water, then



**Figure 5.** Effect of temperature on the adsorption (%A) of Zn<sup>2+</sup> and Cu<sup>2+</sup> ions from water by VPSS and EPSS resins (initial concentration of each metal 100 mg L<sup>-1</sup>; volume of sorption medium, 100 mL; amount of resin, 0.2 g; stirring rate, 180 rpm; agitation time, 1 h; initial pH, 5.2).

**Table II.** Uptake of Zinc and Copper Ions from Water by VPSS and EPSS Resins as a Function of Contact Time (Initial Concentration of Each Metal 100 mg L<sup>-1</sup>; Volume of Sorption Medium, 100 mL; Amount of Resin, 0.2 g; Stirring Rate, 180 rpm; Temperature, 20 ± 1°C; pH Without Adjustment)

t (min)	Uptake (mmol g <sup>-1</sup> )					
	Zn <sup>2+</sup>		Cu <sup>2+</sup>		Zn <sup>2+</sup> + Cu <sup>2+</sup>	
	VPSS	EPSS	VPSS	EPSS	VPSS	EPSS
5	0.32	0.36	0.47	0.38	0.74	0.56
10	0.53	0.47	0.56	0.54	1.06	0.79
15	0.61	0.59	0.64	0.65	1.10	0.95
30	0.72	0.71	0.77	0.76	1.21	1.13
60	0.73	0.73	0.77	0.77	1.19	1.15
90	0.73	0.74	0.78	0.78	1.17	1.15
120	0.74	0.74	0.77	0.78	1.22	1.14

**Figure 6.** Effect of cyclical copper cations adsorption by EPSS resin and cationite regeneration on working ion exchange capacity (IEC) of the resin (column experiment, one cycle: overloaded resin capacity, washed excess of metal ion, regenerated resin with the use of 3% H<sub>2</sub>SO<sub>4</sub> (v/v) solution, and washed excess of acid; mass of dry EPSS resin, 1.5 g; column diameter, 1 cm; room temperature).

regenerated by introducing 5% sulfuric acid, and once again washed with deionized water all cyclically 360 times. Shrinking increased the speed of flow. During regeneration, resin lost color and swelled, which resulted in slowing down the flow. After every 20 cycles and full protonation, working capacity of the resin was determined titrimetrically, that is by measuring amounts of protons revealed by sodium chloride solution. Beads of EPSS cationite were blue and shrunk after treating with copper sulfate. In column, during cycles of adsorption and regeneration, the ability of resin to exchange cations diminished from about 2.5 to 2.3 meq g<sup>-1</sup> (Figure 6). Pattern is nonlinear owing to low repeatability of cation exchange in column. However, it can be concluded that during usage EPSS cationite loses its exchange abilities.

## CONCLUSIONS

The chemical modification of polystyrene and polystyrene waste with the use of solid silica sulfuric acid as sulfonating agent was performed. The exchange of zinc and copper cations by the resins obtained in the batch experiments depended on the adsorbate amount, agitation time, pH, and temperature.

Generally, synthesized resins caused a decrease in concentration of the solved impurities. The amount of synthesized adsorbate which must be used for effective removal of heavy metal ions from water is the same or smaller in comparison to commercial exchangers. However, the great advantage of the obtained sulfonated derivatives of polystyrene is the rate of metal removal. Experimental data showed that these resins can purify water at least twice as fast as the commercial one. The temperature and pH influence the metal adsorption. Low pH of the solution causes the decrease in the removal of metal cations owing to their competition with protons. The competitive adsorption of zinc and copper ions revealed their similar affinity to sulfo-groups. Resins could adsorb much more Zn<sup>2+</sup> and Cu<sup>2+</sup> ions when they were both present in the solution than in the case when adsorption was conducted separately for each of them. After many cyclical adsorption and regeneration, resin was still able to exchange metal cations.

The experiments showed that VPSS and EPSS resins are effective cation exchangers. Thus, the problem of environmental pollution by polystyrene waste and heavy metal ions can be resolved by polymer chemical modification into ion exchange resin.

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