Recovery of platinum group metals using magnetic nanoparticles modified with ionic liquids

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ABSTRACT

The development of a principally new approach to preparation of IL-modified magnetic nanoparticles and their application as sorbent materials for recovery of platinum group metals from model technological solutions are described. The formation of Fe_3O_4 nanoparticles, their simultaneous coating with a polymer shell and an ionic liquid are implemented in aqueous biphasic systems by a single step synthesis. Different ionic liquids have been tested as modifying agents: Cyphos® IL 101, Cyphos® IL 110, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-octyl-3-methylimidazolium hexafluorophosphate. The prepared magnetic nanoparticles have been characterized by scanning and transmission electron microscopy, X-ray diffraction, thermogravimetric analysis and applied as sorbents for magnetic solid-phase extraction of platinum metals from chloride solutions. The results indicate that the recovery of the platinum metals from (0.1 M HCl + 1 M NaCl) solution is 99% for Pd(II) and 98% for Pt(IV) within 30 min and their quantitative stripping can be achieved using 2 M HNO_3 solution.

1. Introduction

Magnetic nanoparticles (MNPs), along with their numerous applications, have received much attention as sorbent materials in separation and purification processes [1-6]. The simplicity of producing and modifying MNPs, their high active surface area, fast kinetic properties, and easy manipulation under an external magnetic field make them suitable for solid-phase extraction of various biomolecules, organic compounds, metal ions, and other inorganic species. The selectivity towards target analytes depends on the active functional groups, which could be chemically or physically grafted on the core-shell structure of MNPs [7]. For these purposes different reagents including ionic liquids (ILs) have been used.

A number of recent studies devoted to combination of MNPs and ILs have demonstrated an improved selectivity and efficiency of separation and preconcentration for a broad range of analytes [8-12]. It became possible owing to the unique features of ILs, the crucial of which are the tunable nature and the ability to a wide variety of interactions (ion exchange, complex forming, hydrogen bonding, hydrophobic and π-π interactions, etc.). The most of the mentioned publications describe the IL attaching to the MNPs based on magnetite nanoparticles (Fe_3O_4). The procedure is usually carried out in three steps including the synthesis of Fe_3O_4, its coating with silica or another kind of shell, and finally the IL

grafting or the synthesis of IL directly on the surface of the coated magnetic core [1]. The most of the prepared magnetic sorbents were applied to separation/analysis of organic compounds and biomolecules, for example, anionic dyes adsorption from industrial effluents [13], determination of plant growth regulators in vegetable samples [14], the extraction of α–chymotrypsin from porcine pancreas crude extract [15], the extraction of the nonsteroidal anti-inflammatory drugs (NSAIDs) from blood samples [16], analysis of human plasma for antidiabetic drugs [17]. Several works are devoted to extraction of metal ions, for examples, Cr(VI) [11] and Pb(II) [18,19]. There is almost no data on platinum metal recovery using IL-modified MNPs.

The novelty of the present work consists in the development of a principally new approach to preparation of IL-containing MNPs and their application as sorbent materials for recovery of platinum metals from technological solutions. The task of selective extraction of platinum metals is the most difficult stage of sample preparation and very important for determination of these metals in samples of complicated composition [20]. The suggested approach involves the use of aqueous biphasic systems based on a water-soluble polymer poly(ethylene glycol) (PEG) and an inorganic phase-forming salt. IL is introduced into the system during the magnetite formation ensuring the simultaneous coating of MNPs with PEG and functionalization with IL active groups.

Different types of ILs were studied as coatings for MNPs for solid-

phase extraction of platinum and palladium. To solve the problem, the phosphonium IL Cyphos® IL 101 was chosen as most efficient one. The prepared magnetic sorbents $Fe_3O_4@PEG@IL$ were characterized by different instrumental techniques and applied to platinum metal separation from model chloride solutions.

2. Materials and methods

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, purity 98%), sodium hydroxide (NaOH, 50 wt%), hydrochloric acid (HCl, 35–38 wt%), nitric acid (HNO_3, 65 wt%), sodium chloride (NaCl, purity 99%), tetraethoxysilane ($C_8H_{20}O_4Si$, purity 98%), ammonium hydroxide solution ($NH_3 \cdot H_2O$, 25 wt%) from Component-reactive (Russia); ammonium sulfate (($NH_4)_2SO_4$, purity 99%), thiourea (Thio, CH_4N_2S, purity 98%) from Vekton (Russia); ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, purity 98%) from Panreac (Spain); ethanol (C_2H_5OH, 95 wt%) from Medhimprom (Russia); poly(ethylene glycol)-4000 (PEG-4000, purity 99%), Cyphos® IL 101 (purity 95%), Cyphos® IL 110 (purity 98%) from Fluka (Switzerland); 1-butyl-3-methylimidazolium hexafluorophosphate ($BMImPF_6$, purity 98%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($BMImTf_2N$, purity 98%), 1-octyl-3-methylimidazolium hexafluorophosphate ($OMImPF6$, purity 97%) from Sigma-Aldrich (Germany); platinum, palladium, rhodium, gold, copper, nickel standard solutions for ICP (purity 99%) from Merck (Germany) were used without further purification. The structure and names of the used ILs are given in Table 1.

2.2. Synthesis of the magnetic sorbent $Fe_3O_4@PEG@IL$

The single step synthesis of MNPs, including their coating and functionalization, was implemented at the liquid–liquid interface in the aqueous biphasic system formed by a water-soluble polymer (PEG-4000, 25 wt%) and a phase-forming salt (ammonium sulfate, 25 wt%). The precursors of magnetite (the mixture of 0.1 M and 0.06 M $FeCl_3$ and $FeCl_2$ correspondingly) were injected into the polymer solution, while 0.93 M NaOH was mixed with the phase-forming salt solution. The weighted amounts of IL were dispersed in both polymer and salt solutions, and treated with ultrasound. After that, the polymer phase was carefully layered onto the salt phase. For a volume of 50 mL of the prepared system it was necessary to use the beaker with a diameter of 70 mm. The MNPs were formed at the PEG-4000 – ($NH_4)_2SO_4$ interface. The MNPs were easily separated from the system using a Nd magnet, washed several times with deionized water and finally dried under vacuum at 55 °C for 5 h.

$Fe_3O_4@SiO_2@IL$ sorbent was also used in this work for comparative evaluation of sorption characteristics. To prepare this sorbent magnetite NPs were synthesized by conventional precipitation way and coated with silica using the Stöber method [21]. The obtained $Fe_3O_4@SiO_2$ NPs were modified with IL in ethanol solution as described in [22].

2.3. Characterization of $Fe_3O_4@PEG@IL$

Scanning electron microscopy (SEM). The samples of MNPs

suspension were examined using a JEOL JSM6700F scanning electron microscope (Japan) equipped with a field emission cathode. An initial MNPs suspension was previously applied onto a cleaned polished silicon substrate, which gave a better contrast in observing individual MNPs particles.

Transmission electron microscopy (TEM). Before measurements, the samples were mounted on a 3-mm copper grid covered with a carbon film taken from isopropanol suspension. Sample morphologies were studied using a Hitachi HT7700 transmission electron microscope. The images were acquired in a bright-field TEM mode at 80 or 100 kV accelerating voltage.

X-ray diffraction (XRD). The samples of MNPs were characterized by a Bruker D8 Advance X-ray Diffractometer using a ($CuK\alpha1$) = 1.5418 Å) Ni-filter (E = 40 keV, I = 40 mA, signal accumulation time 0.3 s/point, step 0.02°).

Thermo-gravimetric analysis (TGA). A dried sample (10 mg) was placed in a TGA furnace SDT Q-600 and the measurements were carried out under an air flow of 250 mL/min with a heating rate of 10 °C/min from 20 °C to 1000 °C.

2.4. A batch solid-phase extraction procedure

5–50 mg of the $Fe_3O_4@PEG@IL$ MNPs were equilibrated with 5–10 mL of metal ion solution after adjusting to various acidities using an orbital shaker (SkyLine ELMI S-3.02L.A10) at 200–250 rpm in 15 mL tubes for 5–60 min. The concentration of Pt(IV) and Pd(II) ions in solution was $2.5 \cdot 10^{-5} – 1.5 \cdot 10^{-4}$ mM. The MNPs were separated from solution by a Nd magnet. The desorption of extracted metal ions was carried out by contacting the MNPs after solid-phase extraction with 2–3 mL of eluent solution for 15 min.

2.5. Determination of platinum metals

The concentrations of metal ions in solutions were determined using a iCAP 6500 Duo inductively coupled plasma atomic emission spectrometer (ICP-AES) from Thermo Fisher Scientific (USA), equipped with a SeaSpray nebulizer, a Spray Chamber Assembly and a quartz torch.

3. Results and discussion

3.1. Synthesis of magnetite nanoparticles, their functionalization with IL and characterization

Aqueous biphasic systems based on water-soluble polymers are well known as unique «green chemistry» extraction systems with a number of advantages over conventional organic solvent-based ones [23,24]. There are some physicochemical features of the aqueous biphasic systems which allow to consider them as the media for synthesis of nanoparticles [25]. The interface between the polymer and the aqueous phase-forming salt represents a uniform Langmuir layer of polymer molecules. The value of a potential jump depends on the composition of the system and on pH. The existence of such a layer makes the transport of ions, containing in the system, to occur through the oriented channels, and the interactions of ions take place at this interface. In our previous work [26], the possibility of the synthesis of magnetite particles (with sizes from 200 nm to 10 μm) was demonstrated on an example of the PEG 3000-ammonium sulfate system. It was found that the particles can be produced only at a certain sequence of reagents addition into the system. In the present work, the method was advanced with the IL injection during the magnetite formation to prepare the novel type of magnetic sorbents. It has been experimentally proved that the precursors should be introduced into the PEG phase, while the IL is necessary to be injected into both phases. The contacting of two solutions leads to the formation of an aqueous biphasic system and production of the nanoparticles at the interface layer.
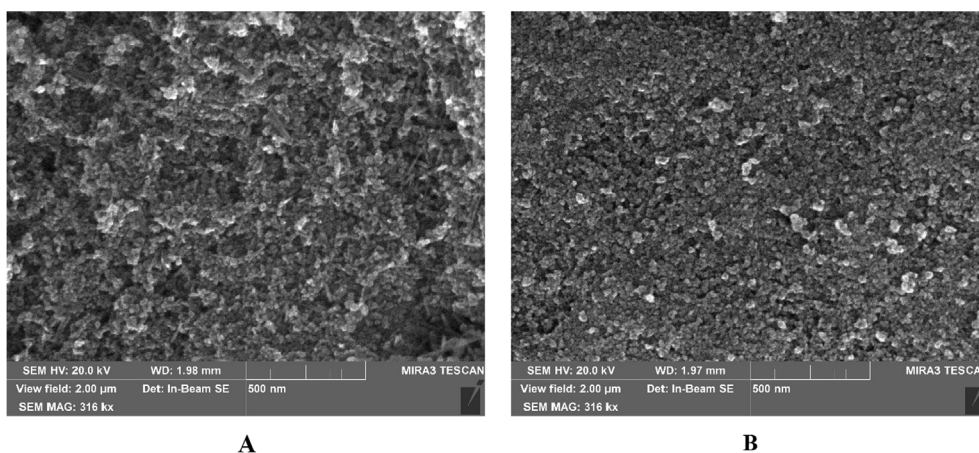
The SEM images of non-modified and IL-modified $Fe_3O_4@PEG$

Table 1
The studied ILs.

IL type	Cation structure	Anions	IL name / abbreviation
Imidazolium	$H_{13}C_6 \overset{C_6H_{13}}{\underset{C_{14}H_{29}}{\overset{\oplus}{P}}} C_6H_{13}$	PF_6^-	$BMImPF_6$ (R = C_4H_9)
		Tf_2N^-	$BMImTf_2N$ (R = C_4H_9)
		PF_6^-	$OMImPF_6$ (R = C_8H_{17})
Phosphonium	$CH_3 \sim N \overset{\oplus}{\underset{N}{\frown}} R$	Cl^-	Cyphos® IL 101
		PF_6^-	Cyphos® IL 110

Fig. 1. SEM images of Fe$_3$O$_4$@PEG nanoparticles (A) and Fe$_3$O$_4$@PEG@Cyphos® IL 101 nanoparticles (B).

nanoparticles (for Cyphos® IL 101 as modifying IL) are presented at Fig. 1. As could be seen the modification of the nanoparticles with IL provides a more homogeneous composition and a narrow size distribution.

The TEM images given at Fig. 2 are indicative of the nanoscale sizes of the prepared magnetic sorbents and the presence of the shell: the average diameter of the nanoparticles is 8–18 nm, the average shell thickness is 2–3 nm.

The XRD spectrum of the IL-modified Fe$_3$O$_4$@PEG nanoparticles (Fig. 3) is almost the same as that for IL-modified Fe$_3$O$_4$ confirming the magnetite structure of the prepared MNPs.

Fig. 4 represents the TGA plots of a multistep thermal

decomposition of Fe$_3$O$_4$@PEG 4000 Fe$_3$O$_4$@PEG@Cyphos® IL 101 nanoparticles. The weight loss below 120 °C for both samples is about of 2.0% and can be attributed to the removal of physically adsorbed water. The weight loss 5.5% between 200 and 550 °C for non-modified nanoparticles (Fig. 5A) corresponds to the endothermic effect due to removal of PEG 4000 molecules. The further weight loss beyond

550 °C can be associated with the phase transformation of magnetite nanoparticles. For IL-modified nanoparticles the exothermic effects could be observed with maxima at 300 and 366 °C (Fig. 5B) accompanied by the weight losses of 2% and 5% respectively. These effects are evidently due to oxidation of the organic components, i.e. IL. A further increase in temperature up to 1000 °C resulted in a slight mass
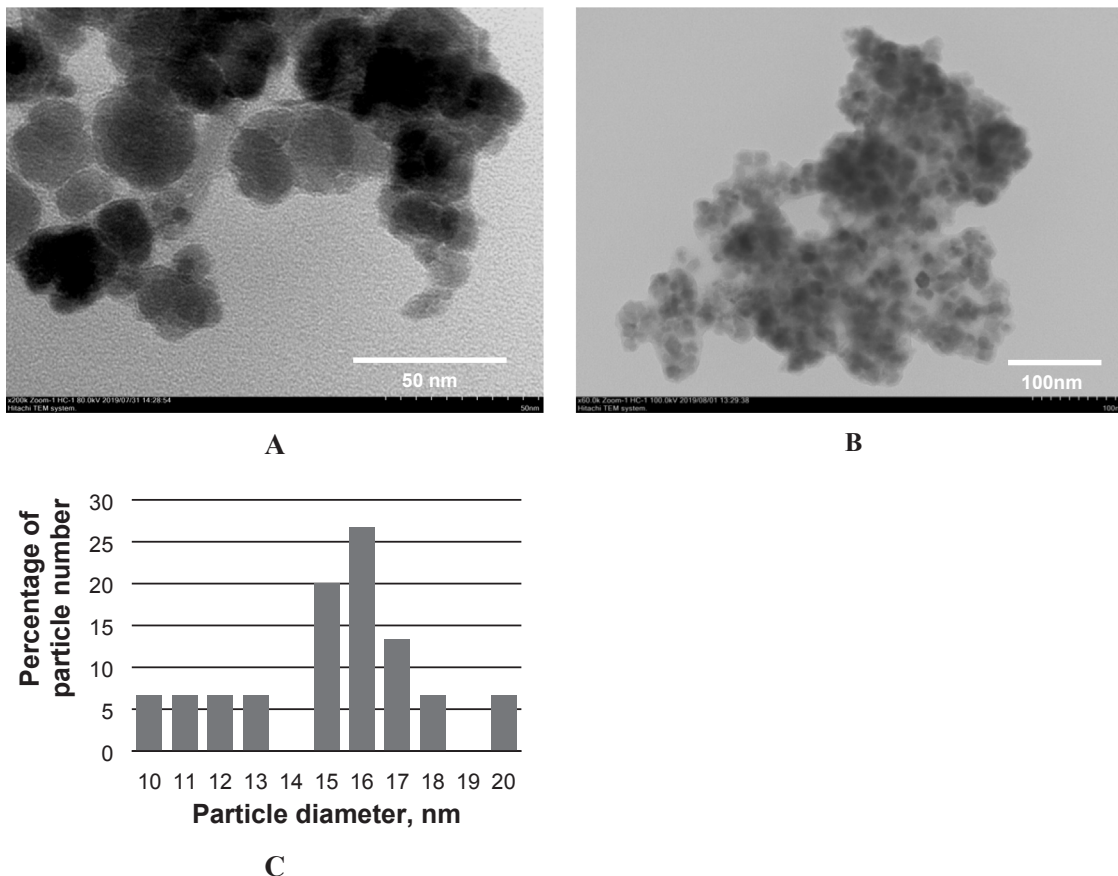

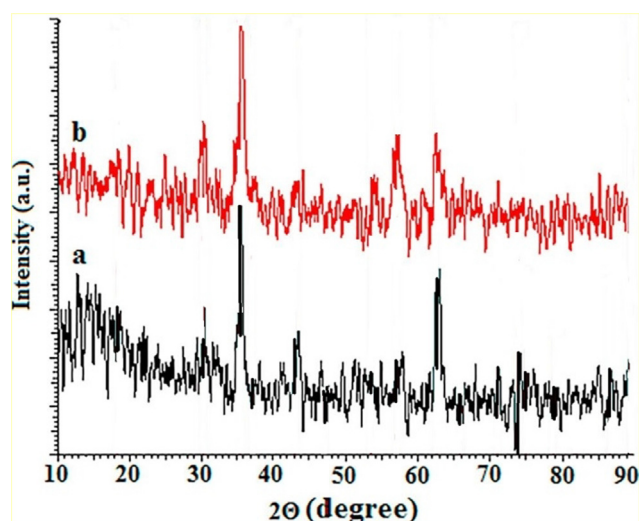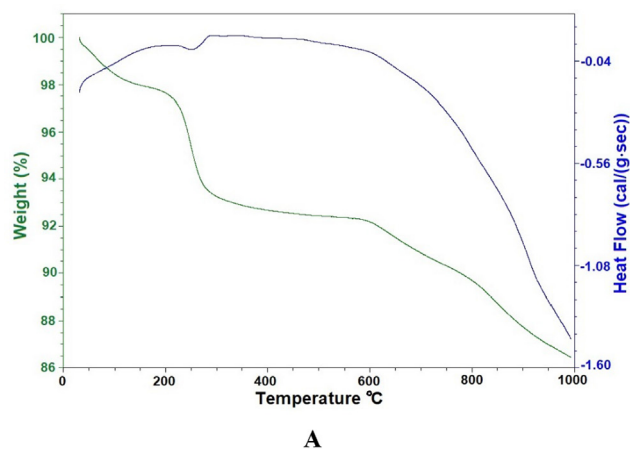**Fig. 2.** TEM images of Fe$_3$O$_4$@PEG@Cyphos® IL 101 nanoparticles (A, B) and their size distribution (C).
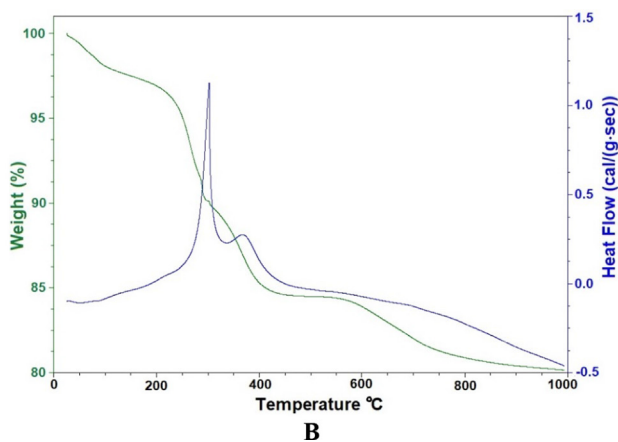
Fig. 3. XRD patterns of Fe_3O_4 (a) and Fe_3O_4@PEG@Cyphos® IL 101 (b) nanoparticles.

A

B

Fig. 4. The thermal analysis of Fe_3O_4@PEG nanoparticles (A) and Fe_3O_4@PEG@Cyphos® IL 101 nanoparticles (B) in air flow.

loss, which can be attributed to residual carbon oxidation and the phase transformation of magnetite nanoparticles.

The modification of the magnetite with IL gives additional advantages which are especially useful for the solid-phase extraction application. It's known that magnetite dissolves in acidic media, while the IL-modified Fe_3O_4 nanoparticles are stable in acid solutions such as hydrochloric and nitric ones until a molarity of at least 1 and 2 M correspondingly. Therefore, the prepared magnetic sorbents with PEG
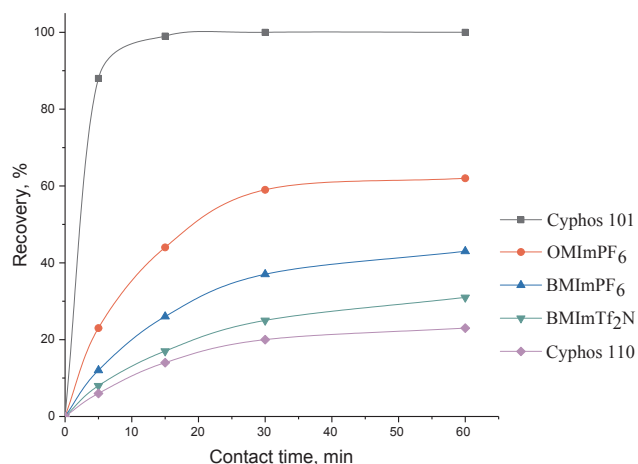

Fig. 5. Recovery of Pd(II) by MNPs coated with different types of ILs: 0.1 M HCl, solution volume 5 mL, sorbent mass 0.02 g, IL content 0.05–0.2 mM/g.

and IL functional groups could be used for solid-phase extraction of a wide variety of analytes from both neutral and acidic media. In the present work we have selected the optimal conditions for recovery of platinum(IV) and palladium(II) from hydrochloric acid solutions (which are typical for separation of platinum metals) using the Fe_3O_4@PEG@IL MNPs, where different phosphonium and imidazolium ILs were tested.

3.2. Solid-phase extraction of platinum metals

There are a lot of sorbents including IL-based ones for recovery of platinum group metals from various solutions [27]. These sorbents are usually synthesized by impregnation of solid supports (such as silica, polystyrene copolymers and others) with phosphonium or imidazolium type ILs [22,28]. There is the publication on the synthesis of magnetic sorbent through chemical grafting task-specific ILs to the core-shell magnetic structure [12].

3.2.1. The effect of IL structure

We studied the influence of the IL composition on the solid-phase extraction of platinum metals using the listed in Table 1 phosphonium or imidazolium ILs as coatings for MNPs. Taking Pd(II) recovery as example (Fig. 5), one can see that both cation and anion structure impact on the extraction capability of the IL-coated MNPs. It is known that the hydrophobicity is one of the most important characteristics affecting the IL retention on a solid support [28]. The more hydrophobic IL, the less its leakage from the support. At the same time, too hydrophobic nature of IL reduces its solubilization and, accordingly, the sorption activity of IL-coated sorbent. It is evident in the case of Cyphos® IL 110 the recovery of Pd(II) does not exceed 20%. The obtained experimental data demonstrated that imidazolium ILs with the C4-C8 alkyl substitutes in the 1-alkyl-3-methylimidazolium cation are not sufficiently effective for palladium recovery, even though there is a slight difference between ILs with [BMIm]$^+$ and [OMIm]$^+$ cations due to a stronger retention of the last one. The quantitative extraction of palladium was obtained only with the MNPs coated by phosphonium IL with halide anion Cyphos® IL 101. This IL is well studied both for solvent and solid-phase extraction of platinum metals [28-30], and it was selected for the further experiments.

3.2.2. The effect of IL content

The determination of optimal IL content is very important from several points of view. As noted by T. Vincent et al. increasing the IL content is favorable for sorption capacity, but the excess of IL-loading causes detrimental effect on the accessibility and reactivity of
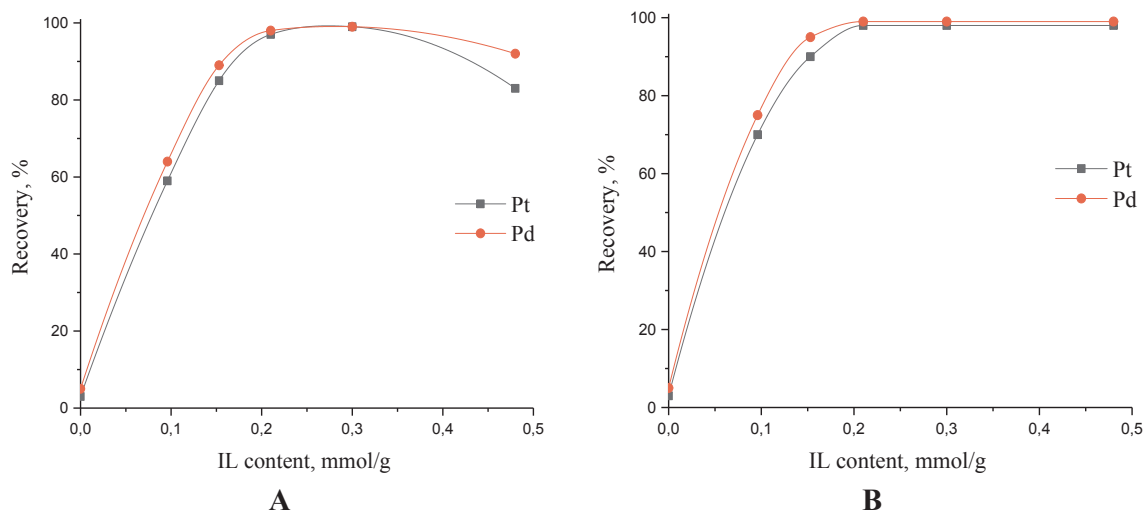
Fig. 6. The effect of IL content on Pt(IV) and Pd(II) recovery: 0.1 M HCl, solution volume 5 mL, sorbent mass 0.02 g, contact time 30 min, Fe$_3$O$_4$@SiO$_2$@Cyphos® IL 101 (A), Fe$_3$O$_4$@PEG@Cyphos® IL 101 (B).

functional groups [31]. It was found that the recovery of platinum(IV) and palladium(II) using magnetic nanoparticles prepared by the conventional precipitation method (Fig. 6A) grows with increasing the coated IL up to the content 0.4 mM IL per 1 g of the sorbent. A further increase in the IL content leads to an increase in hydrophobicity of the sorbent and, as a consequence, to a decrease in sorption activity of the sorbent. A different trend was found for the Fe$_3$O$_4$@PEG@Cyphos® IL 101 sorbent, which retained its sorption activity even with a high content of IL (Fig. 6B). Due to the presence of the PEG shell, the prepared nanoparticles are distinguished by hydrophilic properties in the whole studied range of loaded Cyphos® IL 101 contents. An IL content of 0.2 mM/g was selected as the optimal one for the further experiments.

3.2.3. The effect of acidity and chloride concentration

The acidity of solution is a crucial parameter for platinum group metal extraction. To prevent the hydrolysis of platinum metals and exclude highly concentrated acid solutions, the working range for solid-phase extraction of platinum metals is usually 0.1–1 M HCl. We studied the recovery of Pt(IV) and Pd(II) ions by the Fe$_3$O$_4$@PEG@Cyphos® IL 101 sorbent in this range of HCl concentrations, also in the presence of NaCl. As can be seen from Table 2 the degree of Pt(IV) and Pd(II) recovery in the studied interval is quite high. The presence of additional chloride ions (Cl$^-$) slightly reduces the recovery of metals from 0.5 to 1 M HCl.

3.2.4. The effect of contact time

The kinetic characteristics are determined by the contributions of diffusion processes and the reaction rate. Under the given experimental conditions, the Pt(IV) and Pd(II) extraction is believed to be accomplished through anion exchange between anion chloro complexes of platinum metals and chloride ion of Cyphos® IL 101 [29]. Fig. 7 demonstrates the effect of contact time for IL-modified MNPs prepared by

conventional way (Fe$_3$O$_4$@SiO$_2$@Cyphos® IL 101) and by synthesis in ABS (Fe$_3$O$_4$@PEG@Cyphos® IL 101). As could be seen in both cases Pd (II) recovery is very fast, that is in agreement with the literature data about a significant high reaction rate of Pd(II) extraction by phosphonium ILs [32]. A slight difference is observed for Pt(IV) recovery: the presence of PEG shell provides better kinetics, probably due to a higher hydrophilicity of Fe$_3$O$_4$@PEG@Cyphos® IL 101 particles and, as a consequence, a faster ionic diffusion process. 30 min were chosen as the optimal contact time for both analytes.

3.2.5. Elution experiments

One of the advantages of the IL-modified sorbents is the possibility of elution of platinum metals, which is usually difficult in the case of conventional complexing sorbents. The results of Pt(IV) and Pd(II) elution after their solid-phase extraction by the Fe$_3$O$_4$@PEG@Cyphos® IL 101 sorbent are given in Table 3. Solution of 2 M HNO$_3$ was selected as the most efficient and suitable eluent for the following instrumental determination of platinum metals.

3.2.6. Solid-phase extraction of Pt(IV) and Pd(II) from a model solution

To evaluate the applicability of the synthesized MNPs for platinum metal separation we investigated the solid-phase extraction of Pt(IV) and Pd(II) from solutions, containing other components such as Cu(II), Ni(II), Au(III), Rh(III), which are nearly always accompany platinum and palladium. The selectivity is one of the most important characteristics of the sorbent materials intended to be used for platinum metal refining and their recycling from secondary raw materials. As can be seen from Fig. 8, the solid-phase extraction of Pt(IV) and Pd(II) from model technological chloride solution is not affected by the presence of a 4-fold molar excess of Cu(II) and Ni(II), as well as traces of Rh(III). Under the given conditions Cu(II) and Ni(II) exist in solution in the form of cations, while rhodium forms chloro-aqua complexes, the recovery of those is negligible. The presence of Au(III) in equimolar quantity does not influence Pt(IV) and Pd(II) recovery but is completely extracted along with them. Selective separation of Pt(IV) and Pd(II) ions can be reached under elution with 2 M HNO$_3$ solution.

4. Conclusions

Fe$_3$O$_4$@PEG@Cyphos® IL 101 sorbent was synthesized for magnetic solid-phase extraction of platinum group metals from technological solutions. A single step method has been developed for the synthesis, which includes the formation of magnetite nanoparticles, their coating
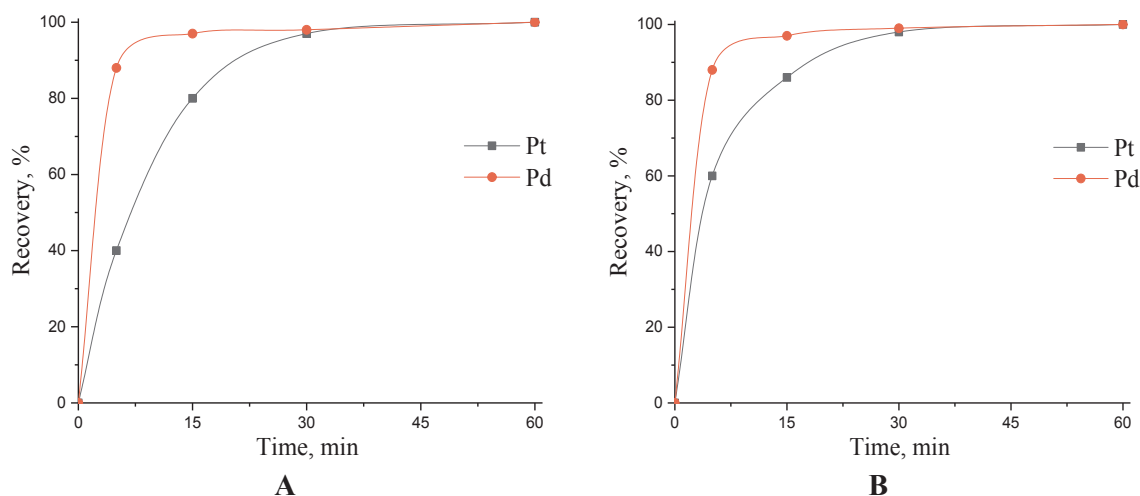
Table 2

Recovery of Pt(IV) and Pd(II) as a function of concentrations of HCl and chloride ions: [Pt,Pd] = $2.5 \cdot 10^{-5}$ mM, solution volume 5 mL, sorbent mass 0.02 g, contact time 30 min, IL content 0.2 mM/g.

[HCl], M	0.1		0.5		1	
[Cl$^-$], M	0	1	0	1	0	1
Recovery of Pt,%	93	92	90	85	88	80
Recovery of Pd,%	95	95	92	88	90	81

Fig. 7. The effect of contact time on Pt(IV) and Pd(II) recovery: 0.1 M HCl, solution volume 5 mL, sorbent mass 0.02 g, IL content 0.2 mM/g, Fe_3O_4@SiO_2@Cyphos® IL 101 (A), Fe_3O_4@PEG@Cyphos® IL 101 (B).

Table 3
Elution of Pt(IV) and Pd(II) with different eluent solutions: eluent volume 3 mL, sorbent mass 0.02 g, contact time 30 min.

Eluent Elution, %	2 M HNO_3	2% Thio in 0.5 M HCl
Pt	98.0	34.3
Pd	98.8	98.2

with polymer shell and modification with IL. The prepared magnetic nanoparticles are characterized by magnetite structure, nanoscale sizes, and the presence of PEG and IL coatings. Fe_3O_4@PEG@Cyphos® IL 101 nanoparticles favorably differ from Fe_3O_4@SiO_2@Cyphos® IL 101 ones and demonstrate a high sorption ability towards platinum and palladium ions in hydrochloric (0.1 M HCl) and chloride (0.1 M HCl + 1 M NaCl) solutions. Selective recovery of Pt(IV) and Pd(II) ions from multi-component solution can be achieved using the prepared IL-modified magnetic nanoparticles and simple elution procedure.

CRediT authorship contribution statement

Olga Mokhodoeva: Conceptualization, Methodology, Writing - original draft. **Valery Shkinev:** Conceptualization, Methodology,

Supervision. **Valeriia Maksimova:** Investigation. **Rustam Dzhenloda:** Investigation, Data curation, Resources. **Boris Spivakov:** Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
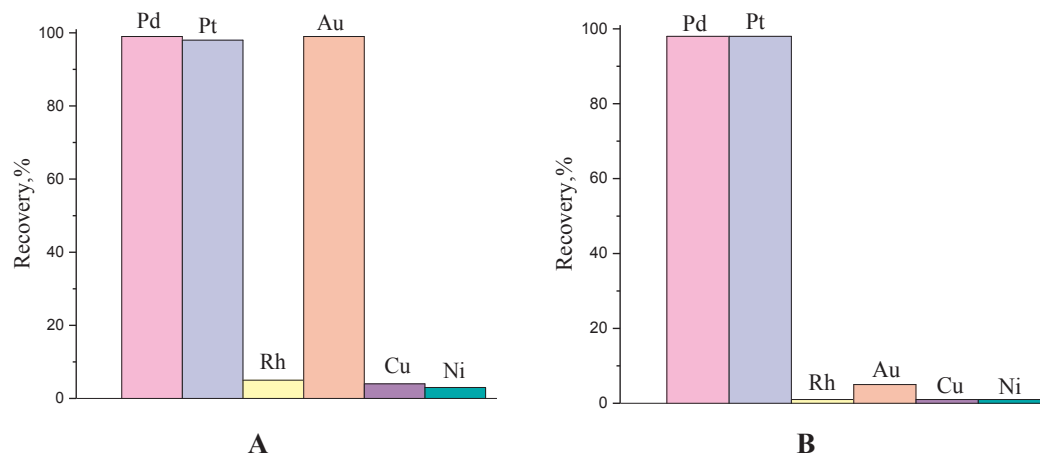
Fig. 8. The recovery of precious metals from the model chloride solution by Fe_3O_4@PEG@Cyphos® IL 101: A) solid-phase extraction: [Pt,Pd,Au] = $1.5 \cdot 10^{-4}$ mM, [Rh] = $3.5 \cdot 10^{-6}$ mM, [Cu,Ni] = 1·mM, 0.1 M HCl + 1 M NaCl, solution volume 5 mL, sorbent mass 0.02 g, contact time 30 min, IL content 0.2 mM/g; B) elution: 2 M HNO_3, eluent volume 3 mL, sorbent mass 0.02 g, contact time 30 min.

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