Vol. **116** (2009) *ACTA PHYSICA POLONICA A* No. 3

Optical and Acoustical Methods in Science and Technology

Application of the FT-IR/PAS Method in Comparison of Ga(III) and In(III) Sorption on Lewatit OC-1026 and Amberlite XAD-7 Impregnated D2EHPA

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The paper makes an attempt to create a polymer sorbent competitive for the commercial Lewatit OC-1026. Therefore the commercial Amberlite XAD-7 was impregnated with the D2EHPA acid. After preparation of both exchangers, their sorption properties towards In(III) and Ga(III) ions were studied [1]. It proved that for pH = 2.17 Amberlite XAD-7 impregnated with D2EHPA acid is characterized by larger sorption capacities than those of commercial Lewatit OC-1026 towards both Ga(III) and In(III) ions. Lewatit OC-1026 as well as the prepared impregnant (XAD-7 + D2EHPA) were examined by means of Raman spectroscopic, FT-IR photoacoustic spectroscopy and FT-IR methods.

PACS numbers: 82.80.Kq, 81.70.Cv, 82.50.−m

1. Introduction

The ion exchanger Lewatit OC-1026 is a polymer sorbent impregnated with D2EHPA. It is applied mainly for removal of Zn(II) and Al(III) ions from the neutral medium. Its commercial form should be suitably prepared before the use. Otherwise, it becomes strongly hydrophobic which makes its application for the column technique impossible. Table I presents the characteristics of the above mentioned ion exchanger. Figure 1 shows the structure of the D2EHPA group which is used for impregnation of the styrene–divinylbenzene skeleton of Lewatit OC-1026. Amberlite XAD-7 (Fig. 1b) is the acrylic ester (dipole moment 1.8) and is the only "moderately polar" XAD resin now available. It has been used to remove relatively polar compounds from non-aqueous solvents, and to remove non-aromatic compounds from polar solvents. Also it has been used for removal of organic pollutants from aqueous wastes, ground water and vapor streams and to remove metal ions from water solvents [1].

2. Experimental

The FT-IR spectra were recorded by means of a Perkin-Elmer FT-IR type 1725X spectrometer. This is the single-beam spectrometer with Fourier transformation, standard range of wavelength: 5800–400 cm^{-1}, maximum resolution: 0.5 cm^{-1}.

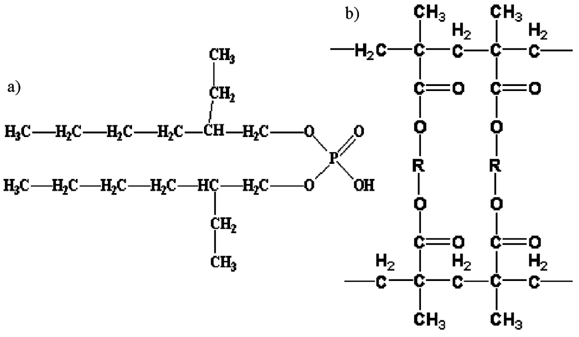

Fig. 1. Molecular structure of: (a) D2EHPA (di-(ethyhexyl) phosphorous acid), (b) the commercial Amberlite XAD-7.

The FT-IR/PAS spectra were recorded by means of a Bio-Rad Excalibur 3000MX spectrometer equipped with the photoacoustic detector MTEC300 (in the helium atmosphere in a detector) over the 4000–400 cm^{-1} range at the resolution of 4 cm^{-1} and a maximum source aperture. The spectra were normalized with reference to MTEC carbon black standard. A stainless steel cup (diameter 10 mm) was filled with powder samples (thickness < 6 mm). Interferograms of 512 scans were averaged for each spectrum.

The Raman spectra were recorded by means of a Renishaw Raman inVia Reflex microscope. This is the automatic, dispersive Raman system with module construction.

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TABLE I

Characteristics of Lewatit OC-1026.

skeleton	SDVB
structure	MACROPOROUS
physical form	transparent grain
form of anion exchanger	D2EHPA
total ion exchange capacity	–
maximum working temperature	90°C
application	electroplating, recovery of heavy metals from hydrometallurgical wastes, chemical industry

3. Results and discussion

Lewatit OC-1026 is a polymer sorbent impregnated with D2EHPA on which gallium(III) and indium(III) ions are evolved. The sorption depends on hydrochloric acid concentrations. For gallium(III) ions the separation coefficient increases insignificantly with the increase of hydrochloric acid 0.01–0.1 M (higher for the acid concentration 0.1 than for 0.01 M) and for indium(III) ions decreases with the increasing acid concentrations. The working capacity of the ion exchanger Lewatite OC-1026 compared with that of gallium(III) with the hydrochloric acid concentration 0.01 M cannot be calculated due to the course of breakthrough curve but for indium(III) ions with the hydrochloric acid concentration 0.01 M is 0.004 g/cm^3.

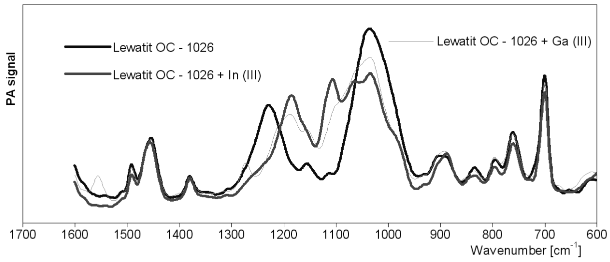

Fig. 2. The parts of FT-IR/PA spectra: Lewatit OC-1026, Lewatit OC-1026 + Ga(III), Lewatit OC-1026 + In(III).

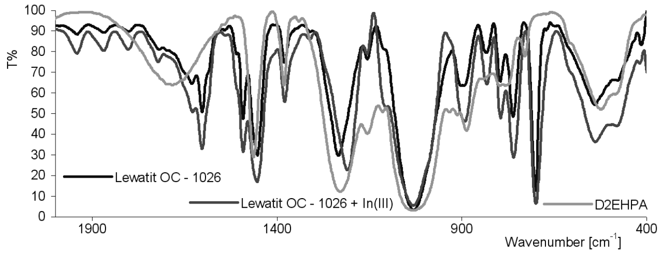

Fig. 3. The parts of FT-IR spectra: Lewatit OC-1026, Lewatit OC-1026 + In(III), D2EHPA acid.

TABLE II

Comparison of characteristic vibrations (cm^{-1}) in the spectra of Lewatit OC-1026 of the polymer sorbent impregnated with D2EHPA (FT-IR/PAS).

Lewatit OC-1026	Lewatit OC-1026–Ga(III)	Lewatit OC-1026–In(III)	Assigned vibrations
2962	2962	2962	C–H stretching of the –CH$_3$ group
2887	2887	2887	C–H stretching of the aliphatic chain
1610	1608	1605	P–O–H stretching
1460	1460	1462	P–CH$_2$ and C–H bending
1384	1384	1384	C–H deformation of the –CH$_3$ group
1234	1195	1190	P=O stretching (–O–P=O)
1043	1047	1139	P–O–C stretching
912	906	896	P–O–C stretching

As follows from the analysis of photoacoustic spectra (FT-IR/PAS) characteristic vibrations in the spectrum of Lewatit OC-1026 originate from D2EHPA in which this sorbent is impregnated. These vibrations are: P=O, P–O–C and P–O–H which are observed in the spectrum at the wavelengths: 1234 cm^{-1}, 1043 cm^{-1} and 1610 cm^{-1} (Fig. 2). Sorption of both Ga(III) and In(III) ions on Lewatite OC-1026 causes significant changes in vibrations of the phosphate group of di-(ethyhexyl) phosphorous (D2EHPA) acid as can be seen in Fig. 1a. Table II describes the spectrum of pure Lewatite OC-1026 as well as that of Lewatite OC-1026 sorbent with Ga(III) and In (III) ions.

As follows from significant changes in the vibrations of the phosphorous group contained in D2EHPA, sorption of Ga(III) and In(III) ions on the polymer sorbent impregnated with di-(ethyhexyl) phosphoric acid is largely of ion exchange character [2, 3]. However, it is not possible to determine accurately the sorption mechanism and the form of complexes created by the phosphate group D2EHPA with the studied ions (Fig. 3).

4. Conclusions

No significant changes were observed for the photoacoustic spectra of Amberlite XAD-7 and Amberlite XAD-7 + D2EHPA and Amberlite XAD-7 + D2EHPA + In(III) (Fig. 4). This may be due to the fact that the peaks originating from the vibrations of the skeleton XAD-7 (polyester skeleton) overlap with those originating from D2EHPA which strengthens the signal for wave numbers with which the peaks originating from D2EHPA appear.

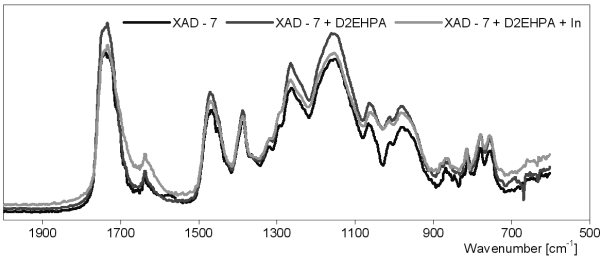

Fig. 4. The parts of FT-IR/PA spectra: Amberlite XAD-7, Amberlite XAD + D2EHPA, Amberlite XAD-7 + D2EHPA + In(III).

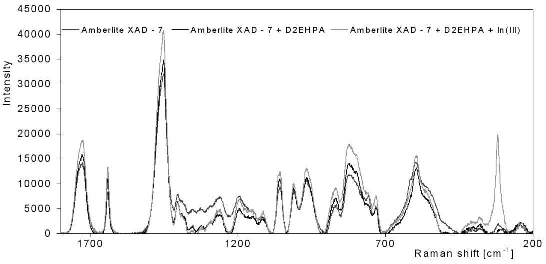

Fig. 5. The parts of Raman spectra: Amberlite XAD-7, Amberlite XAD + D2EHPA, Amberlite XAD-7 + D2EHPA + In(III).

Laser of too large energy (wavelength — 785 nm) was used in Raman spectroscopy (Fig. 5) which resulted in partial destruction of sample structure. After sorption of the impregnated (XAD-7 + D2EHPA) with In(III) ions on the Raman spectrum there was observed a new peak originating from the vibrations of very scarce indium oxide (317 cm^{-1}) which is probably formed due to sample exposure using high energy laser [4–6].

It was proved that for pH = 2.17 Amberlite XAD-7 impregnated with D2EHPA acid is characterized by larger sorption capacities than those of commercial Lewatit OC-1026 towards both Ga(III) and In(III) ions.

The FT-IR spectra made for Lewatit OC-1026 show similar peaks originating from the vibrations similar to those made by FT-IR/PAS which indicates that photoacoustic spectroscopy is as good as the FT-IR method.

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