RECOVERY OF SOME PLATINUM GROUP METALS BY ADSORPTION ON MATERIALS WITH GUIDED FUNCTIONALITY

PhD Thesis – Summary

For obtaining the scientific title of PhD at
Politehnica University Timișoara
In the fields of PhD chemical engineering
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28 January 2022

The doctoral thesis is structured in two parts, containing 8 chapters and 231 pages.

In the first part of the thesis (2 chapters) was performed the literature study, to establish the current state of knowledge in the field of synthesis, characterization and application of new materials to recover PGEs from aqueous solutions.

The Platinum Group Elements (PGE) or Platinum Group Metals (PGM), are six metal elements grouped together in the periodic periodic table of the elements in Groups 8, 9, and 10 and periods 5 and 6 [1]. These metals are concentrated not only at the great depths of the Earth but also in its mantle and tend to appear together in the same mineral deposits, having similar physical and chemical properties [2].

The natural reserves of PGE are rare and spread, being around 31.000 tons. From the total reserves, 81 tons are palladium, 14.000 tons [3] are platinum and 3000 tons are ruthenium [4]. In Crust Earth the concentrations of PGE is about 0,001% and are mostly found in the countries like South Africa, Russia and Zimbabwe [5].

Due to their unique physical and chemical properties, the PGE is used in a variety of industrial products (manufacture of catalytic conversion systems used to reduce emissions of carbon monoxide, hydrocarbons or nitrogen oxides from the exhaust of vehicles) and chemical reagents (catalytic sieves of platinum or platinum-rhodium alloys for the production of nitrogen oxides in the nitric acid production process, raw material used for the manufacture of fertilizers and explosives, refining of crude oil and producing aromatics and high octane ratings) [6]. PGEs are also required in a variety of commercial, industrial, medical and military applications, as well as for a range of existing and emerging technologies such as computer hard drives, hybrid integrated circuits, multi-layer ceramic capacitors, thermocouples, thermoresistors, etc.

Economic, political, environmental and social events could disrupt the availability and accessibility of the PGEs [7]. However, global production of PGEs has been steadily increasing since the years 70 and are increasingly used in various applications [8].

Due to the exponential growth in recent decades of the use of PGEs, their biogeochemical cycle is often disrupted by anthropogenic actions [9]. Numerous studies have shown that PGE's accumulate in the tissues of living organisms and constitute a high risk to them (water pollution, acid water drainage, environmental degradation, allergic reactions, dermatitis, asthma, nausea, hearing loss, nephrotoxicity, etc.) [10]. The primary production of platinum group metals generates a large amount of mining waste, consumes a large amount of energy and water, and produces potentially hazardous gases such as CO2 and SOx. Separation and refinement of each element of PGEs consume significant amounts of water and acid substances that pollute the water and the soil [11]. Currently, 40 % Pt, 58 % Pd, and 83 % Rh are used in the automotive industry for the production of catalytic converters [12].

PGEs also have some disadvantages, such as high prices and non-regeneration, which have a negative impact on the environment. Due to these causes, the interest in recovering these elements from waste, such as spent catalysts, but even from dilute solutions, has increased [13].

Recycling/recovery of PGE is important for ensuring it in the production chain and maintaining a circular economy [14].

Recovery of PGEs from by-products, waste or industrial solutions can be achieved by melting, chlorination, acid digestion, pre-concentration with solvents, co-precipitation, ion exchange, adsorption, etc. Advanced research focuses on the large-scale application of various materials with absorptive properties in order to recover/pre-concentrate PGEs by adsorption. Of these most used adsorbents are activated coal, alumina, silica, metal oxides/hydroxides, zeolites, polyurethane foam, chemically modified commercial or natural polymers, biopolymers, etc.

By physico-chemical modification of the internal and external surface of natural/synthetic adsorbent materials can improve their adsorbing properties [15]. Over the last 50 years researchers have discovered several types of extractants used to improve the properties of adsorbent materials, but only a few of them are also widely used. The extractant must be a good separating agent for metals in the platinum group metals, must have a low cost and shall satisfy industrial requirements.

The selection of the extractant has to fulfill several several requirements. The most important requirement is that the extractant must have at least one functional group and a relatively long hydrocarbon chain or a substituted aromatic nucleus/benzene. Functional groups, containing P, N, O or S, act as a metal complexing agent, the carbon chain being used to enhance the solubility of the extractant in the chosen solvent. In addition, a good extractant must have good selectivity to the metals in the PGEs, excellent chemical stability, low density and viscosity, and high surface tension. Some of these properties are important to prevent emulsifying in the extraction process [16].

According to the literature, it is known that crown ethers can be used for the removal or recovery of metallic ions because they allow chelating and incorporate/ entrapping of metallic ions inside or at the interface [17-19].

In the second part of doctoral thesis (6 chapters) are presented the original research.

Starting from the desire to obtain a series of materials with guided adsorbing properties and knowing that the support material must be inert with good chemical stability in order to be functionalized with different pendant groups, thus in this study crown ethers, were used as extractants. Crown ethers binds strongly certain cations form chelates. Oxygen atoms are well positioned to conordinate with a cation located inside the ring, while the outside of the ring is hydrophobic.

The studies were performed on 75 materials with adsorbent properties. These were obtained by the functionalization using dry method know as SIR (Solvent Impregnated Resin) of three substrates: (i) a polymeric resin in the form of acrylic esters, polar, macroporous (Amberlite XAD7); (ii) a silica matrix with rigid three-dimensional structure (magnesium silicate $MgSiO_3$) and a biopolymer obtained by the alkaline N-deacetylation of chitin (chitosan) with 5 crown ethers (dibenzo-18-crown-6 ether, DB18C6; dibenzo-30-crown-10 ether, DB30C10; dibenzo-24-crown-8 ether, DB24C8; 1-aza-15-crown-5 ether, 1-Aza15C5 and 1-aza-18-crown-6, 1-Aza18C6), varying the solid support: extractant ratio (10:0,5; 10:1, 10:1,5, 10:2 și 10:2,5). Dissolution of the reactants was carried out in nitrobenzen.

The purpose of obtaining these materials was to recover as effectively as possible three of the components of the platinum group (PGEs), palladium ions, Pd(II), platinum, Pt(IV) and ruthenium, Ru(III). These metals are economically valuable and important in terms of physico-chemical properties. For each functionalized materials was varied the support:extractant ratio to establish optimal conditions for the synthesis of materials with adsorbing properties, in pursuit of their adsorption capacity and efficiency for the recovery of the 3 metallic ions, Pd(II), Pt(IV) and Ru(III). In this sense, the residual concentration of metallic ions in the solution was determined by atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). It has been found that the materials obtained by functionalization with DB24C8, 1-Aza15C5 and 1-Aza18C6 behave similar to materials obtained by functionalization with DB18C6 and DB30C10, for which further studies have been carried out on 6 of the materials obtained, namely: XAD7-DB18C6; XAD7-DB30C10; Ch-DB18C6; Ch-DB30C10; $MgSiO_3$-DB18C6 and $MgSiO_3$-DB30C10. These crown ethers was chosen on the grounds that DB18C6 is the crown with the lowest number of oxygen atoms and DB30C10 with the highest number.

The physico-chemical characterization of the materials with adsorbent properties were preformed by scanning electron microscopy SEM, X-ray dispersion spectroscopy (EDX), Fourier transform infrared spectrometry (FT-IR), by determining the specific surface using the Brunauer - Emmett - Teller method (BET) and by determining the point of zero charge (pH_{pZc}).

To highlight the adsorptive performance of the six materials XAD7-DB18C6, XAD7-DB30C10, Ch-DB18C6, Ch-DB30C10, $MgSiO_3$-DB18C6 și $MgSiO_3$-DB30C10 as regards recovery of Pd(II), Pt(IV), Ru(III) ions from aqueous solutions by static and dynamic adsorbtion, the most representative parameters was establish: ratio solid : liquid between adsorbent and adsorbed, pH of the solution which contains metallic ions Me^{n+}(Pd(II), Pt(IV), Ru(III)), contact time between adsorbent and adsorbed, temperature at which the adsorption process occurs, initial concentration of the Me^{n+} ions on the adsorption capacity of the materials obtained and behavior of the materials in the successive adsorption-desorption processes, establishing the number of adsorption-desorption cycles for the obtained materials.

Trying to establish a mechanism for the adsorption of PGEs the kinetic, thermodynamic and equilibrium studies were performed.

Kinetic studies allow an understanding of the mechanism of carrying out the adsorption process, the chemical reactions, the reaction rate and the mass transfer coefficient, and the determined optimal adsorption conditions.

The most common kinetic models are the pseudo-first-order kinetic model (Lagergren model), pseudo-second-order (Ho and McKay model) [20] and the intraparticle diffusion (Weber and Morris model) [21].

Thermodynamic parameters involved in the adsorption process are, standard enthalpy variation ΔH°, standard entropy variation ΔS° and standard variation of free energy Gibbs ΔG°. These parameters give information about the energy changes that occur during the adsorption process [22].

Establish the adsorption capacity at equilibrium is an important parameter for the proper analysis and design of the adsorbent-adsorbed system [23]. Description of the adsorption recovery process of Me^{n+} ions was done by mathematical modeling of the experimental data using three adsorption isotherms, namely Langmuir isotherm which is based on the monomolecular layer adsorption of the adsorbed [24], , the Freundlich isotherm Freundlich isotherm where adsorption occurs on a heterogenous surface [24] and Sips isotherm, an isotherm which combines the two Langmuir and Freundlich isotherms [25].

The application of a material in adsorption processes depends not only on its adsorption capacity but also on the capacity of the material to regenerate for reuse. In order to perform this property it is necessary that the metal ion on the surface of the material to be able to easily desorption with a higher concentration in the eluent so that its recovery is effective. For this purpose, adsorption-desorption cycles have been performed.

Statistical methods play an important role in the planning, management, analysis and interpretation of the data resulting from the experimental determinations. When several variables influence a particular characteristic of a process, the best strategy is to design an experiment so that at the end of the experiment reliable and economically efficient conclusions can be drawn [26].

In order to determine parameters that have a significant influence on the adsorption process (pH, contact time, initial concentration of Me^{n+} and temperature) for establish the process results (maximum adsorption capacity) at the desired values, optimization of the recovery process by adsorption of Me^{n+} ions by factorial design was carried out.

Proposals have also been made for the material synthesis mechanisms as well as for the mechanisms of the recovery processes of Me^{n+} ions. The synthesis mechanism takes place in two stages. In the first phase a operation is performed by hydrogen bridges created on the support surface (XAD7, Ch, $MgSiO_3$) and O from crown ether (DB18C6 or DB30C10). In the second part of the mechanism a chelate is formed between the Me^{n+} and the crown ether.

Conclusions and original contributions

The novelty of this doctoral thesis was to obtain materials with guided properties for the recovery of some metal ions from the platinum group (Pd(II), Pt(IV) and Ru(III)) by adsorption. Thus, by functionalization of inert solid supports (XAD7, Ch and $MgSiO_3$) by impregnation with crown ether (DB18C6, DB30C10, DB24C8, 1-Aza15C5, 1-Aza18C6) on 5 ratios support: extractant was found the following:

- 75 materials were obtained;
- the method used for functionalization of the materials was the dry method (SIR), which consists of bringing the extractant dissolved in the solvent into contact with the solid support at ambient temperature (298K) for 24 h. The resulting suspension has been filtered, washed, dried for 24 hours at a temperature of 323K;
- the solvent used to dissolve the extractant was nitrobenzene;
- regardless of the support nature and metallic ions used in the process, an increase in the adsorption capacity occurs simultaneously with the increase of the mass ratio solid support:extractant, which is why the chosen optim ratio of support:extractant was 10:1 (g/g) for all supports used;
- on the basis of the results obtained for each type of crown ether used for the functionalization and taking into account their structure, it was found that the efficiencies in the recovery of metallic ions are similar, the studies continued with 6 of the materials, namely: XAD7-DB18C6; XAD7-DB30C10; Ch-DB18C6; Ch-DB30C10; $MgSiO_3$-DB18C6 and $MgSiO_3$-DB30C10;

Following the morphological and textural properties of the functionalized materials in order to improve the adsorption capacity of the studied materials by assigning the presence of the pendant groups on the surface of the supports, these the materials were characterized by:

- scanning electron microscopy (SEM) where changes occur in the surface morphology of the material, confirming the presence of crown ethers on the surface of the inert support;
- X-ray diffraction spectroscopy (EDX) in which the semi-quantitative presence of the corresponding atoms of the pendant groups from the crown ethers was shown;
- Fourier transform (FT-IR) infrared spectroscopy were the specific vibrations of the present bindings in the pendant groups from the extractants was revealed;
- Brunauer - Emmett - Teller method (BET) by establishing the size of the specific area, the volume and size of the pores.

In the case of $MgSiO_3$ - DB18C6 the pore size, the specific surface and the pore volume decrease by suggesting that the DB18C6 crown ether can block the pores of the support. In the case of $MgSiO_3$-DB30C10, the pore size increases, which means that the DB30C10 crown ether is larger and can still penetrate into the pores, fixing it to the surface of the support. The polymeric resin type Amberlite XAD7 and chitosan, has a significant specific surface, but after being functionalized it decreases significant. This can be attributed to the fact that during the process of functionalization the pendant group of the extractant enter the pores of the support by blocking them.

- determination of the potential of zero charge, pH_{pZc} to know the acid-base properties of the surface of the materials.

Thus, has been observed that for each initial pH value, between 3-8, all the obtained materials have buffering capacities and the pH corresponding to the potential of zero charge pH_{pZc} for materials was: XAD7-DB18C6 and XAD7-DB30C10 ~ 7,5; Ch-DB18C6 and Ch-DB30C10 ~7,5 and for $MgSiO_3$-DB18C6 and $MgSiO_3$-DB30C10 ~9.

In order to monitor the efficiency of recovering the PGEs, Pd(II), Pt(IV) and Ru(III) by adsorption from aqueous solutions of the six materials (XAD7-DB18C6, XAD7-DB30C10, Ch-DB18C6, Ch-DB30C10, $MgSiO_3$-DB18C6 și $MgSiO_3$-DB30C10), studies were performed in static regime, setting out characteristic parameters, namely: pH, solid:liquid ratio, contact time, temperature, adsorption capacity and the maximum adsorption concentration of the obtained materials.

From experimental data obtained it was found out, that:

- the efficiency of the adsorption process of Me^{n+} increases with the solid-liquid ratio, regardless of the nature of the material and metal ion studied but insignificant, thus it has been established that the optimal solid-liquid ratio was 0,1:25 (g/ml);
- as the pH increases in the range 1-10, the adsorption capacity of the materials increases, reaching the maximum value at pH=3, regardless of the nature of the metal ion. Therefore, the optimal pH for adsorption of the ions Pd(II), Pt(IV) and Ru(III) in aqueous solution on XAD7-DB18C6, XAD7-DB30C10, Ch-DB18C6, Ch-DB30C10, $MgSiO_3$-DB18C6 and $MgSiO_3$-DB30C10 materials was pH<3;
- with increasing contact time, the material's adsorption capacity increases, reaching equilibrium after 180 minutes.
- in the temperature range 298-318K, the adsorption process is positively influenced by the temperature, the adsorption capacity of the materials increases, but not significantly, thus for economic reasons the studies were carried out at a temperature of 298K

In order to have a better visibility on the maximum adsorption capacity of the materials obtained the experimental data are presented in Table 1.

Table 1. The maximum adsorption capacity of PGEs on the obtained materials

Material	**Maximum adsorption capacity, mg/g**		
	Pd(II)	Pt(IV)	Ru(III)
Support Amberlite XAD7			
XAD7-DB18C6	6,50	6,60	10,7
XAD7-DB30C10	12,7	12,3	18,3
Support Chitosan (Ch)			
Ch-DB18C6	17,6	22,4	30,4
Ch-DB30C10	30,0	40,0	52,1
Support $MgSiO_3$			
$MgSiO_3$-DB18C6	21,1	21,1	19,9
$MgSiO_3$-DB30C10	34,8	29,2	32,7

Based on the data presented in Table 1 it can be stated that the materials XAD7-DB30C10, Ch-DB30C10 and $MgSiO_3$-DB30C10 show significant adsorption capacities for recovery of metal ions than XAD7-DB18C6, Ch-DB18C6 and $MgSiO_3$-DB18C6 materials.

To evaluate the kinetic mechanism of the adsorption processes of Me^{n+} on the obtained functionalized materials the experimental data have been modeled using pseudo-first-order kinetic model (Lagergren model), pseudo-second-order (Ho and McKay model) and intraparticle diffusion (Weber and Morris model) at three working temperatures (298, 308 and 318 K).

The correlation coefficient (R^2) closer to unity indicates that the adsorbtion process is modeled by one of the kinetics model presented. Another factor influencing the choice of the kinetic model are the experimentally adsorption capacity ($q_{e,exp}$) to have a value really close to the theoretically predicted adsorption capacity of the kinetic models ($q_{e,calc}$). By analyzing the experimental data obtained, was observed that the correlation coefficient at all used temperatures in cases of pseudo-second-order model is closer to 1, and the $q_{e,exp}$ and $q_{e,calc}$ have closer values. Because of this it can say that the pseudo-second-order kinetic model describe the adsorbtion process of Me^{n+} ions on the studied materials.

In order to distinguish if the intraparticle diffusion or film difussion is the determining stage of speed, experimental kinetic data have been processed according to Weber and Morris's model at 3 working temperatures. It has been observed that the adsorption mechanism of Me^{n+} ions is carried out in several stages, since the straight lines obtained by plotting the dependence of $q_t = f(t_{1/2})$ at different temperatures do not pass through the origin (C = 0). It was found that the both inaparticle diffusion and film diffusion influence the kinetics of the adsorption process.

It was also noted that with the increase of temperature the value of K_{diff} also increases. The diffusion constants for stage 1 are higher than the diffusion constants for stage 2, which allows us to state that the determinant speed is stage 2, where the process is slower.

The activation energy E_a has been determined using the Arrhenius equation and the speed constant of the pseudo-second-order kinetic model, k_2, which is specific to the metal adsorption process on the studied materials.

In cases of XAD7-DB30C10, Ch-DB30C10 and $MgSiO_3$-DB30C10 the activated energy was smaller than was using the XAD7-DB18C6, Ch-DB18C6 and $MgSiO_3$-DB18C6 material, which can be attributed to a good functionalization of Amberlite XAD7, chitosan and $MgSiO_3$ support not beeing necessary a heat to initiate interactions.

Knowing that the value of the E_a can give us information on the nature of the adsorption process, from the experimental data it has been found that the adsorption recovery of the Me^{n+} ions on the 6 materials is of a physical or physico-chemical nature.

In order to establish information on energy changes associated with the adsorption process, thermodynamic studies have been carried out in the temperature range 298-318 K. Thus, the variations of free enthalpy ΔH^0, free energy Gibbs ΔG^0 and free entropy ΔS^0 were determined.

Positive values of free-enthalpy ΔH^0 demonstrate that the energy required for the adsorption process is the energy used for bringing into contact with the surface of the material with adsorbing properties. The affinity to the Me^{n+} ions generates electrostatic interactions and can give complexation by an endotherm process, which is consistent with the abilities of adsorption at high temperatures.

The values of free energy variation, Gibbs ΔG^0, calculated from experimental data, are negative, which in absolute value increase with the temperature, indicating that the adsorption of Me^{n+} ions on all the materials studied is a natural and spontaneous process. This increase of free energy with the temperature can be attributed to the actual increase in the contact surface between the support and the Me^{n+}.

Positive values of free entropy variation ΔS^0, suggest that the adsorption process intensifies at the material/solution interface and the degree of disorder of particles increases as the temperature increases, which can be attributed to the surface change of the material. Thus, the adsorption of Me^{n+} ions on the surface of studied materials is an endothermic and spontaneous process.

The effect of the initial concentration of Me^{n+} ions on the adsorption capacity of the functionalized materials has been established.

The experimental results demonstrate that, with the increase in the initial concentration of the Me^{n+} ions, the amount of adsorbed metallic ions on the surface of the material increases. This is due to the gaps available in the material mass. When the gaps are filling , the amount of adsorbed metallic ions remains constant. This time is assigned to the maximum adsorption capacity of the material.

It has been noted that XAD7-DB30C10, Ch-DB30C10 and $MgSiO_3$-DB30C10 materials have for all the metal ions studied adsorption capacities significantly higher than the XAD7-DB18C6, Ch-DB18C6 and $MgSiO_3$-DB18C6 materials.

In order to identify the adsorption mechanism, it is necessary to describe how the solution interacts with the adsorbent. This can be achieved by using equilibrium isotherms, which show the relationship between the amount of adsorbed substance per gram of equilibrium adsorbent (q_e) and the concentration of metallic ions (C_e) remaining in the aqueous phase. The description of the adsorption process of Me^{n+} ions on synthesized materials was done by mathematical modeling of the experimental data using three adsorption isotherms, namely the Langmuir, Freundlich and Sips isotherm.

For materials investigated for the recovery of the three metallic ions, the value of the coefficient of correlation R^2 closest to 1 was for the Sips isotherm. This allows us to say that the experimental data have best matched this isotherm.

By comparing the adsorption capacities obtained for the Sips isotherm with those experimentally obtained, it was observed that the values are close together, which helped to choose this isotherm as the isotherm describing the adsorption process.

Analyzing the value of the heterogeneity factor, n_s, ($n_s<1$), we can say that the adsorption process is likely to take place by migrating metallic ions from the aqueous phase to the surface of the adsorbent, the process being heterogenous.

It can also be said that: (i) the adsorption process is heterogeneous; (ii) adsorption occurs by the interaction between a molecule of solut and an active center on the surface of the sorbent; (iii) the surface of a sorbent contains a limited number of active centers; (iv) at equilibrium only part of them are occupied, the rest remaining free, irrespective of the temperature at which adsorption takes place; (v) adsorption results on the surface of the sorbent, resulting in a monolayer, the molecules of solut being retained only on the free surface of the sorbent; (vi) not all active centers on the surface of the sorbent are energy-equal; (vii) there may be some interactions between the molecules of solut and therefore, once the surface of the sorbent is covered, additional molecules of solut may still be adsorbed; (viii) can be used to describe the adsorption processes of multi-layer solute molecules.

For dynamic adsorption recovery studies in fixed layer column, it was intended to establish the selectivity of materials (XAD7-DB18C6, XAD7-DB30C10, Ch-DB18C6, Ch-DB30C18, $MgSiO_3$-DB18C6 and $MgSiO_3$-DB30C10), and the competition between the three PGEs ions. For this purpose, the height of the adsorbent material layer, the amount of material, the flow rate of the solution with Me^{n+} and the absorbent-adsorbed contact time was varied.

The performance of the dynamic adsorption process is given by the column breakthrough curves, represented by the dependence of the metal concentration in the fixed layer column on time.

Due to the morphological properties of the surface, structure and the fact that they are in powder form, the materials Ch-DB18C6 and Ch-DB30C18 have led to column clogging, which is why dynamic adsorption studies could not be performed.

By increasing the height of the material layer in the column, the time and volume required for the adsorption process of metallic ions Pd(II), Pt(IV) and Ru(IV) up to the time of breakpoint, when the ratio of the residual concentration (C_{rez}) at time t to the initial concentration (C_0) of the solution against the volume of solution introduced is no longer equal to zero. The area where the ratio of C_{rez}/C_0 is zero corresponds to the mass transfer Zone (MTZ) where the adsorption process is complete. This adsorption area extends over the entire height of the column, depending on the contact time.

After a time, the column is completely saturated, with metal ions from the solution no longer adsorbing, and the ratio of crez/C0 is equal to 1.

The experimental data consisted of the following:

- the breakthrough volume is greater when using XAD7-DB30C10 and MgSiO3-DB30C10 materials than when using XAD7-DB18C6 and MgSiO3-DB18C6 materials;
- the Ru(III) is the least affected metal ion in the competition, since it has been observed that the residual concentration starts to rise after a higher amount of solution passed through the column;
- following the completion of the adsorption-desorption cycles of the material for the three ions Pd(II), Pt(IV) and Ru(III), it has been observed that the volume of eluent until the breakthrough of the column decreases with the increase in the number of adsorption-desorption cycles; the adsorption capacity of the material in the adsorption cycle decreases, the column being breakthrough more quickly.

In order to allow a possible reuse of exhausted materials following the adsorption process, adsorption-desorption studies have been carried out:

- the number of adsorption – desorption cycles for materials XAD7-DB30C10 and $MgSiO_3$-DB30C10 is higher than for materials XAD7-DB18C6 and $MgSiO_3$-DB18C6 for all three metal ions studied;
- the number of adsorption-desorption cycles for Ru(III) ions was 4 cycles, 3 cycles for Pt(IV) ions and 2 cycles for Pd(II) ions for the material XAD7-DB18C6;
- for XAD7-DB30C10, was performed a number of 7 adsorption-desorption cycles for Ru(III), 5 cycles for Pt(IV) ions and 3 cycles for Pd(II) ions;
- the number of adsorption-desorption cycles of the material $MgSiO_3$-DB18C6 for Ru(III) ions was 8 cycles, 6 cycles for Pt(IV) ions and 5 cycles for Pd(II) ions;
- in the case of $MgSiO_3$-DB30C10 was performed 11 adsorption-desorption cycles for Ru(III) ions, 8 cycles for Pt(IV) ions and 6 cycles for Pd(II) ions.

Optimization and design of the dynamic adsorption process was difficult due to the fact that paths may form during the adsorption process, which is not uniform. The results obtained for the four materials are given in Table 2.

Table 2. Dependence of the residual concentration of Me^{n+} on the parameters of the dynamic adsorption process

Material	Layer height, H (cm)	The volume of the solution passed through the column (mL)			Stationary time in column (min)		
		Pd(II)	Pt(IV)	Ru(III)	Pd(II)	Pt(IV)	Ru(III)
XAD7-DB18C6	4,5	40	110	160	6,67	18,33	25,00
	2,5	30	70	70	13,33	11,67	11,67
	1,5	20	40	50	6,67	1,67	8,33
XAD7-DB30C10	4,5	80	140	200	13,33	23,33	33,33
	2,5	60	100	170	10,00	16,67	28,33
	1,5	30	50	80	5,00	8,33	13,33
$MgSiO_3$-DB18C6	4,5	80	130	160	5,00	15,00	20,00
	2,5	60	110	190	6,67	11,67	11,67
	1,5	40	50	60	1,67	1,67	5,00
$MgSiO_3$-DB30C10	4,5	180	190	200	13,33	23,33	33,33
	2,5	170	180	170	10,00	16,67	28,33
	1,5	70	90	80	5,00	8,33	8,33

This doctoral thesis also presented a statistical method, an advanced design and design technique for experiments and industrial processes, which optimizes the controllable variables of the adsorption process.

The purpose of the factorial design modeling study was to determine parameters that have a significant influence on the adsorption process (pH, contact time, initial Me^{n+} concentration and temperature) in order to obtain maximum adsorption capacity. Studies have been conducted for materials obtained by the functionalization of three Amberlite XAD7, chitosan and $MgSiO_3$ media with DB30C10, for recovery of Pt(IV) ions from aqueous solutions.

By optimizing the adsorption process, a maximum adsorption capacity of has been obtained when using the three materials:

- 15,03 mg Pt(IV)/g XAD7-DB30C10 at a control factor setting - contact time of 190 minutes and initial concentration of 141,06 mg/L Pt(IV);
- 44,64 mg Pt(IV)/g Ch-DB30C10 at a control factor setting - contact time of 208 minutes and initial concentration of 225 mg/L Pt(IV);
- 33,2 mg Pt(IV)/g $MgSiO_3$-DB30C10 at a control factor setting - contact time of 240 minutes and initial concentration of 200 mg/L Pt(IV).

Experimental planning has helped to establish optimal settings for chemical processes, with minimal time and cost savings.

In the **final part of the thesis**, the recovery mechanisms of Me^{n+} (Pd(II), Pt(IV) and Ru(III)) by adsorption on the 6 materials (XAD7-DB18C6, XAD7-DB30C10, Ch-DB18C6, Ch-DB30C10, $MgSiO_3$-DB18C6 and $MgSiO_3$-DB30C10) have been proposed.

Due to the large difference in concentrations between target metallic ions and interfering ions in the matrix, the selective extraction of metallic ions in trace levels from unconventional sources is a long-standing challenge.

XAD7-DB18C6, XAD7-DB30C10, $MgSiO_3$-DB18C6 and $MgSiO_3$-DB30C10 materials favor the selective adsorption of Me^{n+} ions in an aqueous solution due to the fact that they have large specific surface structures and a large volume of pores. In the case of the materials Ch-DB18C6 and Ch-DB30C10, they have small-surface structures, the pores being filled with the crown ether used to operate the materials. This functionalization occurs at the support surface (XAD7, Ch, or MgSiO3) by creating hydrogen bridges and O from the crown ether (DB18C6 or DB30C10), being considered as stage I of the mechanism.

The selectivity of the crown ether is influenced by the compatibility between the size of the Me^{n+} ions and the size of the crown cavity (the number of O atoms of the crown), which provides good yields for the recovery of the men ions from aqueous solutions, forming complexes.

In stage II of the mechanism, between the crown ether and Me^{n+} is formed a chelate. Thus, the functionalized materials with DB30C10 crown ether, which has a higher number of O and Catoms than DB18C6 crown ether, allow two Me^{n+} to enter the cavity of the DB30C10 crown, unlike DB18C6 where only one Me^{n+} ion enters.

The original research presented in this doctoral thesis resulted in the publication and/or communication of 12 works in journals indexed in Web of science, Clarivate Analytics or International databases, 1 scientific paper will be published:

- 10 papers published in journals indexed in web of Science, Clarivate Analytics (H-index= 2);
- 1 works being published in magazines indexed in Web of Science, Clarivate Analytics;
- 2 paper published in the volume of an indexed scientific event Web of Science, Clarivate Analytics;
- 2 papers communicated to international scientific events;
- 6 bachelor's and 2 dissertation theses.

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