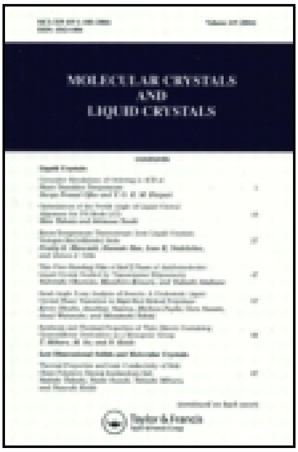

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New Applications of Sulfonated Derivatives of Polystyrene Waste

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New Applications of Sulfonated Derivatives of Polystyrene Waste

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The solid silica sulfuric acid was used to heterogeneous sulfonation of polystyrene waste dissolved in organic solvent. After sulfonation, small suspended particles of polystyrene derivatives were easily separated from much bigger particles of silica sulfuric acid by filtration and from solvent mostly by decantation and additionally by evaporation. The characteristics of adsorption of heavy metal cations on resins from polystyrene were compared with that of commercial resins. It was proved that synthesized resins are effective cation exchangers. The advantage of obtained resins was their high rate of metal removal.

Keywords Heavy metals; ion exchange; polystyrene; sulfonation

Introduction

Unique properties of polymer can arise by incorporating sulfonic groups via sulfonation. The improvement of properties like increased strength, hydrophilicity and proton conductivity have led to an exploration of a variety of applications of sulfonated polymers, such as membranes for fuel cells, plasticizers for macro-defect-free concretes, flocculants and ion-exchange resins [1–4].

The current intense research and general interest in heterogeneous sulfonation are the result of the opportunities such systems present for basic research, and of the undisputable importance such systems have for industry and in developing technologies. Therefore we applied the Neihoff method of sulfonation to convert polystyrene (VPS - virgin polystyrene, EPS - expanded polystyrene) into a polymeric water soluble flocculant [5]. These sulfonated derivatives usually find application in the industrial water treatment due to the lower consumption of the coagulants necessary, short flocculation time and improved sedimentation properties of suspensions [6–8].

Unfortunately the Neihof method of sulfonation poses problems due to the desulfonation processes. Moreover, this method requires a large excess of sulfonation agent, as many sulfonation methods do, because the water by-product slows the reaction down by diluting

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the acid. A large amount of "used acid" obtained in batch reactions is usually neutralized and disposed while in continuous processes it has to be recycled by complex techniques. The separation of the products from the sulfonation agent is a difficult and energy consuming process that habitually implies a basic aqueous work-up. Moreover, many sulfonation agents are corrosive and dangerous to transport and handle. Consequently, any reduction in the amount of the sulfonation agent required and/or any simplification in the handling procedures would be highly convenient in terms of risk reduction, economic advantages and environmental protection.

As it was previously proven [9,10] silica sulfuric acid simplifies the sulfonation of small aromatic compounds in comparison with the conventional sulfonation methods. Therefore the solid silica sulfuric acid was used to heterogeneous sulfonation of virgin polystyrene (VPS) and expanded polystyrene waste (EPS) dissolved in organic solvent.

The presence of heavy metal ions like cadmium, lead, chromium, copper and zinc in water often indicates anthropogenic environmental pollution. These metals are of particular concern because they are non-degradable and can be bioaccumulated. In industrial wastewater streams and urban runoff samples, copper and zinc are detected in over 90% frequency, while cadmium, lead and chromium are detected to a lesser extent [11,12]. Industrial wastewaters usually contain copper in a concentration range from about 5 to 250 mg L^{-1} and zinc in concentration range from 10 to 400 mg L^{-1} [7]. Such amounts of harmful metals discharged without treatment may endanger public health and the environment.

To effectively remove metal ions from metal-laden wastewater, the most commonly used techniques like reduction and precipitation and ion-exchange are used. The main advantages of ion-exchange over chemical precipitation are its recovery of metals, selectivity and the meeting of strict discharge specification [13].

In the present study, adsorption of zinc and copper ions from water using synthesized resins was studied. The cation exchange behavior of chosen metals was studied depending on pH, temperature, agitation time and adsorbate amount. Stability against temperature, oxidizing agent and cyclical adsorption and regeneration of obtained resin were also examined. These experiments were conducted to confirm the usefulness of obtained resins at different conditions and to indicate the best ones for cation exchange.

Experimental

Polystyrene Sulfonation Procedure

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). Chlorosulfonic acid from Sigma-Aldrich was added dropwise over a period of 30 minutes at room temperature. The substrates were mixed with a constant quantity of silica gel: 4.5 g to 1 mL of chlorosulfonic acid [6]. 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 $\equiv$Si$-$OH and silanodiol $=$Si(OH)$_2$ groups from the silica gel surface and in consequence silica sulfuric acid is formed.

Samples consisting of 5 g of virgin polystyrene (VPS from Chemical Company "Dwory" in Oświęcim Poland, $M_{r,vVPS} = 170\,000$) and expanded polystyrene waste (EPS, $M_{r,vEPS} = 110\,000$) 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. Since 2 moles of $ClSO_3H$ were used per 1 monomeric unit of polystyrene to synthesize silica sulfuric acid, the polystyrene to sulfonating agent ratio was 1:2. The experiments were performed with a substrates ratio of 1:2, for 7 hours at 60°C.

The suspended small particles of sulfonated derivatives of virgin polystyrene (VPSS) and sulfonated derivatives of expanded waste polystyrene (EPSS) 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_2SO_4, the by-product of sulfones formation. The products were insoluble in water but absorbed a lot of water. It seems that obtained sulfonated derivatives of polystyrene are cross-linked via intermolecular and intramolecular sulfone bridges.

The resins were then washed with 10% (w/w) HCl solution for full protonation. Then the hydrogenated resins were washed with deionized water to remove excess acid. The dried membrane was crushed with the use of porcelain mortar to make small crumbs.

Cation Exchange, Batch Experiments

The ion exchange capacity *IEC* (with unit of mmol g^{-1} of dry polymer) of sulfonated polystyrene (VPSS, EPSS) was determined by measuring the concentration of H_3O^+ from protons that were exchanged with sodium cations for 24 hours at a constant temperature of 20°C, while acid-form resin samples were equilibrated with 0.20 mol L^{-1} NaCl solution. Before exchange experiments, appropriate amounts of resins were weighted and separately conditioned in distilled water for 24 hours.

Solutions of heavy metals (Zn, Cu as sulfate, reagent grade, POCh) were prepared in deionized water. In order to characterize metals adsorption, stock solutions of 2500 mg L^{-1} of each metal were diluted in water with conditioned resin to obtain samples containing 100 mg L^{-1} of metal ions. Under these experimental conditions, it was confirmed that no chemical precipitation had occurred. The solutions were shaken (180 rpm) in 250 mL flasks with appropriate amounts of resins in an incubator at a temperature of between 20°C and 60°C for a period of 5 min to 150 min. The initial water pH was adjusted with diluted 0.10 M HCl at the range 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 ions concentrations in the original solutions were also determined.

The percentage of separately or simultaneous adsorbed metal ions (*A*) and amount of occupied sulfo groups (*U*) by zinc and copper cations in VPSS and EPSS resins were calculated using the following equations:

$$A = (c_i - c_f)100/c_i[\%] \tag{1}$$

$$U = [(c_i - c_f)zV]/(mM)\,[\text{meq}\,\text{g}^{-1}] \tag{2}$$

$$U = \{[(c_{iCu} - c_{fCu})z_{Cu}/M_{Cu}] + [(c_{iZn} - c_{fZn})z_{Zn}/M_{Zn}]\}V/m[\text{meq}\,\text{g}^{-1}] \tag{3}$$

where: c_i and c_f are the concentrations of the metal ion [mg L^{-1}] in initial and final solutions, respectively, V is the volume of the solution [L], m is the weight of the adsorbent [g], M is the molar mass of metal [g mol^{-1}], z – valence of adsorbed metal.

The Langmiur and Freundlich adsorption isotherms were determined to show relationships between the amount of metal ions for unit weight of adsorbent and the concentration of ions in the liquid at equilibrium. The Langmuir equation usually describes chemical adsorption well. It can be applicable to estimate the amount of metal ions which corresponds with the total covering exchanging places in resin. The Langmuir isotherms were generated by plotting $C/n_a = f(C)$:

$$C/n_a = \frac{1}{K_l n_{a\,\max}} + \frac{C}{n_{a\,\max}} \Rightarrow \frac{c_f m 10^3}{(c_i - c_f)V} = \frac{1}{n_{a\,\max}}\frac{c_f}{M} + \frac{1}{K_l n_{a\,\max}} \tag{4}$$

In turn to theoretically grounded Langmiur isotherms, Freundlich isotherms are empirical fidelity. These equilibrium isotherms were generated by plotting $log\ n_a = f(log\ C)$:

$$n_a = K_f C^n \Rightarrow \log n_a = n \log C + \log K_f \tag{5}$$

where: C – equilibrium metal ions concentration in fluid [mmol L^{-1}], $C = c_f/M$; n_a – amount of metal ions adsorbed by unit of mass of adsorbent [mmol g^{-1}], $n_a = [(c_i - c_f)V/Mm1000]$; K_l, K_f, n – adsorbate, adsorbent and temperature dependent coefficients; $n_{a\,max}$ – amount of metal ions which corresponds to covering all exchanging places in resin [mmol g^{-1}].

Pearson correlation coefficient (R) was used to verify which adsorption isotherm, Langmiur or Freundlich-type, was most suitable for equilibrium studies.

The pH of solution at equilibrium with metal ions was predicted with the assumption that zinc or copper metal ion reveals one (pH_{1H}) and two (pH_{2H}) protons from an ion exchanger. Calculated pH values were then compared with measured pH values.

$$pH_{1H} = -log\left(10^{-pH_i} + \frac{c_i - c_f}{M1000}\right) \tag{6}$$

$$pH_{2H} = -log\left(10^{-pH_i} + \frac{(c_i - c_f)^2}{M1000}\right) \tag{7}$$

where pH_i is initial pH of metal solution.

The stability of the resin during the adsorption of heavy metal ions and EPSS resin regeneration was studied in a column. About 1.5 g of dry resin was overloaded by 10 mL 36 g 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. The working capacity of the resin was determined titrimetrically by measuring the amount of protons revealed by 10 mL sodium chloride 30% (w/v) solution and 100 mL of deionized water.

Results and Discussion

Effect of Resin Dose

The effect of variation of resin dosage on the removal of zinc and copper ions by VPSS and EPSS cation exchange resins are shown in Fig. 1. Amount of resin (m) was tested separately in the range of 0.05–0.40 g and equilibrated for 2 h at 20°C at an initial metals concentration 100 mg L^{-1} in 100 mL solutions.

As expected, the percentage of metal ions adsorbed (A) increased with resin dosage. The adsorption percent approached 100% for 0.20 g of resin for both metals. According to this result, the optimum dosage of resin for adsorption experiments was determined to

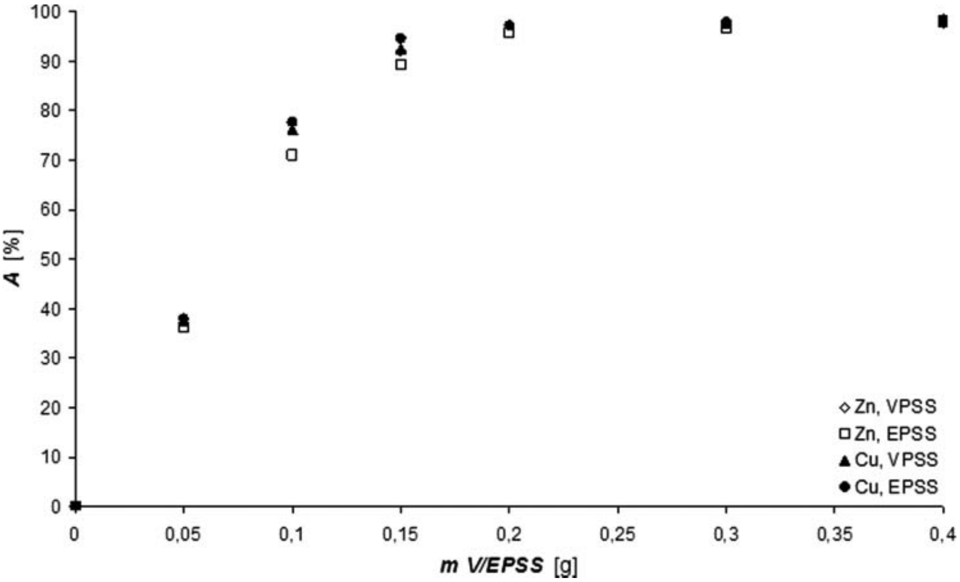

Figure 1. The effect of VPSS and EPSS dosage on the separate adsorption (*A*) of $[Zn(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ from water (initial concentration of each metal 100 mg L^{-1}; volume of sorption medium 100 mL; time of adsorption 2 h; stirring rate 180 rpm; temperature 20 ± 1°C; initial pH about 5.2).

be 0.20 g and it was subsequently used in all of the following batch experiments. Both zinc and copper cations adsorption patterns are similar. This can be explained by the fact that 100 mL of solutions contained similar amounts of hydrated ions as $[Zn(H_2O)_6]^{2+}$ (0.153 mmol) and $[Cu(H_2O)_6]^{2+}$ (0.157 mmol) separately. A similarity in adsorption of these ions is the consequence of identical valency of metals and almost the same molar mass and ionic radius.

Rengaraj et al. [9] reached the same level of adsorption when cleaning 100 mL water solution of $[Co(H_2O)_6]^{2+}$ 0.170 mmol, $[Cr(H_2O)_6]^{3+}$ 0.192 mmol and $[Ni(H_2O)_6]^{2+}$ 0.170 mmol (100 mg L^{-1} each), with the use of 0.20 g Amberlite IRN77 commercial exchange resin containing about 50% of water. However Pehlivan and Altun [14] had to use 0.10 g (with about 50% of water) of the commercial Dowex 50 W resin to remove the zinc and copper cations separately, 100 mg L^{-1} each, from only 20 mL solutions. That means that about 0.50 g of Dowex 50 W of resin needed to be used to clean 100 mL of this solution.

The equilibrium of adsorption of metal ions by VPSS and EPSS cation exchange resin is described by Langmuir (Fig. 2) and Freundlich (Fig. 3) isotherms. These isotherms showed differences in the characteristics of zinc and copper ions exchange by obtained resins. The curses of isotherms were similar for VPSS and EPSS cationites and different for two studied metal ions. The difference was probably caused by the volume of hydrated metal ions. Copper cations have the same charge but a smaller ionic radius than zinc cations. Smaller ions are probably more mobile. Parameter $n_{a\,max}$ verifies this theory. $n_{a\,max}$ as value of metal ions which fill available exchange sites is higher for copper cations than for zinc ions (Table 1).

To verify which isotherm better describes the adsorption of zinc and copper cations by VPSS and EPSS resins, the values of Pearson correlation coefficient (*R*) were determined.

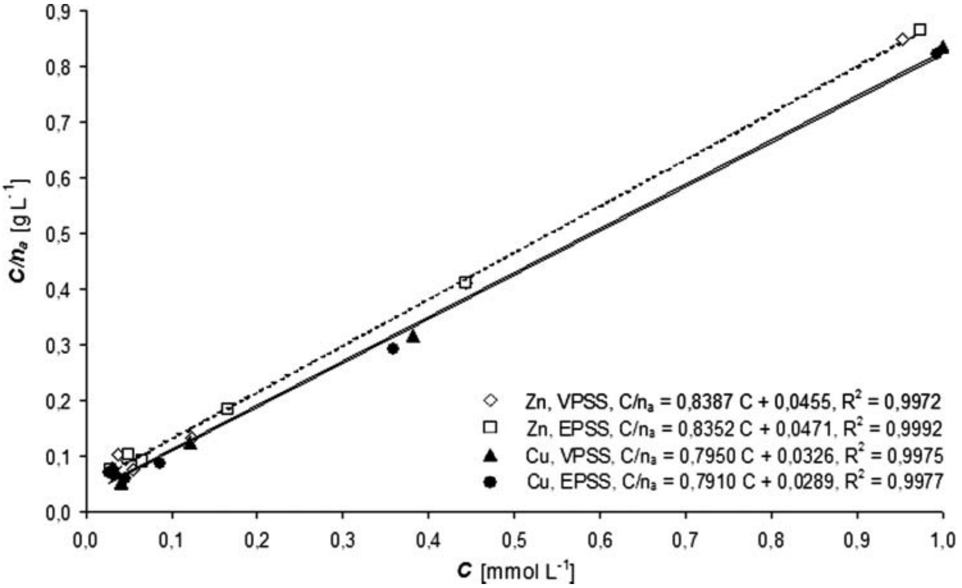

Figure 2. The Langmuir isotherms of separate adsorption of $[Zn(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ from water solutions by VPSS and EPSS resins (initial concentration of each metal ion 100 mg L^{-1}; volume of sorption medium 100 mL; time of adsorption 2 h; stirring rate 180 rpm; temperature 20 ± 1°C; initial pH about 5.2).

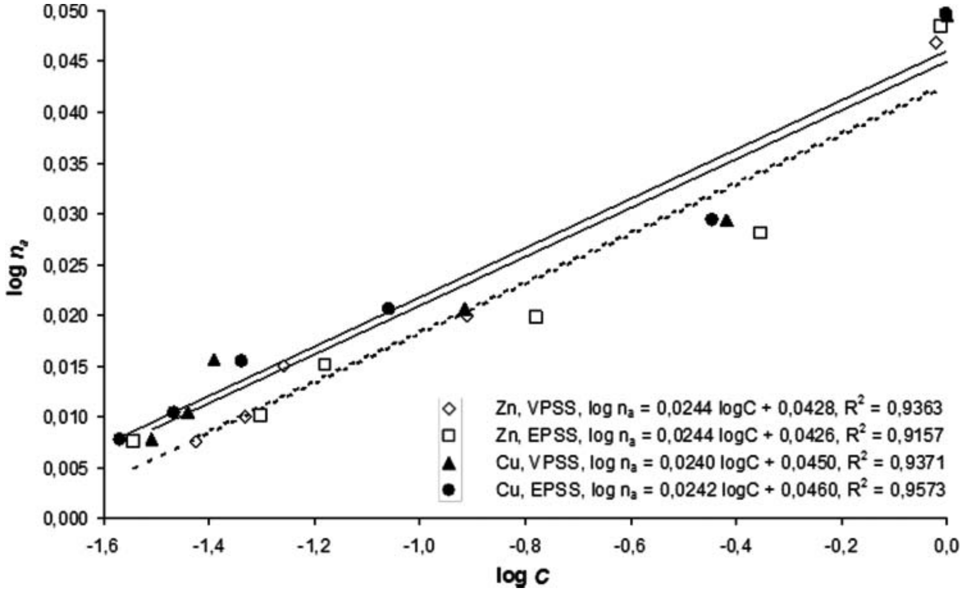

Figure 3. The Freundlich isotherms of the separate adsorption of $[Zn(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ from water solutions by VPSS and EPSS resins (initial concentration of each metal ion 100 mg L^{-1}; volume of sorption medium 100 mL; time of adsorption 2 h; stirring rate 180 rpm; temperature 20 ± 1°C; initial pH about 5.2).

Table 1. Parameters of the Langmuir and Freundlich isotherms of $[Zn(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ of separate adsorption by VPSS and EPSS resins (initial concentration of each metal ion, 100 mg L^{-1}; volume of sorption medium, 100 mL; time of adsorption, 2 h; stirring rate, 180 rpm; temperature, 20 ± 1°C; initial pH about 5.2)

	Langmuir isotherms			Freundlich isotherms		
Metal, resin	$n_{a\,max}$ [mmol g^{-1}]	K_l [L $mmol^{-1}$]	R^2	K_f [L g^{-1}]	n	R^2
Zn, VPSS	1.192	18.43	0.9972	1.104	0.0244	0.9363
Zn, EPSS	1.197	17.73	0.9992	1.103	0.0244	0.9157
Cu, VPSS	1.258	24.39	0.9975	1.109	0.0240	0.9371
Cu, EPSS	1.264	27.37	0.9977	1.112	0.0242	0.9573

R^2 determined for Langmuirs isotherms was closer to 1 than R^2 for Freundlich isoterms. This attests that Langmuir isotherm better describes the studied equilibrium process than the Freundlich isotherm.

Due to ions charge, the zinc and copper cations probably joined to two adjacent $–S(=O)_2(O^-)$ groups. Hence, the number of sulfo groups that are able to attach this cation, i.e. ion exchange capacity (*IEC*) should be at least two-fold higher than the $n_{a\,max}$ value is. The oxidation number +2, $n_{a\,max}$ of zinc and copper was about 1.20 mmol g^{-1} and 1.26 mmol g^{-1} respectively. *IEC* of cationites VPSS and EPSS determined by releasing protons by sodium cations with oxidation number +1, were 2.64 and 2.58 meq g^{-1} (20 ± 1°C) respectively.

Effect of Agitation Time

Adsorption of zinc and copper cations by two different resins VPSS and EPSS was studied by an agitation of the samples for a predetermined time interval in the temperature controlled shaker. Adsorption of heavy metal ions (*A*) was rapid within the first 10 min then continued at a much slower rate and reach a maximum value at about 30 min for both metals (Fig. 4). A similar pattern for zinc and copper cations is probably the result of the comparable physical properties and the valence of the metals. This can reasonably be explained considering diffusion of metals through the ionic membrane which is dependent on its ionic radius and the stability constant of the metal-ligand complex.

It was found that VPSS and EPSS cationites cleaned water from zinc and copper ions much faster than commercial resins do. More than 90% adsorption of cations was achieved after 30 min contact of 0.20 g (dry) VPSS or EPSS resin with 100 mL 100 mg L^{-1} solution containing 0.153 mmol $[Zn(H_2O)_6]^{2+}$ or 0.157 mmol $[Cu(H_2O)_6]^{2+}$ (Fig. 4). A similar effect was reached for 0.10 g (with 50% of water) of Dowex 50W resin after 60 min contact with 20 mL 100 mg L^{-1} solution of these metal ions [10]. To remove more than 90% of cations: $[Co(H_2O)_6]^{2+}$ 0.170 mmol or $[Cr(H_2O)_6]^{3+}$ 0.192 mmol or $[Ni(H_2O)_6]^{2+}$ 0,170 mmol, from 100 mL 100 mg L^{-1} solution with the use of 0.20 g Amberlite IRN77 resin (contained about 50% of water) at least 150 min of contact was needed [9].

The rate of cation exchange by VPSS and EPSS resin in comparison with commercial cation exchangers is probably the consequence of low cross-linking, looser structure

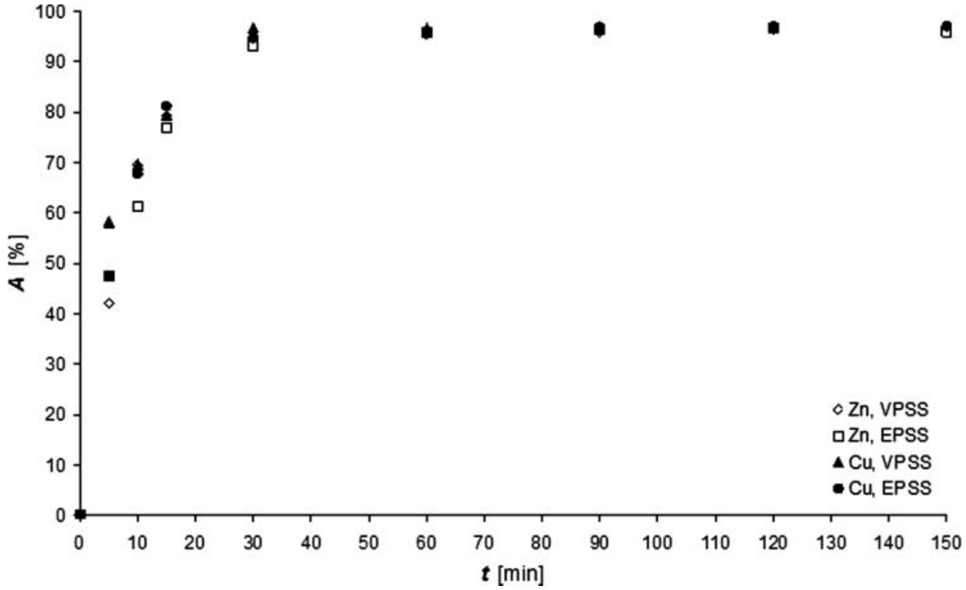

Figure 4. The effect of the contact time on the separate adsorption (*A*) of $[Zn(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ from water by VPSS and EPSS resins (initial concentration of each metal, 100 mg L^{-1}; volume of sorption medium, ~100 mL; amount of resin, ~0.20 g, proportion 100 mL to 0.20 g was kept; stirring rate, 180 rpm; temperature, 20 ± 1°C; initial pH, 5.2).

and a high moisture holding capacity. The obtained resin adsorbs about ten times more water (moisture holding capacity is about 600%) than Dowex 50W and Amberlite IRN77 cationites. We believe that a looser structure and a higher moisture holding capacity determines the availability of functional sulfo groups to cations. Unfortunately, low degrees of cross-linking usually lead to reduced mechanical toughness.

Effect of pH

Due to the formation of metal hydroxides and their precipitation at high pH, the initial pH of the metal ion solutions was shifted below 6. The metal ions adsorption decreases for obtained resins with a decrease of pH (Fig. 5). The lower adsorption of metal cations is probably connected to the high concentration of very mobile hydronium ions at low pH. The H_3O^+ ions can compete with bigger and less mobile solvated metal cations on mutual exchange sites.

Hydronium cations influenced the copper more than the zinc cations. The most apparent differences between adsorption of $[Zn(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ can be observed at pH 2.7 (Fig. 5).

Based on the electron donating nature of $-S(=O)_2(O^-)$ group and the electron-accepting nature of zinc and copper metal cations, the ion exchange mechanism could be preferentially considered. The zinc as well as copper cations may be attached to two hydroxyl groups of two adjacent sulfo groups which can donate two pairs of electrons to the metal ion and release two hydrogen ions into the solution. At low pH the sulfo groups are protonated and the surface charge diminishes due to the numerical dominance of H_3O^+ (0.200 mmol) over metal cations. At pH 2.7, before exchange starts, there are slightly

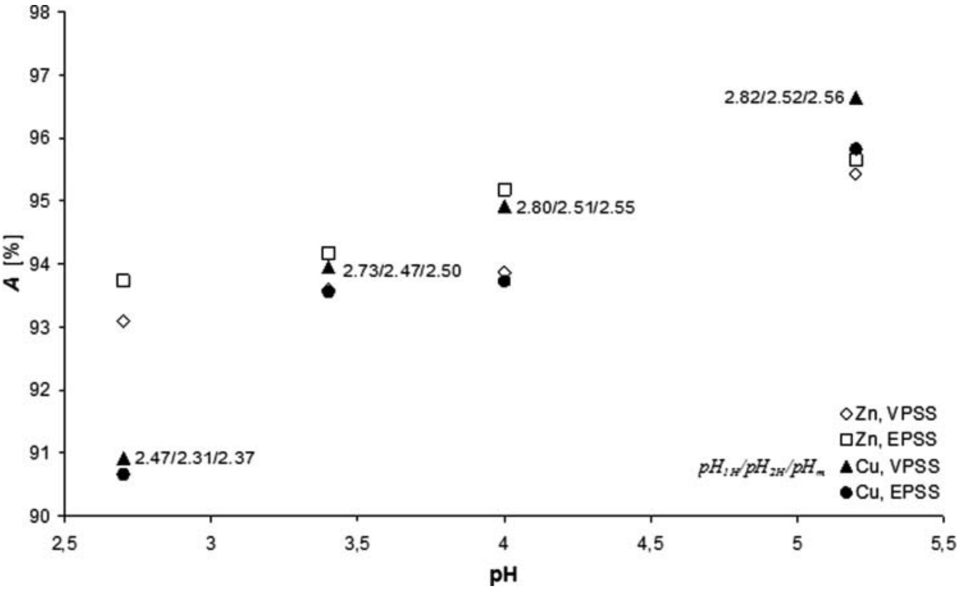

Figure 5. The effect of pH on the separate adsorption (*A*) of $[Zn(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ from water by VPSS and EPSS resins (initial concentration of each metal, 100 mg L^{-1}; volume of sorption medium, ~100 mL; amount of resin, ~0.20 g, proportion 100 mL to 0.20 g was kept; stirring rate, 180 rpm; temperature, 20 ± 1°C; agitation time 1 h); $pH_{1H}/pH_{2H}/pH_m$ - are pH of samples with VPSS and copper cations at equilibrium, pH_{1H} - pH predicted with the assumption that metal ion replaces one H^+ from resin, pH_{2H} - pH predicted with the assumption that metal ion replaces two H^+ from resin, pH_m - pH measured.

(about 1.3 times) more protons than zinc or copper cations in the solution. The removal of metal ions from water is correlated with the release of protons which strengthens the dominance. Based on the pH and adsorption percentage (*A*) from experimental data, it can be calculated that at equilibrium, the dominance of H_3O^+ ions over copper cations is about 30 times and over zinc ions it is about 40 times. The value of the pH measured is close to the pH calculated with the assumption that one copper cation reveals two protons (Fig. 5). The data for zinc (not shown) is similar, which indicates that, generally, metal ions tend to attach to the number of sulfo groups that is their oxidation number.

Generally, the adsorption of metal ion depends on its charge density. Therefore, apart from the same valence of the zinc and copper cations, adsorption of copper cations should be more effective than that of zinc cations due to a smaller radius and a bigger charge density of copper cation. However, at acidic pH, adsorption of zinc cations prevailed over that of copper ions, probably due to the difference in the electrostatic force between the ion pair – sulfo group and counter-ion. This force depends on Lewis acid (which is a metal cation able to accept electron pair) strength and Lewis base (which is a sulfo group with electron pair) strength. Since both metal ions joined to the same Lewis base, $-S(=O)_2(O^-)$ group, the electrostatic force of this connection depends on the difference between the Lewis acid and the Lewis base strength, i.e. when the difference is smaller, the ions have a stronger tendency to pair. Zinc cation (Lewis acid strength 0.36) should form a stronger ion pair with a sulfo group (Lewis base strength about 0.27) than copper cation (Lewis acid strength 0.45) [15].

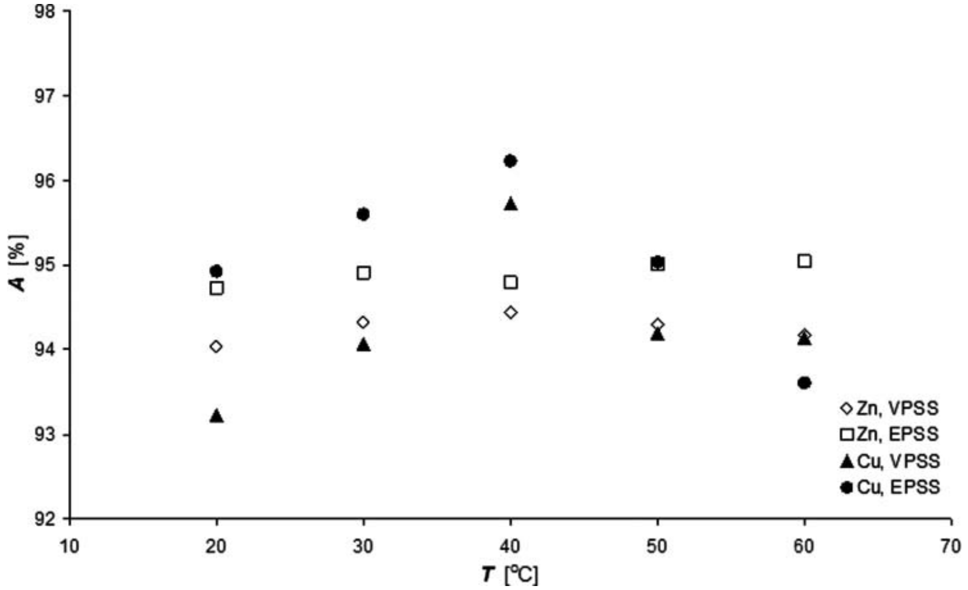

Figure 6. The effect of temperature on the separate adsorption (*A*) of Zn(H_2O)$_6$]$^{2+}$ and [Cu(H_2O)$_6$]$^{2+}$ from water by VPSS and EPSS resins (initial concentration of each metal, 100 mg L^{-1}; volume of sorption medium, ∼100 mL; amount of resin, ∼0.20 g, proportion 100 mL to 0.20 g was kept; stirring rate, 180 rpm; agitation time, 1 h; initial pH, 5.2).

Effect of Temperature

The effect of the temperature on adsorption of zinc and copper ions was investigated in batch type reaction (Fig. 6). The adsorption of zinc cations was very effective and does not change (EPSS) or changes only slightly (VPSS) with temperature (Fig. 6). The stability of zinc ions adsorption at various temperatures is probably the result of the formation of the strong ion pair with a sulfo group. The experimental results suggest that the binding of copper ions is more temperature-dependent (Fig. 6). The adsorption of copper has arisen at the temperature range from 20°C to 40°C. At 40°C, adsorption of this metal was the highest. At higher temperatures, adsorption of copper ions decreased.

Competitive Adsorption Behavior

Competitive adsorption of zinc and copper ions by VPSS and EPSS resins was also studied. The systems reached equilibrium after about 30 min of adsorption (Fig. 7). After this time, about 70% of Zn(H_2O)$_6$]$^{2+}$ and [Cu(H_2O)$_6$]$^{2+}$ was adsorbed. In this case, at equilibrium, more copper and zinc ions were left in the solution than when metal ions were separately adsorbed by the same mass of obtained resins. However, when taking into account the relation of mass of adsorbent to the amounts of exchanged ions, the effectiveness of simultaneous adsorption of metal ions was better. It was found that zinc and copper cations separately adsorbed by resins were attached maximum to 1.48 and 1.56 milli changing places per gram of the exchangers, respectively (*U* parameter in Table 2). When zinc and copper cations were both present in the system at equilibrium, they occupied maximum about 2.44 milli sulfo groups per gram of VPSS resin and 2.28 milli sulfo groups per gram of EPSS resin (Table 2). For comparison, the total ion exchange capacity of VPSS and

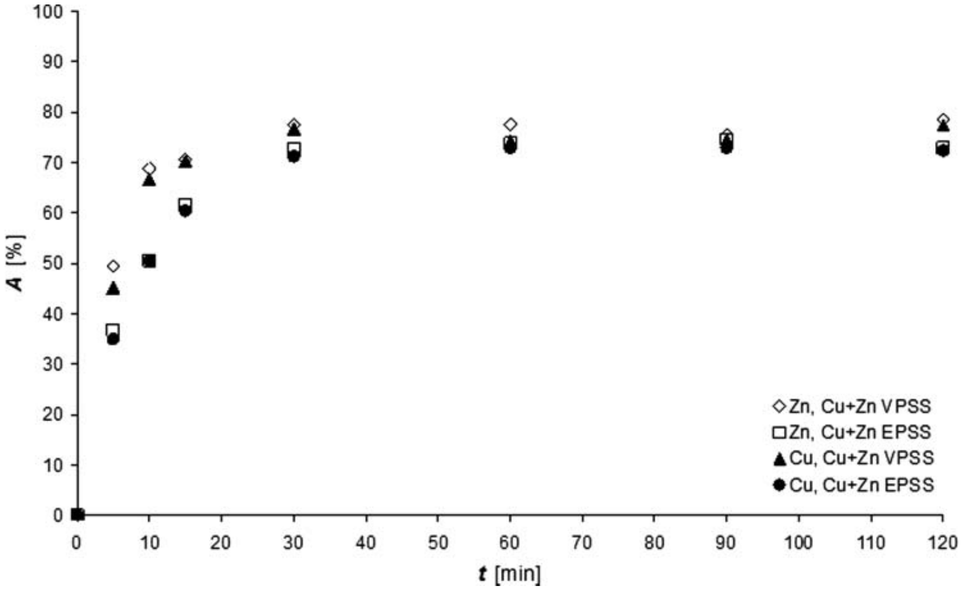

Figure 7. The effect of the contact time on the simultaneous adsorption (*A*) of $[Zn(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ from water by VPSS and EPSS resins (initial concentration of each metal, 100 mg L^{-1}; volume of sorption medium, ~100 mL; amount of resin, ~0.20 g, proportion 100 mL to 0.20 g was kept; stirring rate, 180 rpm; temperature, 20 ± 1°C; initial pH, 5.2).

EPSS resins are 2.64 and 2.58 meq g^{-1} (at 20°C), respectively. That means that in batch experiments, resins may have operational cation exchange capacity close to total *IEC*. An increase of the value of *U* parameter may be the reason for the moving of equilibrium between occupation of sulfo groups by the protons and the metal ions. In the closed system,

Table 2. The amount of occupied sulfo groups (*U*) by zinc and copper cations adsorbed separately or simultaneously in VPSS and EPSS resins versus contact time (initial concentration of each metal, 100 mg L^{-1}; volume of sorption medium, ~100 mL; amount of resin, ~0.20 g, proportion 100 mL to 0.20 g was kept; stirring rate, 180 rpm; temperature, 20 ± 1°C; initial pH. 5.2)

	U [meq g^{-1}]*					
t [min]	Zn, VPSS	Zn, EPSS	Cu, VPSS	Cu, EPSS	Zn+Cu, VPSS	Zn+Cu, EPSS
5	0.64	0.72	0.94	0.76	1.48	1.12
10	1.06	0.94	1.12	1.08	2.12	1.58
15	1.22	1.18	1.28	1.30	2.20	1.90
30	1.44	1.42	1.54	1.52	2.42	2.26
60	1.46	1.46	1.54	1.54	2.38	2.30
90	1.46	1.48	1.56	1.56	2.34	2.30
120	1.48	1.48	1.54	1.56	2.44	2.28

*It was assumed that one zinc or copper cation joints to two $-S(=O)_2(O^-)$ groups.

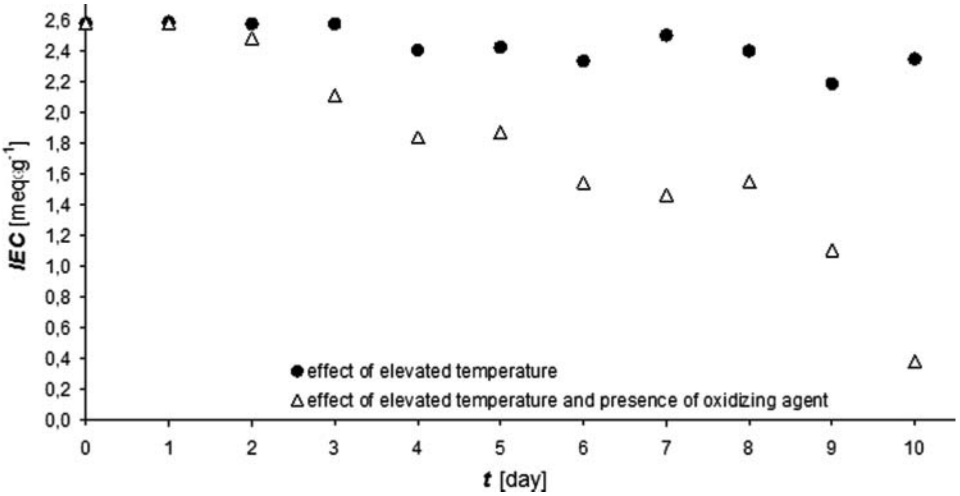

Figure 8. The effect of an elevated temperature and the presence of 3% H_2O_2 on the ion exchange capacity (*IEC*) of EPSS resins (volume of water or 3% H_2O_2, ~50 mL; mass of each sample of resin, ~0.10 g, proportion 50 mL to 0.10 g was kept; stirring rate, 180 rpm; temperature, 60 ± 1°C).

which is a batch method, an introduction of an additional amount of metal ions with high affinity to sulfo group leads to the exchange of a larger amount of adsorbate.

Stability of the Resin

Commercial polystyrene ion exchange resin cross-linked by a divinylbenzene additive may lose its exchange abilities under high temperature and in the presence of oxidants. Therefore, the influence of these conditions on obtained polystyrene derivatives with sulfone bridges was studied. To check the resin stability, the samples of EPSS resins were stored in deionized water at 60°C and in 3% H_2O_2 at 60°C. After each 24 hours, the total *IEC* of resin samples was determined.

It was found that an elevated temperature slightly influenced the total *IEC* of the EPSS ion exchanger (Fig. 8). The initial *IEC* value (about 2.6 meq g^{-1}) diminished after 10 days of experimentation to about 2.4 meq g^{-1} (Fig. 8). A decrease of cation exchange capacity may be connected with losing sulfo groups from the resin as a result of thermal hydrolysis. The hydrogen peroxide content had a greater influence on the exchange ability of the resin than an elevated temperature. Solution turbidity increased within 10 days of experimentation. Finally, *IEC* of this cationite decreased to about 0.4 meq g^{-1} (Fig. 8). Oxidizing agents probably break down bonds of chains in polymer and cause its fragmentation. Then water-soluble poly(styrenesulfonic) acids are extracted from this resin. Therefore, neutralizing oxidants before cation exchange from the solution, which may contain oxidants, is recommended. When cleaned water was chlorinated, cationite may be secured e.g. by water filtration through the activated carbon or by the addition of sodium sulfite.

The stability of the resin during adsorption of heavy metal ions and resin regeneration was also studied. The experiment was performed with the use of EPSS in a column. Resin was overloaded by copper sulfate, washed with deionized water, then regenerated by introducing 5% sulfuric acid and once again washed with deionized water, all cyclically 360 times. Shrinking caused the speed of flow to increase. During regeneration, the resin

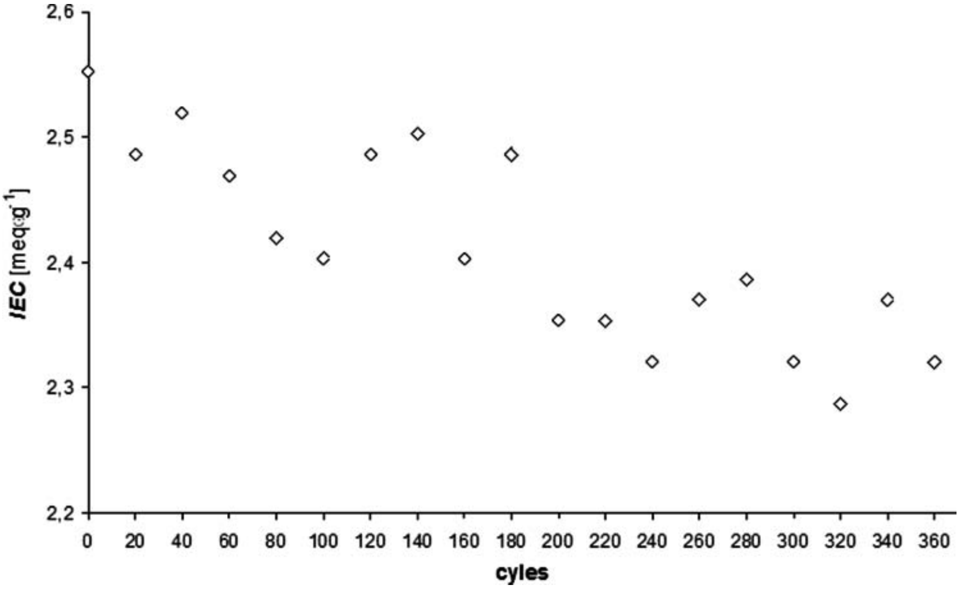

Figure 9. The effect of cyclical copper cations adsorption by EPSS resin and cationite regeneration on resin IEC (column experiment, 1 cycle: overloaded resin capacity, washed excess of metal ion, regenerated resin with the use of 3% H_2SO_4 (v/v) solution and washed excess of acid; mass of dry EPSS resin, 1.5 g; column diameter, 1 cm; room temperature).

lost color and swelled, which resulted in slowing down the flow. After every 20 cycles and full protonation, the working capacity of the resin was determined titrimetrically, i.e. by measuring the amounts of protons revealed by the sodium chloride solution. Beads of EPSS cationite were blue and shrunk after being treated with copper sulfate. In a column, during cycles of adsorption and regeneration, the ability of the resin to exchange cations diminished from about 2.5 meq g^{-1} to about 2.3 meq g^{-1} (Fig. 9). The pattern is non-linear due to the low repeatability of cation exchange in a 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 sulfonatig agent was performed. The exchange of zinc and copper cations by obtained resins in the batch experiments was studied. The dependence on the adsorbate amount, agitation time, pH and temperature were also estimated.

Generally, synthesized resins caused a decrease in concentration of the impurities solved. In comparison to commercial exchangers, obtained resins can purify water at least two times faster. The temperature and pH slightly influenced the metal adsorption. Only a low solution pH caused a decrease in the removal of metal cations due 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 zinc and copper ions when they were both present in the solution than when their adsorption was conducted separately.

The presented 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 the chemical modification of the polymer into the ion exchange resin.

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