Sorption and Thermal Properties of Strongly Basic Cross-Linked Ionic Polymer Modified with Cr(III) Compounds

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ABSTRACT: AV-17(Cr) material was prepared by modifying a commercial polymer AV-17 (initially bearing R4N$^+$ functional groups) with Cr(III) compounds was investigated. Comparative isotherms characterizing the CrO_4^{2-} and $Cr_2O_7^{2-}$ ion sorption from solution with pH values of 3 and 8, respectively, at 19°C and 60°C, were obtained using the raw AV-17(Cl) and the modified AV-17(Cr) material. The sorption process on AV-17(Cr) takes place through the coordination of Cr(VI) ions with Cr(III) ions, while on AV-17(Cl) it is due to an ion exchange mechanism. The sorption isotherms obtained in pH 8 solutions fit perfectly the Langmuir model. The thermodynamic functions ΔG, ΔH, and ΔS characteristic to the adsorption of CrO_4^{2-} ions from K_2CrO_4 solutions with pH = 8 were calculated. The active sites belonging to the AV-17(Cr) material were identified as jarosite type compounds of Cr(III). SEM images show that the Cr(III) compounds are present in the form of ultrafine particles located on the surface and within the bulk phase of the polymer granules. Comparative thermal degradation process of both the AV-17(Cr) and the AV-17(Cl) material was conducted in air and in an inert atmosphere (He). The thermal degradation mechanism of sorbent AV-17(Cr) and exchanger AV-17(Cl) is proposed. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41306.

INTRODUCTION

It is well known that cross-linked ionic polymers bearing R$_4$N$^+$ functional groups are widely used in industry and science. Their main applications in the field of water treatment and waste water purification usually involve the strongly basic anion exchanger property: R$_4$NA + B$^-$ $\leftrightarrow$ R$_4$NB + A. These polymers are nonselective toward sorption of inorganic anions and often it is considered that they are able to participate only in anion exchange processes. Strongly basic anion exchangers do not contain negatively charges or electron donor atoms in their matrix and therefore, theoretically, they may not interact with metallic cations[1]. However, in our previous studies[1–4] we reported that strongly basic anion exchangers are able to retain metallic cations from M$_2$(SO$_4$)$_3$ solutions (M = Fe^{3+}, Cr^{3+}, and Al^{3+}) in certain conditions. The retaining of the mentioned above metallic cations takes place due to the formation in the polymer phase ultra-fine particles of jarosite mineral type compounds: R$_4$N[M$_3$(OH)$_6$(SO$_4$)$_2$] and H$_3$O[M$_3$(OH)$_6$(SO$_4$)$_2$], where R$_4$N$^+$ are the functional groups of the polymer.[2,3] According to Ref. 5,

jarosites are formed as layers of three or six octahedral cycles. The SO$_4^{2-}$ groups are located in the axial position, each coordinating three metal ions belonging to three octahedral and OH$^-$ groups are positioned in the equatorial plane, forming a bridge between two metal cations[1]. Between the jarosite polymer layers there are mobile cations retained by Coulomb's electrostatic interactions. In the jarosite type compounds, formed in the polymer phase, such cations are R$_4$N$^+$ and H$_3$O$^+$. But R$_4$N$^+$ groups are relatively mobile because they belong to the reticulated polymer chains. The H$_3$O$^+$ content in the compounds depends on solution pH in which jarosite type compounds were formed. The solvated mobile cations have different dimensions and influences interactions between polymer layers of jarosite.

Through various methods metal compounds in the polymer phase can be converted to other compounds. For example, the mineral type compounds in the polymer phase in boiling water are converted into β-FeOOH ultrafine particles in super paramagnetic state or in relatively massive and magnetically ordered particles.[2,6] While the synthetic jarosite type Na[Fe$_3$(OH)$_6$(SO$_4$)$_2$]

Additional Supporting Information may be found in the online version of this article.

compounds upon heating in water ($t > 80°C$),[7] are converted into highly dispersed α-FeOOH particles.

The controlled processes of metallic compounds formation within a polymeric support changes considerably the polymer properties and may expand the possible applications of ion-exchange materials by producing selective sorbents[1,6,8] and catalysts.

It is known that chromium (III) compounds are chemically more stable than iron compounds. Using Cr(III) compounds to modify polymeric matrices may therefore offer the advantage of obtaining superior sorbents and catalysts. In order to apply Cr(III)-containing polymers in catalysis, liquids, or gases purification, it is necessary to evaluate their thermal behavior in various media. In previous work,[1] we have investigated chemical and thermal stability of strongly basic anion exchanger modified with compounds of Cr (III). It was shown that the nature of acid solution (HCl, HNO_3, and H_2SO_4) has influenced the chemical and thermal stability of the sorbent obtained by modification of the polymer with compounds of Cr (III).

Modifying commercial cross-linked ionic polymers bearing strongly basic functional (R_4N^+) groups with Cr(III) compounds and subsequently using them as adsorbents for CrO_4^{2-} and $Cr_2O_7^{2-}$ ions is an issue of particular practical interest due to the fact that Cr(VI) is highly toxic and often contaminates technological waters in galvanic sections. In order to apply Cr(III)-containing polymers in water purification, it is necessary to evaluate their sorption properties toward CrO_4^{2-}–$Cr_2O_7^{2-}$ ions and thermal behavior in various media. This study aims to provide an answer to the above mentioned problems.

EXPERIMENTAL

The commercial strongly basic anion exchanger AV-17(Cl) has been used as a starting material. The exchanger AV-17 is a gel-type cross-linked polystyrene-divinylbenzene polymer with $^-N^+(CH_3)_3$ functional groups. Its full anion-exchange capacity is 3.5–4.0 mg of equiv./g.[9]

The process of obtaining the AV-17 modified with Cr(III)-containing compounds (AV-17(Cr)) has been conducted according to Ref. [10. A five grams sample of the AV-17(Cl) material was charged into 0.5 L $Cr_2(SO_4)_3$ solution, containing 2 g Cr L^{-1} at $60 \pm 1°C$ for 8 hr. The pH of the solution was maintained at 4.2 ± 0.1 by using NaOH solution. After 8 hr of contacting with $Cr_2(SO_4)_3$ solution, the polymer sample was filtered, washed with distilled water and dried in air. The Cr^{3+} content in the polymeric phase (32.5 mg G/g) was determined photocolorimetrically[11] after desorption.

To obtain sorption isotherms of Cr(VI)-containing anions, AV-17(Cr) sorbent samples (0.2 g) were placed in contact with 100 mL aliquots of K_2CrO_4 solutions with pH 3.0 or, respectively, 8.0 at temperatures of 19 and, respectively, 60°C for 8 hr. For comparison the Cr(VI)-containing anions sorption was also investigated in the same conditions and on the starting material. The concentration of chromium (VI) ions was determined photocolorimetrically. The sorption was calculated using formula S = (Co − Ceq.)V/m, where S is the sorption value (mmol Cr(VI) g^{-1}), Co and Ceq are the initial and, respectively, at the equilibrium Cr(VI) concentrations (mmol L^{-1}), V is the solution volume that was in contact with the sorbent (L) and m is the sorbent mass (g). For some sorption processes, the thermodynamic functions ΔG, ΔH, and ΔS were calculated.

A scanning electron microscope (Vega II LSH with accelerating voltage of 30 kV—Tescan Company) was used to examine the size and morphology of Cr(III) compound particles on the surface and within the volume of the polymeric granule. The samples were attached to aluminum holders using a silver based adhesive. Samples conductivity was achieved by sputter coating with a 15 nm layer of gold.[1]

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves are recorded in air, at a 20 mL min^{-1} outflow, within 25–900°C temperature range, using a Mettler Toledo TGA-SDTA851[e] thermogravimetric analysis device. The test samples weighed between 2.5 and 4.5 mg, and the preferred rate of heating was 10°C min^{-1}. In order to calculate the apparent activation energy, thermogravimetric curves were also recorded at the following heating rates: 7, 13, and 16°C/min. The derivatograph employed provides a temperature measuring accuracy of $\pm0.25°C$ and a reproducibility of $\pm0.15°C$, whereas the resolution provided by the balance for measuring the sample quantity is 1 μg. The device was temperature and sensitivity calibrated based on the standard melting points of metals such as In, Al, Zn, and Au. Samples of AV-17(Cr) sorbent treated with CrO_4^{2-} solution were investigated by comparison with the raw ion exchanger AV-17(Cl)[1]

The thermal degradation processes conducted both on sorbent and exchanger were also analyzed in an inert atmosphere (He) using a TG/FTIR/MS system, within the 30–600°C temperature range, at the same heating rate of 10°C min^{-1}.[1] The system is equipped with an apparatus of simultaneous thermogravimetric spectrophotometer FTIR model Vertex-70 (Bruker-Germany) and mass spectrometer model QMS 403C Aëolos (Netzsch-Germany).[1] The experiments used samples between 10 and 12 mg. Helium with a flow rate of 50 mL min^{-1} was used as a carrier and as a protective purge for the thermo balance at 20 mL min^{-1}.[1] The thermogravimetric analyzer was calibrated for temperature and sensitivity using the melting points of the standard metals (Hg, In, Sn, Bi, and Zn). Further information on the technical characteristics and operation of the TG/FTIR/MS system is detailed in a previous paper.[12]

RESULTS AND DISCUSSION

Sorption of Cr(VI)-Containing Anions

The AV-17(Cl) polymer contains only one type of functional groups—R_4N^+ that are energetically equivalent. It was therefore expected that the sorption isotherms of Cr(VI)-containing anions will fit the Langmuir model. This was not the case, since the data regarding the sorption process of Cr(VI)-containing anions on the AV-17(Cl) exchanger from solutions with pH 3 do not fit the Langmuir model, as shown in Figure 1a. In aqueous solutions with pH 3 and Cr(VI) concentration of 10^{-1} mol L^{-1}, chromium (VI) ions are known to exist both as $HCrO_4^-$ and as $Cr_2O_7^{2-}$ species, with the latter being preponderant.[13]
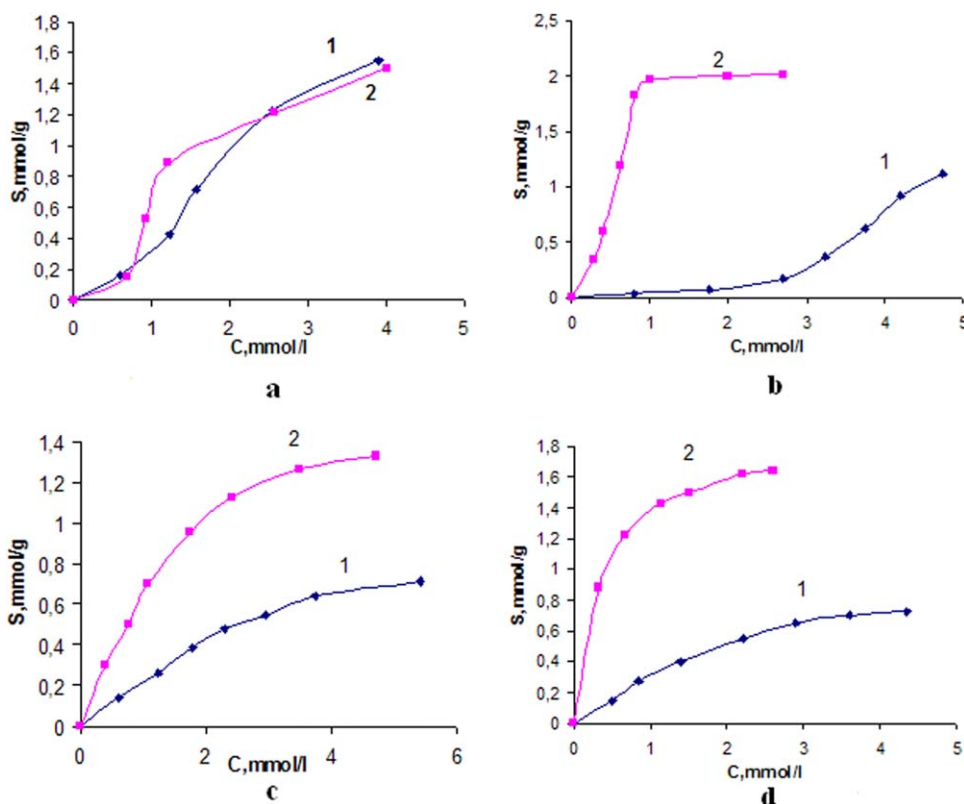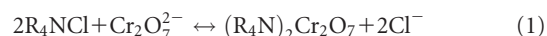
Figure 1. (a) Sorption isotherms of Cr(VI)-containing anions from K_2CrO_4 solutions with pH 3 and temperature of 19 (1) and 60°C(2) on the exchanger AV-17(Cl); (b) Sorption isotherms of Cr(VI)-containing anions from K_2CrO_4 solutions with pH 3 and temperature of 19 (1) and 60°C(2) on the sorbent AV-17(Cr); (c) Sorption isotherms of Cr(VI)-containing anions from K_2CrO_4 solutions with pH 8 and temperature of 19 (1) and 60°C(2) on the exchanger AV-17(Cl); and (d) Sorption isotherms of Cr(VI)-containing anions from K_2CrO_4 solutions with pH 8 and temperature of 19 (1) and 60°C(2) on the sorbent AV-17(Cr). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
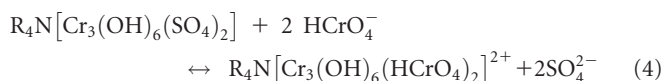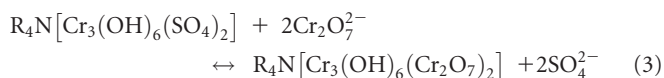
When the ion concentration reaches 10^{-5} mol L^{-1}, at pH 3, all Cr(VI) ions are in the form of $HCrO_4^-$ anions.

The shape of isotherms presented in Figure 1a indicates the presence of interactions between the two Cr(VI) anion species and may be explained by the fact that in the polymeric phase the $HCrO_4^- \leftrightarrow Cr_2O_7^{2-}$ equilibrium is shifted toward the formation of $Cr_2O_7^{2-}$ ions. The temperature increase also influences the equilibrium. It is well known that sorption value of inorganic ions, conditioned by ion exchange processes, practically is not dependent on temperature. The temperature can influence only the sorption kinetics.

The sorption isotherms on the AV-17(Cr) support (Figure 1b) are essentially different from those previously discussed. First of all, it is noticeable that the sorption of Cr(VI)-containing anions at 19°C on AV-17(Cr) is much lower than on AV-17(Cl) and begins at Cr(VI) concentrations that are higher than 2 mol L^{-1} (Figure 1b, curve 1). On the other hand, sorption from solutions with temperature of 60°C is higher on the AV-17 (Cr) sorbent than on the AV-17(Cl) exchanger (Figure 1b, curve 2). The shape of the isotherms in Figure 1(a,b) and their dependence on temperature shows that the sorption mechanism of ions containing Cr (VI), on sorbent AV-17(Cr) is different that on the AV-17(Cl) exchanger. On the AV-17(Cl) exchanger the sorption process may be expressed by Eqs. (1) and (2):

$$2R_4NCl + Cr_2O_7^{2-} \leftrightarrow (R_4N)_2Cr_2O_7 + 2Cl^- \quad (1)$$

$$R_4NCl + HCrO_4^- \leftrightarrow R_4NHCrO_4 + Cl^- \quad (2)$$

The sorption on the AV-17(Cr) sorbent is a chemical process that may be expressed by Eq. (3) and (4):

$$R_4N\left[Cr_3(OH)_6(SO_4)_2\right] + 2Cr_2O_7^{2-}$$
$$\leftrightarrow R_4N\left[Cr_3(OH)_6(Cr_2O_7)_2\right] + 2SO_4^{2-} \quad (3)$$

$$R_4N\left[Cr_3(OH)_6(SO_4)_2\right] + 2HCrO_4^-$$
$$\leftrightarrow R_4N\left[Cr_3(OH)_6(HCrO_4)_2\right]^{2+} + 2SO_4^{2-} \quad (4)$$

It is known that ligands in Cr(III) complexes are nonlabile. That is why the sorption of Cr(VI) from diluted solutions with temperature of 19°C is low (Figure 1b, curve 1). Moreover, in the outcome of the process (4), the SO_4^{2-} anions partially remain in the external sphere of the $R_4N[Cr_3(OH)_6(HCrO_4)_2]SO_4$ complex, thus contributing to the equilibrium (4) shift to the right. In the sorption from solution with temperature of 60°C, process (3) prevails. That is why the sorption from these solutions is higher and takes place in diluted solutions (Figure 1b, curve 2).

In solution of K_2CrO_4 with pH 8, Cr(VI) ions exist only as CrO_4^{2-} species.[13] The sorption of CrO_4^{2-} anions on the AV-17(Cl) exchanger takes places as a result of the anion exchange process described by Eq. (5):
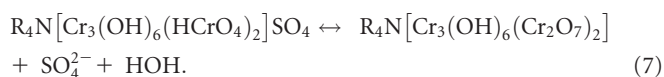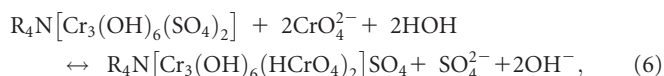
Table I. The Values of Isotherms Constants and Thermodynamic Functions

Sorbent	T (°C)	$S\infty$ (mol g^{-1})	K (L mol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})
AV-17(Cl)	19	1.39	216	−13.05	25.4	131.65
AV-17(Cl)	60	1.40	783	−18.45		131.66
AV-17(Cr)	19	1.44	269	−13.52	52.5	226.05
AV-17(Cr)	60	1.83	3,768	−22.80		226.07

$$2R_4NCl + CrO_4^{2-} \leftrightarrow (R_4N)_2CrO_4 + 2Cl^- \qquad (5)$$

It is surprising that sorption of the CrO_4^{2-} ions on AV-17(Cl) exchanger is strongly influenced by temperature (Figure 1c), although it is known that the ion exchange process is almost independent of temperature. Obviously, at the 19°C process (5) takes place. Although at 60°C, the Cr(VI) ions present in solution exist only in CrO_4^{2-} species, within the polymeric phase they partially reside as $HCrO_4^-$ ions and the sorption process takes place according to Eq. (2).

In solutions with pH 8, the sorption isotherms of CrO_4^{2-} ions on the AV-17(Cr) sorbent (Figure 1d) are similar to those obtained on the AV-17(Cl) support (Figure 1c). The sorption isotherm obtained at 19°C (Figure 1d, curve 1) proceeds according to process (6), while that obtained at 60°C (Figure 1d, curve 2) is characterized by processes (6) and (7):

$$R_4N\left[Cr_3(OH)_6(SO_4)_2\right] + 2CrO_4^{2-} + 2HOH$$
$$\leftrightarrow R_4N\left[Cr_3(OH)_6(HCrO_4)_2\right]SO_4 + SO_4^{2-} + 2OH^-, \qquad (6)$$

$$R_4N\left[Cr_3(OH)_6(HCrO_4)_2\right]SO_4 \leftrightarrow R_4N\left[Cr_3(OH)_6(Cr_2O_7)_2\right]$$
$$+ SO_4^{2-} + HOH. \qquad (7)$$

In solutions with pH 8 and temperature of 60°C sorption of Cr(VI)-containing anions on the AV-17(Cr) material is slightly higher than on the AV-17(Cl). However, this is not the essential difference. The important feature is that sorption on AV-17(Cr) is a chemical process, and therefore, the sorption is selective. The sorbent AV-17(Cr) is able to retain selectively only the anions with tetrahedral configuration from solution.

The isotherms in Figure 1(c,d) may be described by the Langmuir adsorption model: $S = S\infty\, KC/1 + KC$, where S is sorption (mmol Cr(VI) g^{-1}), C—equilibrium concentration of Cr(VI) (mmol L^{-1}), and $S\infty$ and K are isotherm constants. The isotherm constants values are presented in Table I. The data in Table I show that the value of the constant $S\infty$ of Cr(VI) sorption isotherms on the AV-17(Cl) exchanger is the same at 19 and at 60°C. This means that in the limit each active center (R_4N^+) retains a single particle of Cr(VI) (see Eqs. (1), (2), and (5)). The constant $S\infty$ of Cr(VI) sorption isotherms on the AV-17(Cr) sorbent is higher, especially at 60°C. The chemical affinity (K) of Cr(VI)-containing anions for the AV-17(Cr) sorbent, especially at 60°C, is much higher than the one for the AV-17(Cl) exchanger (Table I).

For sorption of Cr(VI)-containing anions in solutions of K_2CrO_4 with pH 8, the thermodynamic functions, namely the variation of Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated using the formulas (8)–(10):

$$\Delta G = -RT \ln K, \text{ where } K \text{ is the constant in Langmuir isotherm,} \qquad (8)$$

$$\Delta H = -R \ln(K_2/K_1) T_2 T_1 / T_1 - T_2, \qquad (9)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (10)$$

The values of these functions are shown in Table I. As evidenced in this table, ΔG depends on the temperature, having a higher value at 60°C. Moreover, ΔS does not depend on temperature, but essentially depends on the sorbent nature, showing a much higher value for the sorption on the AV-17(Cr) sorbent than on the AV-17(Cl) exchanger. The sorption processes are usually exothermic. The calculated values of ΔH indicate that in the sorbent phase the Cr(VI)-containing anions undergo significant changes.

SEM Investigation

In the previous papers,[2,6] we have demonstrated that the jarosite type compounds of Fe(III) in the phase of strongly basic anion exchangers are in the form of ultrafine solid particles. It is naturally to assume that compounds of Cr(III) within the AV-17(Cr) sorbent phase are also in the form of ultrafine particles. The SEM images of samples of AV-17(Cr) sorbent confirmed this assumption [Figure 2(a,b)]. The existence of chromium compounds particles within the phase of the AV-17 (Cr) sorbent and their morphology are the same before and after sorption of Cr(VI)-containing ions [Figure 2(c–f)]. The particles of chromium compounds are distributed chaotically both on the surface and within the volume of sorbent granules. The prior testing of the AV-17(Cr) sorbent samples by using X-ray powder diffraction spectroscopy showed that in the sorbent phase there are no crystalline phases. The SEM images of samples of the AV-17(Cr) sorbent confirm that chromium compounds are amorphous both on the surface and within the volume of sorbent granules.

Thermogravimetric Investigation

As far as the sorbents: raw AV-17(Cr) (Sample **So**), treated with K_2CrO_4 solution at 19°C and pH 3 (sample **1**) and sorbent treated with K_2CrO_4 solution at 19°C and pH 8 (sample **2**) are concerned, the degradation mechanism is influenced by the atmosphere in which the thermal degradation process occurs. Therefore, at temperatures higher than 300°C, the thermal decomposition processes affecting the **1** and **2** samples are separated differently in helium compared to air. P. Kannan[14] pointed out that the working environment influence the thermal degradation mechanism of polystyrene. Thermogravimetric characteristics of the sorbent samples are shown in the Table II at heating rate 10°C/min. He achieved activation energies that
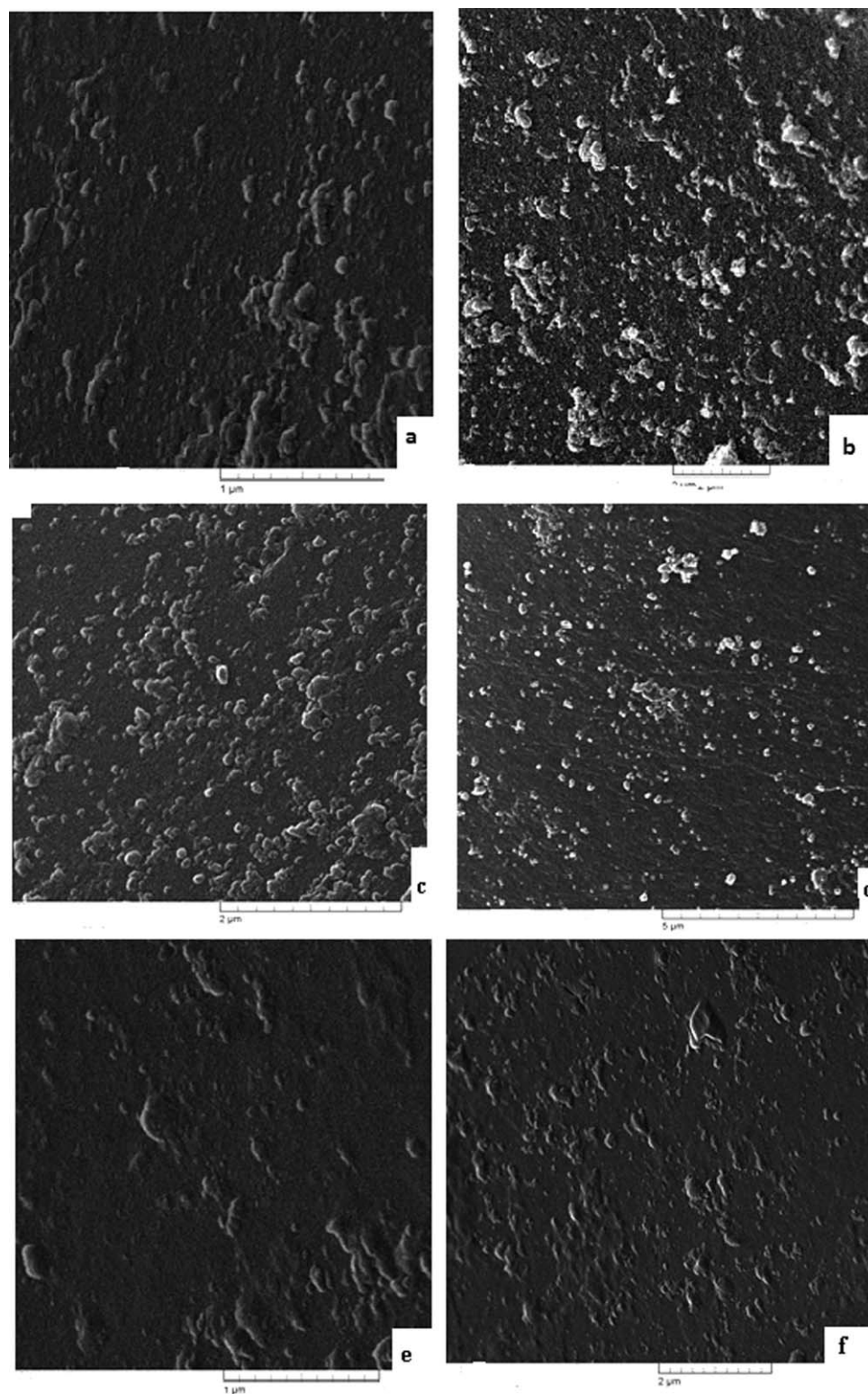
Figure 2. SEM images: of chromium (III) compounds on the surface (a) and in the volume (b) of AV-17(Cr) sorbent granule; of chromium (III) compounds on the surface (c) and in the volume (d) of AV-17(Cr) sorbent granule after sorption of CrO_4^{2-} ions from solution with temperature of 19°C and pH 8; of chromium (III) compounds on the surface (e) and in the volume (f) of AV-17(Cr) sorbent granule after sorption of Cr(VI)-containing anions from solution with temperature of 19°C and pH 3.

Table II. Thermogravimetric Characteristics of the Sorbent Samples

Samples	Thermal degradation stages	Helium				Air			
		T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	W (%)	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	W (%)
AV-17(Cr) (So)	I	37	87	131	7.51	49	71	100	15.54
	II	196	206	252	8.59	100	189	240	4.70
	III	300	324	344	22.42	302	316	328	20.63
	IV	405	428	481	38.33	405	420	438	20.23
	V	–	–	–	–	532	601	622	32.59
	Residue				23.15[a]				6.31[b]
AV-17(Cr)+$Cr_2O_7^{2-}$ (1)	I	38	102	154	4.12	54	75	115	13.93
	II	172	240	330	14.28	218	236	286	9.73
	III	380	417	424	17.78	286	377	416	10.09
	IV	424	432	437	11.29	416	424	428	14.26
	V	437	442	482	16.82	453	464	546	33.76
	Residue				35.71[a]				18.23[b]
AV-17(Cr)+$Cr_2O_4^{2-}$ (2)	I	38	102	157	5.48	57	75	115	12.29
	II	287	345	380	17.12	326	370	390	16.94
	III	380	417	425	27.65	416	423	429	11.00
	IV	425	432	452	21.18	429	461	551	41.89
	Residue				28.57[a]				17.88[b]

[a] Residue at 600°C (Netzsch system).
[b] Residue at 900°C (Mettler Toledo system).

were considerably higher when the degradation occurred in helium (about 190 kJ mol^{-1}) than when it occurred in air (only 120 kJ mol^{-1}). This is probably the case with **1** and **2** samples; considering the steeper TG curve slope in helium than in air (see Figures S1 and S2, Supporting Information), the activation energy values are higher in inert atmosphere and the degradation mechanism is different in the two working atmospheres.

Activation energy variation with the conversion degree was determined by the Friedman[15] method, using thermogravimetric curves recorded in air and helium at the following heating rates: $\beta = 7$, 10, 13, and 16°C/min. This differential method suggested by Friedman does not use any type of approximations. Hence, it is thought to be more accurate than integral isoconversional methods.[16]
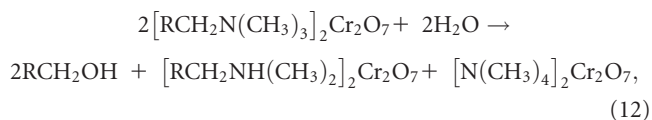
The Friedman method is a generally applicable method allowing apparent activation energy determination by means of the following equation:

$$\ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = \ln\left[F(\alpha)A\right] - \frac{E_\alpha}{RT_\alpha}, \quad (11)$$

when α is constant, the graphical representation of the $\ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = f\left(\frac{1}{T_\alpha}\right)$ values (pairs of values read at the following four heating rates: $\beta = 7$, 10, 13, and 16°C/min) results into a line the inclination of which provides the apparent activation energy value E_α. The correlation coefficients read in samples 1 and 2 on the graphical representation of the $\ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = f\left(\frac{1}{T_\alpha}\right)$ lines for various conversion degree values were higher than 0.9. Apparent activation energy variation calculated by the Friedman method depending on the conversion degree is shown in Figure 3a for sample 1 and Figure 3b for sample 2. Our results support both the complexity of the degradation mechanism and the fact that it is influenced by the environment where the thermal degradation process occur. We also noted that at conversion degrees higher than 0.7 and at temperatures exceeding 380°C the apparent activation energy values are higher in inert atmosphere than in the air. This finding is in agreement with the results of other researchers,[14] considering that the degradation of the basic polymer containing polystyrene–divinylbenzene occurs at temperatures higher than 380°C (according to the TG-MS-FTIR study described hereunder).

The **1** and **2** samples have a degradation mechanism slightly different from the sample of AV-17(Cr) sorbent (see Figure S3, Supporting Information). The **1** sample contains mostly $(R_4N)_2Cr_2O_7$ and $R_4N[Cr_3(OH)_6(Cr_2O_7)_2]$, whereas **2** sample contains $(R_4N)_2CrO_4$ and $R_4N[Cr_3(OH)_6(CrO_4)_2]$. The first stages consist partly of sorbent water removal (phase of hydration and free water) and partly of the following process for the **1** sample:
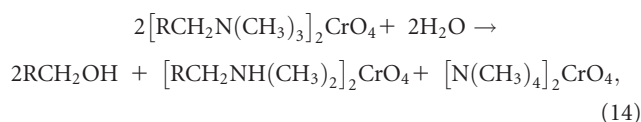
$$2\left[RCH_2N(CH_3)_3\right]_2Cr_2O_7 + 2H_2O \rightarrow$$

$$2RCH_2OH + \left[RCH_2NH(CH_3)_2\right]_2Cr_2O_7 + \left[N(CH_3)_4\right]_2Cr_2O_7, \quad (12)$$

which continues at temperatures higher than 170°C with $[N(CH_3)_4]_2Cr_2O_7$ intermediate decomposition:

$$\left[N(CH_3)_4\right]_2Cr_2O_7 \rightarrow 2N(CH_3)_3 \uparrow + C_2H_6 \uparrow + Cr_2O_3 + 2O_2 \uparrow. \quad (13)$$
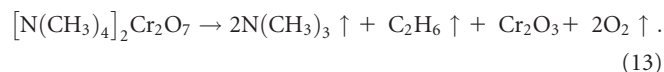
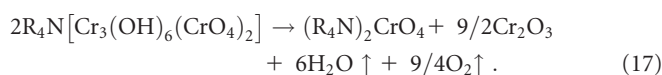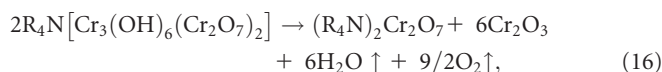The process that may occur in the **2** sample when water is present is shown in the following:
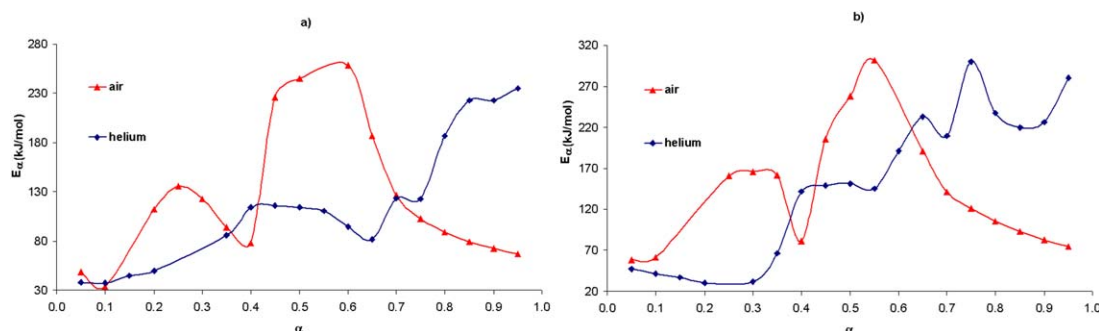
Figure 3. Activation energy variation with the conversion degree for the samples 1 (a) and 2 (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
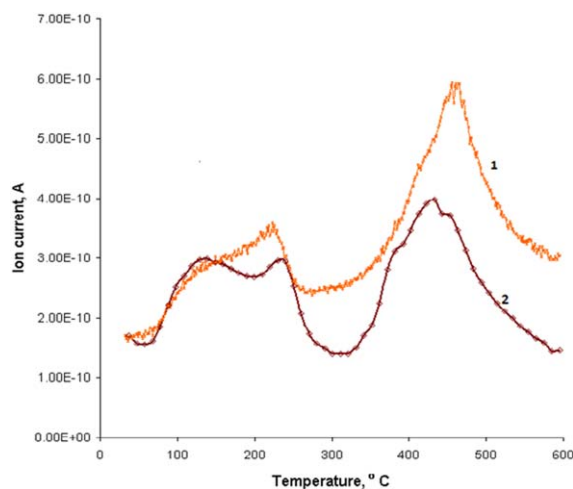
$$2\left[RCH_2N(CH_3)_3\right]_2CrO_4 + 2H_2O \rightarrow$$
$$2RCH_2OH + \left[RCH_2NH(CH_3)_2\right]_2CrO_4 + \left[N(CH_3)_4\right]_2CrO_4, \quad (14)$$

which continues at temperatures higher than 200°C with $[N(CH_3)_4]_2CrO_4$ intermediate decomposition:

$$2\left[N(CH_3)_4\right]_2CrO_4 \rightarrow 4N(CH_3)_3 \uparrow + 2C_2H_6$$
$$\uparrow + Cr_2O_3 + 5/2O_2\uparrow \quad (15)$$
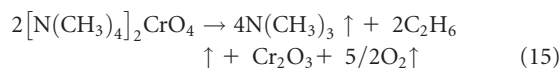
According to the following reaction sequences, an additional amount of water also results for these samples, at temperatures higher than 300°C, due to the dehydroxylation process:

$$2R_4N\left[Cr_3(OH)_6(Cr_2O_7)_2\right] \rightarrow (R_4N)_2Cr_2O_7 + 6Cr_2O_3$$
$$+ 6H_2O \uparrow + 9/2O_2\uparrow, \quad (16)$$

$$2R_4N\left[Cr_3(OH)_6(CrO_4)_2\right] \rightarrow (R_4N)_2CrO_4 + 9/2Cr_2O_3$$
$$+ 6H_2O \uparrow + 9/4O_2\uparrow . \quad (17)$$

The MS spectra recorded for these two test samples (**1** and **2**) support the proposed mechanism. Therefore, Figure 4 shows the ionic current variation for the $m/z = 18$ (H_2O^+) fragment, Figure 5 for the $m/z = 16$ (O^+) fragment, Figure 6 for the $m/z = 30$ ($C_2H_6^+$) fragment, and Figure 7 for $m/z = 59$ ($N(CH_3)_3^+$).

The thermal decomposition processes of the basic structure of the polymer containing polystyrene–divinylbenzene occur at temperatures higher than 380°C.[17] Ionic fragments specific to the styrene monomer, to α-methyl styrene, to dimethylbenzene or to alkylbenzene, etc. are also identified for these polymers. As the **1** and **2** samples are concerned, we also noted a separation tendency of several degradation processes within the 380–480°C temperature range (represented by two or three peaks in the DTG curves, compared to only one peak in the sorbent raw AV-17(Cr)—Sample **So**, see Figures S1–3, Supporting Information). They probably occur due to the different rate at which the random split processes occur, as a result to which various fragments of alkylbenzene result. Figures 8–10 show the MS spectra for the $m/z = 91$ ($C_7H_7^+$), $m/z = 105$ ($C_8H_9^+$), and $m/z = 120$ ($C_9H_{12}^+$) ionic fragments that illustrate the separation of several processes within the above mentioned temperature range.

The FTIR spectra recorded for the **1** and **2** test samples also support the proposed degradation mechanism. According to Figures 11 and 12, the bands specific to water in the vapor state
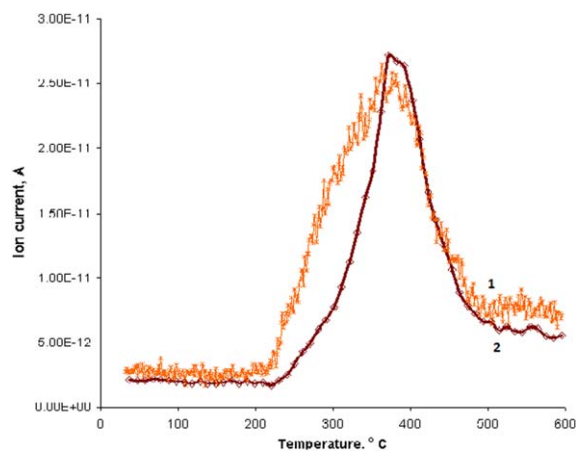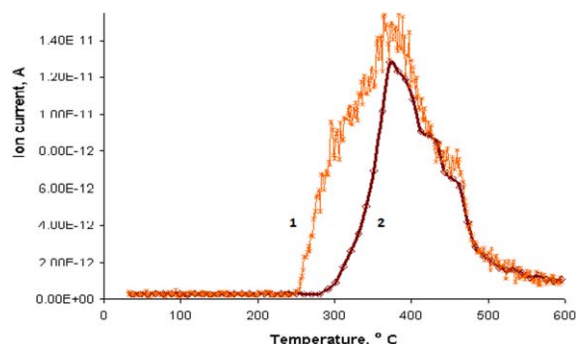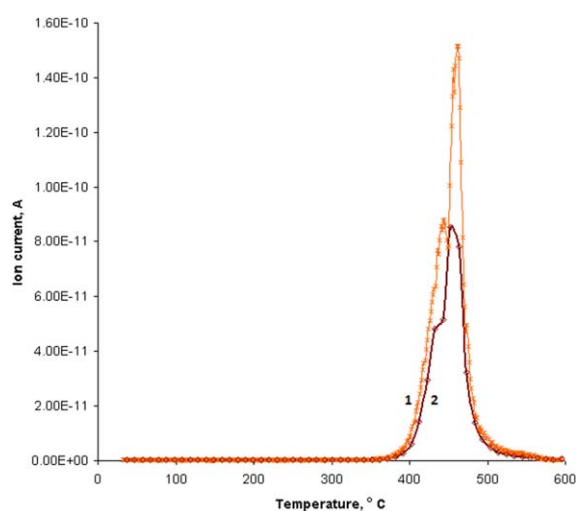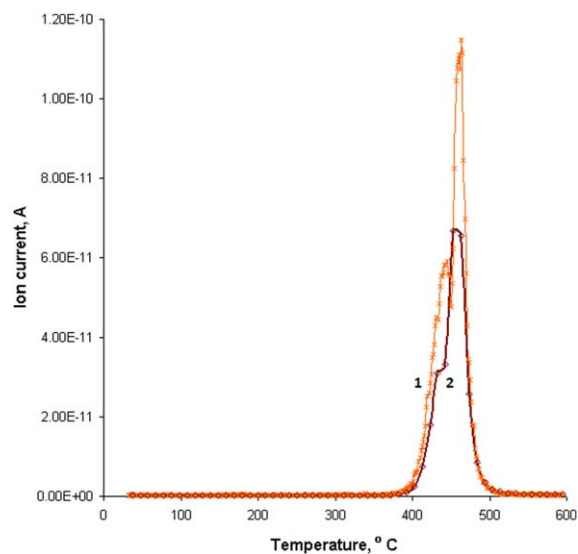

Figure 4. Ionic current variation with temperature for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ (1) and sorbent AV-17(Cr) containing CrO_4^{2-} (2) for the $m/z = 18$ fragment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
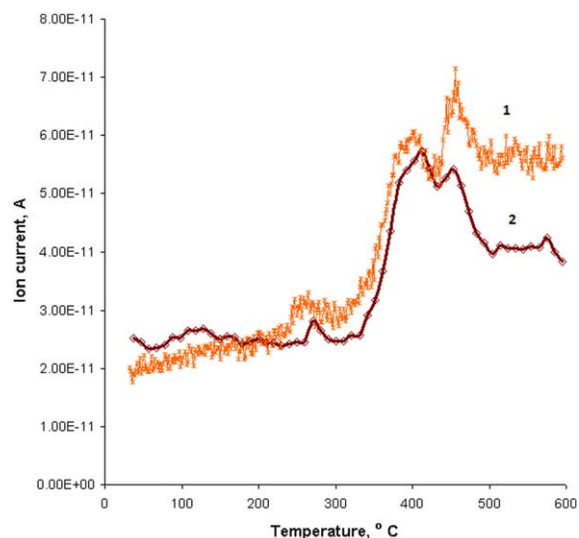
Figure 5. Ionic current variation with temperature for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ (1) and sorbent AV-17(Cr) containing CrO_4^{2-} (2) for the $m/z = 16$ fragment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Ionic current variation with temperature for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ (**1**) and sorbent AV-17(Cr) containing CrO_4^{2-} (**2**) for the m/z = 30 fragment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
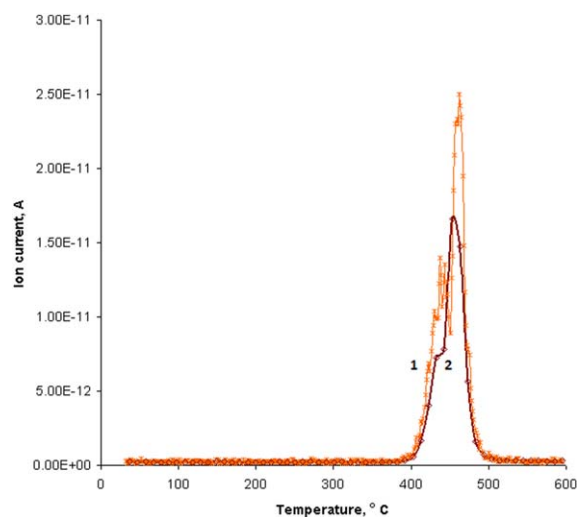

Figure 9. Ionic current variation with temperature for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ (**1**) and sorbent AV-17(Cr) containing CrO_4^{2-} (**2**) for the m/z = 105 fragment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Ionic current variation with temperature for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ (**1**) and sorbent AV-17(Cr) containing CrO_4^{2-} (2) for the m/z = 59 fragment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

occur within the 1390–1860 cm^{-1} and 3500–3900 cm^{-1} ranges, respectively.[18,19] The FTIR bands from 1158 to 1274 cm^{-1} that occur at 240°C for the **1** test sample and at 345°C for the **2** test sample may be connected to C-N bond vibration. The presence of the bands located at 1458 and 2970 cm^{-1} in the FTIR spectrum[20,21] may be connected to the m/z = 30 ($C_2H_6^+$) ionic fragment identified in the MS spectrum.

The FTIR spectra in Figure 11 (spectrum 2 and 3) and in Figure 12 (spectrum 3) support the thermal decomposition theory of the basic structure of polymers containing polystyrene–divinylbenzene, at temperatures higher than 380°C. We noted, for instance, the

Figure 8. Ionic current variation with temperature for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ (**1**) and sorbent AV-17(Cr) containing CrO_4^{2-} (2) for the m/z = 91 fragment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]


Figure 10. Ionic current variation with temperature for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ (**1**) and sorbent AV-17(Cr) containing CrO_4^{2-} (2) for the m/z = 120 fragment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
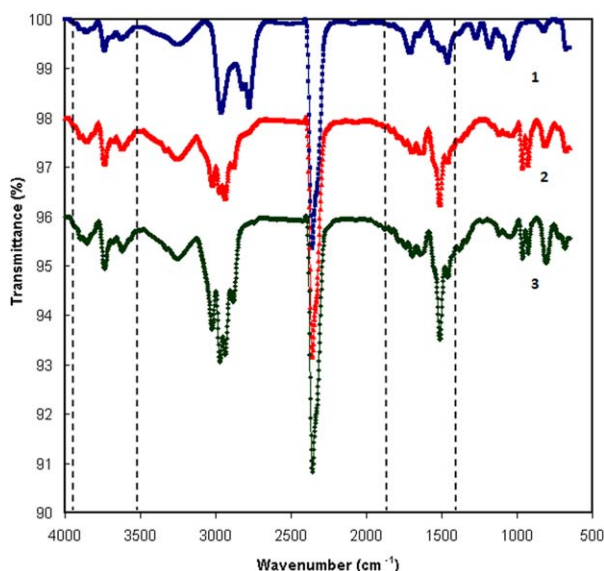
Figure 11. FTIR for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ at 240 (1), 417 (2), and 442°C (3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bands from 3,078 cm^{-1} characteristic to the aromatic cycles of the styrene monomer; those from 2,860 and 2,920 cm^{-1} in connection to the methyl groups belonging α-methyl styrene; the bands specific to aliphatic –CH_2 groups from polystyrene at 3,026 cm^{-1}.[22,23]. As the **1** and **2** sample are concerned, we also identified in the FTIR spectra the bands specific to CO_2 at 672 and 2,352 cm^{-1} at temperatures higher than 200°C.[21] They have a higher intensity for the **1** polymer, the thermal degradation of which results into a higher amount of oxygen that may lead to CO_2 formation.
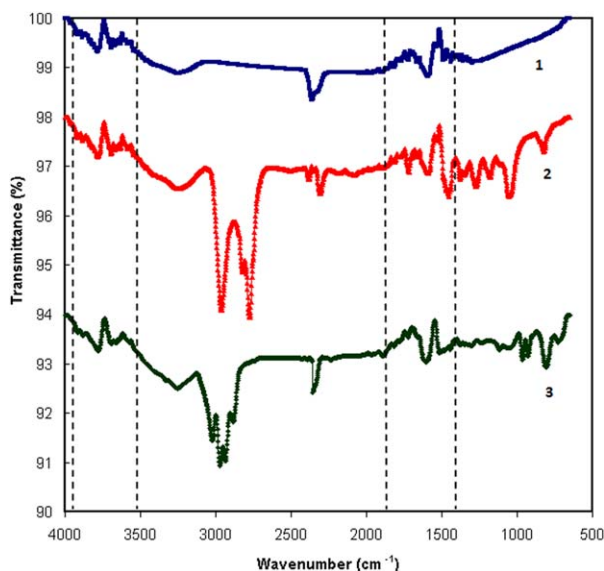
Figure 12. FTIR for the sorbent AV-17(Cr) containing $Cr_2O_7^{2-}$ at 102 (1), 345 (2), and 432°C (3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The strongly basic cross-linked AV-17 ionic polymer (containing R_4N^+ functional groups) modified with Cr(III) compounds becomes a selective sorbent (AV-17(Cr)).

Sorption of CrO_4^{2-}, $Cr_2O_7^{2-}$ ions on the AV-17 (Cr) sorbent and, respectively, on the AV-17 (Cl) exchanger depends strongly on temperature (19°C vs. 60°C) and solution pH (3 vs. 8). It is shown that during sorption in the sorbent phase the chemical (polychromic and complex forming) and physical (anion exchange) processes take place. Sorption isotherms and thermodynamic functions values (ΔG, ΔH, and ΔS) confirm this conclusion. Sorption isotherms of Cr (VI)-containing anions in solutions with pH 8 both on the AV-17(Cr) sorbent and on the AV-17(Cl) exchanger are described by the sorption Langmuir model. The SEM images show that the AV-17 (Cr) sorbent contains ultrafine particles consisting in Cr (III) compounds both on the surface and within the volume of sorbent granules. The Cr(III) compounds are amorphous and the particles morphology is not influenced by the sorption of Cr(VI)-containing anions.

The TG-MS-FTIR study conducted enabled us to propose a degradation mechanism. The AV-17(Cr) sorbent before sorption of Cr(VI) ions (sample **So**), after sorption from solution with pH 3 (sample **1**) and with pH 8 (sample **2**) show a complex degradation mechanism, the first stages of which consist in water removal from the polymer (phase of hydration and free water), followed by trimethylamine ($N(CH_3)_3\uparrow$), ethane ($C_2H_6\uparrow$), sulfur dioxide ($SO_2\uparrow$), and oxygen ($O_2\uparrow$) release at temperatures higher than 300°C and by the release of an additional amount of water ($H_2O\uparrow$) resulted from the dehydoxylation process. The thermal decomposition of the basic structure of the polymers containing polystyrene–divinylbenzene occurs at temperatures higher than 380°C. The **1** and **2** samples also exhibit trimethylamine ($N(CH_3)_3\uparrow$), ethane ($C_2H_6\uparrow$), and oxygen ($O_2\uparrow$) release, yet starting at temperatures that are lower by about 100°C than the temperatures of the other polymers. These polymers also show the release of an additional amount of water ($H_2O\uparrow$) resulted from the dehydoxylation process at temperatures higher than 300°C.

REFERENCES

1. Gutsanu, V.; Tudorachi, N.; Lisa, G. *Thermochim. Acta* **2013**, *574*, 109.
2. Gutsanu, V.; Gafiichuk, V.; Shofransky, V.; Turta, C. *J. Appl. Polym. Sci.* **2006**, *99*, 59.
3. Drutsa, R.; Gutsanu, V.; Rusu, V. *J. Appl. Polym. Sci.* **2006**, *102*, 3978.
4. Gutsanu, V.; Drutsa, R. BOPI, 8, 25, Patent 2241MD, **2003**.
5. Archipenko, D. K.; Devyatkina, E. T.; Palcic, N. A. Cristali Chemical Particularities of Synthetic Jarosites, Nauka, Novosibirsk, **1987** (In Russian).
6. Gutsanu, V.; Schitco, C.; Lisa, G.; Turta, C. *Mater. Chem. Phys.* **2011**, *130*, 853.
7. Ohyabu, M.; Ujihira, I. *J. Inorg. Nucl. Chem.* **1981**, *2*, 1948.
8. Gutsanu, V.; Rosca, I. BOPI, 4, 33, Patent 2746 MD **2005**.
9. Lurie, A. A. Sorbents and Chromatographic Carrier, Nauka: Moscow, **1972** (In Russian).

10. Gutsanu, V.; Drutsa, R. BOPI, 9, 23, Patent 1027 MD **1998**.

11. Marchenco, Z. Photometrical Determination of Elements, Mir, Moscow, **1971** (In Russian).

12. Lisa, G.; Apreutesei Wilson, D.; Scutaru, D.; Tudorachi, N.; Hurduc, N. *Thermochim. Acta* **2010**, *507*, 49.

13. Fishtic, I. F.; Vataman, I. I. Thermodynamics of the Metallic Ions Hydrolysis, Stiintsa, Chisinau, **1988** (In Russian).

14. Kannan, P.; Biernacki, J. J.; Visco Jr, D. P.; Lambert, W. *J. Anal. Appl. Pyrol.* **2009**, *84*, 139.

15. Friedman, H. L. *J. Polym. Sci. Part C* **1964**, *6*, 183.

16. Vyazovkin, S.; Burnham, A. K.; Criadoc, J. M.; Pérez-Maqueda, L. A.; Popescu, C.; Sbirrazzuoli, N. *Thermochim. Acta* **2011**, *520*, 1.

17. Dragan, E. S.; Dinu, M. V.; Lisa, G.; Trochimczuk, A. W. *Eur. Polym. J.* **2009**, *45*, 2119.

18. Tudorachi, N.; Chiriac, A. P. *Polym. Test.* **2011**, *30*, 397.

19. Cervantes-Uc, J. M.; Cauich-Rodriguez, J. V.; Vazquez-Torres, H.; Garfias-Mesias, L. F.; Paul, D. R. *Thermochim. Acta* **2007**, *457*, 92.

20. Kaljuvee, T.; Edro, E.; Kuusik, R. *Oil Shale* **2007**, *24*, 117.

21. Ferrasse, J. H.; Chavez, S.; Arlabosse, P.; Dupuy, N. *Thermochim. Acta*, **2003**, *404*, 97.

22. Singare, P. U.; Lokhande, R. S.; Madyal, R. S. *Russ. J. Gen. Chem.* **2010**, *80*, 527.

23. Yang, M.; Tsukame, T.; Saitoh, H.; Shibasaki, Y. *Polym. Degrad. Stabil.* **2000**, *67*, 479.