



Chemical modification of commercial St-DVB microspheres and their application for metal ions removal

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Abstract

Multistage modification of commercially available styrene with divinylbenzene (St-DVB) microspheres is presented. The new type of modification introducing very attractive thiol (–SH) groups on the surface of polymeric matrices was made. In order to obtain thiol derivatives, the parent St-DVB microspheres were treated by H₂SO₄ with addition of oleum and then conversion of sulfonic groups to chloride acylsulfonic groups in the presence of PCl₅ and POCl₃ was carried out. Finally, the reduction of modified microspheres by using SnCl₂·2H₂O was conducted. The thiol groups content (elemental analysis), thermal properties (TG/DTG, DSC analysis) as well as the swelling characteristics of the functional microspheres were examined. The novel material St-DVB-SH was compared with commercial ion exchanger Ambersept GT74 to removal of heavy metal ions: Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II). In order to investigate the applicability of the obtained microspheres for heavy metal ions removal, the batch method was used. On the basis of studies, the optimal pH of the solution and microspheres dose was determined. Both for St-DVB-SH and Ambersept GT74, the Langmuir and Freundlich isotherm models are used to represent adsorption equilibria. The pseudo first order, pseudo second order and intraparticle diffusion kinetic models were used to fit the adsorption kinetic data. Additionally, dynamic adsorption tests were carried out in order to establish bed exhaustion. Results of a comprehensive comparative analysis indicate that the new synthesized material St-DVB-SH is very effective for removal of heavy metal ions studied.

Keywords St-DVB microspheres · Chemical modification · Thiol groups · Heavy metals · Wastewaters treatment

1 Introduction

Due to the rapid development of the industrial world, there is a significant increase of environmental pollution by heavy metals such as: Hg, Cd, Pb, Co, Zn, Cu. Their harmfulness consists in the possibility of accumulation in living organisms and their chronic toxicity. Health effects of regular consumption of even trace amounts of heavy metals can

appear after a long period of time (Guo et al. 2017; Gode and Pehlivan 2006; Mustafa and Komatsu 2016; Hubicki and Kołodyńska 2012; Hubicki et al. 1999; Carolin et al. 2017). There are many different methods of wastewater treatment containing heavy metal ions. Among others, coagulation, solvent extraction, chemical precipitation, electrolysis, membrane separation, ultrafiltration, adsorption, ion exchange and electrodialysis can be distinguished (Fang et al. 2018; Ko et al. 2017; Huang et al. 2016). Adsorption and ion exchange operations are commonly used with applications such as industrial pollution control or environmental protection, especially in water softening, purification and decontamination. The costs for the ion exchange systems will vary depending on (i) discharge requirements, (ii) volume of water to be treated, (iii) contaminant concentration, (iv) presence of other contaminants, (v) ion exchanger and regenerate utilization etc.

Technical products of most importance are styrene-*co*-divinylbenzene (St-DVB) copolymers and acrylate or methacrylate copolymers with adequate cross-linking

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agents. The structure of the exchanger is dependent on: (i) the degree of cross linking, (ii) type of cross linking agent, (iii) species of inert material and their ratio during polymerization as well as (iv) stabilizers such as styrene-maleic anhydride copolymers, allyl alcohol and vinyl acetate copolymers, polyvinyl alcohol, sodium polymethacrylate, methylcellulose, carboxymethylcellulose, gelatin and starch (Ozkan et al. 2017; Fang et al. 2014; Galadzhiev et al. 2012; Roy et al. 2004). Sometimes inorganic stabilizers as calcium and magnesium hydroxides, talc, alkali silicates and calcium phosphate are used. It is well known that copolymers with the gel structure with low crosslinkage are characterized by no definite pore size and therefore the measurements both pore and volume size as well as inner surface is impossible. Such matrix is also characterized by the difficulty of swelling in order to introduce functional groups. Copolymers with the gel structure contain approx. 2–16% DVB. However, they are not sufficiently effective in many industrial processes because they exhibit unsatisfactory ion exchange rate and have low sorption ability.

Synthesis of the macroporous structure during polymerization process results to the distance formation among the functional groups. Formation of caverns and channels, their amount and size depend on the inert material (pore-forming solvents) used to expand the matrix such as ethanol, toluene, xylene etc. (Mahfouz et al. 2014; Ali et al. 2016). The main factor influencing the developing the inner surface area is application of crosslinkers. The higher the degree of crosslinkage, the larger is the surface. Consequently, ion exchangers with surface area larger than 750 m²/g can be produced by using typical crosslinkers like divinylbenzene (Maciejewska 2012).

Nowadays, the majority of produced the ion-exchange resins are based on the polymer chemistry of styrene (St) crosslinked with divinylbenzene (DVB). The copolymers of St-DVB have well-defined porous structures which make them subject of numerous studies. Furthermore, these materials are mechanically resistant, insoluble in water and strong organic solvents. These copolymers are widely used as ion exchange resins, polymer supported catalysts, precursors for carbon spheres, absorbents and gel permeation chromatography column packings (Fontanals et al. 2015; Bing et al. 2016; Tan and Tan 2017; Tsyurupa and Davankov 2006; Perez-Macia et al. 2015; Podkościelna and Kołodyńska 2013). The diversity of applications is due to modification of the polymer backbone with appropriate ionic functional groups (e.g. sulfonate, acetate, thiol, amine) etc. The cation exchangers with the sulfur atom at varied degree of oxidation state or sulfur atom directly bonded to the benzene ring have the following functional groups: (i) sulfonic, (ii) a sulfinic, (iii) thiol and (iv) isothioureia. In the case of the St-DVB

copolymers, the –SO₃H groups attached to the benzene rings in an aqueous medium are dissociated and strongly acidic (Bogoczec and Kociołek-Balawejder 1987). In the pH range 2–14 they act as cation exchangers with the capacity 4.2–5.0 mval/g. In contrast, the –SO₂H groups attached to the benzene rings are characterized by the average degree of acidity and they are very easily oxidized. These cation exchangers exhibit particularly high affinity for the Pb(II) ions, therefore they are highly selective for them and characterized by good reversibility in the sorption–desorption process. Moreover, copolymers containing the –SOH groups are highly reactive and can be used for the preparation of sulfene derivatives and sulfene cations (Bogoczec and Kociołek-Balawejder 1986, 1987).

Lately, a lot of attention is devoted to polymers containing thiol groups that can be used as selective sorbents for removal of heavy metal ions and other elements in the water and wastewater treatment processes (Zhang et al. 2013; Odio et al. 2016; Abadast et al. 2017; Huang et al. 2017). Thiol groups have a higher affinity to ions of Hg(II), Au(I) and Ag(I) than to the other heavy metal ions, such as Cd(II), Zn(II), Cu(II) or As(III). An example of the ion exchanger containing the thiol groups is Ambersep GT74 (Vudama and Chakraborty 2016). It is a weakly acidic cation exchanger with good selectivity for mercury, rhodium, cadmium, silver, lead and copper. Ambersep GT74 has been designed for the removal of Hg(II) from different solutions. This resin is insoluble in ordinary solvents and stable throughout the pH range. The matrix of this resin is macroporous styrene copolymer. The ionic form as shipped is H⁺. Ambersep GT74 is used in various fields, including waste water treatment, recovery of solutions and metals, removal of interfering ions in hydrometallurgy and the recovery of the catalysts (WHO Regional Office for Europe 2007). However, the most known is macroporous Imac TMR comprising two functional groups: thiol group and sulfonic acid groups.

In the presented paper, multistage modification of commercially available styrene divinylbenzene (St-DVB) microspheres is presented. The new type of modification introducing very attractive thiol (–SH) groups on the surface of polymeric matrices was made. In order to obtain thiol derivatives the parent St-DVB microspheres were treated by H₂SO₄ with addition of oleum and then conversion of sulfonic groups to chloride acylsulfonic groups in the presence of PCl₅ and POCl₃ was carried out. Finally, the reduction of modified microspheres by using SnCl₂·2H₂O was conducted. The obtained novel material based on the St-DVB with the thiol functional groups St-DVB-SH was compared with commercial ion exchanger Ambersept GT74 which is recommended

for removal of heavy metal such ions as Hg(II), Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II).

2 Experimental

2.1 Chemicals and eluents

Commercial St-DVB microspheres were used without any purification. Reagent grade, hydrochloric acid, NaOH, PCl_5 , POCl_3 , CH_3COOH , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, sulfuric(VI) acid, oleum (fuming sulfuric acids), acetone, methanol, hexane, toluene, tetrahydrofuran (THF) and acetonitrile were from Avantor Performance Materials Poland. The initial solutions of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) (1000 mg/L) were prepared by dissolving appropriate amounts of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in deionized water. Then they were diluted to obtain 0.001 M, 0.002 and 0.003 M solution of the appropriate ions at relevant pH. 0.1 M HCl or 0.1 M NaOH solutions was used to adjust pH. The solution of NaNO_3 was of analytical grade.

2.2 Modification of St-DVB microspheres

2.2.1 Sulfonation of St-DVB microspheres

In a 500 mL round-bottomed three-necked flask, equipped with a mechanical stirrer, thermometer and dropping funnel, 50 g of microspheres (St-DVB) was placed and next a solution of 300 mL of H_2SO_4 and 60 mL of oleum (65%) were added very slowly and the whole content were stirred for 1.5 h at 50 °C, next for 3 h at 110 °C and finally for 15 h at room temperature. The obtained modified microspheres were transferred to a glass beaker with ice (1 h), next filtered off and washed with distilled water. The course of the reaction was confirmed by determining the acid number (AN) $L_{\text{AN}} = 4 \text{ mmol/g}$.

2.2.2 Modification II ($-\text{SO}_3\text{Na}$ groups)

Microspheres obtained in reaction of sulfonation (Sect. 2.2.1) were placed together with solution of NaOH (20 g of NaOH and 1 L of water) into a glass beaker. After 3 h the microspheres are filtered and air-dried.

2.2.3 Modification III ($-\text{SO}_2\text{Cl}$ groups)

Ninety five gram of microspheres with $-\text{SO}_3\text{Na}$ groups, 160 g of powdered PCl_5 , 200 mL of POCl_3 were placed

in a 500 mL round-bottomed two-necked flask equipped with a thermometer and air condenser. The reaction was performed for 5 h at 110 °C. Next, modified microspheres with $-\text{SO}_2\text{Cl}$ groups on the surface were very slowly transferred to a glass beaker (2.5 L) with ice. After 0.5 h microspheres were filtered off, washed with water and dried in air. Weight of dry microspheres was 90 g.

2.2.4 Modification IV ($-\text{SH}$ groups)

200 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 700 mL CH_3COOH were placed in a 1000 mL round-bottomed three-necked flask equipped with a mechanical stirrer, thermometer and glass tube (through which hydrogen chloride was added). The flask was placed in an ice bath and hydrogen chloride was dosed until the reducing mixture was clear. Next, 90 g of selected microspheres (St-DVB- SO_2Cl) was placed to the reducing mixture and the whole content was stirred for 5 h. The modified microspheres were left in the flask for 12 h at room temperature. Next, the mixture was heated to 60 °C for 1 h. After this time, microspheres were washed with water in a glass beaker to which 200 mL of HCl was next added. After 0.5 h, microspheres were filtered off, washed with water and dried at 50 °C for 3 h (Podkościelna and Kołodyńska 2013; Podkościelna et al. 2014; Podkościelna 2013).

In the result the new microspheres with very attractive thiol ($-\text{SH}$) groups on the surface of polymeric matrices were made.

2.3 Polymer characterization

Elemental analysis of the modified copolymers was carried out using the Perkin-Elmer CHN 2400 apparatus and elemental analyser Vario EL III Elementar (S).

The KOH/ CH_3OH method was used to determine the acid number (AN). The acid number content was calculated from the difference between the blank and that found for the titration of the sample reaction mixture.

Attenuated total reflectance (ATR-IR) spectra were obtained using a Bruker FTIR spectrophotometer TENSOR 27. The spectra were in the spectral region of 400–4000 cm^{-1} . The resolution was set to 4 cm^{-1} and the number of scans per spectrum was equal to 32.

Differential scanning calorimetry (DSC) thermograms were obtained with the use of a DSC Netzsch 204 calorimeter (Netzsch, Günzburg, Germany). All DSC measurements were carried out in aluminium pans with a pierced lid with the sample weight ~ 5–10 mg under nitrogen atmosphere (30 mL/min). Dynamic scans were performed at a heating rate of 10 K/min in the temperature range 20–450 °C. Curing

characteristics, such as temperature of the peak maximum and final cure temperature were determined.

The thermogravimetric analysis (TG/DTG) was made on a STA 449 Jupiter F1, Netzsch (Germany). The samples were heated from 20 to 1000 °C with a heating rate of 10 °C/min under a dynamic atmosphere of helium (40 mL/min).

Image of microspheres was made using the optical microscope MORPHOLOGI G3 Malvern (Great Britain).

2.4 Kinetic, equilibrium and dynamic adsorption studies

Batch experiments were conducted using 250 mL flask kept at a constant temperature (20 °C) for a period of up to 2 h shaking. For this aim mechanical shaker ELPIN type 357 (Poland) was used. The reaction mixture consisted of 0.5 g of St-DVB-SH or Ambersep GT74 and a known initial concentration of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) in a total volume of 100 mL. All the adsorption experiments were in 0.01 M NaNO₃ background electrolyte to maintain a constant ionic strength. The desired pH was adjusted before the experiments. After the appropriate time (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 60 and 120 min.) or after the reaching equilibrium, the adsorbent was removed by filtration using filtering paper. The concentration of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions was determined by AAS method using AAS 240 FS spectrometer (Varian) at 324,7 nm for Cu(II), 213,9 nm for Zn(II), 228,8 nm for Cd(II), 217 nm for Pb(II) and 232 nm for Ni(II).

The adsorption capacity at time t (q_t) and adsorption percentage ($S\%$) were calculated according to Eqs. 1 and 2 (An et al. 2017).

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (1)$$

$$S\% = \frac{C_0 - C_t}{C_t} \times 100\% \quad (2)$$

where: q_t is the adsorption amount of M(II) ions at time t (mg/g), c_0 is the initial concentration of M(II) in the solution (mg/L), c_t is the concentration of M(II) at time t (mg/L), V is the volume of solution (L), m is the weight of St-DVB-SH or Ambersept GT74 sample (g), $S\%$ is the adsorption percentage (%).

The pseudo first order (PFO), pseudo second order (PSO) and intraparticle diffusion (IPD) kinetic models were used to fit the adsorption kinetic data. They are expressed as:

(a) The pseudo first order (PFO):

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1 t}{2.303} \quad (3)$$

(b) Pseudo second order (PSO):

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} - \frac{t}{q_2} \quad (4)$$

(c) Intraparticle diffusion model (IPD):where:

$$q_t = k_i t^{0.5} + C \quad (5)$$

q_1, q_2 are the amounts of adsorbed metal ions at equilibrium, q_t is defined as previously, k_1 is the pseudo first order rate constant (1/min), k_2 is the pseudo second order rate constant (g/mg/min), k_i is the intraparticle diffusion rate constant (mg/g/min^{0.5}), C is the diffusion constant. Additionally from PSO model the initial sorption rate constant h was calculated.

The isotherms of equilibrium adsorption of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions on St-DVB-SH and Ambersep GT74 were analyzed by means of the Langmuir and Freundlich models:

(a) Langmuir model

$$\frac{1}{q_e} = \frac{1}{q_m K_L c_e} + \frac{1}{q_m} \quad (6)$$

(b) Freundlich model

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (7)$$

where: q_e is the amount of adsorbed metal ions at equilibrium, K_L is the Langmuir constant, q_m is the adsorption capacity of the ion exchanger and C_e is the equilibrium concentration of metal ions in the solution; K_F is the multilayer sorption capacity of sorbent, $1/n$ is the Freundlich constant.

Dynamic adsorption tests were carried out for St-DVB-SH and Ambersep GT74 in order to establish bed exhaustion. Breakthrough curves were plotting as C/C_0 versus V_e , where C_0 is the inlet concentration of metal ions (mg/L) and C is the outlet concentration of metal ion (mg/L), V_e is the outlet fraction volume.

3 Results and discussion

3.1 Properties of the St-DVB microspheres

Figure 1 presents the scheme of modification of commercially available St-DVB microspheres. In a four-step

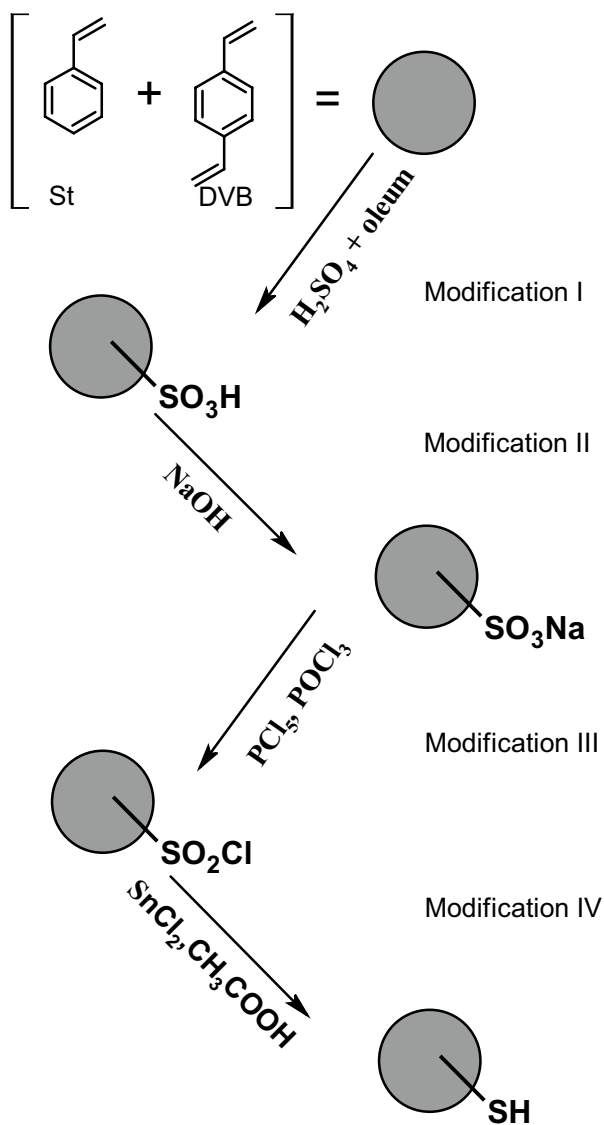


Fig. 1 Scheme of the studied copolymers

modification, St-DVB microspheres with $-SH$ functional groups were obtained. In Fig. 2 the image of microspheres after modification is presented. Some microspheres have damages in form of cracks caused by relatively hard reaction conditions. Elemental analysis confirms the presence of thiol groups on the surface of microspheres. The results show that after modification, 12.94% of the sulfur in form of thiol groups was introduced into the polymeric matrix. This confirms that the proposed modifications are very efficient.

The tendency to swell is an important parameter which determines the use of polymeric microspheres as

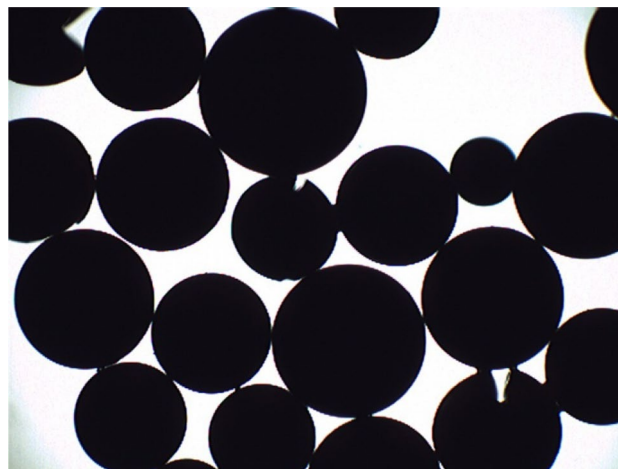


Fig. 2 The image of microspheres after modifications (St-DVB-SH)

a sorbents in different solvents. In order to define the tendency to swell, the swellability coefficient (B) was determined. B is a function of the solvent nature and composition of the copolymers. B was defined by equilibrium swelling in acetone, methanol, acetonitrile, toluene, hexane, THF and water (Tuncel and Piskin 1996; Kesenci et al. 1996). Swellability coefficient is expressed as:

$$B = \frac{V_s - V_d}{V_d} \times 100\% \tag{8}$$

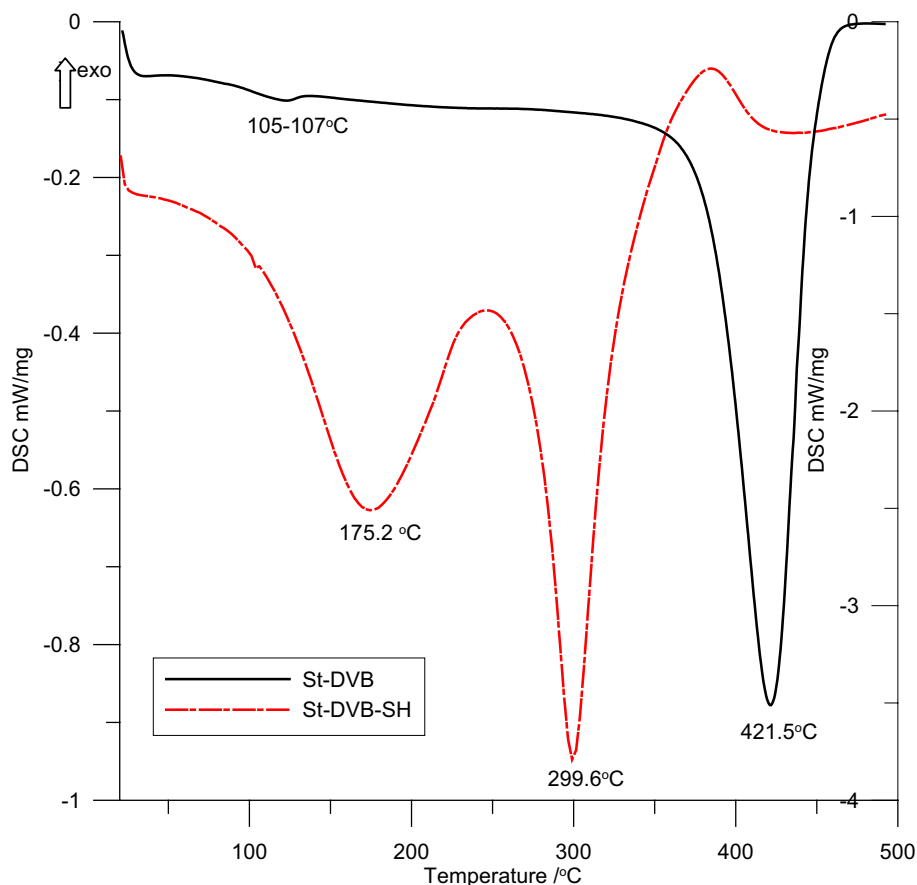
where: V_s is the volume of the copolymer after swelling, V_d is the volume of the dry copolymer.

0.1 g of the sample was transferred into a glass tube (\varnothing 1 cm) with a sinter and immersed in 2 mL of the solvent. Before and after swelling, the volume of the sorbent in the glass tube was measured. Three specimens were tested for each samples and a mean value was taken. The values of B for microspheres vary from 0 to 12% (Table 1). In non-polar solvents (toluene, hexane) copolymers practically not swell. After modification polymers exhibit a slight increase of swelling in polar solvents such as acetone (increase from 4 to 8%), in methanol from 2 to 4% and acetonitrile from 2 to 5%, with the exception of water when the increase of swelling about 12% is observed.

Thermal properties of copolymers were characterized by DSC analysis. The DSC curves are shown in Fig. 3. The obtained results in the range from 25 to 500 °C are measured. The presented curves for parent microspheres (St-DVB) and modified ones with $-SH$ groups (St-DVB-SH) have a different course. Starting material is stable up to 350 °C. On the curve only one endothermic effect at maximum at 421.5 °C,

Table 1 Swelling studies

Copolymer	Swellability coefficient (B) [%]						
	Acetone	Methanol	THF	Toluene	Hexane	Acetonitrile	Water
St-DVB	4	2	5	0	0	2	0
St-DVB-SH	8	4	5	0	0	5	12

Fig. 3 DSC analysis

connected with the thermal degradation of copolymer is visible. The glass transition temperature can be observed at 105–107 °C, which corresponds to the glass transition temperature of polystyrene (Rieger 1996; Ahmed et al. 2017). After modification with thiol groups, the thermal resistance of microspheres is lowered. On the curve, two endothermic effects are noticeable. The first at 175.2 °C is probably associated with cleaving/disconnection of thiol groups. The second one at 299.6 °C is associated with the partial thermal degradation of the sample.

In order to determine of thermal stability of sorbents the TG and DTG measurements in inert atmosphere (helium)

were made. Figure 4 presents the analysis for commercial St-DVB copolymer. It is clearly visible that the commercial sorbent decomposed in one step with the maximum at 420 °C and it is related to the total degradation of aromatic fragments. A completely different course have curves (Fig. 5) for the copolymer with thiol groups. Due to the small weight loss of the St-DVB-SH, sample was heated from 20 to 1000 °C. From the course of TG curve one can see that the process of destruction of the sample, after reaching the temperature of 1000 °C (with a heating rate of 10 °C/min) has not been completed. About 40% of residue of the starting mass of the sample was obtained, probably in the

Fig. 4 TG and DTG analysis for St-DVB copolymer

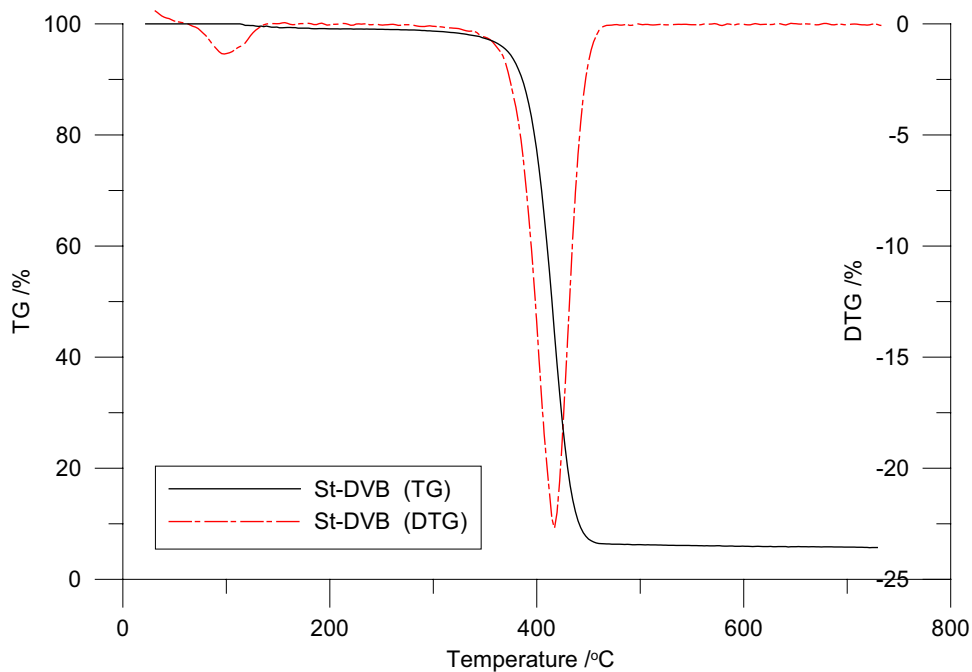
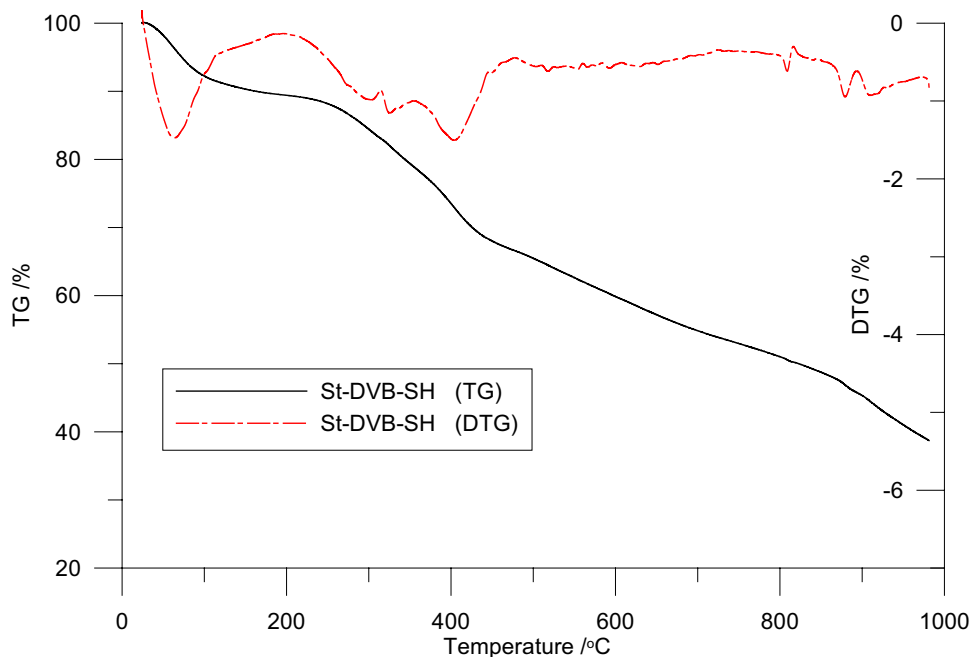


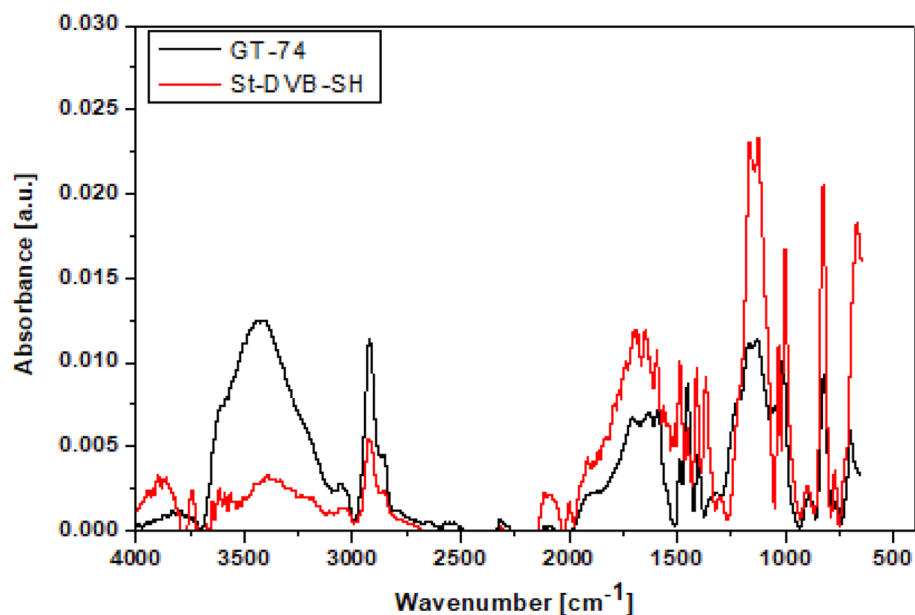
Fig. 5 TG and DTG analysis for St-DVB-SH copolymer



form of difficult to decompose aromatic-sulfur connections. The lower thermal resistance of the sorbents after modification can be related to the partial destruction (cracking) of the microspheres (Fig. 2) due to the drastic synthesis conditions. This results in a faster thermal degradation of the

modified sorbents. Nevertheless, this thermal resistance is sufficient for the sorption process. Figure 6 show the ATR-FTIR spectra of two studied ion exchangers: St-DVB-SH and Ambersep GT-74. In the both spectra, the presence of

Fig. 6 ATR-FTIR spectra of St-DVB-SH and Ambersep GT74



intensive peak located at 3450 cm^{-1} can be assigned to the O–H bands. This peak is connected with presence of hydroscopic water in macroporous structure of polymeric beads. The signals located at $2920\text{--}2875\text{ cm}^{-1}$ are derived from the stretching vibrations of aromatic and aliphatic --CH , --CH_2 groups. The aromatic group $\text{C}=\text{C}$ gives a shape signal at 1620 cm^{-1} . The signals about 830 cm^{-1} can be assigned to the C–H vibrations from the benzene ring. The small typical signals at 2300 cm^{-1} are derived from thiol (--SH) groups.

3.2 Studies of kinetics and equilibrium adsorption

After estimation of the optimum sorbent mass from the range $0.05\text{--}0.1\text{ g}$ of the each ion exchanger St-DVB-SH and Ambersep GT74 (data not presented) the sorption process was carried out for the concentrations in the range $0.001\text{--}0.003\text{ M}$ of the initial solution of the above-mentioned ions, weight of 0.1 g (as the optimal), shaking speed of 180 rpm and at temperature of 293 K (Figs. 7a–f, 8a–f, 9a–f). The next tests were carried out to determine the optimal pH of the solution for sorption of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions on the St-DVB-SH and Ambersep GT74. It is well-known that in the solution copper(II) in the pH range from 1 to 7 occurs as Cu^{2+} cation. In the pH range 6–10 there are other cationic forms CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$. At higher pH values i.e. in the range of 7–12, precipitation of copper(II) hydroxide occurs. Above pH 9, anionic forms

$\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$, dominate. As for zinc(II), up to pH 8 it is in the form of Zn^{2+} cation. The precipitation of the amphoteric zinc hydroxide(II) starts at pH 8. At pH 10 there are also the co-existing anionic forms, i.e. $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$. Cadmium and lead also exist as Cd^{2+} and Pb^{2+} ions. In literature it has been mentioned (Carolin et al. 2017; Fang et al. 2018; Hubicki et al. 1999) that prevalence of free cadmium ions at pH below 8 after which hydroxyls are formed. Lead also precipitates at pH 8. Cationic combinations of PbOH^+ and $\text{Pb}_3(\text{OH})_4^{2+}$ are also formed at pH in the range of 6–12. A small percentage of the Pb_2OH_3^+ cation exists at pH from 7 to 9. $\text{Pb}(\text{OH})_2$ hydroxide inclusions occur in the pH range of 8–13. The anionic form of $\text{Pb}(\text{OH})_3^-$ occurs at pH 9 and dominates at higher values. Similar behavior is observed in the case of nickel.

The pH value is one of crucial parameters which influence the efficiency of the process of heavy metal ions uptake. Therefore, the pH value of the solution affects the sorption of metal ions and their interactions with the functional groups of St-DVB-SH and Ambersep GT74. Based on the conducted tests, it can be concluded that for St-DVB-SH and Ambersep GT74, the amount of adsorbed ions increases gradually with increasing pH and the highest value reaches at pH 5, therefore this pH value was chosen for further studies on the effect of phase contact time and initial concentration on the sorption process. In addition, the choice of pH 5 for the

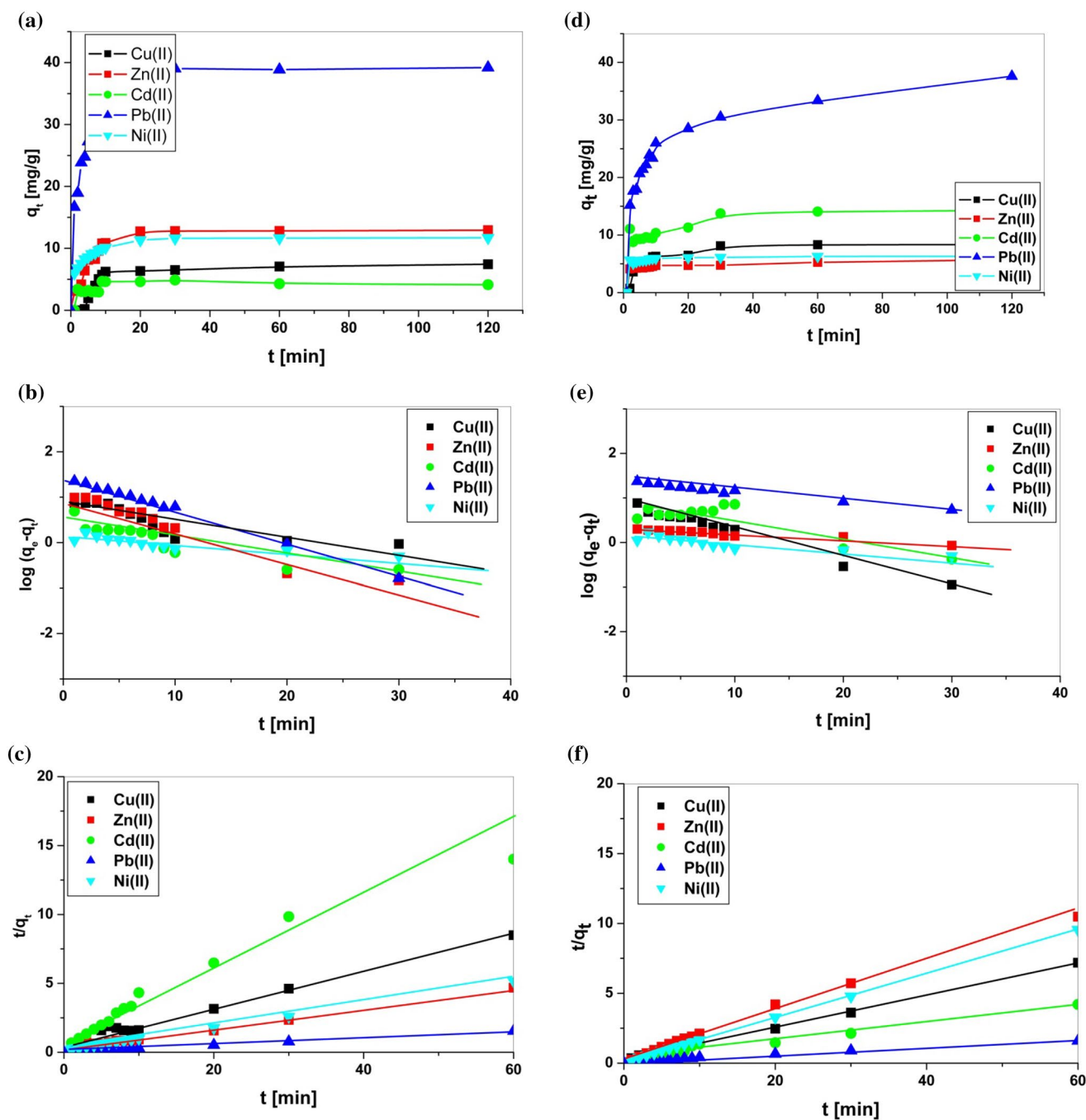


Fig. 7 a–f Comparison of sorption capacities q_t (a, d); linear plot for PFO kinetic model (b, e) and PSO kinetic model (c, f) for Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions on St-DVB-SH (a–c) and Ambersep GT74 (d–f). Initial concentration is equal to 0.001 M

sorption process is consistent with the speciation of the above-mentioned metal ions as was discussed above. These results confirm the presence of metals in the form of two-positive cations and the lack of other forms that can reduce the effectiveness of the process (precipitation effect).

As for kinetic analysis, it was found that removal of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) on St-DVB-SH and Ambersep GT74 increases with time and reaches a maximum value at about 90 min. Changing the initial concentration metal ions from 0.001 to 0.003 M the

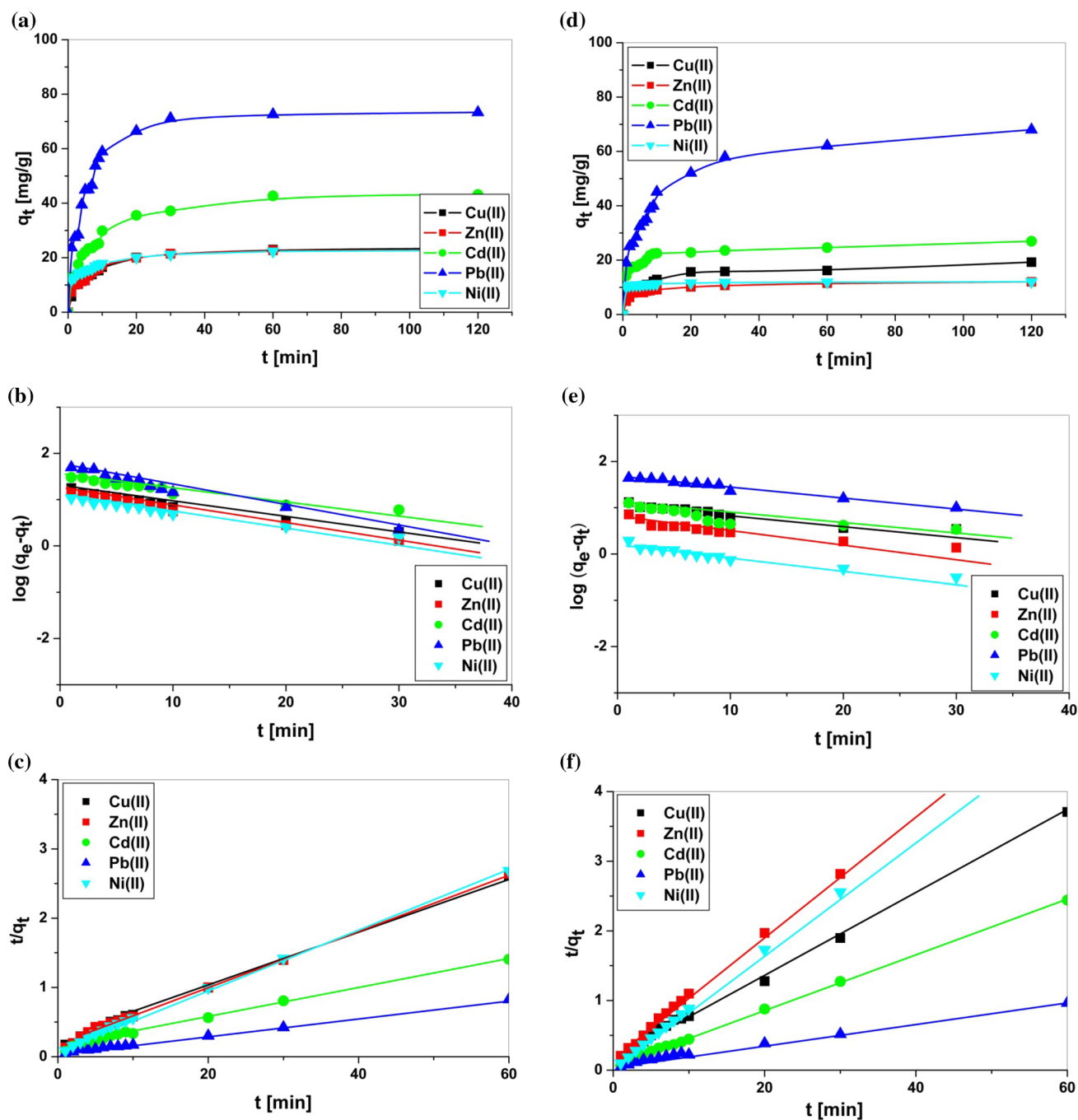


Fig. 8 a–f Comparison of sorption capacities q_t (a, d); linear plot for PFO kinetic model (b, e) and PSO kinetic model (c, f) for Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions on St-DVB-SH (a–c) and Ambersep GT74 (d–f). Initial concentration is equal to 0.002 M

amount adsorbed also increases for all metal ions. The pseudo-second kinetic model (PSO) correlates best the uptake rate ($R^2 > 0.99$) and it is important in water treatment process design using St-DVB-SH and Ambersep

GT74 (Tables 2, 3). Good fits were observed for all initial concentration of studied metal ions indicating that sorption reaction can be approximated with the second order kinetics model (Figs. 7c, f, 8c, f, 9c, f).

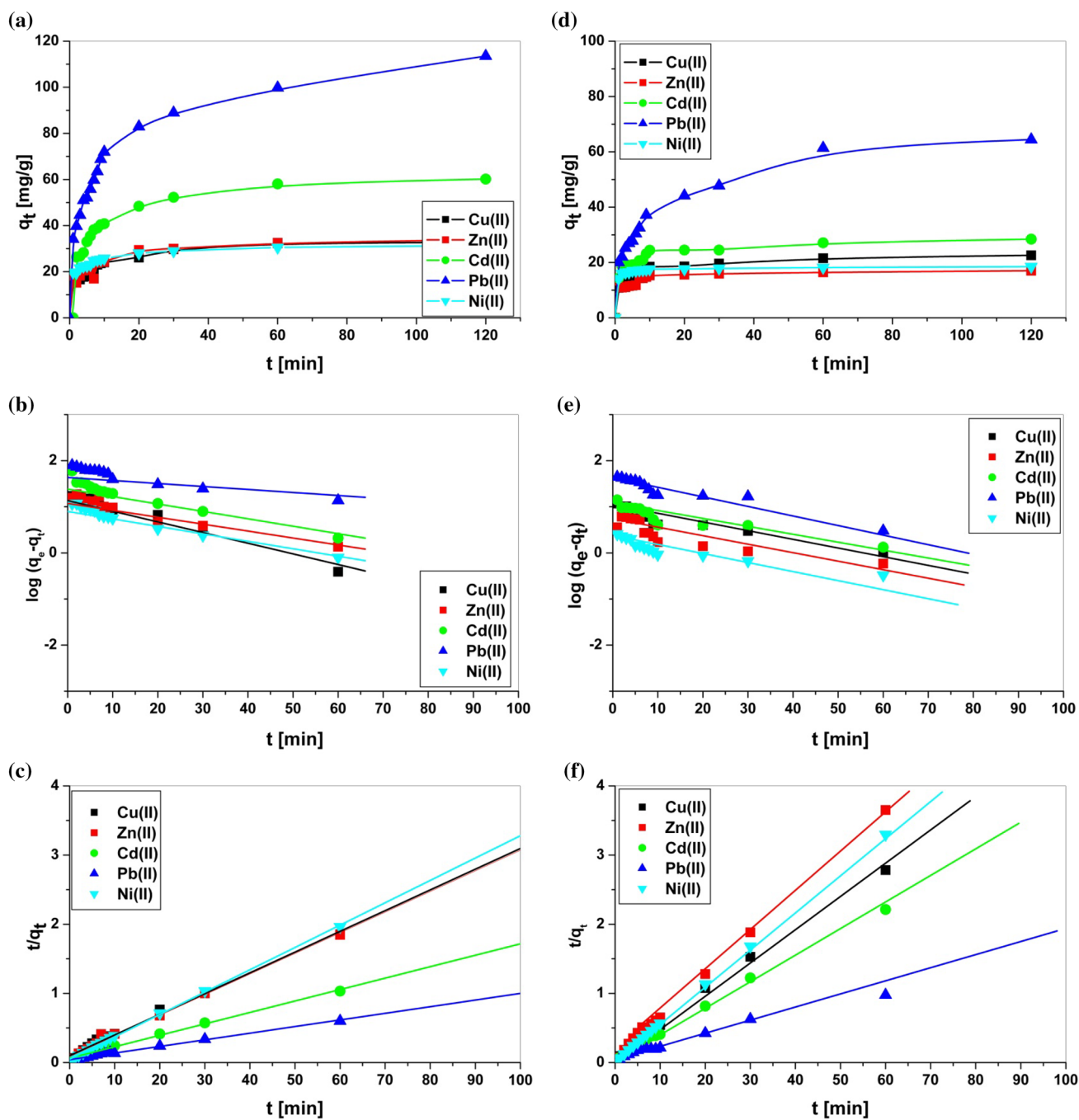


Fig. 9 a–f Comparison of sorption capacities q_t (a, d); linear plot for PFO kinetic model (b, e) and PSO kinetic model (c, f) for Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions on St-DVB-SH (a–c) and Ambersep GT74 (d–f). Initial concentration is equal to 0.003 M

The Langmuir model is widely applied for indicating the adsorption isotherm type. The adsorbate e.g. metal ions adsorbed only on the specific number of sites of ion exchanger are characterized by the same energy of

sorption and any interactions between them. The obtained sorption isotherms of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) on St-DVB-SH and Ambersep GT74 at 20, 40 and 60 °C are presented in Fig. 10a–e. The parameters

Table 2 Kinetic models and best-fit parameters for Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) sorption on St-DVB-SH

C_0 [M]	q_{exp} [mg/g]	Parameters									
		PFO			PSO				IPD		
		q_1 [mg/g]	k_1 [1/min]	R^2	q_2 [mg/g]	k_2 [g/mg min]	h	R^2	k_i [mg/g min ^{0.5}]	C	R^2
Cu(II)											
0.001	7.43	4.10	0.064	0.724	7.43	0.047	0.079	0.996	2.420	0.235	0.958
0.002	23.44	14.35	0.062	0.985	22.99	0.039	7.873	0.999	5.106	8.101	0.987
0.003	32.78	19.06	0.025	0.989	31.96	0.018	29.427	0.998	6.12	14.24	0.891
Zn(II)											
0.001	12.93	6.59	0.857	0.764	12.85	0.045	3.338	0.992	1.527	4.505	0.987
0.002	22.76	19.78	0.118	0.975	22.75	0.037	10.746	0.998	2.342	8.590	0.892
0.003	33.88	25.89	0.044	0.954	31.48	0.028	34.751	0.998	3.487	12.415	0.697
Cd(II)											
0.001	4.38	2.11	0.067	0.827	5.22	0.038	1.038	0.996	1.530	4.278	0.689
0.002	43.16	31.29	0.067	0.985	43.08	0.015	16.76	0.999	4.710	13.022	0.758
0.003	60.18	36.24	0.050	0.964	59.06	0.007	20.574	0.988	7.412	14.07	0.987
Pb(II)											
0.001	39.20	14.86	0.084	0.756	39.20	0.019	26.215	0.994	3.25	20.987	0.897
0.002	73.30	40.97	0.075	0.936	74.00	0.011	30.976	0.999	7.66	28.59	0.944
0.003	113.51	67.34	0.029	0.934	112.58	0.008	48.091	0.995	11.52	33.18	0.862
Ni(II)											
0.001	11.71	4.11	0.083	0.856	10.91	0.067	11.28	0.996	0.82	7.03	0.987
0.002	22.67	19.82	0.059	0.741	22.18	0.067	24.576	0.999	1.17	10.554	0.789
0.003	31.36	22.58	0.044	0.987	31.07	0.003	36.578	0.999	2.35	16.58	0.857

obtained from the isotherm equation are listed in Table 4. Based on the results presented in Table 4, it was found that sorption of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions in a one component system both on St-DVB-SH and Ambersep GT74 is well described by the Langmuir model. This is confirmed by the high values of the determination coefficients ($R^2 > 0.997$). Additionally, the agreement between the experimental data ($q_{e,exp}$) and the model predicted values of adsorption capacities (q_2 from PSO) was evident. The maximum adsorption capacities of the St-DVB-SH for the Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions are 45.26 mg/g, 32.42 mg/g, 62.77 mg/g, 135.85 mg/g and 49.88 mg/g at a pH of 5, respectively. These values were higher than for commercially available Ambersep GT74. Better results were also obtained for higher temperatures (Fig. 10), except for Ni(II).

In the next step, the results were evaluated by the dynamic method. The performance of a column was evaluated based on the shape of the breakthrough curve obtained from the plot of C/C_0 vs. V_e . The breakthrough curve of Cu(II), Cd(II) and Ni(II) on St-DVB-SH (closed symbols) and Ambersep GT74 (open symbols) are presented in Fig. 11. As follows from the breakthrough curves, Cu(II), Cd(II) and Ni(II) exhibit higher affinity for the St-DVB-SH than for the corresponding ion exchanger Ambersep GT74. The greatest differentiation in affinity of the metal ions sorption was found on the St-DVB-SH. The shape of the curves for Cu(II), Cd(II) and Ni(II) at pH 5.0 suggests possible separation of these metal ions according to the affinity series: Cd(II) > Cu(II) > Ni(II).

Table 3 Kinetic models and best-fit parameters for Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) sorption on Ambersept GT74

C_0 [M]	q_{exp} [mg/g]	Parameters									
		PFO			PSO				IPD		
		q_1 [mg/g]	k_1 [1/min]	R^2	q_2 [mg/g]	k_2 [g/mg min]	h	R^2	k_i [mg/g min ^{0.5}]	C	R^2
Cu(II)											
0.001	8.42	4.68	0.085	0.754	8.41	0.083	0.002	0.996	0.259	4.156	0.843
0.002	19.27	9.83	0.038	0.753	19.58	0.055	9.826	0.999	0.425	7.623	0.987
0.003	22.61	19.06	0.025	0.846	22.07	0.046	20.467	0.995	1.137	12.405	0.998
Zn(II)											
0.001	5.72	1.47	0.059	0.828	4.85	0.782	8.219	0.998	0.178	0.458	0.921
0.002	12.20	5.44	0.038	0.975	10.97	0.228	18.462	0.997	0.664	6.643	0.851
0.003	17.70	4.57	0.023	0.987	14.42	0.046	22.489	0.998	1.125	14.59	0.777
Cd(II)											
0.001	14.30	6.84	0.114	0.946	11.27	0.352	31.725	0.997	0.225	8.678	0.867
0.002	26.95	8.55	0.095	0.707	26.17	0.259	35.692	0.998	1.117	16.528	0.853
0.003	28.44	16.92	0.026	0.946	28.44	0.050	44.085	0.999	1.333	22.117	0.998
Pb(II)											
0.001	38.00	23.42	0.065	0.982	29.72	0.028	16.098	0.997	2.472	16.613	0.895
0.002	67.97	41.40	0.046	0.925	67.92	0.019	25.566	0.999	5.062	29.26	0.841
0.003	69.78	44.07	0.037	0.996	69.99	0.016	29.016	0.998	7.312	32.04	0.954
Ni(II)											
0.001	6.30	4.25	0.084	0.897	6.21	1.671	57.358	0.998	0.101	5.47	0.745
0.002	12.05	11.34	0.040	0.855	11.98	0.546	71.018	0.998	6.321	14.46	0.888
0.003	18.52	19.52	0.022	0.764	18.44	0.032	75.479	0.999	9.472	16.333	0.847

4 Conclusions

A four-step modification of commercial styrene with divinylbenzene (St-DVB) microspheres was carried out in order to obtain novel materials with very attractive thiol functional groups (St-DVB-SH). Elemental analysis confirmed the presence of thiol groups (12.94% of S) on the surface of modified microspheres. The synthesized materials have a low tendency to swell in organic solvents (max 8%). The novel material St-DVB-SH was compared with commercial ion exchanger Ambersept GT74 to removal of heavy metal ions: Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II). Based on the conducted tests, pH 5 was chosen for all adsorption studies which guarantees the presence of metals ions in the form of two-positive cations and the lack of other forms that can reduce the effectiveness of the process. Kinetic studies indicate that efficiency of metal

ions removal is greater for St-DVB-SH than for Ambersept GT74. It is particularly evident at higher initial concentrations of 0.002 and 0.003 M. The pseudo-second kinetic model (PSO) correlates best the uptake rate ($R^2 > 0.99$) for both St-DVB-SH and Ambersept GT74. It was found that sorption of metal ions studied is well described by the Langmuir model, which is confirmed by high values of determination coefficients. The maximum adsorption capacities of the St-DVB-SH for the Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) ions were distinctly higher than for Ambersept GT74. The obtained results and comparative studies with commercial ion exchanger (Ambersept GT74) indicate that the new synthesized St-DVB-SH material can be successfully used for sorption of the heavy metals ions studied.

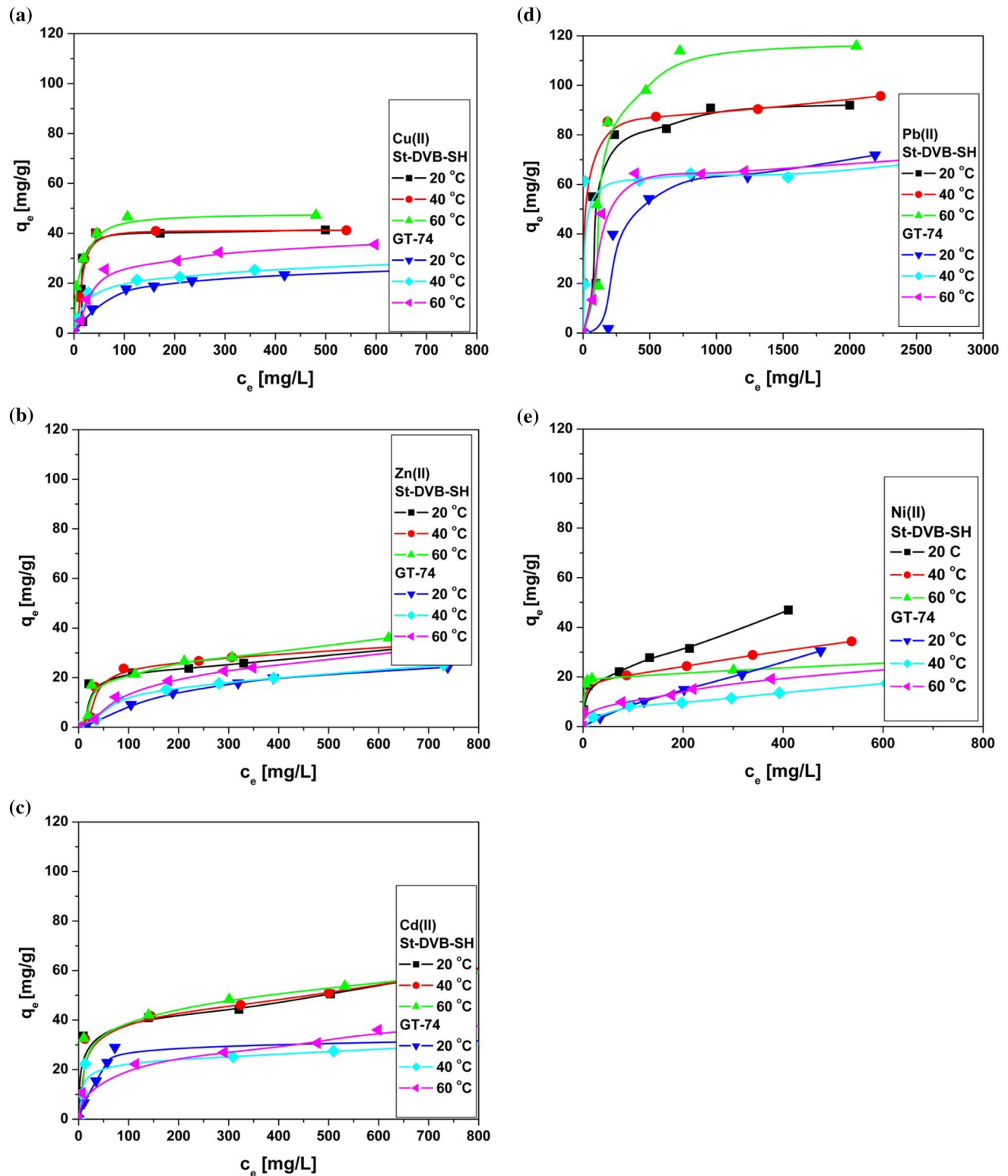
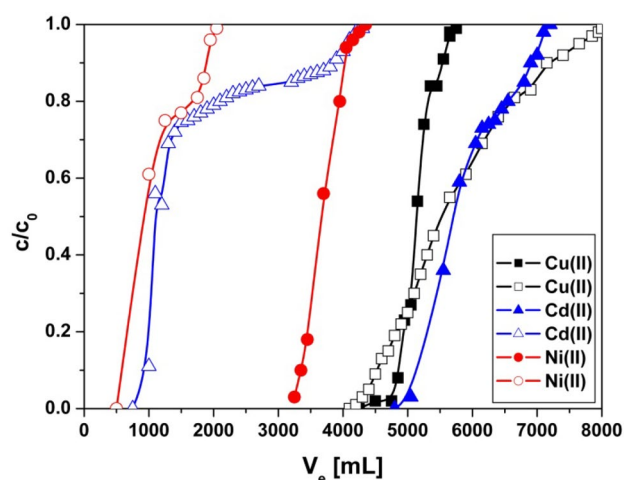


Fig. 10 a–e Sorption isotherms of Cu(II) (a), Zn(II) (b), Cd(II) (c), Pb(II) (d) and Ni(II) (e) ions on St-DVB-SH and Ambersep GT74 at 20, 40 and 60 °C

Table 4 Langmuir and Freundlich isotherm parameters as well as correlation coefficients for Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) sorption on St-DVB-SH and Ambersep GT74

Isotherm model	Parameters	ST-DVB-SH	GT74
Cu(II)			
Langmuir	$q_{e,exp}$ [mg/g]	47.38	35.54
	q_m [mg/g]	45.26	36.00
	K_L [L/mg]	0.063	0.068
	R^2	0.878	0.920
Freundlich	K_F [mg/g]	1.527	1.253
	$1/n$	0.175	0.164
	R^2	0.789	0.812
Zn(II)			
Langmuir	$q_{e,exp}$ [mg/g]	36.05	31.05
	q_m [mg/g]	32.42	30.00
	K_L [L/mg]	0.067	0.058
	R^2	0.999	0.986
Freundlich	K_F [mg/g]	1.054	1.034
	$1/n$	0.187	0.183
	R^2	0.986	0.975
Cd(II)			
Langmuir	$q_{e,exp}$ [mg/g]	67.62	47.14
	q_m [mg/g]	62.77	40.54
	K_L [L/mg]	0.112	0.114
	R^2	0.999	0.999
Freundlich	K_F [mg/g]	2.365	2.478
	$1/n$	0.257	0.284
	R^2	0.987	0.938
Pb(II)			
Langmuir	$q_{e,exp}$ [mg/g]	135.85	69.84
	q_m [mg/g]	137.54	73.33
	K_L [L/mg]	0.234	0.309
	R^2	0.999	0.997
Freundlich	K_F [mg/g]	2.447	2.687
	$1/n$	0.263	0.259
	R^2	0.998	0.999
Ni(II)			
Langmuir	$q_{e,exp}$ [mg/g]	46.89	30.53
	q_m [mg/g]	49.85	34.47
	K_L [L/mg]	0.457	0.353
	R^2	0.992	0.999
Freundlich	K_F [mg/g]	1.066	1.112
	$1/n$	0.235	0.242
	R^2	0.999	0.999

**Fig. 11** The breakthrough curves of Cu(II), Cd(II) and Ni(II) on St-DVB-SH (closed symbols) and Ambersep GT74 (open symbols)

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