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The use of the chelating resin of a new generation Lewatit MonoPlus TP-220 with the bis-picolylamine functional groups in the removal of selected metal ions from acidic solutions

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HIGHLIGHTS

- ▶ Bis-picolylamine ion exchangers efficient sorbents in metal ions removal.
- ▶ Good kinetic properties of Lewatit MonoPlus TP-220 result in fast M(II, IV) sorption.
- ▶ M(II, IV) sorption process follows the pseudo-second order kinetic equation.
- ▶ Lewatit MonoPlus TP-220 is reused and capacity reduction is small.

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ABSTRACT

A chelating resin of a new generation with the bis-picolylamine functional groups namely Lewatit MonoPlus TP-220 was applied in selected noble metal recovery such as palladium(II), platinum(IV), gold(III) and base metals such as Cu(II), Co(II), Ni(II) and Zn(II). Characterization of the ion exchanger including the contents of H, C and N atoms and the type of functional groups was carried out using the elementary analysis and FT-IR methods. Surface morphology (AFM and SEM pictures) of the commercially available Lewatit MonoPlus TP-220 resin was presented. Based on the batch method it was found that Lewatit MonoPlus TP-220 removed palladium(II), platinum(IV), gold(III) and cooper(II) form acidic solution very efficiently whereas zinc(II), nickel(II) and cobalt(II) to a smaller extend but the resin shows negligible higher selectivity for palladium(II) ions compared to others. The series can be presented as follows: Pd(II) > Au(III) > Pt(IV) > Cu(II) > Zn(II) > Co(II) > Ni(II). Due to this fact, the surface morphology of Lewatit MonoPlus TP-220 and the FT-IR spectrum after the Pd(II) sorption were also presented and the column studies were carried out in order to find the working ion exchange capacities for palladium(II) ions and to check how acids (nitric and hydrochloric) concentrations influence the sorption efficiency. The kinetic analysis, one of the most important factors making the metal ions removal economical and short time consuming, was discussed in this paper.

1. Introduction

Chelating ion exchange resin, in general, coordinating copolymers possesses covalently bonded side chains which contain one, two or more (multiple) donor atoms. Due to this fact, as a Lewis base, they are able to form coordinating bonds with Lewis acids such as the most toxic metal ions. The coordination-type interactions between the chelating resins and the metal ions sorbed provide their extremely high selectivity toward commonly encountered metal ions, M(II). The sorption efficiency mainly depends on the types of resin functional groups and to a smaller extent on resin beads size and its other physicochemical properties. The reciprocal position of functional groups, their spatial configuration and matrix properties play also a role in the M(II) sorption efficiency [1–4]. In a chelating resin, the functional groups containing donor atoms are rigidly bound to repeating monomers (like styrene) which again, are fixed as part of the three-dimensional network cross-linked through divinylbenzene. Depending on the number of donor atoms in pendant ligands of resin the functional groups are mono-, bi- or polydentate. The chosen examples of chelating resins with different types of functional groups are included in Table 1. As can be seen the presented resins can be divided into two groups. The first one includes three resins which are quite common and are found in many industrial applications. These resins possess iminodiacetate, carboxylate and aminophosphonate functional groups resulting in

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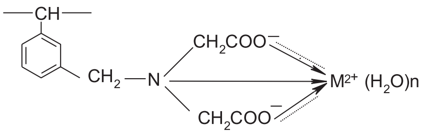
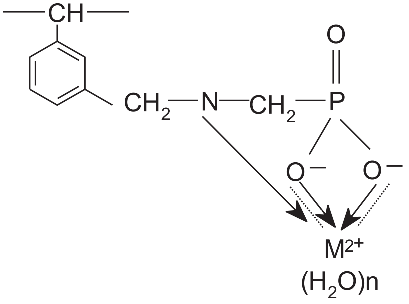
metal(II) ions binding using one nitrogen and two oxygen atoms – three dentate ligands (iminodiacetate or aminophosphonate type ion exchangers) or two oxygen atoms from two neighbouring carboxylate groups – bidentate ligands (carboxylate type resin) by cation exchange accompanied by chelation (→ coordinate bonds, . . . electrostatic bonds):

- Iminodiacetate:



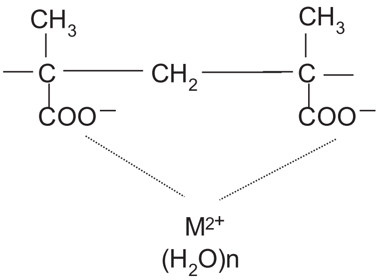
(1)

- Aminophosphonate:



(2)

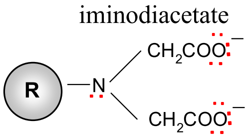
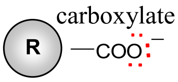
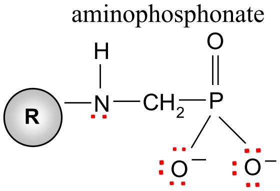
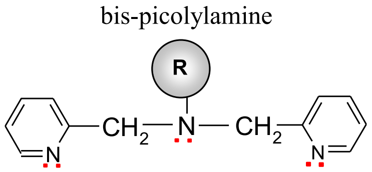
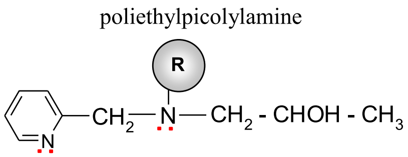
- Carboxylate:



(3)

In these three cases positive charges of metal ions are neutralized by the fixed negative charges in the resin phase resulting in the anion excluded from the polymeric exchangers due to the Donnan co-ions exclusion effect [2]. The last two chelating resins with only nitrogen donor atoms from weak-base pyridine and tertiary amine functional groups as resins of new generation exhibit some unusual properties in relation to other commonly used chelating ones and offer new application opportunities. Nowadays, this type of resins with the picolylamine functional groups has been met with great interest. More frequently, their applicability for removal, separation, preconcentration and purification of metal ions from water, solid waste, wastewater, etc. is considered [3–8]. The main advantages of such type of resins compared to other with not only nitrogen donor atoms are presented below:

Table 1
Characterisation of different types of chelating ion exchangers (chosen examples).

Trade name, manufacturer	Matrix	Functional groups (FG)	Donor atoms per FG	Acid-base characteristic
Amberlite IRC – 718, Dow Chemicals	Polystyrene		One N and two O	Weak base and weak acid
Amberlite DP-1, Dow Chemicals Bio-rex 70, Biorad Inc.	Polymetacrylate		One O	Weak acid
Amberlite ES-467, Dow Chemicals	Polystyrene		One N and two O	Weak base and weak acid
Dowex XFS 4195, DOW 3N, Dow Chemicals	Polystyrene		Three N	Weak base
Dowex XFS 43084, DOW 2N, Dow Chemicals	Polystyrene		Two N	Weak base

- Metal removal capacities remain almost unaffected at pH as low as 1.

It was found that the resins of new generation offer significant metal(II) ions removal capacities at very low pH (around 1) resulting in removal of metal ions even from highly acidic solutions. For the commercial, frequently used chelating resins due to the weak-acid and/or weak-base functional groups these resins show high affinities for hydrogen ions, therefore in highly acidic conditions (pH < 2) the metal(II) ions uptake is reduced drastically due to formidable competition from hydrogen ions [2].

- Resins regeneration loaded by metal ions is possible and very efficient with the ammonia solution whereas ineffective by using acids.

Greater than 90% regeneration efficiency of the chelating resins loaded by M(II) ions is observed with 2–4% acid solutions such hydrochloric, sulfuric acids, etc., but in the case of the resins of new generation such as DOW 3N and DOW 2N the resin regeneration is possible only by ammonia solutions. Such a drastic difference of these two groups of chelating resins is unexpected and requires explanation [2].

- The metal ion uptake increases with an increase in competing Ca^{2+} and Na^{+} ion concentrations e.g. copper or nickel removal.
- Cations as well as anions can be removed simultaneously from the aqueous phase. In the frequently used chelating resins the anions are excluded as mentioned.

More details and explanations of the resins with only weak-base functionality behaviour can be found in [2].

The main object of this work was to investigate of Lewatit MonoPlus TP-220 – the resin of a new generation applicability in selected metal ions removal from acidic solution and to study the isotherms and kinetic equations that fit the experimental findings. These studies are continuation of our previous investigations and deal with application of chelating resins with bis-picolylamine ligands namely Dowex M-4195 [3] in palladium(II) recovery. The new findings for Lewatit MonoPlus TP-220 were discussed in relation to the obtained results for Dowex M-4195.

2. Experimental

2.1. Column, batch, and kinetic studies

Lewatit MonoPlus TP-220 applicability in removal of selected noble metals was evaluated using the column (Pd(II), Pt(IV), Au(III)) and batch methods (Pd(II), Pt(IV), Au(III), Cu(II), Co(II), Zn(II), Ni(II)). In the former the solution containing 100 mg/L of selected noble metal ions is allowed to percolate through a column (∅1 cm) filled with 10 cm^3 of swollen Lewatit MonoPlus TP-220 resin with flow rate equal to 0.4 cm^3/min. In the batch operation (thermostatic shaker, Elpin+, Poland), air dry resin in 0.5 g amount was mixed with 50 ml of acidic solution (0.1–6.0 M HCl; 0.1–0.9 M HCl to 0.9–0.1 M HNO_3) containing metal ions in concentration of 100 mg/dm^3 and the system was kept in agitation for a period from 1 min to 24 h. The batch experimental conditions were following: the agitation speed – 180 stock per min, the amplitude = 8; the ambient temperature. The residual concentrations of metal ions were determined using the AAS method (Fast Sequential Atomic Absorption Spectrometer, Varian AA240FS with SIPS autosampler). The wavelength [nm] was 242.8, 265.9, 247.6, 232.0, 213.9, 324.8, 240.7; the lamp current [mA] was 4, 7, 10, 4, 5, 4, 7; slit width [nm] was 1, 0.2, 0.2, 0.2, 1.0, 0.5, 0.2 for Au(III), Pt(IV), Pd(II), Ni(II), Zn(II), Cu(II), Co(II) respectively and the air/acetylene flow [L/min] was usually 13.5/2 in all cases.

Successful application of the sorbent demands innovation of cheap, easily available, abundant sorbents of known kinetic parameters and sorption behaviour. Due to this fact, the kinetic analysis of the obtained time dependent experimental sorption data were interpreted using the kinetic equations such as:

- The Lagergren equation [9,10], the pseudo-first order kinetic equation, PFO given as:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{4}$$

- The Ho and McKay [11,12] equation, the pseudo-second order kinetic equation, PSO given as:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \tag{5}$$

where q_e and q_t are the amounts of noble metals sorbed on Lewatit MonoPlus TP-220 at equilibrium and after time t (mg/g), k_1 is the rate constant of the Lagergren equation (1/min), k_2 is the rate constant for the pseudo-second order equation (g/mg min).

2.2. Chemical and porous structure of Lewatit MonoPlus TP-220 analysis

The resin of new generation namely Lewatit MonoPlus TP-220 was used in selected metal ions sorption studies. Chelating resins properties were collected in Table 2. It is worth highlighting that this resin similar to Dowex M-4195 possesses the same functional groups i.e. the bis-picolylamine ligands. This fact found confirmation in the FT-IR spectrum analysis of Lewatit MonoPlus TP-220 obtained before the sorption process. A similar spectrum was also obtained for Dowex M-4195 and both were compared. Contrary to Dowex M-4195 whose properties and sorption behaviour towards selected base and noble metals were known, Lewatit MonoPlus TP-220 is hardly ever found in literature. In order to obtain more complete information about the weak base chelating resin Lewatit MonoPlus TP-220 the FT-IR and elementary analysis (Perkin Elmer CHN 2400 analyzer and the Sartorius microbalance M2P) of the resin were made. Moreover, its surface morphology was analyzed using the scanning electron BS: 301 (Telsa) and atomic force NanoScope V (Veeco, USA) microscopes.

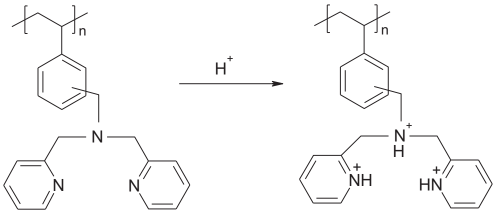
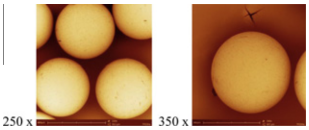
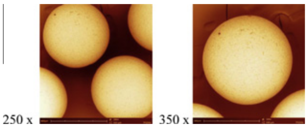
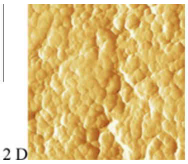
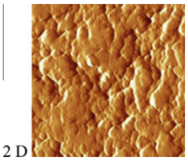
3. Results and discussion

3.1. Bis-picolylamine chelating resins functionality and properties

As can be seen in Table 2 Lewatit MonoPlus TP-220 is a resin of bis-picolylamine (bis-(2-pyridylmethyl)amine) functional groups, similar to Dowex M-4195. Both resins are characterized by macroporous structure, polystyrene matrix but different beads size [3,4].

The bis-picolylamine ligand is polydentate (threedentate) containing three nitrogen donor atoms: two atoms in the pyridyl groups ($-NC_5H_4$) and the last one in the tertiary amine functional group (3N – 2 aromatic, 1 aliphatic) [5,13–14]. Nitrogen atoms are donors of electron pairs (three, free electron pairs), whereas nitrogen atom of the pyridyl group is a stronger reducing agent than nitrogen atom of the amine group. The dissociation constants for bis(2-pyridylomethyl)amine groups are following $pK_1 = 1.12$; $pK_2 = 2.6$; $pK_3 = 7.3$ (298 K, 0.1 M KNO_3) [15]. As was mentioned by Grinstead' [15] at low pH all nitrogen atoms of bis(2-pyridylmethyl)amine functional groups are protonated, whereas at medium and high pH one or any nitrogen atoms are protonated, respectively. After functional groups attachment to styrene–divinylbenzene matrix nitrogen atoms can be deprotonated in chloride solutions. At pH higher than 4.21 these functional groups are not protonated.

Table 2
Salient properties of the chelating resin Lewatit MonoPlus TP-220.

Trade name	Resin type	Matrix	Structure	Ionic form as shipped	Appearance	Mean bead size	Uniform coefficient	Water retention
Lewatit MonoPlus TP-220	Chelating resin	Crosslinked polystyrene	Macroporous	Fully protonated	Opaque beads	0.62 (±0.05)	1.1	48–60%
Functional groups								
	Before sorption				After Pd(II) sorption			
SEM								
AFM								

As results from our investigations of C, H, N content in Lewatit MonoPlus TP-220 the amount of nitrogen atoms was equal to 10.86% whereas the carbon and hydrogen contents were following: %C = 74.3, %H = 7.06%. Compared to Dowex M-4195 negligibly higher nitrogen content was found (%N = 9.43; %C = 80.24; %H = 6.95).

In order to confirm the presence of functional groups of Lewatit MonoPlus TP-220 resin the FT-IR spectrum was recorded and presented accompanied by the FT-IR spectrum of Dowex M-4195 (Dow 3 N) – the resin of the same type (see Fig. 1a–c). As can be easily seen, these spectra are similar. The peaks appearing in the FT-IR spectrum of Lewatit MonoPlus TP-220 were assigned to various groups and bonds in accordance with their respective wavenumbers (cm^{-1}). In Dowex M-4195 as well as Lewatit MonoPlus TP-220 the peaks related to the resin matrix and their functional groups are observed. For Lewatit MonoPlus TP-220 in the higher frequency region at 3329 cm^{-1} the broad and intense peak was assigned to the stretching vibrations of the —OH group [16–22]. On the lower frequency side (3000–2800 cm^{-1}) of this band, the peaks related to the asymmetric stretching vibration of —C—H bonds of the ring (ν_{as}(C—H), 3051 cm^{-1}), symmetric and asymmetric stretching bonds of —CH_2 groups (ν_s(—CH_2), 2840 cm^{-1}, ν_{as}(—CH_2), 3009, 2918 cm^{-1})) of cross-linked polystyrene are observed [16,17,20–22]. At 1630 cm^{-1} the peak related to the vibration of —OH groups from water present in the resin phase (δ—OH) [16,17,20]. The ring C=C stretching vibration (ν_{as}(C=C), 1509, 1493 cm^{-1}) and the asymmetric scissoring vibration of the methylene groups (δ_{as}(—CH_2), 1432, 1362 cm^{-1}) are found. Moreover, the vibration of the atoms from the functional groups that means the vibration of the tertiary amine, pyridine ring and quaternary nitrogen is found. The peaks related to the quaternary nitrogen appear at 978 cm^{-1}. The peaks of vibrations of the amine groups are present in the wavelength region 1100–1200 cm^{-3} and 3000–3200 cm^{-1} [1]. The ring stretching vibration of C=N and C=C is observed in the region 1690–630 cm^{-1}. Moreover, new peaks of N-metal vibration appear in Fig. 1f.

As can be seen in Fig. 1d–f comparing the spectra of Lewatit MonoPlus TP-220 before and after Pd(II) sorption some changes can be found. In the 2800–3000 and 1400–1600 cm^{-1} frequency regions some of the peaks disappeared. In these frequency regions the peaks are related to the vibration of the functional groups atoms, therefore this fact can indicate that the functional groups can participate in Pd(II) binding, but the mechanism of Pd(II) sorption cannot be exactly described based on the FT-IR analysis. Probably, the Pd(II) mechanism could be coordination, due to the bis-picolylamine functional groups properties.

The SEM studies confirmed the spherical beads of Lewatit MonoPlus TP-220 and also the monodispersity of this ion exchange resin. As can be seen in Table 2 all beads possess a similar size. Moreover, the surface morphology obtained by the AFM method is typical of porous materials that means is rougher and highly porous. Pores can be also present in the SEM pictures where the bead looks like to be cutting.

3.2. Evaluation of batch sorption of noble (Pd, Pt, Au) and base (Zn, Cu, Co, Ni) metals

3.2.1. Noble metal sorption on Lewatit MonoPlus TP-220 – batch evaluation, kinetic studies

Palladium(II), platinum(IV) and gold(III) sorption onto Lewatit MonoPlus TP-220 as a function of acids concentration and the phases contact time was studied by varying the phases contact time from 1 to 240 min, hydrochloric acid from 1.0 to 6.0 M and hydrochloric mixed with nitric acid from 0.1 to 0.9 M and 0.9 to 0.1 M, respectively. The chosen results are presented in Fig. 2 and Table 3. As can be seen based on the obtained results noble metal ions sorption on Lewatit MonoPlus TP-220 is very effective. In the case of Pd(II) ion the affinity of chelating resin under discussion is negligibly higher than the case of platinum(IV) and gold(III). The selectivity series can be presented as follows: Pd(II) > Au(III) > Pt(IV). The batch sorption capacities of noble metal ions uptake are high and they are in the range from 9.94 to 10.0 mg/g; from 9.44 to 9.84 mg/g and from 9.84 to 9.96 mg/g for Pd(II), Pt(IV) and Au(III), respectively in the 0.1–6.0 M HCl solutions. As can be seen, the q_e values is the highest in the 0.1 M HCl system. The batch sorption capacities decreased with the increasing hydrochloric acid concentration (q_e values are lower 0.6%, 4% and 1.2% for Pd(II), Pt(IV) and Au(III) respectively compared to those obtained in 0.1 M HCl), therefore one can state that the hydrochloric acid

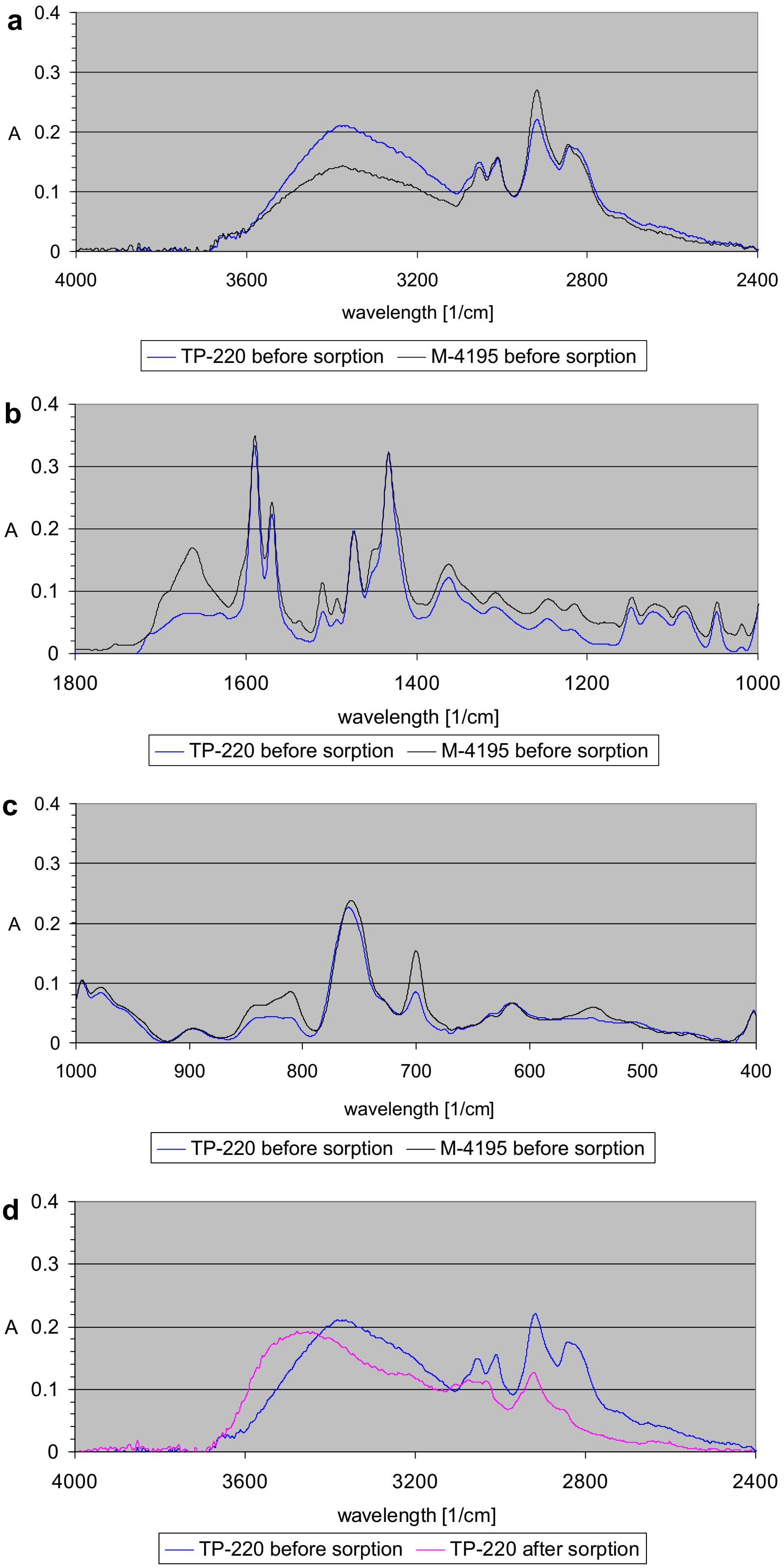


Fig. 1. Comparison of FT-IR spectra for the commercial chelating resin with bis(2-pyridylmethyl)amine functional groups: (a)–(c) Lewatit MonoPlus TP-220 and Dowex M-4195 before Pd(II) sorption and (d)–(f) Lewatit MonoPlus TP-220 before and after Pd(II) sorption.

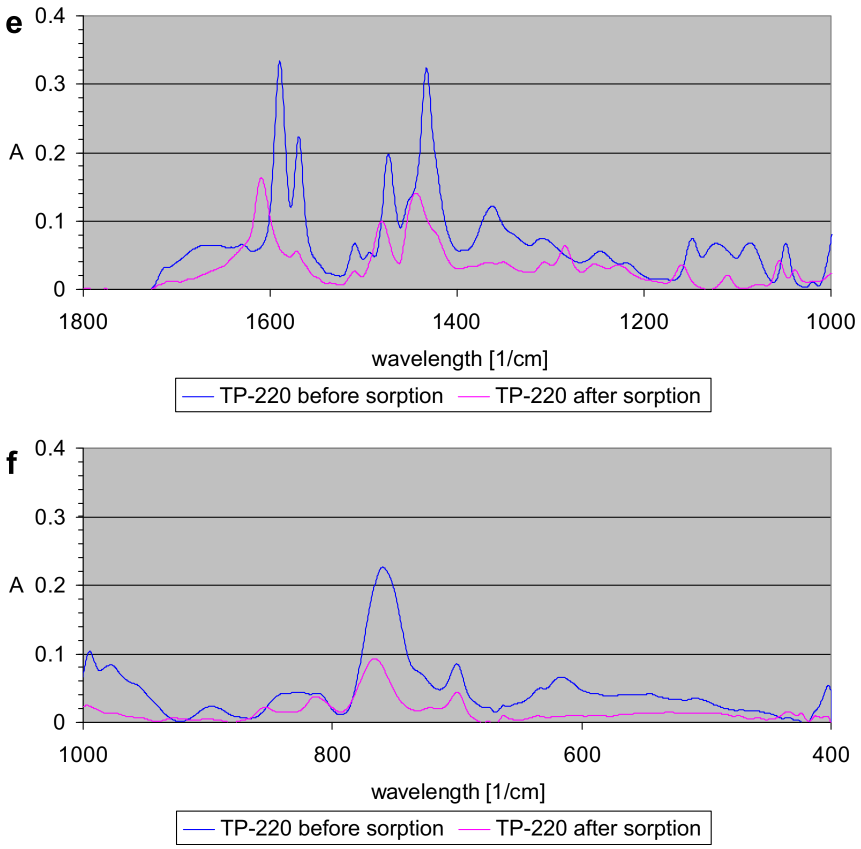


Fig. 1 (*continued*)

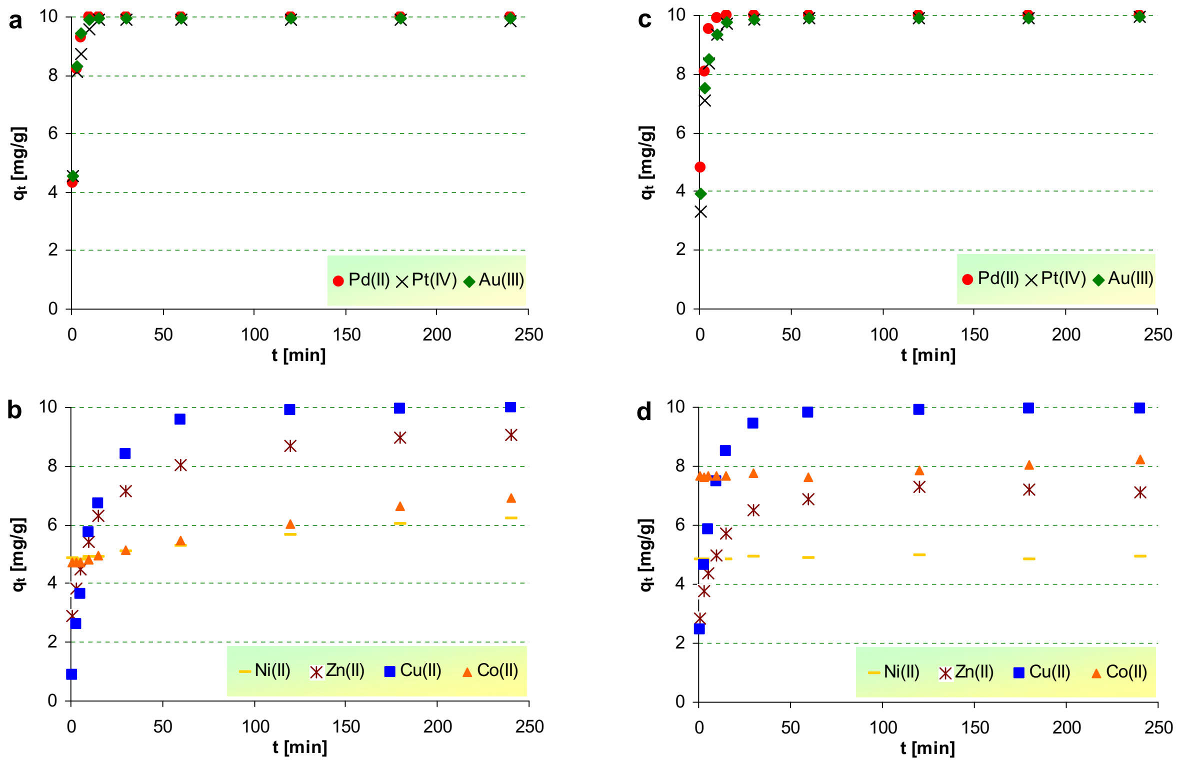


Fig. 2. Effect of phases contact time and acids concentration on (a) and (c) noble and (b) and (d) base metal ions sorption from (a) and (b) 0.1 M HCl – 100 mg M/L and (c) and (d) 0.9 M HCl – 0.1 M HNO_3 – 100 mg M/L solutions.

Table 3
Comparison of amount of metal ions sorbed on Lewatit MonoPlus TP-220 at equilibrium and the time required to reach equilibrium by the system (resin dose 0.5 ± 0.0005 g, volume of solution 50 mL, initial concentration of solution 100 mg/L, agitation speed 180 rpm, amplitude 8, ambient temperature).

Metals	0.1 M HCl		1.0 M HCl		3.0 M HCl		6.0 M HCl		0.1 M HCl – 0.9 M HNO_3		0.2 M HCl – 0.8 M HNO_3		0.5 M HCl – 0.5 M HNO_3		0.8 M HCl – 0.2 M HNO_3		0.9 M HCl – 0.1 M HNO_3	
	q_e (mg/g)	t_{eq} (min)	q_e (mg/g)	t_{eq} (min)	q_e (mg/g)	t_{eq} (min)	q_e (mg/g)	t_{eq} (min)	q_e (mg/g)	t_{eq} (min)	q_e (mg/g)	t_{eq} (min)	q_e (mg/g)	t_{eq} (min)	q_e (mg/g)	t_{eq} (min)	q_e (mg/g)	t_{eq} (min)
Pd(II)	10.0	15	10.0	15	10.0	15	9.94	60	9.99	15	9.98	10	9.99	5	9.99	5	10.0	5
Pt(IV)	9.84	15	9.77	15	9.62	30	9.44	60	9.73	120	9.77	60	9.78	60	9.91	30	9.93	15
Au(III)	9.96	15	9.95	30	9.91	60	9.84	60	9.89	30	9.88	30	9.89	15	9.96	30	9.94	15
Zn(II)	9.09	>240	8.74	180	9.49	120	9.15	120	1.96	–	2.11	–	2.16	–	7.81	120	7.15	180
Ni(II)	6.24	>240	4.93	–	4.68	–	4.89	–	4.88	–	4.93	–	4.91	–	5.00	–	4.95	–
Co(II)	6.90	>240	4.8	–	4.66	–	6.62	–	7.16	–	7.56	–	7.66	–	7.89	–	8.22	–
Cu(II)	9.98	240	9.95	120	9.87	120	9.12	180	9.75	180	9.84	120	9.90	120	9.94	60	9.95	120

t_{eq} – the time required to reach equilibrium by the system, q_e – the amount of metal ions sorbed at Lewatit MonoPlus TP-220 at equilibrium time, – effects of phases contact time on q_e values are not observed, q_e reached close values in the whole sorption time range (1–240 min).

concentration up to 6 M can negligibly influence on the sorption efficiency for Pd(II) and Au(III). Moreover, in the case of the above mentioned solutions, the time required to reach equilibrium by the system is short, that means that sorption kinetics of noble metal ions onto Lewatit MonoPlus TP-220 is fast. This fact found confirmation in the shape of the kinetic curves (q_e vs. t). As Fig. 2 shows the noble metal ions uptake, as a function of phases contact time, was noted to occur in two phases. The first phase involved very rapid metal uptake during 5 min of sorbent (Lewatit MonoPlus TP-220) – sorbate (Pd(II), Pt(IV), Au(III)) contact, which was followed by a slow phase of noble metal removal spread over a negligibly longer period of time until the equilibrium is reached. Time required to reach equilibrium as shown in Table 3, is very short, usually 15 min for all metals in the 0.1 M HCl solution and is dependent on hydrochloric acid concentration. With the increasing hydrochloric acid concentration, the time required to reach equilibrium also increased to 60 min in the 6.0 M HCl solutions. The two-step metal uptake process, the first being rapid and the second slower, has been extensively reported in literature e.g. [23,24]. The rapid step is probably due to the abundant availability of active sites on Lewatit MonoPlus TP-220, whereas with the gradual occupancy of these sites, sorption of metals under discussion becomes less efficient during the slower step.

In the case of noble metal ions sorption on Lewatit MonoPlus TP-220 from the chloride–nitrate(V) solutions the following observations were made: (1) q_e values usually negligibly increase with the increasing hydrochloric acid concentration and decreasing nitric acid – 0.1%, 2% and 0.7% increase of q_e values was observed, (2) q_e values increase rapidly with the phases contact time increase, and (3) time required to reach equilibrium is short (5–120 min) and decreases with the hydrochloric acid concentration increase and that of nitric acid decrease. The fastest kinetics of sorption process was observed for Pd(II) ions. As shown in Table 2 [25] which describes the ion exchangers properties under the batch sorption experimental conditions and compares of the time required to reach equilibrium during the Pd(II) sorption, the t_{eq} values are in many cases higher or much higher than those obtained for Lewatit MonoPlus TP-220 e.g. for Dowex MSA-2 t_{eq} is in the range from 60 to 120 min (the experimental conditions were the same as in this paper) whereas for Lewatit MonoPlus TP-220 t_{eq} = 5–60 min. Comparing t_{eq} of the ion exchangers of the same type: Lewatit MonoPlus TP-220 and Dowex M-4195 [3] the kinetics of Pd(II) sorption process is faster in the case of Lewatit MonoPlus TP-220. This is a very important factor which affects on the practical applicability of this resin for metal ions recovery.

The ionic radius for noble metals under discussion is similar for Pd^{2+} (86 pm) and Au^{3+} (85 pm) and higher than for Pt^{4+} (62.5 pm) [23]. In the chloride solution palladium(II), platinum(II), platinum(IV) and gold(III) can exist in different forms depending on the pH of solution and total concentration of the chloride ions (see Fig. 3a–c for Pd(II), Pt(IV), Au(III)). In the chloride solutions (0.1–6.0 M HCl) the noble metal ions form anionic chlorocomplexes such as $PdCl_4^{2-}$, $PtCl_6^{2-}$, $AuCl_4^-$ (log Cl^- is in the range from −1 to 0.8) [3,26,27]. In these ionic species $\left(PdCl_4^{2-}, AuCl_4^-\right)$ both metals' chloride complex ions have the same electronic configuration d^8 and both complexes exhibit a square planar stereochemistry results in similar chemical coordination behaviour, therefore these meal ions can adsorb onto the same types of sorption sites [28]. In the platinum(IV) complex $PtCl_6^{2-}$ metal has a different electronic configuration from that of Pd(II) and Au(III), d^6 and the complex exhibits octahedral stereochemistry. According to the HSAB theory all noble metal ions are classified as soft acid [29]. Due to the above mentioned facts these noble metals show strong affinity for Lewatit MonoPlus TP-220 and behave similar which results in high batch sorption capacities, but negligibly smaller platinum(IV) sorption can be caused by different stereochemistry of the complex. The degree of ion-pair formation depends on the size of anionic chlorocomplexes and the ionic charge and increases from MCl_4^-, MCl_6^{2-} to MCl_4^{2-} to MCl_6^{3-} [30]. Based on the bis(2-pyridylmethyl)amine functional groups functionality, the efficiency of metal ions sorption depends on the total chloride anion concentration, pH of solution and protonation degree of functional groups as well as pH. At pH higher than 4.21 these functional groups are not protonated. According to [15] if n values (n – the average amount of accepted protons) is lower than 2 (pH > 1.4) the increase of chloride anions causes the increase of metal ions sorption efficiency. In the case of $n = 2$ (pH = 1.4) metal ions sorption is independent of chloride anion concentration and when n is higher than 2 (pH < 1.4) chloride anions concentration increase reduces the sorption efficiency. In the case presented here the decrease of batch sorption capacities with the increasing concentration of hydrochloric acid is observed.

3.2.2. Base metal sorption on Lewatit MonoPlus TP-220 – batch evaluation

Metal ions uptake capacities were determined as a function of time to determine an optimum contact time for the adsorption of zinc(II), copper(II), nickel(II) and cobalt(II) metal ions on Lewatit MonoPlus TP-220. Fig. 2b and d shows time course of the sorption of Zn(II), Co(II), Ni(II) and Cu(II) metal ions on Lewatit MonoPlus TP-220 (chosen examples). As it can be seen from the figure, these metals behave differently in the system of sorbate (metal ions) – sorbent (Lewatit MonoPlus TP-220). As results from Table 3, there is rapid uptake kinetics but slower or much slower than in the case of the selected noble metal ions. The time required to reach equilibrium is attained after 60, 120, 180 and 240 min whereas in the case of Pd(II), Pt(IV) and Au(III) it was in the range 5–120 min. Table 3 also shows that the affinity of Lewatit MonoPlus TP-220

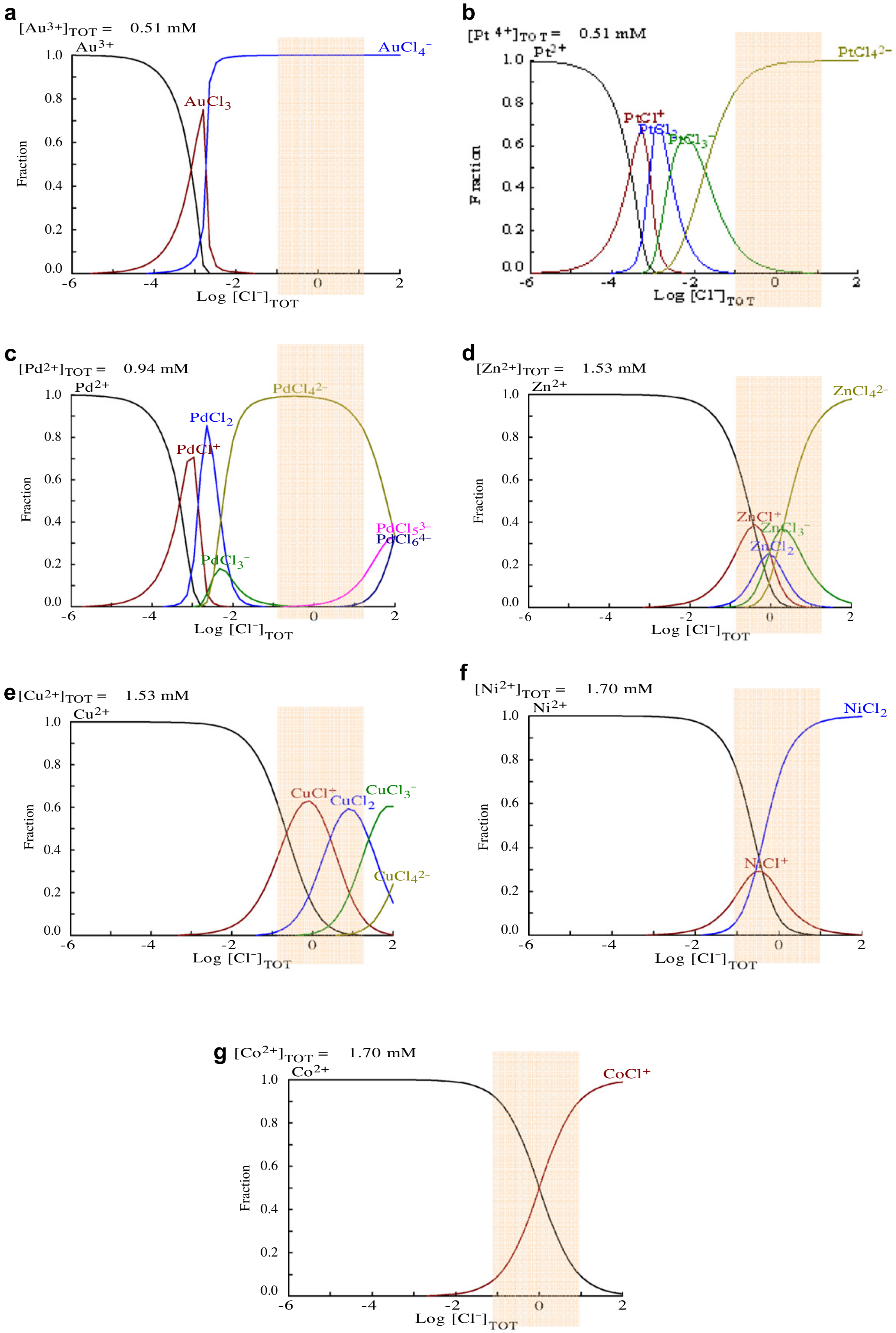
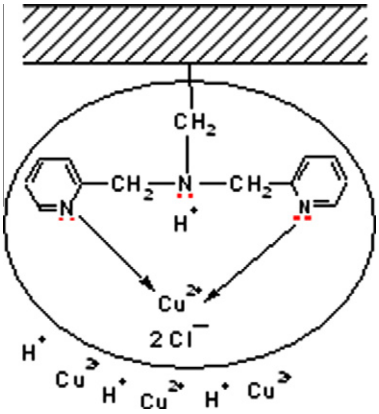


Fig. 3. Speciation of metal ions (a) Au(III), (b) Pt(II), (c) Pd(II), (d) Zn(II), (e) Cu(II), (f) Ni(II), and (g) Co(II) as a function of log from the total chloride concentration (metal concentration 100 mg/L).

for base metal ions is weaker than for the noble ones. Kinetic characteristics for the chelating ion exchangers depends on many conditions such as: the presence of chelating functional groups and their accessibility without sterical hindrance which is greatly determined by the polymeric matrices, structural properties of the sorbent (size, surface area, porosity), metal ion properties (e.g. hydrated ionic radius, speciation), initial concentration of metal ions, pH, temperature, chelate formation rate or presence of the competing ions. Fig. 3d–g presents the speciation of metal ions in the chloride solutions.

As for the copper(II) sorption on Lewatit MonoPlus TP-220 this metal exists in the form of positive metal ions or in the form of cationic complexes $CuCl^+$. The metal ions ionic radius is equal to 73 pm. Lewatit MonoPlus TP-220 shows the highest affinity for copper(II) ions compared to others under discussion. Similar observation was made by other researchers [5,6,31]. In the selectivity series shown by Diniz et al. which examined the sorption of copper(II), nickel(II), lead(II), iron(III), cobalt(II) and manganese onto Dowex M-4195 (bis-picolylamine functional groups similar to Lewatit MonoPlus TP-220) from the single-metal (Cu > Ni > Co > Pb > Fe > Mn) and multicomponent (Cu > Ni > Pb > Fe > Co > Mn) solutions the copper is in the first position. Copper(II) usually shows high sorption affinity for chelating ion exchangers containing only nitrogen atoms under acidic conditions [2,31,32]. Copper(II) is a borderline soft metal cation and due to its incomplete 3d orbital in the electronic configuration as a Lewis acid is able to coordinate and form inner-sphere complexes with Lewis base or a ligand (electron pair donor). Lewatit MonoPlus TP-220, similar to Dowex M-4195 shows distinctive sorption properties compared to the IDA resin. In this case copper(II) at as low pH as 1.5 is sorbed with high efficiency. It is caused by the fact that Lewatit MonoPlus TP-220 compared to the IDA resin (one donor atom) contains three nitrogen donor atoms (two aromatic and one aliphatic). Due to the electron withdrawing effect of the aromatic groups, the negative logarithm of the acid dissociation constant, the pK_a values are quite low and remain deprotonated even at pH 1.5, therefore the two pyridyl nitrogen donor atoms are still available at acidic pH and the bidentate complex with Cu(II) can be formed. The Cu(II) binding mechanism during the Cu(II) sorption onto Lewatit MonoPlus TP-220 is Lewis acid–base interaction and contrary to the IDA resin the electrostatic interactions are absent [1,2,31], only one functional group is used for one Cu(II) binding [14]:



(6)

where → denotes the Lewis acid–base (LAB) interactions.

Lewatit MonoPlus TP-220 as a resin containing three donor atoms (soft Lewis base) shows also high affinity for other metal ions such as zinc(II), cobalt(II) and nickel(II) – soft Lewis acid and forms coordinate bonds [2]. The selectivity series can be presented as follows:

- 0.1 M HCl: Cu(II) > Zn(II) > Co(II) ≈ Ni(II),
- 1.0 and 3.0 M HCl: Cu(II) > Zn(II) > Ni(II) ≈ Co(II),
- 6.0 M HCl: Zn(II) ≈ Cu(II) > Co(II) > Ni(II),
- 0.1 M HCl – 0.9 M HNO_3, 0.2 M HCl – 0.8 M HNO_3, 0.5 M HCl – 0.5 M HNO_3: Cu(II) > Co(II) > Ni(II) > Zn(II),
- 0.8 M HCl – 0.2 M HNO_3, 0.9 M HCl – 0.1 M HNO_3: Cu(II) > Co(II) > Zn(II) > Ni(II).

As follows from Fig. 3 such metal ions are present in the solution in the form of metal ions, positive charge or inert complexes. Only in the case of zinc the anionic species can be present in the solutions of the concentrations under discussion. The ionic state of zinc depends on both its concentration in solutions and composition as well as acidity of these solutions. The tetrachlorozincate complex $[ZnCl_4]^{2-}$ is formed in strong acidic solutions in which HCl concentration is in the range from 1 to 6 mol/L. The amounts of coexisting anionic and cationic forms of aquacomplexes such as $[ZnCl_4(H_2O)_2]^{2-}$, $[Zn(H_2O)_6]^{2+}$ increase with the decrease in acidity to 10^{-2}–10^{-3} mol/L [33]. As was mentioned by Kononova et al. high zinc(II) sorption onto strongly and weakly basic anion exchangers (recovery of zinc(II) – 75–80%) results from mixed mechanism of Zn(II) binding. In the case of zinc sorption on the weakly basic anion exchange resin not only the chelating mechanism but also the anion exchange one take part [33]. In the case of the strongly basic anion exchangers their functional groups (quaternary ammonium) have no ability for complexation, but on the other hand they show high sorption ability in a wide range of pH values. High sorption of zinc(II), but smaller than for Cu(II) and some noble metal ions onto Lewatit MonoPlus TP-220 can be caused by the dual nature of ion exchange resins which can act as the chelating or anion exchanger [7]. The ionic radii of metal ions under discussion are following: Zn(II) = 74 pm, Ni(II) = 69 pm, Co(II) = 65 pm [23]. Zinc(II) possesses the negligibly higher ionic radius but the sorption is higher than for metal ions with smaller ionic radius. This fact indicates that the binding mechanism plays a more significant role than the size of metal ions during the sorption onto Lewatit MonoPlus TP-220.

The sorption mechanism plays also an important role in the sorption kinetics. As mentioned the ion exchange resin under discussion can act as a chelating or anion exchange resin. The form in which metal ions exist in the solution is also very important. As shown in Fig. 3 in the case of the noble metal ions the anionic chlorocomplex is the most predominant form. The positively charged groups on the resin attract the anionic PGM complex ions, which exist as chloride anions in the acidic medium, by means of electrostatic attraction. At the acidic pH, the resin acquires a positive charge due to the protonation of the amino groups, which removes noble metal ions by means of anion exchange mechanism.

In the case of base metal ions the metals bind on the resin by chelating mechanism or by mixed mechanism chelating with anion exchange mechanism depending on the form in which exist the base metal ions. In some cases the ion exchange mechanism can be involved e.g. sorption of Cu(II) in the presence of Fe(III) similar to those on the strongly basic anion exchange resnin Dowex 21K [1].

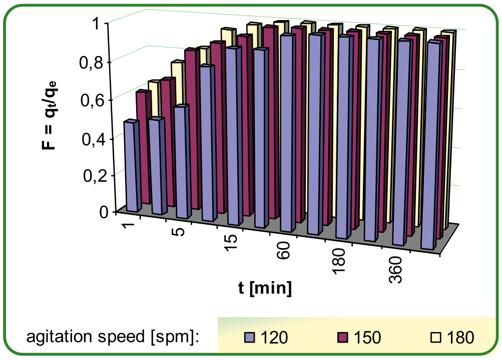
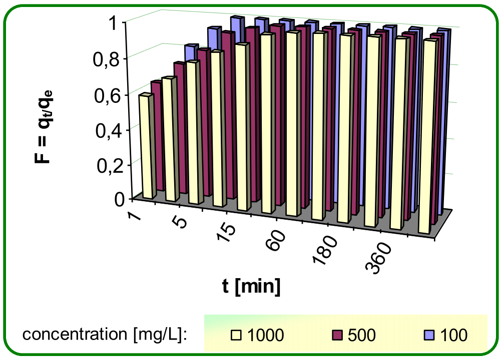
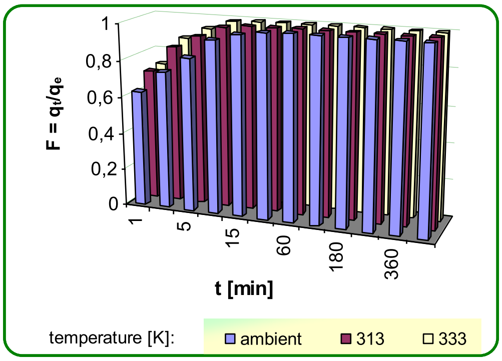
3.3. Kinetic studies of Pd(II) sorption onto Lewatit MonoPlus TP-220

It is known that the sorption process could be dependent on and controlled with different kinds of mechanisms, like mass transfer, diffusion control, chemical reactions and particle diffusion. In order to clarify the palladium(II) sorption process the Lagergren's pseudo-first and pseudo-second order kinetic equations were used. The effects of initial Pd(II) concentration, temperature and agitation speed were tested. The results of different experimental parameters effects on the Pd(II) sorption process are presented in

Table 4. In all cases the phases contact time was 24 h, but in the figures the presented time was shorter to the values changes will be easer observed, if any.

A series of experiments was performed using the agitation speeds of 120, 150 and 180 rpm, and a particle size range of 0.57–0.67 mm. The initial palladium(II) concentration was 500 mg/L. As can be seen from Fig. included in Table 4 the agitation speed affects the kinetics but negligibly and only at the beginning of the sorption process. After 60 min no changes of q_t values are observed. For 150 and 180 rpm the changes are not visible in the whole range of phases contact time. With increasing the agitation speed, the rate of diffusion of Pd(II) molecules from the bulk liquid to the liquid boundary layer surrounding the particle is improved. Increase in the amount of Pd(II) sorbed on Lewatit MonoPlus

Table 4
Effects of selected experimental conditions on Pd(II) sorption on Lewatit MonoPlus TP-220.

Experimental conditions	Particle diffusion control	Film diffusion control	Figures
Rate of agitation speed[a]	No effect	Increase with agitation speed beyond a critical agitation speed	
Concentration of solution	No effect	~C	
Temperature[b]	Increase with temperature ca. 4–8% per degree Centigrade	ca. 3–5% per degree Centigrade	
Particle size	Inversely proportional $\sim 1/r_o^2$	Inversely proportional $\sim 1/r_o$	

[a] 0.1 M HCl – 500 mg Pd/L, V = 0.05 L, m = 0.5 g, ambient temperature, 120–180 rpm, A = 8.

[b] 0.1 M HCl – 500 mg Pd/L, V = 0.05 L, m = 0.5 g, ambient temperature, 313 K, 333 K, 180 rpm, A = 8.

TP-220 with increasing agitation speed at the beginning of the sorption process is due to the change in the boundary layer resistance of the system. The boundary layer resistance to the mass transfer will be affected by the rate of the sorption process and the increasing degree of agitation will reduce this resistance and increase the mobility of the system (increase of the driving force of Pd(II)). Similar effects of agitation speed on the Pd(II) sorption on Dowex M-4195 were obtained in our previous studies [3]. In both cases 180 rpm was chosen as the optimal agitation speed. As follows from the kinetic parameters (see Table 5) obtained for the pseudo-first (PSO) and pseudo-second (PSO) kinetic order equations with the increasing agitation speed the kinetic rate constant for PSO also increased, which is in agreement with that mentioned above. As commonly observed, also in this case PSO fits well the experimental data (high determination coefficient, good correlation between sorption capacity obtained experimentally and calculated from the PSO equation) e.g. [3,34].

The influence of palladium initial concentration on the sorption kinetics was studied changing the concentration from 100 to 1000 mg/L. Increasing the palladium(II) initial concentration results in the increasing amount of Pd(II) sorbed on Lewatit MonoPlus TP-220. Moreover, the shape of kinetic curves changed. For the solution of higher initial concentration at the beginning of the sorption process the curves seem to be more sloping which indicates that the kinetics is slower for the solution of 1000 mg/L concentration. The time required to reach equilibrium is prolonged 10 min for 100 mg/L solution to 120 min for 1000 mg/L solution. This fact was confirmed by the kinetic parameters such as k_2 values which slightly decreased with the concentration increase (Table 5). Equilibrium uptake increased with the increasing initial palladium(II) concentration due to the increase in the driving force of concentration gradient. For the initial concentrations of 100 and 1000 mg/L, the ability of Lewatit MonoPlus TP-220 to sorb the maximum amount of Pd(II) within 10–120 min indicates that it is an effective sorbent for the removal of Pd(II) from acidic solutions. When the initial palladium(II) concentration increased from 100 to 1000 mg/L, the equilibrium sorption capacity increased from 10.0 to 99.95 mg/g. Similar observations during the studies of Pd(II) sorption onto sorbents from the solution of different initial Pd(II) concentrations were found by Parodi et al. [35] and Ruiz et al. [36].

The effect of temperature on sorption of Pd(II) by Lewatit MonoPlus TP-220 was studied using 500 mg/L initial metal concentration at ambient, 313 and 333 K. The results show that the sorption capacity negligibly increase or is unchanged with the increasing temperature. The slight increase of the amount of Pd(II) sorbed was observed at the beginning of the sorption process with the increasing temperature. Increase of temperature causes the decrease of film thickness of the boundary layer surrounding Lewatit MonoPlus TP-220 beads which results in the decrease of mass transfer resistance and the increase of Pd(II) ion mobility. Additionally, the increase of temperature changes the swelling properties of ion exchange resin under discussion. As was concluded by Sánchez et al. [37] faster kinetics of the sorption process of palladium and gold ions results from the temperature increase and this effect is higher for gold ions as a result of greater changes in its diffusivity. Based on the k_2 parameters (Table 5) in our cases this conclusion cannot be exactly repeated, but the initial sorption rate increases with the temperature (ambient and 313) what corresponds to the q_t values presented in the figure in Table 4.

Based on the kinetic studies it can be concluded that the Pd(II) sorption process is governed by the film diffusion rather that by the particle diffusion. The Weber and Morris model which was described in [3] indicates that the intra-particle diffusion is not the rate controlling step (the second part of the kinetic parts shows low R^2).

Table 5
Kinetics parameters for Pd(II) sorption process.

Experimental conditions	Kinetic parameters								
Rate of agitation speed	speed [rpm]	$q_{e,exp}$	PFO			PSO			
			q_e	k_1	R^2	q_e	k_2	h	R^2
	120	49.97	8.73	0.03	0.843	50.05	0.01	30.8	1.000
	150	49.87	17.60	0.12	0.987	49.90	0.04	107.2	1.000
	180	50.00	2.16	0.02	0.577	49.96	0.06	139.3	1.000
Concentration of solution	Co [mg/L]	$q_{e,exp}$	PFO			PSO			
			q_e	k_1	R^2	q_e	k_2	h	R^2
	100	10.00	13.13	0.66	0.991	10.00	0.40	40.3	1.000
	500	49.94	18.01	0.16	0.997	49.96	0.06	139.3	1.000
	1000	99.95	15.11	0.03	0.904	100.03	0.01	128.2	1.000
Temperature	temp. [K]	$q_{e,exp}$	PFO			PSO			
			q_e	k_1	R^2	q_e	k_2	h	R^2
	ambient	49.94	18.01	0.16	0.997	49.96	0.06	139.3	1.000
	313	49.88	7.60	0.15	0.777	49.89	0.16	385.8	1.000
	333	49.90	2.81	0.07	0.548	49.91	0.13	332.0	1.000
Particle size	The kinetic parameters were not obtained.								

$q_{e,exp}$ (mg/g), q_e (mg/g), k_1 (1/min), k_2 (g/mg min), and h (mg/g min).

3.4. Dynamic studies of Pd(II) onto Lewatit MonoPlus TP-220

Dynamic experiments on the sorption on Lewatit MonoPlus TP-220 were carried out taking into account our data on sorption on noble metal ions on the same resins under static conditions. Due to the fact that the affinity of Lewatit MonoPlus TP-220 is the highest for Pd(II) ions, only in this case the breakthrough curves were obtained and presented. Based on the breakthrough curves the following parameters were calculated:

— working ion exchange capacity, $C_r[\mathrm{g/cm^3}]$:

$$C_r = (V_p \cdot C_o)/V_j \tag{7}$$

— weight distribution coefficient, D_w:

$$D_w = (U - U_o - V_v)/m_j \tag{8}$$

— bead distribution coefficient, D_b:

$$D_v = D_w d_z \tag{9}$$

— number of theoretical plates, N:

$$N = \frac{(U - U_o)(U' - U_o)}{(U - U')^2} \tag{10}$$

where V_p – collected volume of effluent between the first fraction and that to the breakthrough point (cm^3), C_o – initial concentration of palladium(II) ions (mg/dm^3); V_j – volume of the anion exchanger bed put into the columns (10 cm^3), U – effluent volume at $C = 0.5C/C_o$ (cm^3), U_o – dead volume in the column (cm^3), V_v – void (interparticle) anion exchanger bed volume (which amounts to ca. 0.4), m_j – dry anion exchanger weight (g), d_z – anion exchanger bed density, U' – effluent volume at $C = 0.159C/C_o$ (cm^3).

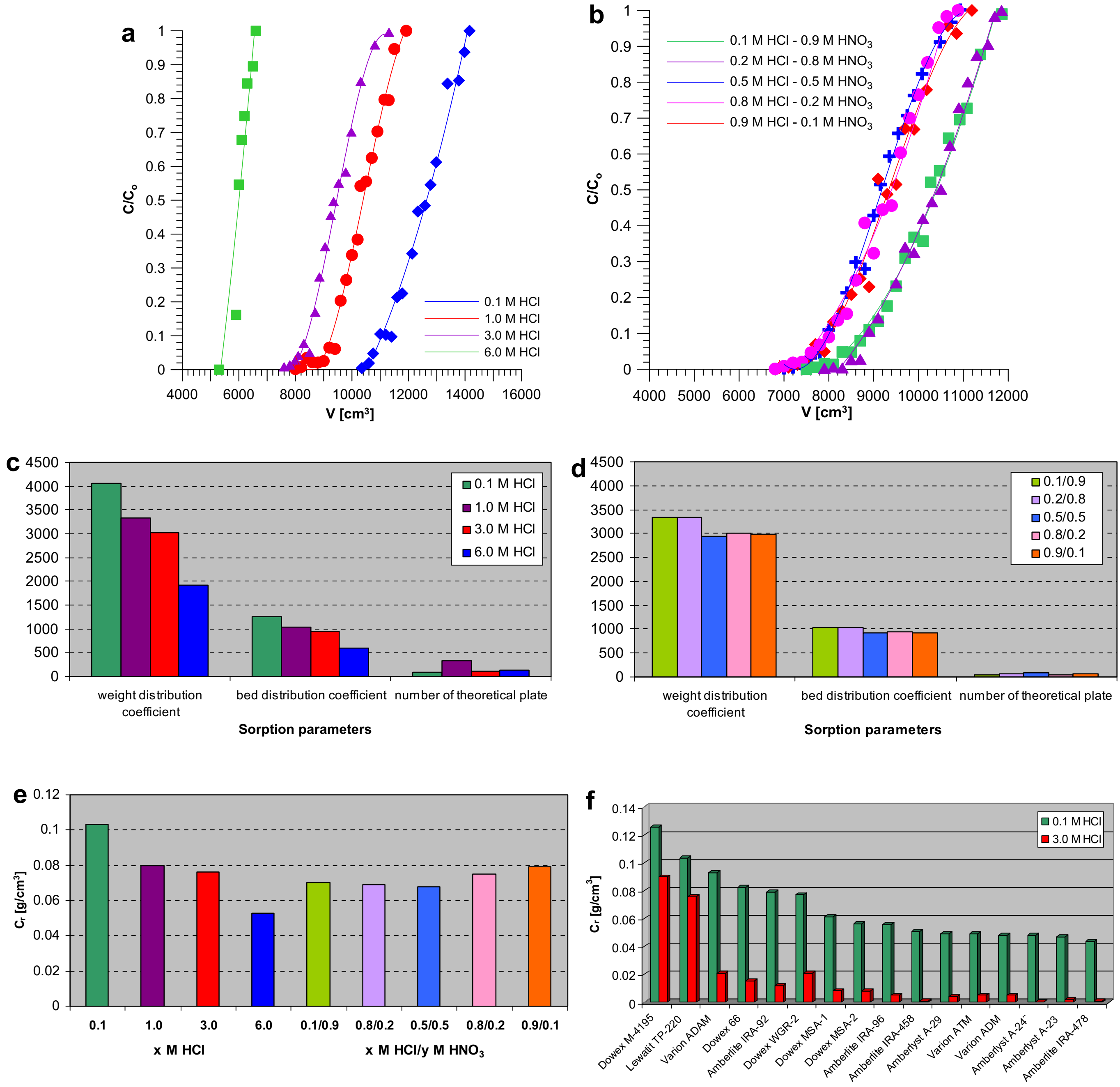


Fig. 4. (a–b) Breakthrough curves and (c–f) sorption parameters obtained for Pd(II) sorption onto Lewatit MonoPlus TP-220.

Fig. 4 shows the series of breakthrough curves obtained from the solutions of different compositions containing hydrochloric acid or the mixture of hydrochloric and nitric acids. As can be seen from Fig. 4a, b, e and f Lewatit MonoPlus TP-220 is a very effective sorbent for Pd(II) removal from the acidic solution. The working ion exchange capacity is in the range from 0.0530 to 0.1035 g/cm^3 and from 0.0680 to 0.0790 g/cm^3 for the HCl and HCl–HNO_3 solutions, respectively. Moreover, based on Fig. 4f, this ion exchanger shows high working ion exchange capacity compared to the other ion exchangers but lower than the resin Dowex M-4195 of the same type containing also the bis(picolylamine) functional groups. Typical tendency in changes of the working ion exchange capacities and the bed and weight distribution coefficients with the increasing concentrations of hydrochloric acid and with the increasing and decreasing concentration of nitric and hydrochloric acids concentrations, respectively were observed (decrease – the HCl system, the increase – HCl – HNO_3 system) (Fig. 4c–e). What is worth emphasizing is the fact that the sorption parameters, particularly the C_e values decrease with the hydrochloric acid concentration increase but the reduction of capacity is much lower compared to the other ion exchangers e.g. Lewatit MonoPlus TP-220 capacity reduction is of about 26.6%, whereas for Dowex M-4195 of about 28.6%. Compared to the other ion exchangers the reduction of the working ion exchange capacity is much higher and is in the range from 72.8% to 99%. These results indicate that the resins under discussion possess a negligible smaller capacity C_r than Dowex M-4195, but on the other hand, the reduction of capacity is negligibly smaller for this resin, therefore it can be used in the solution with higher HCl concentration with good results. It is worth mentioning that with the high acid concentration the stability of the resin should be checked to be sure that the destruction of the resin is excluded.

The SEM and AFM analysis of the ion exchange resin and the surface morphology of Lewatit MonoPlus TP-220 before and after the Pd(II) sorption process confirmed that the sorption process takes place on the ion exchange resins. Making comparison between the AFM picture before and after the Pd(II) sorption it can be concluded that after the sorption process the surface seems to be smoother than before. In this case the AFM picture after the Pd(II) sorption process possesses the regions where the porous structure becomes visible to a smaller extent. The pores are blocked and become shallower. It must be highlighted that it is difficult to show the same two pieces of ion exchange resin surface before and after the sorption process, therefore sometimes the changes of the surface morphology cannot be easily observed.

3.5. Desorption and reused test of Lewatit MonoPlus TP-220

The batch desorption experiments were performed as follows: Lewatit MonoPlus TP-220 previously exposed to a noble metal ions (Pd(II), Pt(IV), Au(III)) containing solutions (initial concentration of single metal ions was 100 mg/dm^3) was contacted with 50 cm^3 of a proper eluting agent for 2 h. After that time the phases was separated and the second sorption was carried out. The sorption–desorption cycles (S1-D1-S2-D2-S3-D3, where S-means the sorption and D – the desorption process and the number indicate the following steps of sorption or desorption, respectively) were repeated threefold. The metal ion concentrations in the eluent solution were analyzed with the AAS method. As eluting agents there were applied: hydrochloric, nitric and sulfuric acids of 0.1–6.0 M HCl, 0.1–4.0 M HNO_3, 0.1–4 M H_2SO_4 concentration, respectively as well as the ammonia (0.5–4.0 M NH_4OH), sodium hydroxide and thiourea and acidic thiourea (0.1 M TU, 0.1 M TU – 0.1 M HCl, 0.1 M TU – 0.1 M HNO_3) solutions. Time 2 h was higher than that required to reach equilibrium by the ion exchanger-eluting agent system. The desorption and sorption efficiency was calculated after all steps. The main observations and conclusions are presented below:

- The sorption process efficiency in the first step was effective, in most cases nearly quantitatively, particularly in the case of palladium(II). The removal of palladium(II) was higher than 99.9% whereas the platinum(IV) and gold(III) removal was about 99.3% and 97.91%, respectively. These results are compatible with the selectivity series written previously based on the batch methods: Pd(II) > Pt(IV) > Au(III).
- The sorption process efficiency for palladium(II) is high in the second and third steps as in the first sorption steps (%S2, %S3 higher than 99%) in all cases without sorption when as the eluting agent was acidic thiourea. Pd(II) %S decreases to 75.66–77.88% (S2), 68.49–71.05% (S3). For platinum(IV) sorption efficiency in S2 and S3 steps decrease in all cases despite the eluting agents used, but the reduction is small (from 1% to 7% for acids, ammonia and sodium hydroxide applied as the eluting agent) or higher (16–19% for thiourea and acidic thiourea regeneration solutions). %S2 decreases to 80.88–84.43% and %S3 decreases to 84.6–98.95%. In the systems containing gold(III) slightly different observation was made. The %S2 and S3 efficiency is at the level similar to that in the first sorption step, is negligibly higher or slightly smaller than %S1. In the sorption–desorption cycle in which the thiourea (0.1 M TU) and acidic thiourea (0.1 M TU – 0.1 M HCl, 0.1 M TU – 0.1 M HNO_3) solutions were applied as the regeneration agents sorption of gold(III) in the second and third steps is really small.
- Desorption % yields of selected noble metals under discussion are different for Pd, Pt, and Au for the same eluting agents. As results from Fig. 5 the acids are not effective eluting agents. The desorption of all noble metals is small and close to 0, particularly for Pd(II) and Pt(IV). Slightly higher desorption yields are achieved for gold(III), but these results are not still satisfactory (%D > 0 and <20%).
- Thiourea and acidic thiourea solutions make the quantitative gold(III) removal, whereas Pd(II) and Pt(IV) desorption is <41% and decreases with the desorption cycles increase. Moreover, after the first desorption cycle, another gold sorption is not observed.
- Ammonia solutions are the most effective eluting agents of those under discussion for Pd(II), Pt(IV) and Au(III). In the three cases the regeneration of resins was high and reached about 70% in some cases.
- Platinum can be effectively eluted by the sodium hydroxide solutions. Desorption by means of 4 M NaOH gives 71% recovery of Pt(IV) in D1, whereas the recovery of Pd(II) and Au(III) is small and equal to 0.09% and 1.66%, respectively.

As the literature data show the noble metals under discussion can be desorbed by means of different techniques, eluting agents with different efficiency. Gold can be removed from the loaded ion exchangers either via a chemical reaction or by displacement. The gold cyanide complex sorbed onto resin is decomposed and the cationic species of gold are formed and removed from the resin (chemical reaction) or the eluant which displays high affinity for the resin is applied for gold removal (displacement method). In the presence of thiourea, the aurocyanide complex is unstable in the acidic solution which results in forming a cationic gold thiourea complex ($Au[CS(NH_2)_2]_2^+$, $\beta_2 = 2 \times 10^{32}$) and hydrocyanic acid (HCN) [38]. Similarly, gold desorption was obtained by Jermakowicz-Bartkowiak and Kolarz [39] who quantitatively desorbed gold(III) from weak base anion exchange resin with aminoguanidyl functional groups using the 5% TU + 0.1 M HCl, but the authors did not observe the lack of sorption of gold in the next sorption cycles. Additionally, as was observed by Campos

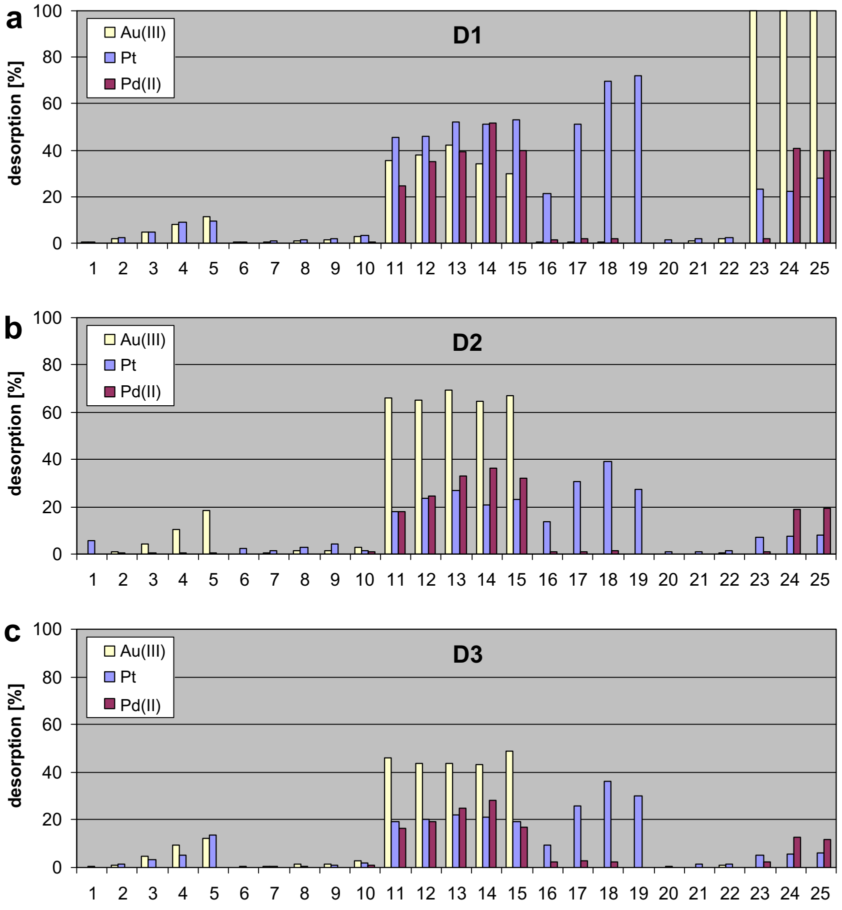


Fig. 5. Desorption % yield of Pd(II), Pt(IV) and Au(III) from Lewatit TP-220 (1–0.1 M HNO_3; 2–1.0 M HNO_3; 3–2.0 M HNO_3; 4–3.0 M HNO_3; 5–4.0 M HNO_3; 6–0.1 M HCl, 7–1.0 M HCl, 8–2.0 M HCl, 9–3.0 M HCl, 10–6.0 M HCl; 11–0.5 M NH_4OH, 12–1.0 M NH_4OH; 13–2.0 M NH_4OH, 14–3.0 M NH_4OH; 15–4.0 M NH_4OH; 16–0.5 M NaOH, 17–1.0 M NaOH, 18–2.0 M NaOH, 19–3.0 M NaOH, 20–0.5 M H_2SO_4, 21–2.0 M H_2SO_4, 22–4.0 M H_2SO_4, 23–0.1 M TU, 24–0.1 M TU – 0.1 M HCl, 25–0.1 M TU – 0.1 M HNO_3).

et al. [40] the desorption of gold was not satisfactory using nitric acid (6 M HNO_3 – %D – close to 20% after 2 h, in our cases using 4 M HNO_3 %D was from 11.5% to 18.60% after 2 h) and significantly faster than the sorption process (after 2 h 93% of gold was desorbed whereas the sorption needs 48 h). It was possible but we have not examined the effect of phases contact time on the % of desorption, but similar to Campos et al. [40] we also obtained 100% elution after 2 h, but in our cases the sorption was much faster than 48 h. The fast desorption is explained in different ways e.g. Michard et al. [41] postulated that uranium ions adsorbed on silica gel as polynuclear species and desorbed in the form of mononuclear species result in the decrease of ionic size of diffusing species, Alguacil et al. [42] indicate a dual mechanism during the gold desorption by acidic thiourea solution (Lewatit MP-64) in which gold(III) is reduced to gold(I) and then complexed with thiourea which is released to the bulk solution. The elution reaction can be presented as follows:

$$R_4N^+AuCl_4^- + 2TU \rightarrow R_4N^+Cl^- + Au(TU)_2^+Cl^- + Cl_2 \qquad (11)$$

In our case due to the chelating mechanism of Pd(II) binding onto Lewatit MonoPlus TP-220 the second explanation seems to be more appropriate, but not quite certain. To explain this fact additional studies should be carried out. As mentioned by Jermakowicz-Bartkowiak et al. [43] during the gold(III) sorption onto resin with guanidine ligand incorporation into the VBC/DVB copolymer the existence of reduced form of gold e.g. Au(I) was ruled out (AuCl species participation was 14% only, changes of the colour of the resin surface on yellow-green was not observed and the XPS analysis did not confirm the existence of metallic gold Au(0)). Gold(III) desorption using HCl solutions of different concentrations was not satisfactory. It was comparable with other results obtained e.g. by Pilśniak et al. [44].

Desorption of palladium(II) ions by HCl solutions was lower than 50–60% (0–5 M HCl, imidazol containing resin)) [35], 0% (1–12 M HCl, PUFIX – strong base anion exchanger) [45], 5.28–9.62% (0.5–3.0 M HCl, glycine modified chitosan) [46], 3.18–6.74% (0.5–5 M HCl, lysine modified chitosan) [47] and there was small similarity to our results. Higher regeneration was obtained by means of HNO_3 and ammonia solutions, comparable to [48,49] (4–14 M HNO_3, 30–96%, Pd(II) desorption from activated carbon; 1–10% NH_3, >80–100%, Pd(II) desorption from Amberlite IRA-93). Many other desorption agents and results can be found in literature not only for the Pd(II) desorption but also Pt(IV), e.g. [35,45–47,50,51].

3.6. Isotherm studies

The equilibrium studies were carried out and the isotherm for Pd(II) at different temperatures were obtained (initial Pd(II) concentration was in the range from 200 to 14,000 mg/dm^3). The Langmuir and Freundlich isotherm parameters at different temperature were obtained (using Eqs. (9) and (10) included in Table 2 in [3]) and presented in Table 6 in comparison to isotherm parameters for Dowex M-4195. Based on the obtained parameters and determination coefficients it can be concluded that for Lewatit MonoPlus TP-220 any Langmuir any Freundlich models fits well the experimental data. The determination coefficient is higher for the Lang-

Table 6
Isotherm parameters obtained for Lewatit MonoPlus TP-220 at different temperature.

Isotherm model	Parameters	Temperature (K)					
		Dowex M-4195			Lewatit MonoPlus TP-220		
		Ambient	308	318	Ambient	313	333
Langmuir	Q_0 (mg/g)	342.3	342.3	338.4	837.0	963.8	939.3
	b (dm^3/mg)	0.118	0.118	0.109	0.006	0.004	0.004
	R_L	0.017	0.017	0.018	0.641	0.710	0.709
	R^2	0.999	0.999	0.999	0.953	0.936	0.921
Freundlich	K_F (mg/g)	92.6	92.6	89.34	115.4	102.3	106.2
	$1/n$	0.207	0.207	0.210	0.243	0.268	0.260
	R^2	0.691	0.691	0.665	0.616	0.700	0.679
Ref. [3]					This paper		

muir model but still not satisfy (0.921–0.953). In all cases published previously e.g. [3,25] such situation was not observed, and the Langmuir model fitted very well the experimental data. This facts found also confirmation in curve course (not presented here) which is different – continuously increase of q_e values is observed and the curve did not achieved the equilibrium. Maybe mixed Langmuir–Freundlich isotherm should be applied in this case or other one. Making comparison between Lewatit MonoPlus TP-220 and Dowex M-4195 ion exchange resins the first one possess higher total Langmuir capacity at all presented temperature. The total sorption capacity is higher for 313 K but smaller for 333 K.

3.7. Future studies

The column studies for Pt(IV) and Au(III) as well as the sorption of metal ions from the three component mixture solution containing the noble metal in different metal ratio (batch method) are in progress. Preliminary studies suggested that the selectivity series obtained by means of column studies will be different from that in batch studies and indicate that in the tertiary solutions the ion exchange resin sorbed the metal ions without preference to one of them.

4. Conclusions

From the results of the present study, it is concluded that, the sorption process is very effective for all noble metal ions. The selectivity series can be presented as follows: Pd(II) > Au(III) > Pt(IV) (batch method). The resin shows also high affinity for copper(II) ions and the selectivity series for base metals are following: 0.1 M HCl: Cu(II) > Zn(II) > Co(II) ≈ Ni(II), 1.0 and 3.0 M HCl: Cu(II) > Zn(II) > Ni(II) ≈ Co(II), 6.0 M HCl: Zn(II) ≈ Cu(II) > Co(II) > Ni(II), 0.1 M HCl – 0.9 M HNO_3, 0.2 M HCl – 0.8 M HNO_3, 0.5 M HCl – 0.5 M HNO_3: Cu(II) > Co(II) > Ni(II) > Zn(II), 0.8 M HCl – 0.2 M HNO_3, 0.9 M HCl – 0.1 M HNO_3: Cu(II) > Co(II) > Zn(II) > Ni(II). Moreover, the resin is characterized by good kinetics – the time required to reach equilibrium is attained after 60, 120, 180 and 240 min for base metals whereas in the case of Pd(II), Pt(IV) and Au(III) was in the range 5–120 min. Kinetic studies show that PSO fits well the experimental data (high determination coefficient, good correlation between sorption capacity obtained experimentally and calculated from the PSO equation). Desorption of loaded resin by noble metals is possible and in some cases satisfactory, but the elution of Pd(II) needs improvement. The AFM and SEM studies confirmed the porous structure of Lewatit MonoPlus TP-220 and the spherical shape of the resin beads. This resin seems to be promising in application, but the future studies are needed and they are in progress.

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