ADVANCED MATERIALS CHEMICALLY MODIFIED THROUGH FUNCTIONALISATION WITH APPLICATION IN ENVIRONMENTAL PROTECTION

PhD Thesis - Summary

For obtaining the scientific title of PhD at
Polythenica University of Timișoara
In the fiels of PhD chemical engineering

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June 2019

The doctoral thesis is structured in two parts, containing 7 chapters and 314 pages.

Part I contains the literature study to establish the current state of knowledge in the field of synthesis, characterization and applications of new materials in order to recover REEs from aqueous solutions.

Rare earth-RE consist of seventeen elements and are divided into two categories, i.e. light rare earth-LRE and heavy rare earth-HRE. LRE include cerium (Ce), lanthanum (La), neodymium (Nd), praseodymium (Pr), samarium (Sm), and HRE include gadolinium (Gd), europium (Eu), terbium (Tb), dysprosium (Dy), thulium (Tm), ytterbium (YB), lutetium (Lu), yttrium (Y), holmium (Ho) and erbium (Er) [1,2]. Due to various chemical, electrical, metallurgical, magnetic, optical and catalytic properties, RE are part of a group of elements with multiple applications in important economic sectors, in high performance technologies such as batteries, lasers, super magnets, fluorescent lamps.

China, the United States of America (USA) and Australia are the main producers, of which China brings about 90% of the world's rare earth-elements (REEs) production [3, 4, 5, 6]. In addition, the development of the nuclear industry has the effect of producing waste, containing various toxic pollutants, including lanthanides and actinides with long-term radiotoxicity. Accordingly, the treatment of the above-mentioned waste is important for environmental protection and safety.

Of the lanthanide group, the most important elements in terms of applicability are lanthanum, europium and neodymium. Although the three elements do not show severe environmental toxicity, because of their importance in advanced technologies, in medical domain and because natural reserves are becoming poorer in these elements, it is necessary to recover them even from dilute solutions [7, 8, 9, 10].

Separation, purification and preconcentration of REEs are accomplished by several methods, such as adsorption, extraction, crystallization, chemical precipitation and ion exchange. Among these, adsorption has been recognized as one of the most promising methods due to its simplicity, high efficiency and availability on a large scale [11]. There are various materials with adsorbant properties (synthesized or chemically modified by functionalization) used to recover REEs from aqueous solutions. These materials include granular activated carbon, carbon nanotubes, modified red clays, chemically modified chitosan by functionalization, magnetic nanoparticle materials, modified silicagel with pendant groups, marine sediments, commercial or natural chemically modified polymers, as well as biopolymers [12].

The adsorbent properties can be improved by chemical modification of the support material or by functionalization with heteroatoms-containing pendant groups such as nitrogen, sulfur, phosphorus or oxygen [13]. In order to obtain such materials, the support has to be an inert material with very good chemical stability, and the extractant (the material containing the

pendant groups) is indicated to be of organic nature. Such materials are usually in the liquid state or may be brought into liquid state by dissolving in a solvent (it is indicated that the extractant and the solvent have minimal solubility).

Part II of the thesis includes original research.

The purpose of this doctoral thesis was to develop new materials with adsorbent properties to be used for the recovery of REEs from aqueous solutions by adsorption. The conditions that such materials have to fulfill in order to be successfully applied in the studied processes are: to be cheap, to be in granular form, to have high capacity and selectivity of adsorption, high physical strength so that it does not disintegrate in water and be regenerated or reused.

The studies were performed on 432 materials with adsorbent properties. These were obtained by the functionalization of three substrates: one of an inorganic nature – florisil (magnesium silicate), one of the class of commercial polymers - Amberlite XAD7 polymer and one of the biopolymers class - cellulose (Avicel PH-101). The used extractant were four environmentally friendly and relatively unexpansive organic compounds with structures containing pendant groups with nitrogen, phosphorus and sulfur heteroatoms, namely sodium β-glycerophosphate, tetraethylammonium bromide, thiourea and tetrabutylammonium dihydrogen phosphate. Dissolution of the reactants was carried out in organic solvents: absolute ethanol, acetone, toluene and n-hexane.

Three different methods were used to perform the support materials: the dry method known as SIR (solvent impregnated resin) method, the solvent evaporation method under vacuum and the ultrasonication method.

The materials with adsorbent properties obtained by functionalization of the support with the extractants Na-β-gli-P, TEABr, thiourea and TBAH2P were characterized by scanning electron microscopy SEM, X-ray dispersion spectroscopy (EDX), Fourier transform infrared spectrometry (FTIR), by determining the specific surface using the Brunauer - Emmett - Teller method (BET) and by determining the point of zero charge (pZc).

Since adsorption is an advanced purification/recovery method, the obtained and characterized materials were studied for their adsorbent properties, trying to establish a mechanism for the adsorption of REEs.

The adsorption studies were conducted both statically and dynamically for a number of 36 materials, considered to be the most representative, establishing the characteristic parameters, namely: pH, ratio solid : liquid, contact time, temperature, adsorption capacity, maximum concentration of adsorption, and behavior of the materials in the successive adsorption-desorption processes, establishing the number of adsorption-desorption cycles for the obtained materials.

Based on the obtained experimental data, kinetic, thermodynamic and equilibrium studies were performed. The kinetic studies of the adsorption processes of REEs on the obtained functionalized materials were made by modeling the experimental data using pseudo-first-order kinetic model (Lagergren model) [14] and pseudo-second-order (Ho and McKay model) [15, 16, 17].

Thermodynamic studies included determination of activation energy, standard variation of free energy Gibbs ΔG°, standard enthalpy variation ΔH° and standard entropy variation ΔS°. Using the values of the k_2, the rate constant, obtained from the pseudo-second-order kinetic model for the adsorption processes of Eu (III), Nd (III) and La (III) on the functionalized materials and the Arrhenius equation, the values of the associated activation energies were calculated. Next, to elucidate how adsorption of metal ions results on the adsorbent material, the Gibbs free energy value is calculated using the Gibbs-Helmholtz equation [11]. In order to determine the values of the variation of the standard enthalpy and the standard entropy

associated with the metal ion adsorption process, the van't Hoff equation is used.

Three of the most commonly used isotherms in classical adsorption processes are Langmuir isotherm, which is based on the monomolecular layer adsorption of the adsorbed, the Freundlich isotherm which was originally developed for heterogeneous adsorption surfaces and Sips isotherm, an isotherm which combines the two Langmuir and Freundlich isotherms [18, 19, 20, 21, 22]. Based on the data from adsorption experiments, the three isotherms can provide information about the maximum adsorption capacity of materials with adsorbent properties, but also about a possible mechanism of the process.

The statistical method is an advanced design and experimentation technique that helps researchers better understand and optimize process-controllable variables, playing an important role in planning, analyzing, interpreting data from experimental determinations, allowing optimal leadership of industrial processes.

Factorial design is one of the most common methods by which an objective function is established. In this case, the objective function is to determine the adsorption capacity as a function of two or more controllable factors, such as: the pH of the metal ion solution studied, the contact time, the solution temperature, and the initial concentration of the metal ion in the solution [23].

After modeling the data by factorial design, it has been established that several variables influence the adsorption process, so designing an experiment is indicated, at the end of which there is given the possibility of choosing reliable and economically efficient solutions.

Final conclusions. Original contributions

Following the functionalization of the support materials we found out:

- the nature of the used extractant and the used method of functionalization influences the adsorption capacity of the material obtained;
- the most effective dissolution medium is ethyl alcohol;
- regardless of the support nature used in the process, an increase in the adsorption capacity occurs simultaneously with the increase of the mass ratio extractant:solid support, but this increase is very small, which is why the chosen ratio of extractant : support was 0.1: 1 for all supports used, and for the three methods of operation.

Based on the obtained experimental data, it was found out, that of the three functionalization methods used:

- *the solvent evaporation method under vacuum* has the most advantages, namely: it is a quick method, it does not require the drying of the material after the functionalization process;
- *the ultrasonication method* is a relatively quick method, having the disadvantage that after the functinalization of the support, it requires a drying time of about 24 hours;
- *the dry method* is of maximum efficiency but requires a long functionalization time of approximately 24 hours and a drying time of 24 hours.

Materials with adsorbent properties obtained by support functionalization with the extractants Na-β-gli-P, TEABr, thiourea and TBAH2P were characterized by scanning electron microscopy SEM, X-ray dispersion spectroscopy (EDX), Fourier transform infrared spectrometry (FTIR) by determining the specific surface using the Brunauer - Emmett - Teller method (BET) and by determining the potential of zero charge (pZc).

Following the morphological and textural properties of the functionalized inorganic or organic polymer matrices, we can conclude that the improvement of the adsorption capacity of the studied materials can be attributed to the presence of the pendant groups of the extractants on the surface of the support.

By X-ray diffraction spectroscopy, EDX, has been qualitatively highlighted the presence of characteristic peaks for the corresponding atoms of the pendant groups from the

extractants.

Scanning electron microscopy images, SEM, confirm the presence of these extractants on the surface of the support, and by Fourier transform (FT-IR) infrared spectroscopy, the specific vibrations of the present bindings in the pendant groups from the extractants were revealed.

Also, the specific surface area of the materials was determined, and it was found out, that:

- by functionalization of magnesium silicate, having a crystalline structure, the specific surface area decreases because the extractant penetrates into the pores of the solid support
- the polymeric resin type Amberlite XAD7 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
- in the case of cellulose, which is a natural microcrystalline polymer with a low specific surface area, it was found out, that after the functionalization the material showed a small value of the specific surface.

The potential of zero charge, pH_{pZc} was determined for the obtained materials, being observed that for each initial pH value, between 4-10, all the obtained materials have buffering capacities and the final pH value is approximately the same and represents the pH-corresponding to the potential of zero charge $pH_{pZc} \sim 8$.

The adsorption studies were performed both in static and dynamic regime, setting out characteristic parameters, namely: pH, solid:liquid ratio, contact time, temperature, adsorption capacity, maximum adsorption concentration, and also the behavior of the materials in successive adsorption-desorption processes, establishing the number of cycles of the obtained materials.

In order to monitor the efficiency of recovering the REEs, La(III), Eu(III) and Nd(III) by adsorption from aqueous solutions, studies have been carried out on the obtained materials. The first batch was obtained by chemical modification of magnesium silicate by functionalization with Na-β-gli-P, thiourea, TEABr and TBAH2P, by various methods of functionalization, namely: dry method, solvent evaporation method under vacuum and ultrasonication method.

The most important and first determined parameter, was the pH. Thus, it has been found that adsorption studies can be performed at $pH<6$, since over this value, the studied REEs precipitates.

Since the solid:liquid ratio is another important parameter in adsorption processes, and since it may differ from one material to another but depend on the methods by which it is functionalized, the studies continued by establishing this ratio for each material obtained by the functionalization of magnesium silicate by the three methods. From the data obtained it was established that with the increase of the quantity of solid material, the adsorption capacity of the material increases. This does not depend on the functionalization method by which the material with adsorbent properties was obtained, on the nature of the extractant and on the metal studied. Thus, subsequent studies were performed at the solid:liquid ratio = 0.1:25.

Kinetic, thermodynamic and equilibrium studies were performed to establish the REEs adsorption mechanism on the 12 obtained materials by chemical modification by functionalization of magnesium silicate. For this purpose, the influence of the contact time and the temperature was determined establishing the kinetic parameters of the adsorption process and the influence of the initial concentration of the metal ion on the adsorption capacity, establishing the best isotherm describing the studied adsorption processes.

Thereby:

- it was found out, that with the increase of the contact time, the adsorption capacity of the material increased, establishing that after 60 minutes the equilibrium was reached. At the same time, it was observed that with increasing temperature the increase of the adsorption capacity of the studied materials is insignificant.
- it was found out, that the adsorption processes for all studied cases fit to the kinetic pseudo-second-order model**,** due to the value close to 1 of the regression coefficient R^2.
- based on the activated energy, it can be stated that the adsorption processes are physical processes, E_a<8 kJ/mol
- the experimental data were fitted with the adsorption isotherms, Langmuir, Freundlich and Sips, it was found out, that most of the studied materials fit to the Sips isotherm model, confirming the regression coefficient R^2 approaching 1 and the calculated maximum adsorption capacity ($q_{e,calc}$) is close, as the value, to the experimental set ($q_{e,exp}$).

The next support in the study was the polymer Amberlite XAD7, which was functionalized with the same extractants and methods previously described.

The studies were similar, the results being as follows:

- adsorption studies can be performed at pH<6, since over this value the studied REEs precipitates.
- solid:liquid ratio = 0.1:25.

Following the kinetic, thermodynamic and balance studies, the conclusions are:

- with increasing contact time, the material's adsorption capacity increases, reaching equilibrium after 30 minutes. At the same time, it has been observed that with the increase of temperature there is an insignificant increase in the adsorption capacity of the studied materials.
- it was found out that the adsorption processes for all studied cases fit to the kinetic pseudo-second-order model due to the value close to 1 of the regression coefficient R^2.
- based on the activated energy it can be stated that the adsorption processes are physical processes, E_a<8 kJ/mol
- experimental data fitted with the adsorption isotherms, Langmuir, Freundlich and Sips leads to the conclusion that most of the studied materials fit to the Sips isotherm model, the confirmation being the regression coefficient R^2 approaching 1 and the calculated maximum adsorption capacity ($q_{e,calc}$), that is close to the experimental value ($q_{e,exp}$).

In case of cellulose used as a support for obtaining new materials by functionalization with the four extractants listed above, for the recovery of La(III), Eu(III) and Nd(III) by adsorption from aqueous solutions, the studies were similar, being:

- adsorption studies can be performed at pH<6 since over this value the studied REEs precipitates as hydroxides.
- solid:liquid ratio = 0.1:25.

After the performed kinetic, thermodynamic and balance studies, the obtained results are:

- with increasing contact time, the material's adsorption capacity increases, reaching equilibrium after 30 minutes. At the same time, it was observed that with increasing temperature the adsorption capacity increased, but insignificant.
- the adsorption processes, for all the studied cases fit the kinetic pseudo-second-order model, as a result of the value close to 1 of the regression coefficients, R^2.
- adsorption processes are physical processes, E_a<8 kJ/mol
- most of the studied materials fit to the Sips isotherm model, the confirmation being the coefficient of regression R^2 approaching 1 and the value of the calculated maximum adsorption capacity ($q_{e,\ calc}$), which is close to the experimental value ($q_{e,\ exp}$).

In order to have a better visibility on the maximum adsorption capacity of the materials obtained and presented during this doctoral thesis, as well as to facilitate a possible choice of one of them for each studied metal ion, the experimental data on the adsorption capacity depending on the nature of the material and the functionalization method chosen, are presented in Table 1.

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

Material	Maximum adsorption capacity, mg/g			Functionalization method
	Eu(III)	Nd(III)	La(III)	
Support-$MgSiO_3$				
$MgSiO_3$-Na-β-gli-P	**10.46**	10.45	11.55	Dry method
$MgSiO_3$-TEABr	10.23	10.38	**12.45**	
$MgSiO_3$-thiourea	10.27	10.52	**10.56**	
$MgSiO_3$-TBAH2P	**10.76**	10.01	9.05	
Support-Amberlite XAD7				
XAD7-Na-β-gli-P	36.21	64.74	**31.77**	
XAD7-TEABr	32.90	72.21	25.17	
XAD7-thiourea	30.03	**75.62**	24.80	
XAD7-TBAH2P	**74.23**	74.87	24.20	
Support-Cellulose				
Cellulose-Na-β-gli-P	30,4	66.2	43,4	
Cellulose-TEABr	30,2	**76,1**	29.4	
Cellulose-thiourea	22,4	70,3	26,7	
Cellulose-TBAH2P	**38,65**	61,7	**58,0**	
Support-$MgSiO_3$				The solvent evaporation method under vacuum
$MgSiO_3$-Na-β-gli-P	**13.58**	11.50	10.71	
$MgSiO_3$-TEABr	**15.64**	13.19	10.73	
$MgSiO_3$-thiourea	**16.20**	14.52	11.55	
$MgSiO_3$-TBAH2P	10.10	**11.31**	8.86	
Support- Amberlite XAD7				
XAD7-Na-β-gli-P	71.92	12.11	**39.75**	
XAD7-TEABr	33.64	74.38	24.15	
XAD7-thiourea	29.09	74.30	24.57	
XAD7-TBAH2P	**72.00**	**76.12**	24.24	
Support-Cellulose				
Cellulose-Na-β-gli-P	30,8	67,2	52,0	
Cellulose-TEABr	28,1	**72,1**	31,0	
Cellulose-thiourea	22,5	68,3	28,1	
Cellulose-TBAH2P	**35,5**	66,1	**57,1**	
Support-$MgSiO_3$				Ultrasonication method
$MgSiO_3$-Na-β-gli-P	8.61	8.81	**9.37**	
$MgSiO_3$-TEABr	8.10	8.09	**9.40**	
$MgSiO_3$-thiourea	8.34	8.57	**8.79**	
$MgSiO_3$-TBAH2P	8.63	8.85	**8.91**	
Support- Amberlite XAD7				
XAD7-Na-β-gli-P	7.59	7.53	4.29	
XAD7-TEABr	7.55	15.05	12.72	
XAD7-thiourea	15.42	20.74	**13.63**	
XAD7-TBAH2P	**29.96**	**32.43**	12.44	

Support-Cellulose				
Cellulose-Na-β-gli-P	**20,5**	45,6	21,1	
Cellulose-TEABr	18,9	**53,6**	20,6	
Cellulose-thiourea	11,3	22,8	20,3	
Cellulose-TBAH2P	15,8	20,6	**22,2**	

Based on the data presented in Table 1 it can be stated that:

- the materials obtained by functionalization through the dry method of Amberlite XAD7 with TBAH2P or thiourea show significant results for recovery both Eu(III) and Nd(III), with adsorption capacities ranging from 74-76 mg/g ;
- the material Amberlite XAD7-Na-β-gli-P also obtained by functionalization with the dry method is effective in La(III) recovery, with an adsorption capacity of about 32 mg/g;
- the results obtained using functionalization of $MgSiO_3$ by the dry method are much lower for all three metal ions, the adsorption capacities being between 10 and 12,45 mg/g for Eu(III) and La(III);
- the materials obtained by functionalization of cellulose by dry method can be used with good efficiency to recover the three metal ions, the adsorption capacities being 38,65 mg/g (in the case of Eu(III) adsorption recovery by cellulose-TBAH2P), 58 mg/g (in the case of Nd(III) adsorption recovery by cellulose-thiourea) and 76,1 mg/g (for Nd(III) recovery by cellulose-TEABr adsorption);
- the materials obtained by the functionalization of $MgSiO_3$ by the vacuum evaporation method showed good results in the recovery of Eu(III), namely, adsorption capacities of 13.58 mg/g, 15.64 mg/g and 16.2 mg respectively ($MgSiO_3$-Na-β-gli-P, $MgSiO_3$-TEABr and $MgSiO_3$-thiourea), and for the recovery of Nd(III) the $MgSiO_3$-TBAH2P material has a relatively good adsorption capacity of 11.31 mg/g;
- Amberlite XAD7 resin functionalized materials by the vacuum evaporation method have significant adsorption capacities for Eu(III) and Nd(III), but also for La(III): 72 mg/g, 76.12 mg/g and 39.75 mg/g;
- materials obtained by the functionalization of cellulose by the vacuum evaporation method have significant adsorption capacities for the three elements, namely 35,5 mg/g, 72,1 mg/g and 57,1 mg/g;
- the materials obtained by functionalization by the ultrasonication method have the lowest but not neglected efficiency for all three used supports. Materials with Amberlite XAD7 support have the highest adsorption capacities (13.63 mg/g-32.43 mg/g), and the materials obtained by functionalization of $MgSiO_3$ have the lowest adsorption capacities (8.91 mg/g- 9.40 mg/g).

Based on these experimental data, one can choose the optimal functionalization method depending on the nature of the support material, the extractant and the metal ion to be recovered.

So:

- for Eu(III) recovery, the best-performing material is Amberlite XAD7-TBAH2P, obtained by functionalzation by the dry method;
- for the recovery of Nd (III), the best material is cellulose-TEABr, obtained by functionalzation by the dry method, but also Amberlite XAD7-TBAH2P, obtained by vacuum evaporation method;
- for La(III) recovery, the best material is Amberlite XAD7-TBAH2P, obtained by functionalization by dry method or vacuum evaporation method;

It can be concluded, that the Amberlite XAD7-TBAH2P material obtained by

functionalization by the dry method shows the best adsorbtion capacities for the recovery of the three metal ions.

In terms of dynamic studies, in order to predict the breakthrough curve for effluent, which is an essential factor in the design of a dynamic adsorption process, it was necessary to investigate the effect of the layer thickness of adsorbent material, as well as the effluent flow on the breakthrough curve. The studies were carried out in the case of the adsorption process of La(III) on the $MgSiO_3$-TBAH2P, Amberlite XAD7-TBAH2P and Cellulose-TBAH2P, all materials being functionalized by the dry method.

It has been found out, that with increasing the height of the adsorbent material layer, the time and volume of solution required for the adsorption process of La(III) also increases until the column of adsorbent material penetrates.

At the same time, for a possible re-use of material from adsorption processes, it is necessary that they can be easy regenerated by desorbing metallic ions from their surface, concomitant with the need to carry out a significant or even total desorption of the metal ions, so that the reuse of the adsorbent material to be profitable. In this regard, the possibility of re-utilization of the three materials, $MgSiO_3$-TBAH2P, Amberlite XAD7-TBAH2P and Cellulose-TBAH2P, after desorption La(III) was studied, and the number of adsorption-desorption cycles was determined.

The obtained results for the three cases are centrally presented in Table 2.

Table 2. The obtained results for the La(III) recovery process by dynamic adsorption

Material	The height of the layer, (H), cm	The volume of the passed La (III) solution, mL	Adsorption capacity (q), mg/g	The number of adsorption-desorption cycles
$MgSiO_3$-TBAH2P	3	3000	26,2	4
	2	2000	28,3	
	1	1000	35,0	
XAD7-TBAH2P	6	3000	28,5	11
	4	2000	36,7	
	1,5	1000	25,86	
Cellulose-TBAH2P	4,4	3000	23,85	6
	2,4	2000	24,01	
	1	675	25,78	

It can be said that even in this case the Amberlite XAD7-TBAH2P material presents the best efficiency for the studied adsorption processes.

At the end of the Ph.D. thesis, is presented a statistical method, that is an advanced design and experimental technique, that helps researchers understand better and optimize the controllable variables of the studied processes, playing an important role in planning, analysing and interpretation of data resulting from experimental determinations, which allows the optimal management of industrial processes.

The purpose of these modeling studies by factorial design was to optimize the process of recovery of lanthanum from aqueous solutions by adsorption onto cellulose-Na-β-gli-P. In this regard, parameters having a significant influence on the adsorption capacity (q) were determined and the optimal values of the controllable factors (pH, contact time, initial concentration and temperature) were established in order to determine the results of the adsorption process at the desired values, in short time and with minimal resources.

By optimizing the adsorption process, it was found out, that at pH=6 and an initial concentration of La(III) of 256 mg/L, adsorption capacity between 30.87mg/g and 36.73mg/g with a 95% confidence interval is obtained.

The experimentally obtained data is confirmed by the data obtained through the factorial design. Thus, the optimal values of experimentally determined parameters are: pH=6, contact time 60 minutes, temperature 25 °C, and initial La(III) concentration of 250 mg/L. The maximum adsorption capacity experimentally obtained was 31.58 mg/L. At the same time, the optimum values of parameters influencing lanthanum adsorption on functionalized cellulose obtained by factorial design were pH=6, contact time 60 minutes, temperature 25 °C, and initial lanthanum concentration of 256 mg/L. The values of the adsorption capacity predicted by the factorial design were between 30.87 mg/g and 36.73 mg/g.

The original research presented in this doctoral thesis resulted in the publication and/or communication of 19 works in journals indexed in Web of science, Clarivate Analytics or International databases, 1 scientific paper will be published:

- 11 papers published in journals indexed in web of Science, Clarivate Analytics (H-index-3);
- 1 works being published in magazines indexed in Web of Science, Clarivate Analytics;
- 1 paper published in the volume of an indexed scientific event Web of Science, Clarivate Analytics;
- 5 papers communicated to international scientific events;
- 3 bachelor's and 2 dissertation theses.

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