

CHELATING ION EXCHANGERS IN HEAVY METAL IONS REMOVAL FROM ACIDIC STREAMS

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Abstract

The aim of the presented study was to investigate the physicochemical properties of chelating ion exchangers Dowex M 4195 and Lewatit[®] MonoPlus TP 220 with bis(2-pyridylmethyl)amine functional groups before and after Co(II) and Fe(III) sorption. For the practical use their sorption capacities were determined by static method depending on the contact time and the initial concentration. The kinetic parameters were determined in order to optimize the sorption of Co(II) and Fe(III) ions including the influence of chloride ions.

The content of Co(II) and Fe(III) ions was determined by the atomic absorption spectrometry method. Optical microscopy and scanning electron microscopy were used in order to determine physicochemical properties of Dowex M 4195 and Lewatit[®] MonoPlus TP 220. The results of X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy with attenuated total reflection analyses were also presented, especially the linear maps of the elemental composition of the cut ion exchangers beads after Co(II) and Fe(III) sorption. These studies show the distribution of cobalt and iron in the whole volume of the ion exchanger beads after the sorption process.

The studies reveal that Dowex M 4195 has a far less developed surface area as compared to Lewatit[®] MonoPlus TP 220. Microscopic examination also showed that the percentage content of the sorbed Co(II) and Fe(III) ions has not changed in the entire volume of the beads.

Studied ion exchangers can be used in the removal of metal ions from the acidic industrial streams.

Keywords: heavy metals, Dowex M 4195, Lewatit[®] MonoPlus TP 220, capacity, optical studies

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1. Introduction

Metals of the density larger than $4.5 \times 10^3 \text{ g/dm}^3$ are classified as those belonging to the heavy metal groups [1]. In chemical reactions they tend to donate electrons forming simple cations. As well as in solid and liquid states they show good thermal and electrical conductivity, have gloss and are opaque. They have high melting and boiling points. They are characterized by reducing properties. The heavy metal group includes: Cu, Co, Cr, Cd, Fe, Zn, Pb, Sn, Hg, Mn, Ni, Mo, V and W as well as non-metal Se. Among the heavy metals there are elements essential for living organisms - microelements (copper, zinc, nickel, chromium) as well as those of unknown physiological role (cadmium, mercury, lead, arsenic and others). These elements are considered toxic. Metals which act as microelements in living organisms appear usually in trace amounts, strictly characterised for particular species. Their deficiency or excess may have harmful effects on living organisms [2]. In contrast, metals regarded as toxic are common pollutants of the ecosystem. The strongest toxic properties are exhibited by inorganic metal compounds, which easily dissolve and decompose, due to easy pass through cell membranes and entering internal organs.

Toxic effects of heavy metals on humans and animals are numerous [3]. These metals are readily accumulated in specific organs and their carcinogenic impact occurs when the level of metal in the body reaches or exceeds the threshold dose. The most attacked organs are often those which are associated with detoxification and elimination of a particular metal. Therefore, heavy metals mostly affect the liver and kidneys [4]. Furthermore, their frequent accumulation can be found in the brain, bones and muscles. Heavy metals can cause immediate acute poisoning or chronic conditions. Acute poisoning is caused by such metals as As, Zn, Cd, Cu and Hg. Whereas chronic poisoning can be due, among others, to As, Zn, Cd, Cr, Cu, Hg, Pb, Sn, Co, Ni, Mn, Se, Fe, and Ag.

Circulation of heavy metals in the natural environment is mainly associated with such processes as rocks weathering, volcanic eruptions, evaporation of the oceans, and soil-forming processes. However, the development of technology and many industries resulted in the increased exposure of the environment to the toxic effects of these metals. The main sources of pollution are the following industries: chemical, metallurgical, electrotechnical, mining and energy. The heavy metal used in almost each industry branch is iron. It is included in the steel used, inter alia, in shipbuilding, automotive, armament and construction industry. Another very important element for many industries is cobalt. Thanks to its unique properties and applications, it has the status of a strategic metal. In many countries the main and traditional area of its use is the production of super alloys used in medicine, aviation and energy industry. Significant and in some countries dominant share in the consumption structure of cobalt has gained the rapidly growing sector of

batteries (e.g. Li-CoO₂ type), commonly used in the electronic industry, particularly in wireless devices for different purposes [5].

Due to such widespread use of iron and cobalt, effective methods of industrial wastewater treatment containing these elements are being searched. The recovery of these metals from industrial wastewaters is also important from an economic and environmental perspective.

Development of manufacturing technology of ion exchangers was due to the need of water purification for many years. As a result of the development of various industry branches, ion exchangers began to be used for the treatment of industrial wastewater, from which there both toxic components and valuable precious metals are recovered [6, 7]. Chelating ion exchangers are used for the treatment of industrial wastewaters. They constitute a separate group of ion exchangers. The selective sorption of transition metals constitutes a special feature of this type of ion exchangers [8]. Sorptive abilities of this type of ion exchangers depend on the type of functional groups to a large extent [9]. Among the commercially available chelating ion exchangers, there can be distinguished the following functional groups: bispicolylamine, for example Dowex M 4195 and Lewatit[®] MonoPlus TP 220, amidooxime, for example Duolite ES 346 and Chelit N, aminophosphonic, for example Duolite C 467, Purolite S 94, Purolite S 950 or Chelit P as well as iminodiacetate, for example Lewatit TP 207, Lewatit TP 208, Purolite S-930. The ability of selective sorption of one ion of metal in the presence of others is a distinctive feature of chelating ion exchangers, since this is not generally possible to achieve in the case of conventional ion exchangers, where the affinity for the ion in the solution is solely determined by the electrostatic influence of the ion and the dissociated functional group. Therefore selective capacity of the sorption of chelating ion exchangers predisposes them to be used for the recovery of valuable metals from ores or sludges or to remove toxic metals from water and wastewater. These characteristics give them an advantage over traditional liquid-liquid or liquid-solid extraction methods, in which there is a need for using solutions of strong acids or solvents oppressive for the environments [10, 11].

In the group of chelating ion exchangers, there are those of the functional groups bis(2-pyridylmethyl)amine, also called bispicolylamine which show beneficial properties. This type of ion exchangers is represented by Dowex M 4195 and Lewatit[®] MonoPlus TP 220 [12]. The matrix of these ion exchangers is a styrene-divinylbenzene copolymer. According to the literature data, ions exchangers of bispicolylamine groups are capable of selective removal of Cu(II) ions [13]. Diniz and co-workers [14, 15] presented a series of affinity for metal ions selected from single-component solutions for the Dowex M 4195 ion exchanger. It is as follows: Cu (II)> Ni (II)> Co(II)> Pb (II)> Fe(III)> Mn (II). This series is slightly different from the affinity selected from a multi-component solution: Cu (II)> Ni (II)> Pb (II)> Fe(III)> Co(II)> Mn (II).

The aim of the presented paper was to compare the removal of Co(II) and Fe(III) ions using Dowex M 4195 and Lewatit[®] MonoPlus TP 220 from acidic streams. The research was carried out under different operation conditions. The parameters determined for the sorption process were correlated with the detailed microscopic characteristics of Dowex M 4195 and Lewatit[®] MonoPlus TP 220. The obtained results can be useful for development and optimalization of simple and economical methods to separate heavy metal ions from acidic streams in industrial and environmental operations.

2. Materials and Methods

2.1. Basic characteristics of used ion exchangers

Two chelating ion exchangers with the bis(2-pyridylmethyl)amine (also called) bispicolylamine functional groups were used in the investigations. The selected physicochemical parameters of Dowex M 4195 and Lewatit[®] MonoPlus TP 220 are presented in Table 1.

2.2. Adsorption capacity and kinetic analysis

One component solutions containing Co(II) and Fe(III) ions at pH=2.5 were prepared mixing suitable amounts of the salts CoCl₂·6H₂O and FeCl₃. 250 mL conical flasks were used for the studies on the sorption of Co(II) and Fe(III) on Dowex M 4195 and Lewatit[®] MonoPlus TP 220. The flasks were filled with 0.5 g of the ion exchanger and 100 cm³ of a suitable solution. They were placed in a mechanical shaker with a water bath (Elpin 357, Elpin-Plus, Poland). During shaking after 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 60, 120 minutes appropriate fractions were collected. Then the measurements of Co(II) and Fe(III) ions sorption on the studied ion exchangers depending on the phase contact time were made. The content of the above mentioned ions in the samples was determined by the atomic absorption spectrometry method (AAS) using spectrometer SpectrAA240 FS (Varian, Australia). The sorption processes of Co(II) and Fe(III) ions on the Dowex M 4195 and Lewatit[®] MonoPlus TP 220 were performed by the static method from the 0.001M CoCl₂·6H₂O and 0.001M FeCl₃ solutions. Sorption capacity q_t [mg/g] of appropriate ions on the selected ions was determined on from the formula (1):

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

where: c_0 is the initial concentration of Co(II) and Fe(III) ions, (mg/L); c_t is the concentration of Co(II) and Fe(III) ions at time t , (mg/L); V is the volume of the solution, (L); m is the mass of the chelating ion exchanger, (g).

The efficiency of Co(II) and Fe(III) ion removal expressed as the percentage of removed ions (R%) can be calculated from the equation (2):

$$\%R = \frac{c_0 - c_t}{c_0} \times 100\% \quad (2)$$

where: c_0 is the initial concentration of Co(II) and Fe(III) ions, (mg/L); c_t is the concentration of Co(II) and Fe(III) ions at time t , (mg/L);

2.3. Analysis of sorption process

X-ray photoelectron spectroscopy (XPS)

There are many research techniques used to obtain information on the physicochemical properties of ion exchangers and sorbents after sorption process. The most preferred technique is photoelectron spectroscopy. This method measures distribution of the energy of electrons emitted from the sample which has absorbed ultraviolet photons (ultraviolet photoelectron spectroscopy, UPS) or X-rays radiation (X-ray photoelectron spectroscopy, XPS) [19].

In order to investigate the chemical structure of the Dowex M 4195 and Lewatit[®] MonoPlus TP 220, the studies were carried out by means of Ultra High Vacuum multi-chamber analytical system (Prevac, Poland). After being fixed on a molybdenum carrier, the samples were degassed at room temperature to the high constant vacuum of about $\sim 5 \times 10^{-8}$ mbar, in the UHV system sluice. After their introduction into the analytical chamber of the system, the appropriate analysis was performed by means of XPS spectroscopy method. AlK_{α} monochromatic radiation was used as a source of photoelectrons. Photoelectrons were stimulated by X-ray of a characteristic line AlK_{α} of 1486.7 eV energy, generated by a VG Scienta SAX 100 lamp with an aluminum anode with a VG Scienta XM 780 monochromator. The pressure in the chamber during measurements was 2×10^{-8} mbar. The X-ray tube operating parameters were as follows: $U = 12$ kV, $I_e = 30$ mA. Photoelectrons recorded by the hemispherical analyzer Scienta R4000. The measurements were made under the following basic parameters: operating mode - sweeping, pass energy - 200 eV, measured range of the binding energy of photoelectrons 0-1200 eV, measuring step 0.5 eV, collection time in a single step 0.2 s and the number of iterations 5. The parameters of the analyzer for the high resolution spectra: operating mode - sweeping, pass energy 50 eV, measuring step 0.1 eV and collection time in a single step 0.667 s.

Fourier Transform Infrared Spectroscopy with attenuated total reflection (FTIR-ATR)

The main task of the spectroscopic methods is to provide information about the structure of the organic material. This knowledge is based on the familiarity with the characteristic absorption bands describing the selected functional group of the organic compounds. Position of the absorption bands in the FTIR (Fourier Transform Infrared Spectroscopy) is related to the change of particles energy resulting from stretching and deformation vibrations of interconnected atoms [20].

In order to investigate the structure of ion exchangers before and after the Co(II) and Fe(III) sorption the FTIR-ATR spectra of Dowex M 4195 and Lewatit[®] MonoPlus TP 220 using the Thermo Scientific FTIR Nicolet 8700 spectrometer were recorded. They were performed by means of an ATR method with a diamond crystal in the range of wave numbers 4000-400 cm^{-1} and the spectral resolution of 4 cm^{-1} . The spectra were recorded directly from the surface of the samples at room temperature.

Microscopy analysis

In order to examine the surface of the Dowex M 4195 and Lewatit[®] MonoPlus TP 220 microscopic images were taken by means of the Fei Phenom scanning electron microscope. Moreover, in order to investigate the internal structure of the above mentioned ion exchangers, the beads were cut by means of ultramicrotome. The cut beads of the ion exchangers were examined using the Nikon optical SMZ 1500 stereoscopic microscope. In order to examine the distribution of elements and the sorbed metals, the linear profiles of elemental compositions for the cut beads after Co(II) and Fe(III) sorption were prepared. In this stage of studies the scanning electron microscope Quanta 3D FEG with EDS/EBSD system was used.

3. Results

3.1. X-ray photoelectron spectroscopy analysis

The results of the studies of the surface of Dowex M 4195 and Lewatit[®] MonoPlus TP 220 ion exchangers carried out by the XPS method before the Co(II) and Fe(III) sorption are shown in Table 2.

The analysis of the spectra shows that the surface of the examined ion exchangers is composed of carbon, oxygen, nitrogen and sulphur (the analysis did not include the hydrogen content). The study shows that the elemental composition of Dowex M 4195 from the surface of ion exchangers is slightly different from that determined theoretically. Out of the total number of carbon atoms approximately 79%, 66% constitute the C-C and C-H bonds from both the ion matrix and the functional groups. In the case of the Lewatit[®]

MonoPlus TP 220 the elemental composition determined by the XPS method from the surface of the ion exchange resins is slightly different from the one specified in theory. Of the total number of carbon atoms approximately 70.5%, 56% are in the C-C and C-H bonds from both the resin matrix and the functional groups. In Figs.1 and 2 spectra of Dowex M 4195 and MonoPlus Lewatit® TP 220 ions made by XPS are presented.

In order to measure the percentage content of the elements after Co(II) and Fe(III) sorption, XPS survey spectra of the studied chelating ion exchangers were recorded. The research shows that the ratio of iron atoms to the nitrogen atoms on the surface of the studied material is 1:6.7. It may reflect the fact that in the case of Dowex M 4195, every second functional group participated in the process of Fe(III) sorption. In the case of Co(II) sorption, the presence of this element on the surface of Dowex M 4195 was not recorded by XPS. This may indicate very low Co(II) sorption on the studied resins. The high resolution XPS analysis showed that Fe(III) constitutes 100% of the iron present on the resin surface.

Comparison of the results of the Dowex M 4195 resin surface test carried out by the XPS method after Co(II) and Fe(III) sorption are shown in Table 3. The XPS spectrum for the Dowex M 4195 ion exchanger resin after Co(II) and Fe(III) sorption is shown in Fig.3.

XPS spectra were made for the Lewatit® MonoPlus TP 220 after Co(II) and Fe(III) sorption. The research shows that the ratio of iron atoms to the nitrogen atoms on the surface of the studied material is 1:18.7. It may reflect the fact that in the case of the Lewatit® MonoPlus TP 220 ion exchanger, every sixth functional group participated in the Fe(III) sorption process. In the case of Co(II) sorption, the ratio of cobalt atoms to nitrogen atoms on the surface of the studied material is 1:14.2. It may reflect the fact that in the case of the Lewatit® MonoPlus TP 220, every fifth functional group participates in the Co(II) sorption process. The XPS spectrum of the Lewatit® MonoPlus TP 220 surface after Co(II) and Fe(III) sorption is shown in Fig.4. The analysis of high resolution XPS shows that Fe(III) constitutes 100% of the iron present on the resin surface. However, in the case of Co(II) sorption, cobalt constitutes 100% of cobalt present on the resin surface. The results for the Lewatit® MonoPlus TP 220 obtained by the XPS method after Co(II) and Fe(III) sorption are shown in Table 4.

3.2. FTIR-ATR spectroscopy

The FTIR-ATR spectra of the Dowex M 4195 and Lewatit® MonoPlus TP 220 before and after Co(II) and Fe(III) sorption are shown in Figs.5 and 6. In the recorded spectra, characteristic bands, connected with the polystyrene-divinylbenzene matrix as well as the bis(2-pyridylmethyl)amine functional groups can be distinguished. The FTIR-ATR spectra after Co(II) and Fe(III) sorption had a high intensity band at approximately 3400 cm^{-1} . This band corresponds to the stretching vibration of the hydroxyl group $\nu(\text{O-H})$, originating from the matrix. Aromatic CH stretching vibrations derived from bis(2-pyridylmethyl)amine unit of the functional group [21, 22] appear at a wavelength $3090\text{-}3000\text{ cm}^{-1}$. The recorded FTIR-ATR spectra show characteristic for the functional group, ring stretching vibrations C=C and C=N at a wavelength of $1600\text{-}1430\text{ cm}^{-1}$ [20,23]. As a result of Co(II) and Fe(III) sorption an increase in the intensity of the band at the wavelength $3090\text{-}3000\text{ cm}^{-1}$ and the band at the wave length $1600\text{-}1430\text{ cm}^{-1}$ can be observed.

3.3. Microscopy Analysis

In order to study the internal structure of Dowex M 4195 and Lewatit® MonoPlus TP 220, the beads were cut by means of ultramicrotome. The cut beads were examined under the microscope. Microscopic images were taken using the optical stereoscopic microscope Nikon SMZ 1500. The pictures of ion exchange resins were taken in the eightfold magnification. The images of the cut beads are shown in Figs.7a-d.

The study shows that Dowex M 4195 has a two-layer structure, while Lewatit® MonoPlus TP 220 has a homogeneous internal structure. There were also carried out studies of the surface of ion exchangers by means of Fei Phenom scanning electron microscope. The images were taken from the surface of the beads after spraying the samples with gold in 10 000 fold magnification. As follows from the literature [18], Lewatit® MonoPlus TP 220 has a much more developed specific surface area compared to that of Dowex M 4195. The studies using scanning electron microscopy confirmed the literature data on the specific surface area of the studied ion exchangers. The results are shown in Figs.8a-d.

In order to examine the distribution of the elements in the whole volume of the ion exchangers after Co(II) and Fe(III) sorption, there was made the linear profile of elemental composition for the radius of the cut beads of Dowex M 4195 and Lewatit® MonoPlus TP 220 ion exchangers (200 points from the center of the cut bead towards the edge of the ion exchanger). The lengths of the rays are shown in Figs.9a-d.

According to the obtained results Dowex M 4195 sorbs Co(II) and Fe(III) ions evenly throughout the volume. In the case of Dowex M 4195 after the Co(II) sorption a slight decrease in the carbon content by about $150\text{ }\mu\text{m}$ from the edge of the bead can be observed. In the same distance the increased percentage of oxygen, nitrogen and cobalt(II) can be also observed. This may be due to the two-layer structure of the studied beads of Dowex M 4195. In the case of Dowex M 4195 after the Fe(III) sorption, elemental

composition of carbon, oxygen, nitrogen, iron and sulfur remained unchanged throughout the resin volume. In the case of Lewatit® MonoPlus TP 220 a uniform distribution of cobalt(II) and iron(III) in the volume of the ion exchanger can be also observed. The elemental composition of carbon, oxygen, nitrogen, sulphur is not changed throughout the volume of the studied bead. The obtained results are shown in Fig10.

3.4. Adsorption capacity and kinetic analysis

For the practical use of ion exchangers in the process of wastewaters purification, determination of sorption capacities depending on the phase contact time and initial concentration is very important. The kinetic parameters were determined in order to optimize Co(II) and Fe(III) sorption with regard to the influence of chloride ions. The study was carried out for the 0.001M initial concentration of Co(II) and Fe(III). A similar study was also carried out with the addition of HCl. The kinetic studies confirm the analysis made by XPS as well as SEM with the EDX detector. Lower percentage of the removal (%R) was observed for Co(II) on Dowex M 4195. Higher percentage of removal was obtained for Fe(III). The obtained results are shown in Figs.11a-f.

4. Conclusions

The studies show that Dowex M 4195 has a much less developed surface area in comparison to the Lewatit® MonoPlus TP 220. The studied bead of Dowex M 4195 has a two-layer internal structure after the process of the Co(II) sorption. The remaining beads have a uniform internal structure. The kinetic studies confirm the results of the analysis made by XPS method. They also confirm the results obtained by scanning electron microscopy with the EDX detector. Lower percentage of the removed ions was observed for Co(II) ions sorbed on Dowex M 4195 whereas higher percentage was obtained for Fe(III) ions. These results are similar to those obtained from the analysis made by the XPS method. In the case of Co(II) sorption, the presence of this element was not registered on the surface of Dowex M 4195 by the XPS method. This may be due to insufficient sorption of this ion on Dowex M 4195. Higher concentration measured by the XPS method was obtained for Fe(III) ions sorbed on Dowex M 4195. The microscopic examination also showed the greatest sorption of Fe(III) ions on Dowex M 4195. Therefore it can be assumed that XPS and SEM methods are effective and practical complementary of studying ion exchangers.

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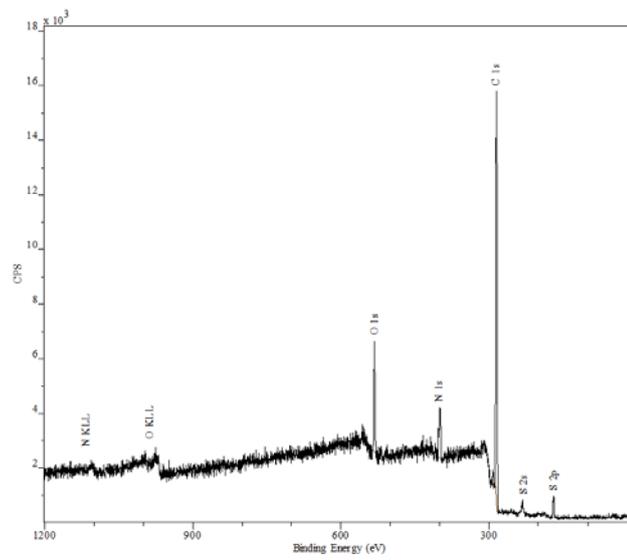


Fig.1. The XPS spectrum of Dowex M 4195 before the sorption process.

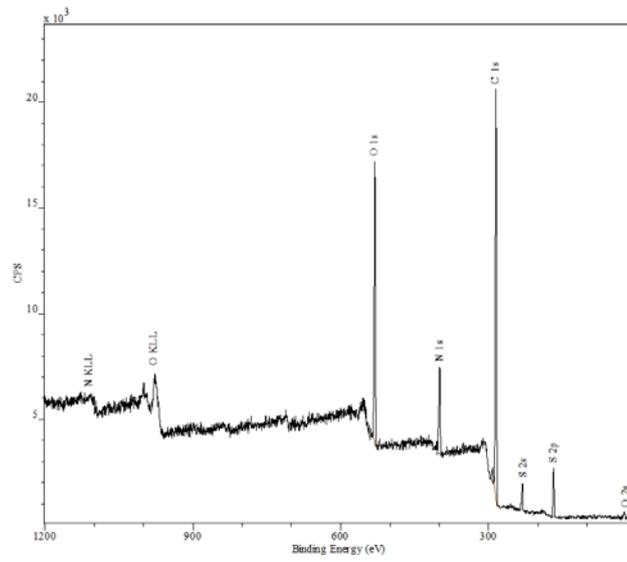


Fig.2. The XPS spectrum of Lewatit® MonoPlus TP 220 before the sorption process.

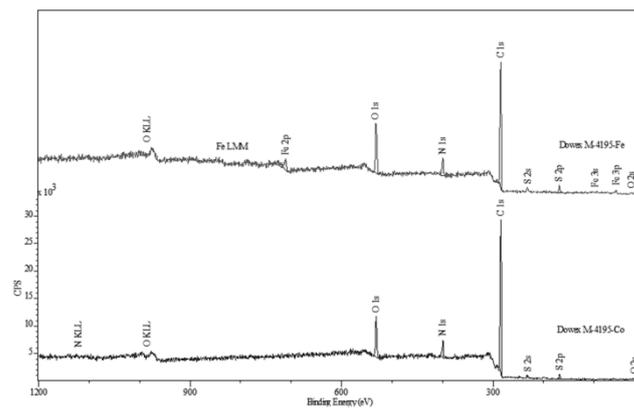


Fig.3. The XPS spectrum of Dowex M 4195 after the Co(II) and Fe(III) sorption process.

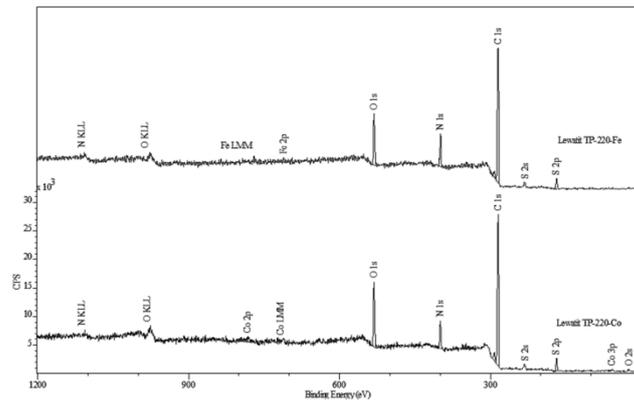


Fig.4. The XPS survey spectrum of Lewatit® MonoPlus TP 220 after the Co(II) and Fe(III) sorption.

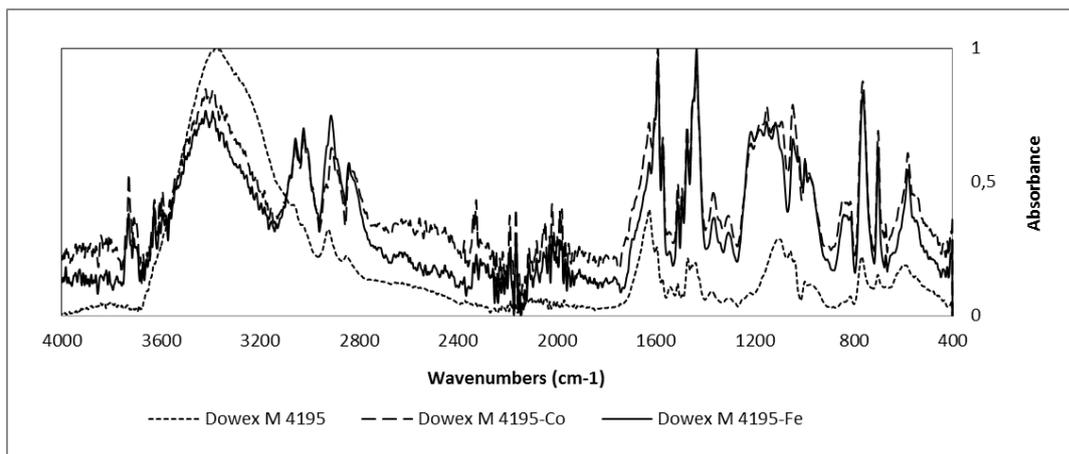


Fig.5. The FTIR-ATR spectrum of Dowex M 4195 before and after the sorption process of Co(II) and Fe(III).

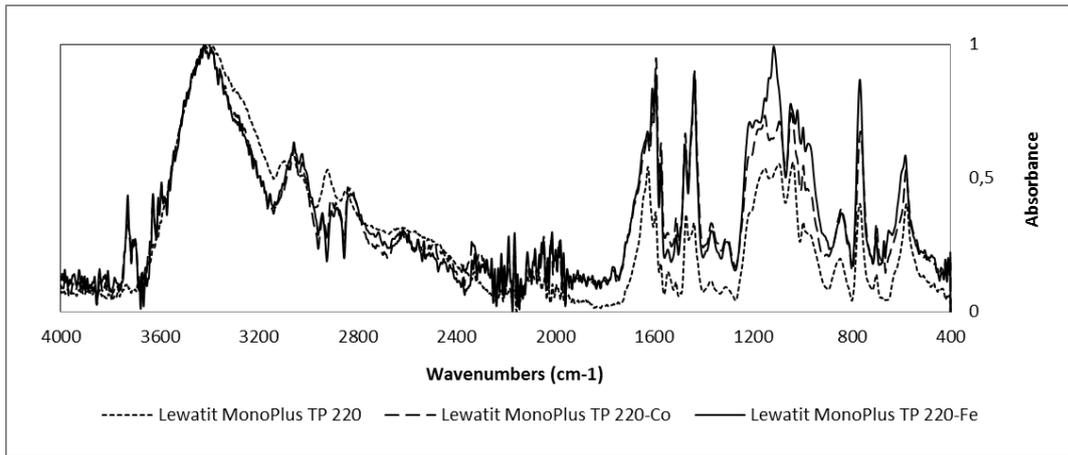
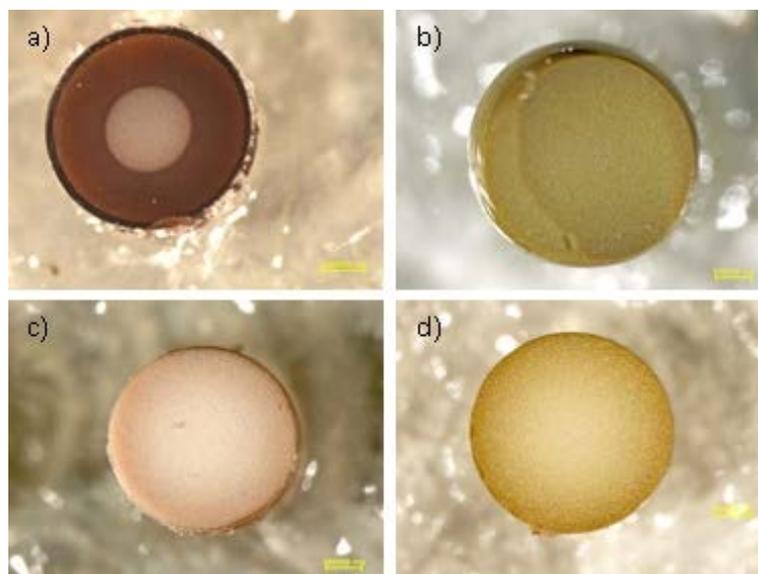
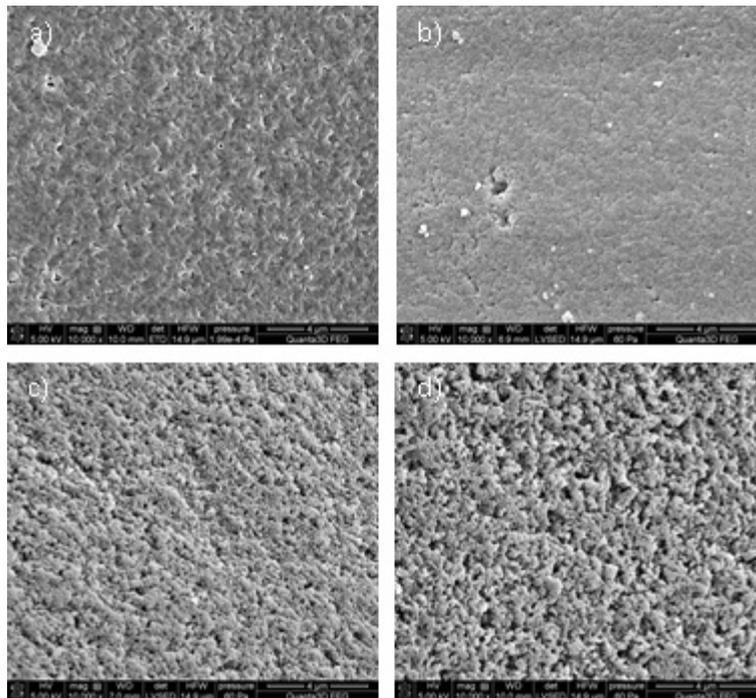


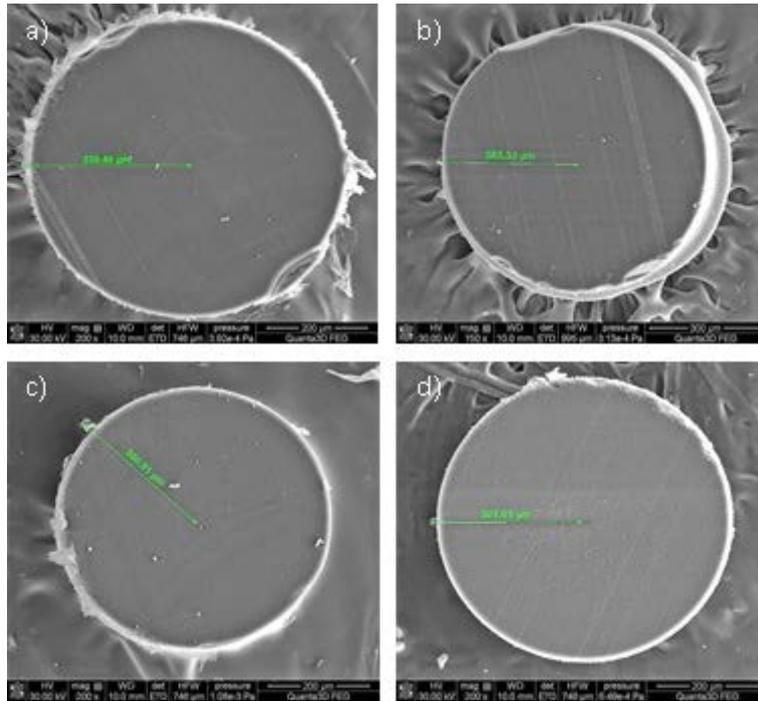
Fig.6. The FTIR-ATR spectrum of Lewatit[®] MonoPlus TP 220 before and after the sorption process of Co(II) and Fe(III).



Figs.7a-d. The images obtained from the microscopic analysis: (a) the cut bead of Dowex M 4195 after the sorption of Co(II), (b) the cut bead of Dowex M 4195 after the sorption of Fe(III), (c) the cut bead of Lewatit[®] MonoPlus TP 220 after the sorption of Co(II), (d) the cut bead of Lewatit[®] MonoPlus TP 220 after the sorption of Fe(III) (mag. 8x).



Figs.8a-d. The images obtained from the microscopic analysis: (a) Dowex M 4195 after the sorption of Co(II), (b) Dowex M 4195 after the sorption of Fe(III), (c) Lewatit® MonoPlus TP 220 after the sorption of Co(II), (d) Lewatit® MonoPlus TP 220 after the sorption of Fe(III). (mag. 10 000x).



Figs.9a-d. The images obtained from the microscopic analysis: (a) the cut bead of Dowex M 4195 after the sorption process of Co(II), (mag. 200x), (b) the cut bead of Dowex M 4195 after the sorption process of Fe(III) (mag.150x), (c) the cut bead of Lewatit[®] MonoPlus TP 220 after the sorption process of Co(II) (mag.200x), (d) the cut bead of Lewatit[®] MonoPlus TP 220 after the sorption process of Fe(III) (mag.150x).

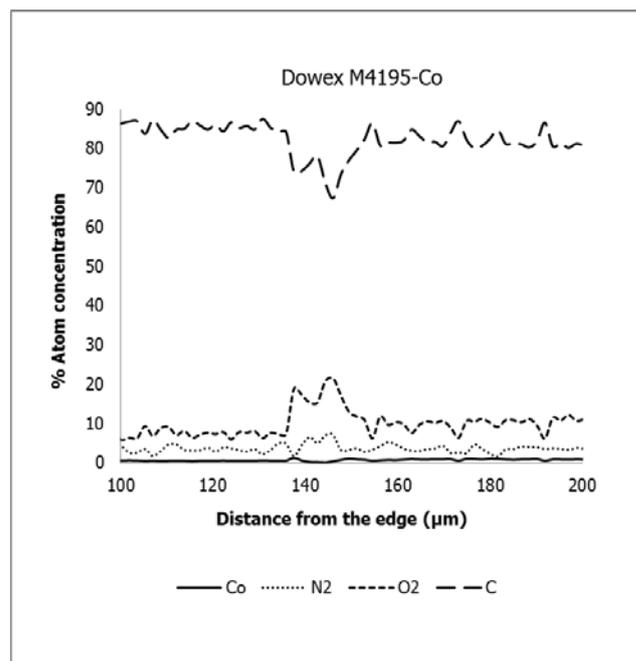


Fig.10. Distribution of carbon, oxygen, nitrogen and cobalt in Dowex M 4195 after the Co(II) sorption.

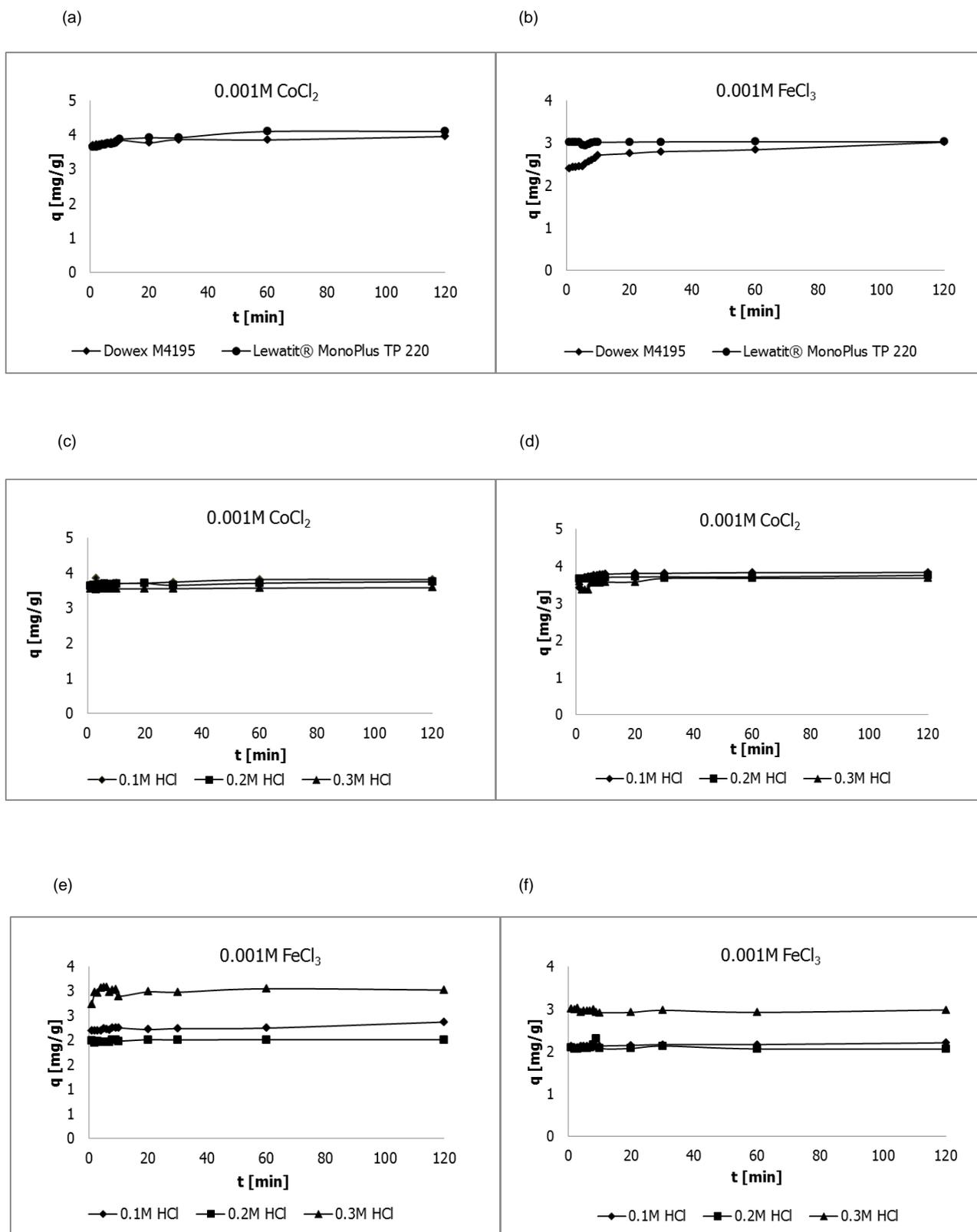


Fig.11a-f. The effect of the phase contact time on (a) Co(II) sorption on Dowex M 4195 and Lewatit® MonoPlus TP220 at the 0.001M CoCl₂, (b) Fe(III) sorption on Dowex M 4195 and Lewatit® MonoPlus TP220 at 0.001M FeCl₃, (c) Co(II) sorption on Dowex M 4195 at different initial concentrations in the chloride system, (d) Co(II) sorption on Lewatit® MonoPlus TP220 at different initial concentrations in the chloride system, (e) Fe(III) sorption on Dowex M 4195 at different initial concentrations in the chloride systems, (f) Fe(III) sorption on Lewatit® MonoPlus TP220 at different initial concentrations in the chloride system.

Table 1. The physicochemical properties of Dowex M 4195 and Lewatit® MonoPlus TP 220 [16-18].

Parameter	Dowex M 4195	Lewatit® MonoPlus TP 220
Manufacturer	Dow Chemical Co.	Lanxess
Form	SO ₄ ²⁻	OH ⁻
Appearance	brown	white
Capacity	1.4 eq/L 35-42 mg/g (6 g Cu(II)/L feed)	2.2 eq/L
Beads size	0.3-1.2 mm	0.67-0.69 mm
Max. temp.	354 K	354 K
pH	0-14	0-14
Uniform coefficient	n.a.	1.1
Water retention	40-60%	48-60%
Ion exchanger before the sorption process		

n.a – not available

Table 2. The elemental composition of Dowex M 4195 and Lewatit® MonoPlus TP 220 determined by the XPS method.

Dowex M 4195						
Name	Position	FWHM	Area	% Mass Concentration	%Atom Concentration	% Theoretical Atom Concentration
C 1s	284.7	2.65	42140.11	76.23	82.24	78.95
O 1s	531.6	2.73	11815.51	9.72	7.87	10.5
N 1s	399.3	3.2	6908.79	8.1	7.49	7.9
S 2p	168.3	2.79	2069.96	5.95	2.4	2.65
Lewatit® MonoPlus TP 220						
C 1s	284.7	2.6	54841.11	61.48	70.39	78.95
O 1s	531	2.5	36142.59	18.42	15.83	10.5
N 1s	399	3.08	12865.13	9.34	9.17	7.9
S 2p	168	2.53	6033.3	10.75	4.61	2.65

FWHM - full width at half maximum

Table 3. The elemental composition of Dowex M 4195 after Co(II) and Fe(III) sorption process measured by the XPS method.

	Name	Position	FWHM	Raw Area	Library RSF	Area/RSF	% Atom Concentration	% Mass Concentration
Dowex M 4195-Fe	C 1s	284.7	2.47	60488.8	1	60488.8	75.9	66.5
	O 1s	531.7	3.03	29868.6	2.93	10194.1	12.8	14.9
	N 1s	399.2	2.81	10583	1.8	5879.5	7.4	7.5
	S 2p	168.2	2.04	3653.07	1.68	2174.5	2.7	6.4
	Fe 2p	710.7	3.55	14940.6	16.4	911.0	1.1	4.7
Dowex M 4195-Co	C 1s	284.7	2.42	70715.7	1	70715.7	83	77.4
	O 1s	531.2	3.07	22356.6	2.93	7630.2	9	11.1
	N 1s	398.7	2.29	9374.52	1.8	5208.1	6.1	6.7
	S 2p	167.2	2.36	2753.25	1.68	1638.8	1.9	4.8

FWHM - full width at half maximum , Library RSF - relative sensitivity factor, Area/RSF- Area/ relative sensitivity factor

Table 4. The elemental composition of Lewatit® MonoPlus TP 220 after Co(II) and Fe(III) sorption process determined by the XPS method.

	Name	Position	FWHM	Raw Area	Library RSF	Area/RSF	% Atom Concentration	% Mass Concentration
Lewatit® MonoPlus TP 220-Fe	C 1s	284..7	2,78	71840.8	1	71840.8	77.1	68.7
	O 1s	531.2	2.66	26017.1	2.93	8879.6	9.5	11.3
	N 1s	399.2	2.32	15698.3	1.8	8721.3	9.4	9.7
	S 2p	168.2	2.9	5470.37	1.68	3256.2	3.5	8.3
	Fe 2p	711.2	2.16	7260.17	16.4	442.7	0.5	2
Lewatit® MonoPlus TP 220-Co	C 1s	284.7	2.59	77050.1	1	77050.1	75.9	66.8
	O 1s	531.2	2.66	33522.8	2.93	11441.2	11.3	13.2
	N 1s	398.7	3.01	15779.3	1.8	8766.3	8.6	8.9
	S 2p	167.7	2.63	6228.15	1.68	3707.2	3.6	8.6
	Co 2p	782.2	1.72	11588	19.2	603.5	0.6	2.6

FWHM - full width at half maximum , Library RSF - relative sensitivity factor, Area/RSF- Area/ relative sensitivity factor