Fe^{2+} and Fe^{3+} Adsorption on 2-Vinylpyridine–Divinylbenzene Copolymers and Acrylonitrile–Methyl Methacrylate–Divinylbenzene Terpolymers

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ABSTRACT: The adsorption of Fe^{2+} and Fe^{3+} ions on 2-vinylpyridine–divinylbenzene copolymer and acrylonitrile–methyl methacrylate–divinylbenzene terpolymer was investigated. In general, the adsorption of Fe^{2+} and Fe^{3+} in both resins increased with the enhancement of hydrochloric acid and metal concentration. The metal adsorption on the terpolymer increased sharply with the addition of small portions of ethanol, whereas the adsorption on the copolymer practically was not affected by the presence of the alcohol. An increase in temperature produced a small increase in iron adsorption for both resins. Fourier transform infrared spectra showed that nitrile and ester groups of the terpolymer did not suffer hydrolysis during metal adsorption, even for the highest HCl concentration and the highest temperature applied. A mechanism of iron adsorption through the ion exchange of chloride anions by tetrahedral $[FeCl_4]^{2-}$ or $[FeCl_4]^{-}$ anions is proposed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3905–3912, 2003

Key words: ion exchangers; macroporous polymers; swelling; transition metal chemistry

INTRODUCTION

Interest in chelating and ion-exchange resins has been growing during the last decades because of their diverse applications in analytical chemistry,[1] hydrometallurgy,[2] wastewater treatment,[3,4] catalysis,[5,6] and removal and separation of metal ions from aqueous solution.[7–11] In general, desirable properties of the resins are a high capacity for the metal ions of interest, high selectivity, fast kinetics, high mechanical strength, and toughness of the exchanger particles. The performance of these polymers in their different applications depends on several factors, including functional group type, pH of the medium, solvent, ion concentration, porous structure, crosslinking degree, and swelling properties of the resin.

It is well known that polymers based on vinylpyridine (VPy) can form polymer–metal complexes.[12] Gutanu et al. found that 4-VPy–divinilbenzene copolymer retain Fe^{3+} ions by nitrogen atoms–Fe^{3+} complexes, whereas the chemically modified copolymer containing a quaternary ammonium nitrogen will retain Fe^{3+} through ion exchange as the $R_4N^+[Fe_3(SO_4)_2(OH)_6]^-$ complex anion.[13] Sugii et al. also proposed that polymers containing pyridine groups can retain metal ions by two mechanisms: conventional ion exchange and complexation.[14] Recently, Rivas et al. described the high selective binding of mercury ions by poly(4-vinylpyridine) hydrochloride resin. The Hg retention occurred in an acid medium through the ion-exchange process of the chloride anions by tetrahedral $[HgCl_4]^{2-}$ anions.[15]

Although polymers based on acrylonitrile (AN) have nitrogen groups that are able to form complexes with metal ions like polymers based on VPy, they have not been applied in the sorption of metal ions from aqueous solutions without previous chemical modification. In general, they are used as weak-base anion exchangers and polymeric carriers after the aminolysis of nitrile groups.[16,17] The aminolysis reaction to produce amidoxime groups is one of the most frequent chemical modifications of nitrile-containing polymers used in hydrometallurgy.[18–20] It is known that the strong interactions between nitrile groups reduce the swelling in aqueous media and the hydrophilicity of porous polymer surface.[21] This is probably one of the reasons that nitrile-containing polymers

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have not been extensively used in metal sorption from aqueous solutions without chemical modification.

This article deals with the study of Fe^{2+} and Fe^{3+} adsorption on 2-VPy–divinylbenzene (DVB) copolymer and AN–methyl methacrylate (MMA)–DVB terpolymer from hydrochloric acid solutions. The aim was to compare the behavior of different nitrogen-containing polymers in relation to iron ion uptake. The retention of iron ions in the terpolymer increased sharply with the addition of small portions of ethanol to the aqueous solution. The effects of HCl, metal concentration, and temperature on the iron ion adsorption were also investigated.

EXPERIMENTAL

Materials

Commercial 2-VPy, AN, MMA, and DVB were vacuum-distilled. All of the other chemicals were used as received. Standard solutions of HCl were prepared by the mixture of an appropriate amount of concentrated acid in deionized water. Standard Fe^{2+} and Fe^{3+} solutions were prepared by the dissolution of appropriate amounts of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$) in acid solutions with different concentrations.

Polymer synthesis

2-VPy–DVB copolymer was obtained by the suspension polymerization of 2-VPy and DVB at a molar ratio of 5:1. Ethyl acetate and heptane were used as pore-forming agents at proportions of 30 and 70% of the total monomer volume, respectively. The aqueous phase contained 2% (w/w) NaCl, 0.6% (w/w) hydroxyethyl–cellulose, and 0.3% (w/w) gelatine. AN–MMA–DVB terpolymer was obtained by the suspension polymerization of AN, MMA, and DVB at a molar ratio of 10:1:2. Toluene was used as a pore-forming agent at a proportion of 100% of the total monomer volume. The aqueous phase contained 2% (w/w) poly(vinyl alcohol). For both reactions, 1% (mol/mol) 2,2′-azobis(2-methylbutane-nitrile) (Vazo-67) was used as an initiator. The organic phase/aqueous phase ratio was 1:5 v/v for the polymerization processes. The reactions were allowed to proceed for 24 h at 60°C, and the stirring speed was kept at 400 rpm. The copolymers and terpolymers beads were washed with warm deionized water, ethanol, and methanol and were then dried at 70°C for 24 h.

Polymer characterization

Apparent densities (d_a's) of the resins were determined in a graduated cylinder.[20] The specific surface area (S), pore volume (V_p), and average pore diameter (D) were obtained from N_2 adsorption measurements by automatic physisorption analyzer micromeritics (ASAP 2010; Micrometrics Instrument Corp., Norcross, GA). Water and organic solvent uptakes were determined by the centrifugation method used by Rabelo and Coutinho.[22–23] The terpolymer had to be treated with methanol before water uptake measurements, but for the copolymer, that was not necessary. The total nitrogen analysis of the resins was performed by an adaptation of the Kjeldahl method.[24] The ion-exchange capacity (IEC) of the 2-VPy–DVB copolymer was determined through a method described by Warshawsky et al.[1] IR spectra of the polymers with and without iron ions were obtained on a Fourier transform infrared (FTIR) spectrometer (Bomem, MB Series; Hartmann & Braun, Quebec, Canada) at room temperature. The samples were run as cold-pressure powders in a KBr medium with a composition of 5% (w/w).

Iron sorption experiments

The iron sorptions were performed in 125-mL Erlenmeyer flasks with 0.2 g of resin and 20 mL of acid solutions containing Fe^{2+} or Fe^{3+} ions. The two phases were shaken in a mechanical shaker with a thermostatic bath for 24 h. After shaking, the two phases were separated, and the supernatant solutions were analyzed by atomic absorption spectrometry. The amount of metal ion in the supernatant subtracted from the amount initially added provided the amount of metal ion adsorbed on the resin. Some experiments were performed with the addition of ethanol to the resin/iron solution mixtures. The HCl concentration varied from 1.0 to 6.0 mol L^{-1}. The metal concentration in initial solutions varied from 100 to 1000 mg L^{-1}. The bath temperatures were 25, 35, and 45°C. The ethanol amounts varied from 5 to 40% iron solution volume.

RESULTS AND DISCUSSION

Polymer characterization

The physicochemical properties of the 2-VPy–DVB copolymer and the AN–MMA–DVB terpolymer synthesized are listed in Table I. The calculated nitrogen contents for the copolymer and terpolymer were 7.6 and 12.6 mmol g^{-1}, respectively. Nitrogen analysis showed a high incorporation of pyridinic and nitrilic units in the polymer chains (65 and 79% monomer charge, respectively). The partial solubility of pyridine and AN in water explained the loss of functional monomer in relation to the initial composition. Calculated and experimental nitrogen contents for the terpolymer were higher than for the copolymer.

In general, ion-exchange resins are classified as gel type, mesoporous, and macroporous, depending on their properties in the dry state. The solvent uptakes

TABLE I
Physicochemical Properties of the Resins

Resin	N (mmol g^{-1})	IEC (mmol g^{-1})	S (m^2 g^{-1})	V_p (cm^3 g^{-1})	D (nm)	d_a (g cm^{-3})	Appearance
2-VPy–DVB	6.07	5.07	2.9	0.01	4.1	0.49	Translucid
AN–MMA–DVB	9.97	—	54.9	0.51	12.5	0.37	Opaque

are also useful for classifying the porous structures of crosslinked polymers.[23,25] The 2-VPy–DVB copolymer synthesized in the presence of a solvating/nonsolvating diluent mixture presented characteristics of mesoporous resins: low S, small V_p, small D, moderated d_a, and low opacity, whereas the AN–MMA–DVB terpolymer synthesized in the presence of a nonsolvating diluent presented characteristics of macroporous resins: high S, large V_p, large D, low d_a, and high opacity.

The solvent uptakes in Table II can be interpreted according to the different porous structures presented by the resins. Because V_p of the 2-VPy–DVB copolymer was very small, the high uptakes of water, ethanol, and toluene could be considered as solvent retention due to swelling of the polymeric structure. The small heptane uptake showed that it was a bad solvent for the copolymer chains. The pyridine groups provided hydrophilic characteristics to the copolymer so that water retention occurred by direct contact. For the macroporous terpolymer, the solvent uptake could be considered a result of three contributions: macropore filling, macropore expansion, and gel structure swelling.[23] Toluene uptake of the terpolymer could be considered a result of macropore filling because the retention volume was practically equal to V_p determined in the dry state. Ethanol retention was a result of the three mentioned contributions. Therefore, the terpolymer had a higher thermodynamic affinity for ethanol than for toluene. The terpolymer had hydrophobic characteristics because water could not penetrate its porous structure without previous contact with an alcohol. This effect was also observed for macroporous styrene–DVB copolymers, which retained water only after methanol treatment. These polymers had water uptakes very close to the V_p determined by mercury porosimetry.[22] Indeed, the water uptake of the terpolymer in Table II was obtained after methanol treatment and a thorough washing with water. Perhaps methanol was not totally washed, so the water uptake was larger than the fixed V_p. Heptane uptake was very small probably because it is difficult to penetrate a polar porous structure. The low thermodynamic affinity of the terpolymer for water and heptane could be explained by the strong dipole–dipole interactions between nitrile groups of the polymeric chains.[21]

Iron adsorption properties

Figure 1 shows the results of Fe^{2+} and Fe^{3+} adsorption on the AN–MMA–DVB terpolymer. The terpolymer beads floated in contact with aqueous solution because of its hydrophobic characteristics, as discussed before. The adsorption of the iron ions in the HCl solutions was preferentially low because aqueous solutions could not penetrate the macroporous structure. The addition of a small amount of ethanol (5% v/v) significantly increased the iron adsorption because the surface tension between the polymer and the aqueous solutions decreased so that the nitrile groups inside the porous beads became accessible. Figure 1 also shows that iron ion adsorption increased with increasing HCl concentration. Therefore, the iron ion adsorption on the terpolymers increased because of two factors: the presence of ethanol in the aqueous solution and the enhancement of HCl concentration.

Figure 2 shows the results of Fe^{2+} and Fe^{3+} adsorption on the 2-VPy–DVB copolymer. In this case, ethanol addition did not produce a significant effect on the iron adsorption as it did for the terpolymer. This could be explained by the hydrophilic properties of the pyridine groups present in the copolymer, which did not need ethanol addition to the iron solution to penetrate and swell the beads. Iron ion adsorption on the copolymer increased slightly with increasing HCl concentration. Figures 1 and 2 show that in the presence of ethanol and for 100 mg L^{-1} iron solution, the adsorption was higher on the terpolymer than on the copol-

TABLE II
Solvent Uptake Values of the Resins

Resin	Water (cm^3 g^{-1})	Ethanol (cm^3 g^{-1})	Toluene (cm^3 g^{-1})	Heptane (cm^3 g^{-1})
2-VPy–DVB	0.58	1.60	0.49	0.01
AN–MMA–DVB	0.68	0.87	0.54	0.20

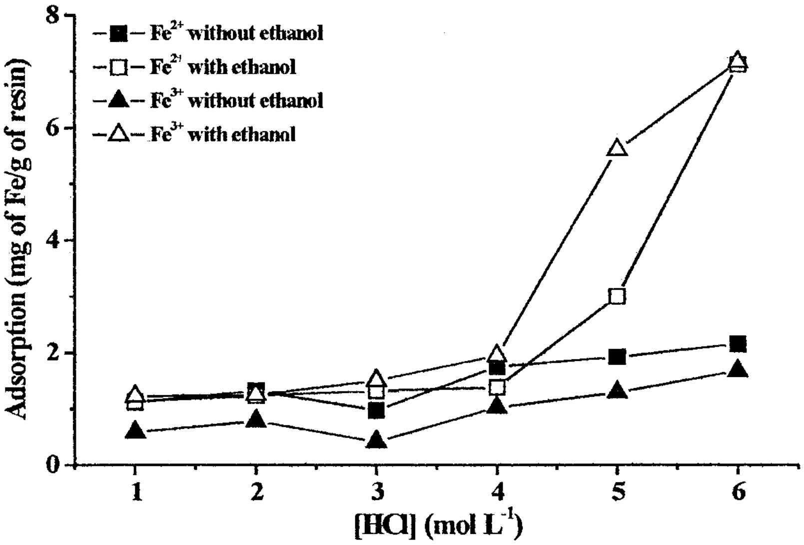

Figure 1 Effects of ethanol addition and HCl concentration on Fe^{2+} and Fe^{3+} ion adsorption on the AN–MMA–DVB terpolymer (iron concentration = 100 mg L^{-1}).

ymer. The higher nitrogen content in the terpolymer in comparison to the copolymer explained these results.

Figure 3 illustrates the relation between the metal concentration and the Fe^{2+} and Fe^{3+} sorption properties in the presence of 5% ethanol. Generally, the adsorption capacity for both ions increased with the enhancement of metal concentration in solution. The Fe^{3+} ion adsorption on both resins was slightly higher than Fe^{2+} ion adsorption. The Fe^{2+} and Fe^{3+} adsorptions on the terpolymer were higher than on the copolymer for low metal concentration, whereas contrary behavior was observed for high metal concentration. This could be explained by the differences in the porous structure and the swelling properties of the resins. The terpolymer had a macroporous structure with a small swelling capacity in aqueous media, so the available surface for iron adsorption became saturated in the range of metal concentration used. Although the copolymer presented a high swelling capacity in aqueous media, which increased with the increasing solution ionic strength, this probably promoted higher iron adsorption on the copolymer at a high metal concentrations.

The effect of ethanol concentration on the Fe^{3+} ion adsorption is illustrated in Figure 4. The adsorption capacity of Fe^{3+} on the 2-VPy–DVB copolymer practically did not change with increasing ethanol concentration until 20% and suffered a slight decrease at 40%. For the AN–MMA–DVB terpolymer, the maximum adsorption capacity of Fe^{3+} occurred at

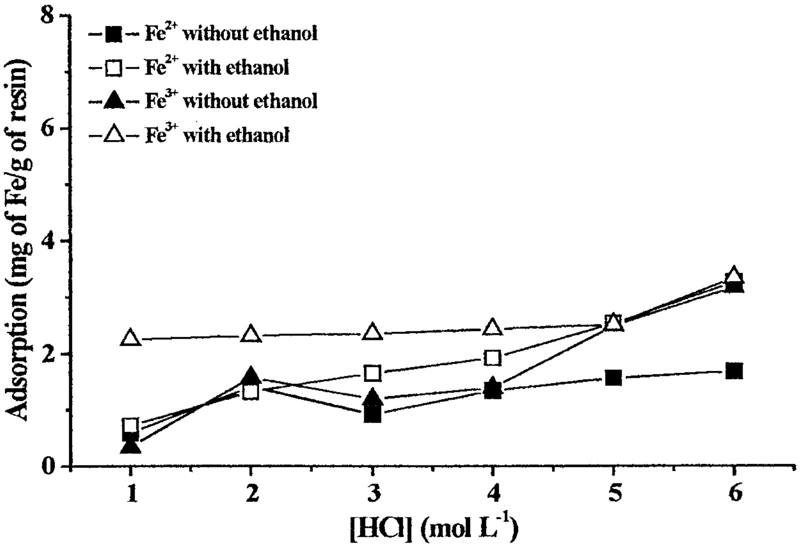

Figure 2 Effects of ethanol addition and HCl concentration on Fe^{2+} and Fe^{3+} ion adsorption on the 2-VPy–DVB copolymer (iron concentration 100 mg L^{-1}).

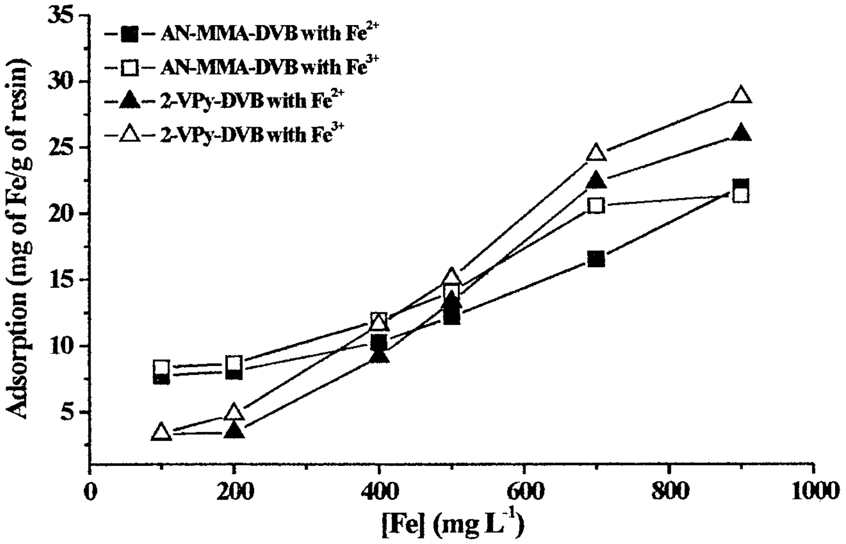

Figure 3 Effect of metal concentration on Fe^{2+} and Fe^{3+} ion adsorption on the 2-VPy–DVB copolymer and the AN–MMA–DVB terpolymer in the presence of 5% (v/v) ethanol (HCl concentration = 6.0 mol L^{-1}).

an ethanol concentration of 5%. After that, the increase in ethanol concentration diminished the iron adsorption. At low concentrations, ethanol promoted the penetration of aqueous solutions in the terpolymer porous structure. At high concentrations, ethanol competed with iron ions for adsorption sites on the terpolymer surface.

Figures 5 and 6 show the effect of temperature on Fe^{2+} and Fe^{3+} adsorption on the 2-VPy–DVB copolymer and AN–MMA–DVB terpolymer, respectively. Only a small increase in iron ion adsorption was observed when the temperature increased. This behavior indicates that adsorption of the Fe^{2+} and Fe^{3+} ions on both resins was not physical. The iron-retention mechanism could be by ion exchange or by complexation. Because equilibrium adsorption increased slightly at higher temperatures, the process could be considered endothermic. Examples of endothermic ion exchange and even endothermic complexation can be found in the literature.[26,27] Ivanov et al. also found an extremely weak influence of temperature on nickel adsorption on polyvinylpyridine.[28]

Investigation of metal–polymer interactions

The interactions between metal ions and the polymer functional groups were investigated by IR spectroscopy. The FTIR spectrum of pure 2-VPy–DVB [Fig. 7(a)] showed characteristic absorption bands at 1589 cm^{-1}, which could be assigned to the in-plane CN

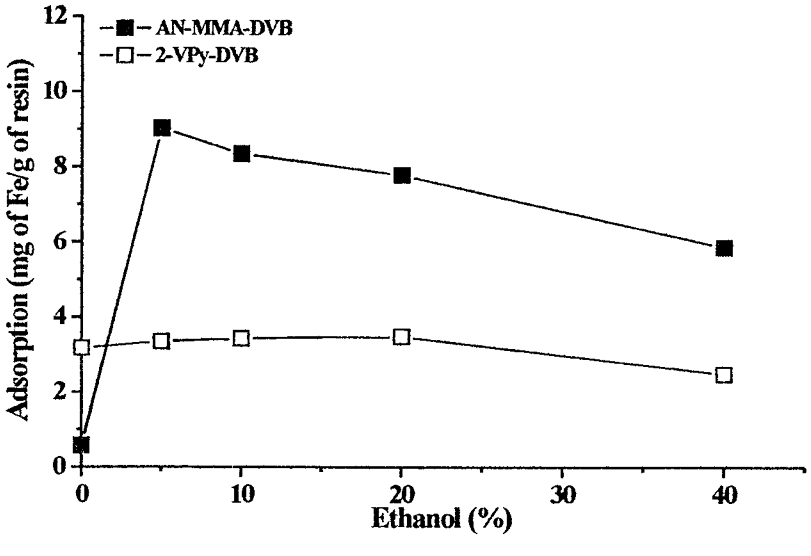

Figure 4 Effect of ethanol concentration on Fe^{3+} ion adsorption on the 2-VPy–DVB copolymer and the AN–MMA–DVB terpolymer (iron concentration = 100 mg L^{-1}; [HCl] = 6.0 mol L^{-1}).

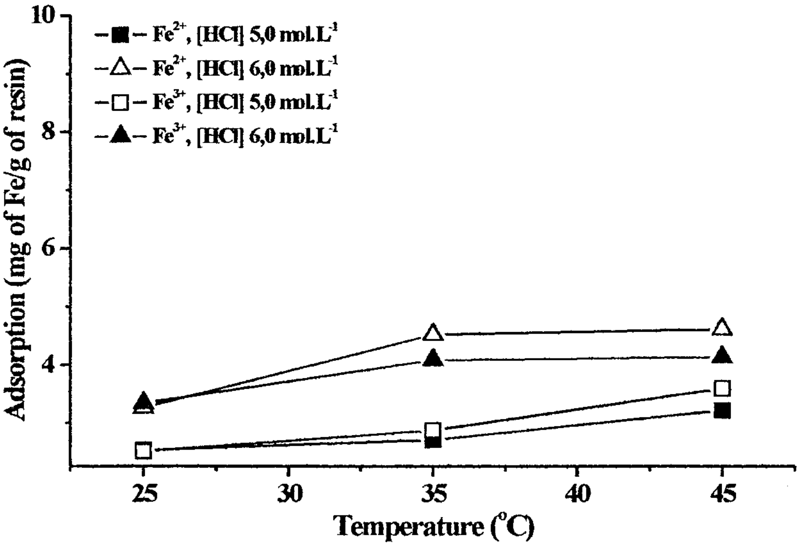

Figure 5 Effect of temperature on the adsorption of Fe^{2+} and Fe^{3+} ions on the 2-VPy–DVB copolymer (iron concentration = 100 mg L^{-1}).

stretching vibration of the free pyridine ring.[12] The FTIR spectrum of 2-VPy–DVB treated with 1.0 mol L^{-1} HCl solution [Fig. 7(b)] presented a shift of in-plane CN stretching to 1615 cm^{-1}, which could be attributed to pyridine groups protonation. 2-VPy–DVB treated with HCl solution presented —NH^+A^- groups, where A^- is a chloride anion. Therefore, the nitrogen atom of hydrochloride pyridine groups did not have a free electronic pair to form coordination bonds with iron ions.[15]

The FTIR spectra of protonated 2-VPy–DVB copolymer with Fe^{2+} and Fe^{3+} ions adsorbed at 45°C from 6.0 mol L^- HCl solutions are shown in Figure 8. The three spectra were identical, indicating that Fe^{2+} and Fe^{3+} ion adsorption did not occur by metal complexation. At high HCl concentration, the chloride ions complexed to Fe^{2+} and Fe^{3+} ions, forming the tetrahedral $[FeCl_4]^{2-}$ and $[FeCl_4]^-$ anions, respectively.[29,30] Probably, the iron ions were adsorbed in the form of these anion complexes by electrostatic interactions with protonated pyridinic groups present in the copolymer.[31] Therefore, the mechanism of iron adsorption on the copolymer could occur in hydrochloric media through an ion-exchange process of the chloride anion by $[FeCl_4]^{2-}$ and $[FeCl_4]^-$ anions.

The FTIR spectra of pure AN–MMA–DVB terpolymer with Fe^{2+} and Fe^{3+} ions adsorbed at 45°C from 6.0 mol L^{-1} HCl solutions are shown in Figure 9. The infrared spectrum of the pure AN–MMA–DVB ter-

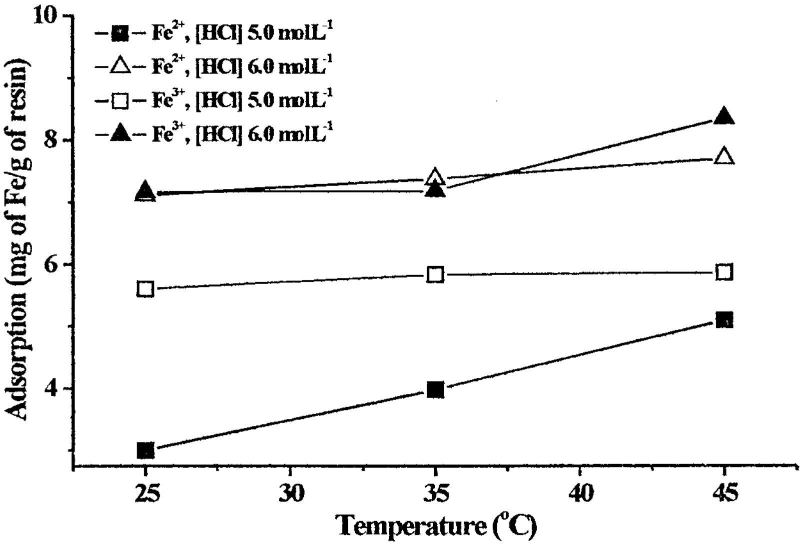

Figure 6 Effect of temperature on the adsorption of Fe^{2+} and Fe^{3+} ions on the AN–MMA–DVB terpolymer (iron concentration = 100 mg L^{-1}).

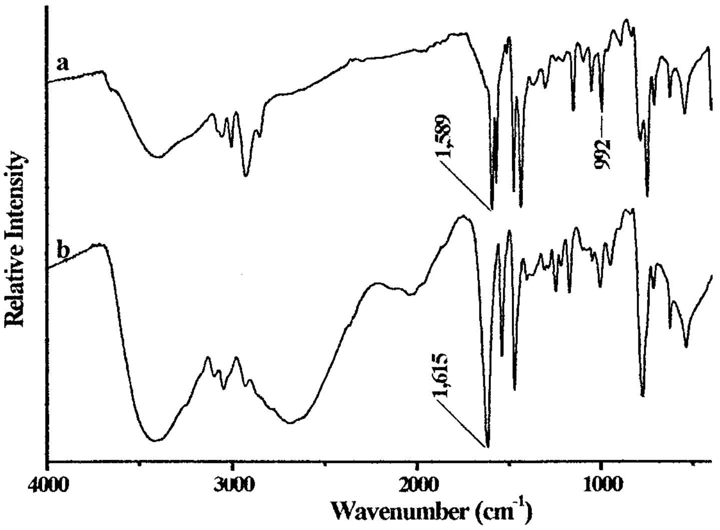

Figure 7 FTIR spectra of the 2-VPy–DVB copolymer: (a) pure and (b) protonated.

polymer [Fig. 9(a)] presented characteristic absorption bands at 2241 cm^{-1}, which was assigned to the stretching of the nitrile group, and 1727 cm^{-1}, which was assigned to the axial deformation of the C=O ester of the MMA units. Because the three spectra were identical, we concluded that the acid hydrolysis of nitrile and ester groups of the terpolymer did not occur during Fe^{2+} and Fe^{3+} ion adsorption at high HCl concentrations and high temperature. There was no evidence in the FTIR spectra for the protonation of nitrile or ester groups and, consequently, for iron ion adsorption on the terpolymer through an ion-exchange process of the chloride anion by Fe anion complexes.

Figure 10 shows the Mössbauer spectrum at 77 K of 2-VPy–DVB copolymer with Fe^{3+} adsorbed. A single peak was found with an isomer shift (δ) of approximately 0.30 mm s^{-1}. This is consistent for high-spin iron(III) in the form of $[FeCl_4]^-$, according to well-established data.[32] All of the other systems presented similar Mössbauer spectra; these details will be discussed in a future article.

CONCLUSIONS

The results obtained in this work demonstrate the production of ion-exchange resins in the form of a 2-VPy–DVB copolymer and AN–MMA–DVB terpolymer with good stability and significant Fe^{2+} and Fe^{3+} ion-adsorption properties. The iron ion adsorption increased with the enhancement of HCl and metal concentrations. The Fe^{2+} and Fe^{3+} ion adsorptions from aqueous solutions were higher on the terpolymer than on the copolymer at low metal concentrations, whereas the contrary effect was observed at high con-

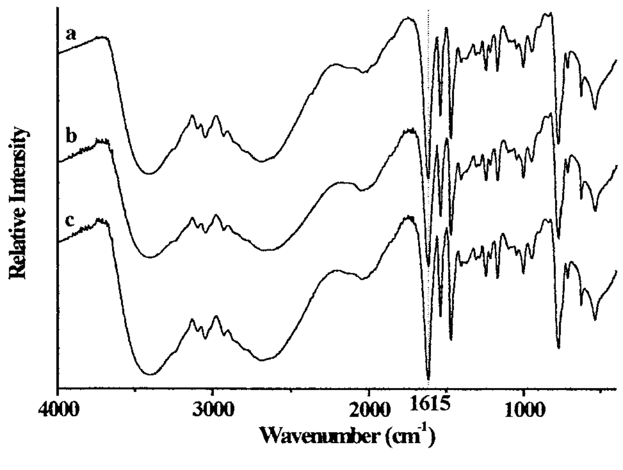

Figure 8 FTIR spectra of the 2-VPy–DVB copolymer: (a) protonated, (b) with Fe^{2+} ions adsorbed, and (c) with Fe^{3+} ions adsorbed.

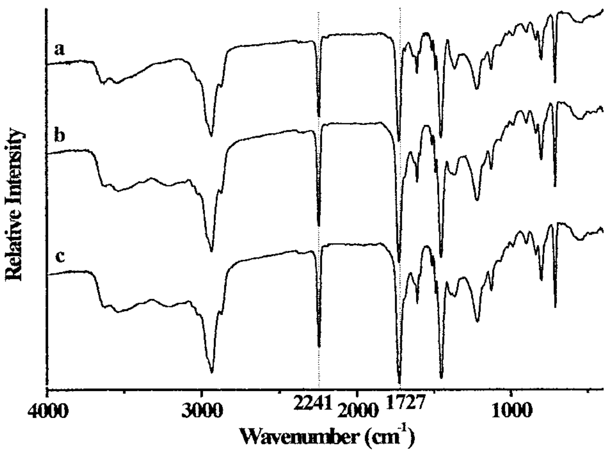

Figure 9 FTIR spectra of the AN–MMA–DVB terpolymer: (a) pure, (b) with Fe^{2+} ions adsorbed, and (c) with Fe^{3+} ions adsorbed.

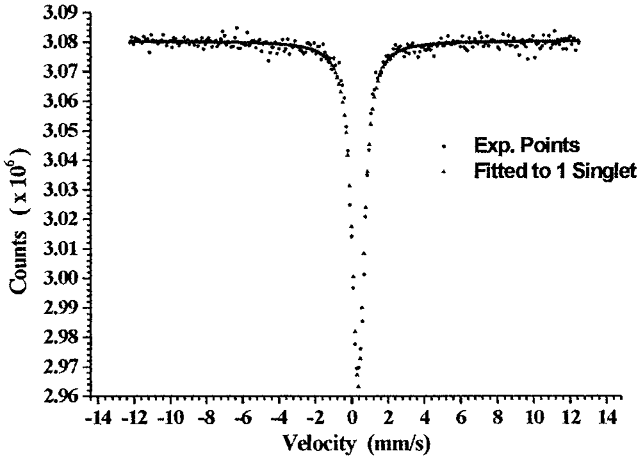

Figure 10 Mössbauer spectrum at 77 K of 2-VPy–DVB copolymer with Fe^{3+} ions adsorbed.

centrations. The enhancement of temperature produced a small increase in iron adsorption on both resins. The polarity reduction of the medium by the addition of a small amount of ethanol was fundamental for iron adsorption on the hydrophobic macroporous structure of AN–MMA–DVB terpolymer. The Fe^{2+} and Fe^{3+} ion adsorption on both resins in the presence of high HCl concentration occurred probably by electrostatic interaction between protonated functional groups and $[FeCl_4]^{2-}$ and $[FeCl_4]^{-}$ anions, respectively.

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