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IR SPECTRA OF DUOLITE C 467, AMBERLITE IRP 64 TYPE SORBENTS TREATED WITH Cu^{2+} AND Pb^{2+} IONS

Abstract

In this study, based on infrared (IR) spectral data, the sorption mechanism of ions with macroporous amino-phosphonic functional ($-\text{CH}_2-\text{NH}-\text{CH}_2-\text{PO}(\text{ONa})_2$) group Duolite C 467 and carboxyl functional group Amberlite IRP 64 ($-\text{COOH}$) ionites was studied. The structure of sorbents, the changes in their functional groups after their interaction with ions have been discussed. During the interaction of Cu^{2+} and Pb^{2+} ions with Duolite C 467 and Amberlite IRP 64, the frequencies of their functional groups shift occurs.

Keywords: IR – spectroscopy method, ion exchangers, the absorption bands, sorption, functional groups, molecular fragments, communication exchanger Cu^{2+} və Pb^{2+}

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Cu^{2+} və Pb^{2+} ionları ilə işlənmiş duolite C 467, amberlite İRP64 tipli sorbentlərinin İQ-spektrləri

Xülasə

Bu araşdırmada infraqırmızı (İQ) spektral məlumatlara əsaslanaraq ionların makroməsəməli amino-fosfonik funksional ($-\text{CH}_2-\text{NH}-\text{CH}_2-\text{PO}(\text{ONa})_2$) qruplu Duolite C 467 və karboksil funksional qruplu Amberlite İRP 64 ($-\text{COOH}$) ionitləri ilə sorbsiya mexanizm öyrənilmişdir. Sorbentlərin strukturları, onların ionlarla qarşılıqlı təsirindən sonra funksional qruplarında yaranan dəyişikliklər haqqında fikir yürüdülmüşdür. Cu^{2+} və Pb^{2+} ionlarının Duolite C 467 və Amberlite İRP 64 ilə qarşılıqlı təsiri zamanı onların funksional qruplarının tezliklərinin sürüşməsi baş verir.

Açar sözlər: İQS metodu, ionitlər, udulma zolaqları, funksional qruplar, sorbsiya, molekulun fraqmentləri, Cu^{2+} və Pb^{2+} - ionit rəbitəsi

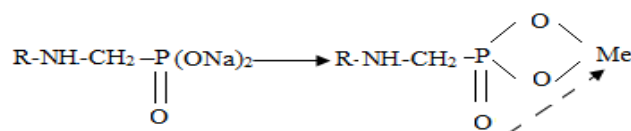
Introduction

The main task of spectroscopic methods is to provide information about the structure of organic materials. This information is based on affinity with characteristic absorption bands describing the selected functional group of organic compounds. In physical and analytical chemistry, infrared

spectroscopy (IR-spectroscopy) is a method used to identify chemical compounds based on the way infrared radiation is absorbed by the compound (Kharitonov, 2005: 615).

Experimental part. In the same way as all ionites, 1.00 grams of samples were crushed in an agate mortar and made into powder, the samples were pressed with KBr and made into pills, and the spectra of the samples were recorded in the range of 4000-400 cm^{-1} in the "Nicolet IS-10" IR-spectrometer. Amberlite IRP64 (-COOH) ionites with phosphonic functional group (- $\text{CH}_2\text{-NH-CH}_2\text{-PO (ONa)}_2$) group Duolite C 467 with carboxyl functional group were involved in research (Jafarli, Abbasov, 2017: 449-462; Jafarli, 2022: 26-28; Pehlivan, Altun, 2006: 149-156; Wolowicz, Hubicki, 2010: 124-159; 6). Their initial and after interaction with Cu^{2+} and Pb^{2+} metal ion IR spectra were taken., the structures of ionites were judged based on the resulting absorption bands.

Since the studied ionites contain phospho- and carboxyl groups, let's take a look at the general spectroscopic properties of the ionites included in these groups. According to the catalog data, the brief characteristics of ionites are as follows (Chromatography, 2003-2004). Duolite C467 has an ion-exchange phosphonic (- PO_3H_2) functional group. This group is acidic in nature and dissociates from solution by exchanging H^+ or Na^+ ions for other cations. The negative charge of the functional groups is replaced by an equivalent number of mobile cations called counterions. Ionic ions can be exchanged with other ions due to the fact that the solution is in contact with the ionic phase.



According to the catalog information, the mass of 1 liter of ionite is 740 g. Regeneration is carried out with 1-2 N hydrochloric acid. 1-2 N NaOH solution is used to convert to Na-form. Since the H-Na transition is reversible, 11% reversibility was noted. The optimal acidity mode of ionite is pH=1-10, the total capacity is 3.5 g Eq/g. The size of the ionite grains is 16-50 mesh, the maximum temperature limit is 650C.

Duolite C467: these are the main absorption bands of this ionite with an amino-phosphonic functional group: the bands at 702.66 cm^{-1} and 760.73 cm^{-1} in the spectrum represent the out-of-plane deformation oscillations of C-H fragments of two substituted benzene rings; 982.66 cm^{-1} characterize asymmetric and symmetric vibrations of P-OH groups, deformation vibrations of OH-groups. The band observed at 1060.42 cm^{-1} represents the vibrations of R- $\text{PO}_2\text{(OH)}$ groups, 1118.71 cm^{-1} - the valence vibrations of P=O groups in the phosphate acid residue connected with hydrogen bond, 1452.18 cm^{-1} - vibrations of C=C bond of benzene ring and deformation vibrations of C-H fragments of - CH_2 groups, 1657.12 cm^{-1} characterize the deformation oscillations of the OH group of the water molecule. According to the literature, the shift frequency of the phosphoryl group is in the region of 950-1200 cm^{-1} (Silverstein, Bassler, Morrill, 1977: 593; Nakomoto, 1991: 536). The spectra of the Na-form ion exchanger are observed in the characteristic absorption bands of the R- PO_3^{2-} ion. In the spectrum of the ion exchanger in the form of Na, the characteristic absorption bands of its ion are observed. The spectrum of an ion exchanger with used metal ions differs from the spectrum of the first ion exchanger by the appearance of absorption bands at 1087.67 and 1041.29 cm^{-1} , which characterize the symmetric and asymmetric waves of R- PO_3^{2-} . The absorption band at 1118.71 cm^{-1} disappears, forming copper and lead forms, new absorption bands appear in ionite samples at 1002.58 and 971.50 cm^{-1} . These changes in the spectrum indicate the formation of strong coordination bonds between copper and lead ions and ionic groups of the sorbent (Fig. 1).

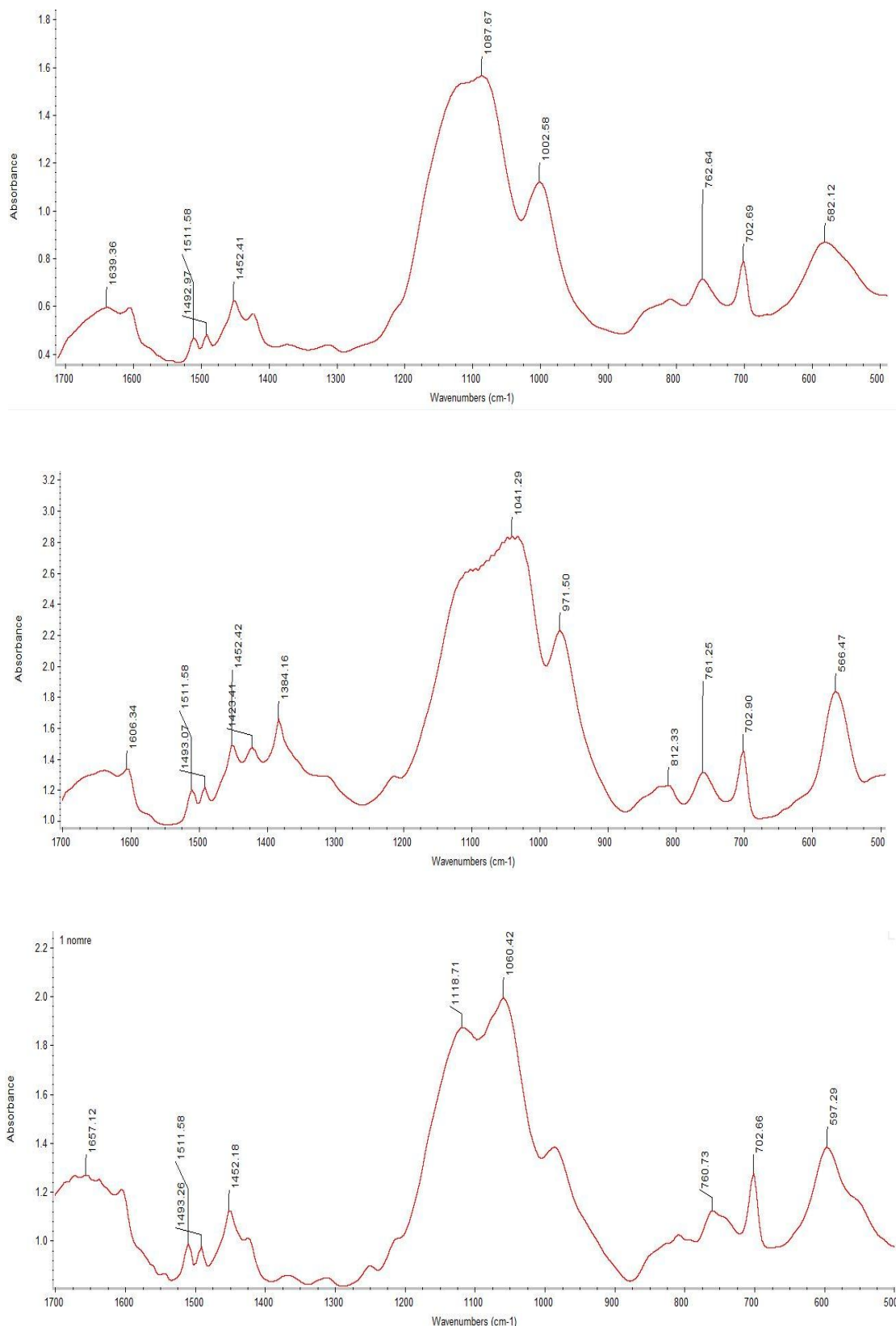


Fig.1. IR spectra of Duolite C467 (1) and post-sorption copper (2) and lead (3) ions.

Amberlite IRP64 (Polacrillex Resin) is a cationite with a carboxyl functional group, a weak acid character, H^+ form, and a macroreticular structural cation with a dry exchange capacity of 10 mg-eq/g. Amberlite IRP64 is obtained from a porous copolymer of methacrylic acid and divinylbenzene. The chemical structure of Amberlite IRP64 is shown in figure 2.

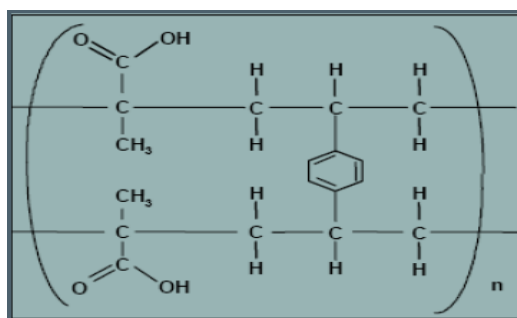


Fig.2. Chemical structure of Amberlite IRP64.

The exchangeable cation in Amberlite IRP64 ionite is the hydrogen ion. In acidic environments (generally up to pH 4), Amberlite IRP64 ionite exists mainly as the free acid in the non-ionized state (Pharmaceutical Grade Cation Exchange Resin).

Absorption bands at $1720\text{-}1660\text{ cm}^{-1}$ belonging to C=O bonds of carboxyl groups are characteristic in IR-spectra of carboxyl cations. When ionites are in acid form, a very strong absorption band is observed at $1280\text{-}1250\text{ cm}^{-1}$ related to valence vibrations of C–O bonds. These vibrations also belong to the in-plane and out-of-plane valence vibrations of the OH-groups noted at $980\text{-}950\text{ cm}^{-1}$. A rather broad band observed at $2700\text{-}2500\text{ cm}^{-1}$ indicates the presence of hydrogen bonds of different strength through OH dimers. In carboxyl-type ionites synthesized using aliphatic monomers, peaks characterizing the aromatic building ring are observed at $795\text{-}790$ and $710\text{-}700\text{ cm}^{-1}$.

Amberlite IRP-64: 517.50 in the spectrum taken in the range of $4000\text{-}500\text{ cm}^{-1}$; 829.23 ; 963.31 ; 1173.36 ; 1266.57 ; 1390.31 ; 1451.07 ; 1483.62 ; 1702.36 ; Clearly defined peaks at 2997.63 and 3476.32 cm^{-1} are observed. Amberlite IRP-64 has carboxyl groups, so the identification of these groups in the spectra will be preferred. The characteristic feature of carboxyl cationites in H^+ form is strong, well-defined bands at $1720\text{-}1660\text{ cm}^{-1}$ corresponding to C=O absorption region of carboxyl groups. It characterizes the valence oscillations (1702.36 cm^{-1}) of the C=O bond in the carboxyl group (-COOH). It is interesting that the maximum of this band is observed at 1702.36 cm^{-1} in Amberlite IRP64. The absorption bands observed in the regions of 3476.32 cm^{-1} and 2997.63 cm^{-1} in Amberlite IRP64 ionite characterize the valence vibrations of OH^- groups of water molecules and carboxyl groups. Amberlite IRP-64 has carboxyl groups, so the identification of these groups in the spectra will be preferred. The characteristic feature of carboxyl cationites in H^+ form is strong, well-defined bands at $1720\text{-}1660\text{ cm}^{-1}$ corresponding to C=O absorption region of carboxyl groups. It characterizes the valence oscillations (1702.36 cm^{-1}) of the C=O bond in the carboxyl group (-COOH). It is interesting that the maximum of this band is observed at 1702.36 cm^{-1} in Amberlite IRP64. The absorption bands observed in the regions of 3476.32 cm^{-1} and 2997.63 cm^{-1} in Amberlite IRP64 ionite characterize the valence vibrations of OH^- groups of water molecules and carboxyl groups. 517.50 ; The absorption bands of 829.23 and 963.31 cm^{-1} represent the vibrational oscillations of methylene- CH_2 groups, 1173.36 and 1266.57 cm^{-1} the fan-shaped deformation oscillations of those groups, 1390.31 ; 1451.07 and 1483.62 cm^{-1} represent deformation oscillations of C-H bonds of methyl and methylene groups. When carboxyl cations are transferred from the acid form to the salt form, absorption bands in the region of $1720\text{-}1660\text{ cm}^{-1}$ belonging to carbonyl groups are lost due to the ionization of COOH groups, and new absorption bands in the region of $1570\text{-}1550$ and 1400 cm^{-1} appear due to ionized -COO^- groups (Bellamy, 1971: 318; Prech, Bulmann, Affolter, 2006: 438).

The clearly observed absorption band in the region of 1702.36 cm^{-1} disappears completely after sorption by Pb^{2+} -ion, and partially splits into a large number of absorption bands with weak intensity. In the Amberlite IRP-64- Pb^{2+} system, a shift of the band to 1172.96 cm^{-1} and a partial weakening of the intensity are observed. 1390.31 belonging to unprocessed Amberlite IRP 64 ionite; 1451.07 ; Absorption bands at 1483.62 and 1702.36 cm^{-1} are either completely lost or

significantly shifted after treatment with the mentioned ions. In the IR-spectrum of ionite taken after sorption by Pb^{2+} ion, extremely weak, barely perceptible absorption bands are observed at 1390.68 and 1478.43 cm^{-1} . Since the coordination bond between this ionite and metal ions can be realized only due to the free electrons of oxygen, special attention was paid to these areas. Comparison of spectra and location of carboxyl groups in the $400-600$ cm^{-1} interval. The clearly observed absorption bands in the region of 2997.63 cm^{-1} and very broad absorption bands at 3476.32 cm^{-1} are significantly changed after sorption by Pb^{2+} ion and split into absorption bands of weak intensity. This confirms that the sorption processes are accompanied by significant complexation along with ion exchange.

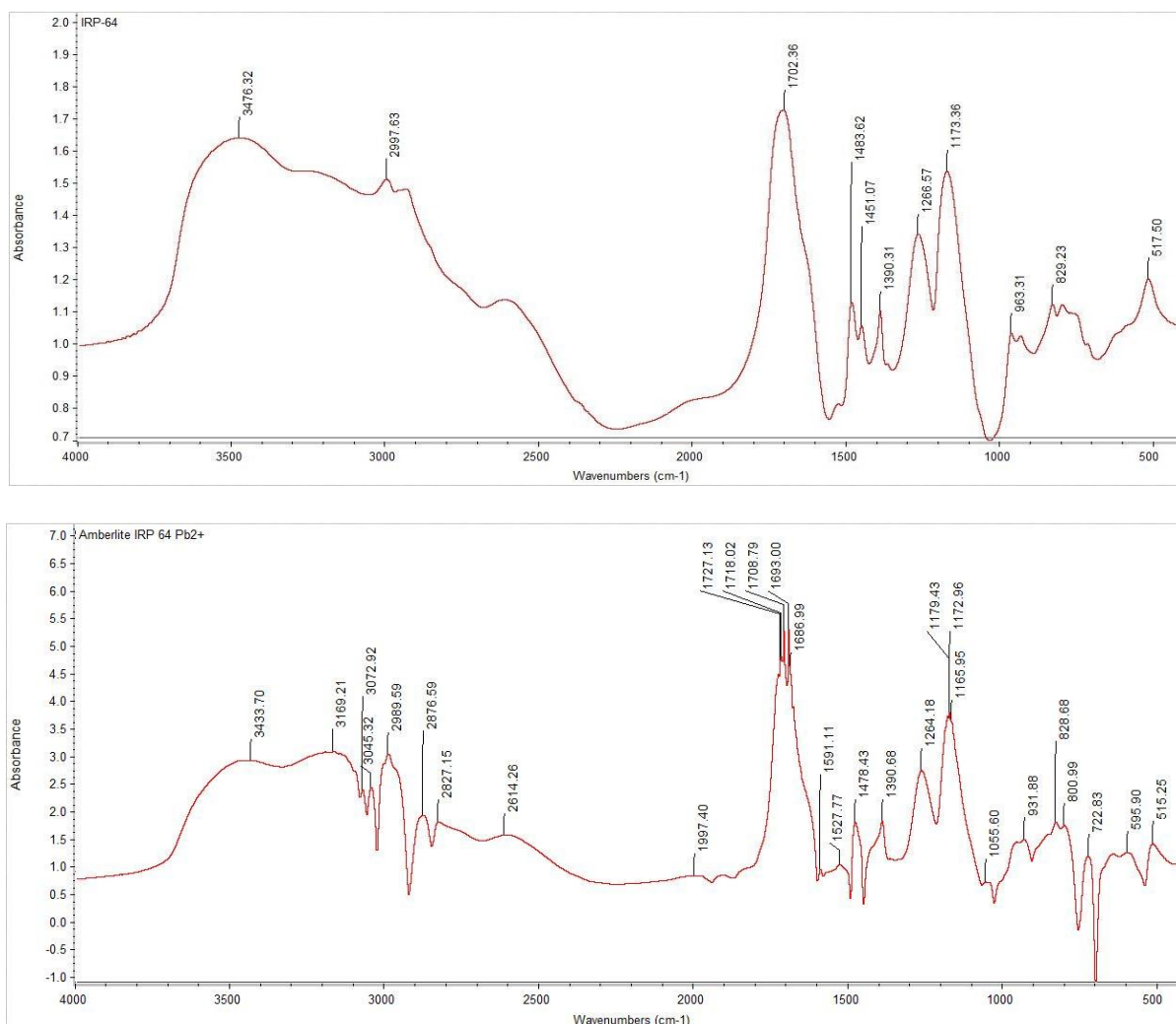


Fig.4. IR spectra of Amberlite IRP-64 Pb^{2+} (1) and lead (2) ions after sorption.

Conclusion

IR spectra of ionite samples were taken, and in the spectra of cationites treated with Pb^{2+} ions, an increase in the intensity of absorption bands in the region of $500-850$ cm^{-1} is observed. The sorption regions at 1060.42 cm^{-1} of phosphoryl groups in the IR spectrum of Duolite C467 ionite treated with Cu^{2+} and Pb^{2+} ions shifted to 1087.67 (Cu^{2+} -form) and 1041.29 cm^{-1} (Pb^{2+} -form). These changes in the spectrum confirm the sorption of ionogenic groups and the formation of bonds between copper and lead ions. Duolite C467 was shown to be a more kinetically effective sorbent. It was shown that the studied sorbent absorbs Pb (II) ion more than other ions. In IRP-64 cationites with carboxyl groups, the shifts and intensity changes of bands related to carboxyl groups result from the nature of the bond between those groups and Pb^{2+} ions. Since the absorption spectra of metal ions in the IR region are mainly observed at $200-400$ cm^{-1} , it is not possible to mention the

lower region (Nakomoto, 1991: 536). However, the clear differences observed in the IR-spectra allow to interpret the nature of sorption not on the basis of hypothetical ideas, but on the instrumental level.

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