

CONTRIBUTIONS TO THE DESIGN OF NEW MATERIALS USED FOR THE RECOVERY OF INDIUM AND GALLIUM IONS

Doctoral Thesis – Abstract

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CONTENT

NOTATIONS. ABBREVIATIONS. ACRONYMS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

PART I. LITERATURE REVIEW

CHAPTER 1. General Considerations

1.1. Indium

1.1.1. Introduction

1.1.2. Applications of Indium

1.2. Gallium

1.2.1. Introduction

1.2.2. Applications

CHAPTER 2. Methods for the recovery of gallium and indium ions

2.1. Methods for the recovery of In(III)

2.2. Methods for the recovery of Ga(III)

2.3. Adsorption of In(III) and Ga(III)

CHAPTER 3. Methods for synthesis and characterization of materials with adsorbent properties

3.1. Methods for synthesis of materials with adsorbent properties

3.1.1. Composite materials

3.1.2. Materials chemically modified by functionalization

3.2. Methods for characterization of materials with adsorbent properties

3.2.1. Physico-chemical methods useful for structural characterization

3.2.1.1. Raman spectroscopy

3.2.1.2. Fourier transform infrared spectroscopy, FT-IR

3.2.1.3. Fourier transform infrared spectroscopy with attenuated total reflectance, ATR-FTIR

3.2.1.4. Magnetism, VSM

3.2.1.5. UV-VIS spectroscopy

3.2.2. Physico-chemical methods used for surface characterization

3.2.2.1. XPS spectroscopy

3.2.2.2. Low-energy ion scattering spectroscopy LEIS

3.2.2.3. Time-of-flight secondary ion mass spectrometry, ToF-SIMS

3.2.3. Physicochemical methods used for elemental analysis

3.2.3.1. Mass spectrometry

3.2.3.2. Energy-dispersive X-ray spectroscopy, EDX

3.2.3.3. X-ray fluorescence spectroscopy, XRF

3.2.4. Physicochemical methods used for determining crystalline properties

3.2.4.1. X-ray diffraction, XRD

3.2.4.2. Small-angle X-ray scattering, SAXS

3.2.5. Physicochemical methods used for morphological analysis

3.2.5.1. Scanning electron microscopy, SEM

3.2.5.2. Transmission electron microscopy, TEM

3.2.5.3. Atomic force microscopy, AFM

3.2.5.4. Determination of specific surface area by the BET method (Brunauer, Emmett, Teller)

3.2.5.5. Dynamic light scattering, DLS

PART II-A. ORIGINAL CONTRIBUTIONS

CHAPTER 4. MgFe₂O₄ spinel used for the recovery of indium and gallium ions in batch mode

4.1. Synthesis and characterization of MgFe₂O₄ spinel

4.1.1. Synthesis of MgFe₂O₄ spinel

4.1.2. Characterization of MgFe₂O₄ spinel by physicochemical methods

4.1.2.1. Differential thermal analysis, DTG

4.1.2.2. X-ray diffraction, XRD

4.1.2.3. Analysis by Fourier transform infrared spectroscopy

4.1.2.4. Analysis by atomic force microscopy (AFM)

4.1.2.5. Magnetic measurements (VSM)

4.1.3.6. Determination of the point of zero charge (pHpzc)

4.1.3. Conclusions

4.2. Recovery of indium and gallium ions by adsorption in static mode, using spinel MgFe₂O₄

4.2.1. Recovery of indium ions from aqueous solutions by adsorption

4.2.1.1. Specific parameters of the adsorption process in static mode

4.2.1.2. Mechanism of the In(III) recovery process by adsorption on MgFe₂O₄ spinel

4.2.1.3. Conclusions

4.2.2. Recovery of gallium ions from aqueous solutions by adsorption

4.2.2.1. Specific parameters of the adsorption process in static mode

4.2.2.2. Mechanism of the Ga(III) recovery process by adsorption on MgFe₂O₄ spinel

4.2.2.3. Conclusions

4.3. Studies on the regeneration capacity of MgFe₂O₄ spinel.

Determination of the number of adsorption-desorption cycles.

CHAPTER 5. Materials obtained by functionalization by impregnation with the amino acid L-valine of Amberlite XAD resins for the recovery of indium and gallium ions in batch conditions

5.1. Synthesis and characterization of materials obtained by functionalization by impregnation

5.1.1. Testing of materials obtained by functionalization by impregnation for the recovery of indium and gallium ions by adsorption from aqueous solutions

5.1.2. Characterization by physicochemical methods of the XAD7-Val material

5.1.2.1. Scanning electron microscopy, SEM

5.1.2.2. Energy dispersive X-ray spectroscopy, EDX

5.1.2.3. Fourier transform infrared spectroscopy, FT-IR

5.1.2.4. Zero point of charge, (pHPZC)

5.1.3. Conclusions

5.2. Applications of Amberlite XAD 7 resin functionalized with L-valine for the recovery of indium and gallium from aqueous solutions by adsorption

5.2.1. Recovery of indium ions from aqueous solutions by adsorption

5.2.1.1. Specific parameters of the adsorption process in static mode

5.2.1.2. Mechanism of the recovery process of In(III) by adsorption on the XAD7-Val material

5.2.1.3. Conclusions

5.2.2. Recovery of gallium ions from aqueous solutions by adsorption

5.2.2.1. Specific parameters of the adsorption process in static mode

5.2.2.2. Mechanism of the recovery process of Ga(III) by adsorption on the XAD7-Val material

5.2.2.3. Conclusions

5.3. Studies on the regeneration capacity of the XAD7-Val material.

Determination of the number of adsorption-desorption cycles

CHAPTER 6. Optimization of the adsorption process of indium and gallium by factorial design

6.1. Optimization of adsorption processes

6.2. Optimization of the adsorption process of indium on the material $MgFe_2O_4$ by factorial design

6.3. Optimization of the adsorption process of gallium on the material $MgFe_2O_4$ by factorial design

6.4. Conclusions

CHAPTER 7. Final conclusions. Original contributions

BIBLIOGRAPHY

EXTENDED SUMMARY OF THE DOCTORAL THESIS

Research in materials science focuses on the development of new synthesis and material production processes, with particular emphasis on methods that limit pollution, are easy to use; and at the same time offer excellent performance at low production costs.

The continued development of applications involving advanced technologies in areas such as communications, renewable energy production, and display technology depends largely on technologically critical elements such as **indium and gallium**.

These elements play essential roles in the functionality of devices such as liquid crystal displays (LCD), light-emitting diodes (LED), photovoltaic cells and optical fibers. Indium, for example, is predominantly used in indium tin oxide (ITO) thin films in flat panel displays found in smartphones, tablets and televisions, accounting for up to 80% of global indium consumption. Gallium, in turn, is vital to the modern electronics industry, being used in gallium arsenide (GaAs) and gallium nitride (GaN) components for integrated circuits and LED.

Ensuring a sustainable supply of indium and gallium is a pressing concern, given their high economic value and supply risks, especially in the European Union, where they are classified as critical raw materials.

In this context, it is necessary to identify and use secondary sources of raw materials, such as waste from various industries, which makes the development of an efficient process for the recovery of these elements extremely important. Conventional methods for the recovery of indium and gallium from secondary resources (such as industrial wastewater) include precipitation, solvent extraction, ion exchange, nanofiltration membranes, chemical reduction and electrochemical techniques. All of these are well-known recovery methods, but they generate potential environmental problems: caused by the use of large amounts of chemicals and organic solvents, low selectivity or high costs. Adsorption is expected to be the most suitable method for the recovery of indium and gallium due to its simple concept, high safety and environmentally friendly process.

The topic of this doctoral thesis was **the design and production of new materials** with selective adsorbent properties, capable of allowing the recovery of **indium (In)** and **gallium (Ga)** from aqueous solutions.

The doctoral thesis is structured in 2 parts and 7 chapters, includes 50 tables and 91 figures, accompanied by 159 bibliographical references, which extend over 160 pages.

In the first part of the doctoral thesis - LITERATURE REVIEW, the current state of knowledge in the field of materials used for the recovery of indium and gallium ions is presented.

The recovery of indium and gallium ions from aqueous solutions, through adsorption processes, is a crucial area of research. These metals are essential for modern technologies such as LEDs and LCD screens, but are considered critical and dispersed, meaning they are difficult to obtain from primary sources. Therefore, the development of new efficient, selective and sustainable adsorbent materials is vital to valorize secondary sources, such as electronic waste, and to promote a circular economy.

Adsorption is one of the most suitable methods for the recovery of indium and gallium from aqueous solutions, due to its simple concept, high efficiency and the fact that it is an environmentally friendly process. The adsorbent material is of great importance because both the effectiveness and the total costs depend on its nature and characteristics.

In Part II of the doctoral thesis, **the original contributions** are presented.

The general objective of the doctoral thesis was to obtain materials through the chemical synthesis of spinel of the $MgFe_2O_4$ form by the co-precipitation method and materials obtained by functionalization by impregnation of Amberlite XAD resins with active groups starting from amino acids, friendly to the environment, in order to recover indium and gallium ions by adsorption.

The specific objectives of the thesis were:

(i) synthesis of spinel in the form of $MgFe_2O_4$ by the co-precipitation method and of materials obtained by functionalization by impregnation of resins in the form of Amberlite XAD with active groups;

(ii) characterization by physico-chemical investigation methods and testing of the obtained materials, in order to recover indium and gallium ions by adsorption;

(iii) establishment of specific adsorption parameters in static regime;

(iv) establishment of mechanisms of recovery processes by adsorption of indium and gallium ions;

(v) adsorption - desorption studies, establishing the number of adsorption-desorption cycles;

(vi) optimization of the recovery process by adsorption in static regime of indium and gallium ions by factorial design.

The activities carried out to achieve the objectives of the doctoral thesis were:

- establishing the optimal method for the synthesis of materials;
- synthesis of spinel in the form of $MgFe_2O_4$ by the co-precipitation method;
- synthesis of functionalized materials by impregnation with active groups starting from amino acids;
- physico-chemical characterization of the obtained materials to highlight their adsorption properties, using various investigation methods, such as: differential

thermal analysis, DTG, X-ray diffraction, XRD, Fourier transform infrared spectroscopy, FT-IR, atomic force microscopy, AFM, scanning electron microscopy, SEM and energy dispersive X-ray spectroscopy, EDX, also determining the zero charge potential, pH_{pZc} ;

- selection of functionalized materials by impregnation with active groups that are highlighted by good adsorbent properties for the recovery of indium and gallium ions;
- establishing the specific parameters of the adsorption process for the recovery of indium and gallium ions by adsorption in a static regime, namely: S:L ratio, pH, contact time, temperature, initial concentration of metal ions;
- establishing the mechanisms of the recovery processes by adsorption of indium and gallium ions through kinetic, thermodynamic and equilibrium studies, in the case of adsorption in a static regime;
- establishing the efficiency of materials through adsorption-desorption studies, also establishing the number of cycles;
- optimizing the recovery process by adsorption in a static regime of indium and gallium ions, through factorial design experiments in order to select reliable and efficient solutions.

A first objective of this study was to synthesize and characterize spinel-structured magnesium ferrite, belonging to the class of oxide magnetic materials for the recovery of indium and gallium by adsorption from aqueous media (**Chapter 4**).

Spinel $MgFe_2O_4$ was synthesized by the co-precipitation method, using magnesium carbonate as the magnesium source. The co-precipitation method is a popular wet chemical approach for the synthesis of magnesium ferrite particles, due to its simplicity and relatively low cost.

As the pH increases, the metal ions form insoluble hydroxides, which precipitate from the solution as colloidal particles. The resulting suspension is allowed to "age", allowing the particles to grow and stabilize, reducing aggregation and improving crystallinity. The washed, dried precipitate is heat-treated to remove organic components and crystallize the hydroxides into the desired magnesium ferrite spinel phase ($MgFe_2O_4$). The structure, morphology, composition and adsorbent properties are revealed by physicochemical methods. Thus:

- From a thermal point of view, by thermogravimetric analysis, it was established that spinel is formed up to $260^\circ C$.
- By X-ray diffraction, XRD, the phases present were identified and the parameters of the crystal lattice were determined, calculating the average size of the crystallites, using the Scherrer formula.
- By Fourier transform infrared spectroscopy, FT-IR, the formation of metal-oxygen bonds characteristic of spinel ferrites was confirmed.

- By atomic force microscopy, AFM, the surface of the material could be visualized and characterized, at nanometric or even atomic dimensions. The results obtained show the presence of roughness, as a result of the modification of the morphology.
- At the same time, the magnification of the prepared material was determined, presenting a superparamagnetic behavior.
- A pH_{pZc} (point of zero charge) of 9.2 was obtained for magnesium ferrite spinel (MgFe_2O_4), which is key information in understanding its surface behavior, especially in aqueous solutions.

Also in Chapter 4, the recovery of indium and gallium ions by static adsorption using spinel MgFe_2O_4 is presented. The recovery of indium (In) and gallium (Ga) by adsorption is an efficient and environmentally friendly process, essential for the valorization of these rare metals, used in the high-tech industry. Recovery by adsorption presents major advantages compared to traditional methods, such as: low cost, high efficiency, selective recovery and sustainability.

Specific parameters of the static adsorption process are essential. These are: the S:L ratio, the pH of the indium ion solution, the contact time, the temperature and the initial concentration of indium ions.

In the case of In(III) recovery by adsorption on MgFe_2O_4 spinel, specific parameters are:

- the optimal S:L ratio is 0.1 g : 25 mL;
- the optimal pH range is $\text{pH} > 2$;
- the contact time is 90 minutes and the temperature is 298 K;
- the maximum concentration is 200 mg In(III)/L, when an adsorption capacity of 46.4 mg/g is obtained.

To study the mechanism of the adsorption process, kinetic, equilibrium and thermodynamic studies were performed. Thus:

- The experimental data obtained were modeled using three different kinetic models: Lagergren, Ho and McKay and Weber-Morris. The pseudo-second-order kinetic model is the one that models the experimental data best, because the regression coefficient is closer to 1, $R^2 \sim 1$. Moreover, the value of $q_{e,calc}$ calculated based on the pseudo-second-order model is close to the experimental one ($q_{e,exp}$).

- The rate determinant is stage 1, according to the Weber and Morris model.
- The activation energy value ($E_a = 7.46$ kJ/mol), which shows us that the adsorption process studied is a physical one.

- Maximum adsorption capacity obtained experimentally, $q_{e,exp} \sim 46.4$ mg In (III)/g. The model that best describes the adsorption process is the Sips model, because the regression coefficient, R^2 , is closest to 1 ($R^2 = 0.9877$), and the calculated adsorption capacity is ~ 47.5 mg In(III)/g, being close to the experimental one.

- From the thermodynamic studies it was found that ΔH^0 has a positive value, which means that the adsorption process of In(III) is endothermic. It was also found that ΔG^0 has negative values, increasing in absolute value with increasing temperature, indicating that the adsorption process is spontaneous and influenced by temperature. The value of ΔS^0 is positive, which indicates that the adsorption process occurs at the interface of the $MgFe_2O_4$ material/In(III) solution.

Spinel $MgFe_2O_4$, used as a material with adsorbent properties, can be used with good results for the recovery of indium ions from aqueous solutions by adsorption.

In the case of Ga(III) recovery by adsorption on spinel $MgFe_2O_4$, specific parameters are:

- optimal ratio S:L = 0.1 g:25 mL;
- optimal contact time is 90 min;
- temperature 298 K;
- initial concentration is 120 mg Ga(III)/L.

By performing the experiments under these conditions, a maximum adsorption capacity of ~ 24.7 mg Ga(III)/g was obtained.

Studies on the mechanism of the adsorption process have shown that:

- The pseudo-second-order kinetic model is the one that models the experimental data best, because the regression coefficient has a value closer to 1, $R^2 \sim 1$. Moreover, the value of $q_{e,calc}$ calculated based on the pseudo-second-order model is close to the experimental one ($q_{e,exp}$).

- The rate determinant is stage 1, according to the Weber and Morris model.

- The activation energy value is $E_a = 4.2$ kJ/mol, according to which the studied adsorption process is a physical one.

- Maximum adsorption capacity obtained experimentally, $q_{e,exp} \sim 24.7$ mg Ga(III)/g. The model that best describes the adsorption process is the Sips model, because the regression coefficient, R^2 , is closest to 1 ($R^2 = 0.9877$), and the calculated adsorption capacity is ~ 24.8 mg Ga(III)/g, being close to the experimental one.

- From the thermodynamic studies it was found that the free enthalpy, ΔH^0 , has a positive value, which means that the adsorption process of Ga(III) is endothermic. It was also found that the free energy, ΔG^0 , has negative values, increasing in absolute value with increasing temperature, indicating that the adsorption process is spontaneous and influenced by temperature. The value of ΔS^0 is positive, which indicates that the adsorption process occurs at the interface of the $MgFe_2O_4$ material/Ga(III) solution.

Adsorption-desorption studies are essential in the complete characterization of an adsorbent material and its performance in separation or purification processes. They provide crucial information not only on how well a material can retain a particular compound (adsorption), but also on how easily and efficiently the compound can be released later (desorption). This release capacity (regeneration) is vital for the reuse of the adsorbent and for the recovery of the adsorbate.

It was observed that after indium adsorption, the spinel adsorbent material was reused 11 times, and after gallium adsorption, the material was reused 7 times.

The second objective was to obtain a group of materials by functionalizing by impregnation with "active groups" a pre-existing, porous support material (**Chapter 5**). The impregnation method is preferred because it allows the controlled distribution of the active groups over a large surface area, without fundamentally altering the structural integrity of the support. The support in question was a synthetic polymeric resin of the Amberlite XAD form, and the extractants were from the amino acid group.

The functionalization method used is the solvent impregnation resin method (SIR-Solvent Impregnated Resin), designed to improve the adsorbent properties of the inert support, i.e. Amberlite XAD7 and Amberlite XAD4 resin. The amino acid L-Valine, selected as the extractant, is distinguished by its environmental friendliness, cost-effectiveness and the presence of active functional groups (-NH₂ and -COOH) in its molecular structure, which increases the adsorption capacities of the material.

To highlight the presence of the amino acid L-valine on the surface of the Amberlite XAD7 resin, the synthesized material was characterized by scanning electron microscopy (SEM) and elemental analysis by energy dispersive X-ray spectroscopy (EDX). Also, the functional groups specific to the support, but especially to the extractant/amino acid, were highlighted by Fourier transform infrared spectroscopy. The zero charge point, pH_{PZC}, was determined using the method of bringing the studied system to equilibrium. Thus:

- From the SEM micrographs, the presence of some points on the surface of the spheres was observed, indicating the presence of the amino acid L-valine;
- From the EDX spectra, the presence of a nitrogen-specific peak was observed, confirming the successful functionalization of the XAD7 support surface, corroborated by the absence of this peak in the EDX spectrum of the unmodified XAD7 resin;
- Specific to the Amberlite XAD7 type polymeric support, the FT-IR spectrum reveals distinct vibrational bonds specific to the polymeric resin and the amino acid L-Valine.
- The zero charge point (pH_{PZC}) for the studied material is approximately 6.4, indicating the pH at which the electrical charge on the surface of the material is neutral.

A possible mechanism for obtaining the XAD7-Val material is based on the following theories:

(i) The XAD7-Val adsorbent material was obtained by impregnating an Amberlite XAD7 type polymeric support, which is a macroporous aliphatic acrylic, non-ionic resin, with a large specific surface area (around 450-750 m²/g) and high porosity. Due to its aliphatic nature, it can adsorb non-polar compounds from aqueous solutions, but also polar compounds from non-polar solvents;

(ii) The extractant was the amino acid L-valine whose specific functional groups are: amino groups (-NH₂), which are basic groups that can be protonated in acidic

solutions. They can participate in electrostatic interactions (ionic attraction) and in the formation of hydrogen bonds. Carboxylic groups (-COOH) are acidic groups that can deprotonate in basic solutions, forming -COO-. They can also participate in electrostatic interactions and hydrogen bonds.

The L-valine impregnation method (Solvent-Impregnated Resin - SIR) ensures the presence of these active groups on the surface and in the pores of the resin.

Also in **Chapter 5**, the efficiency with which In(III) and Ga(III) can be recovered from aqueous solutions was investigated, by adsorption on the material obtained by modifying the Amberlite XAD7 resin by impregnation with the amino acid L-valine.

In the case of In(III) recovery by adsorption, the following were found:

- The most important parameter, whose influence was established first of all, was the pH. Thus, it was found that adsorption studies can be carried out at $\text{pH} > 3$.

- Since the S:L ratio is another important parameter in adsorption processes, from the data obtained it was established that with the increase in the amount of solid material the adsorption capacity of the material increases, but not significantly. Thus, the studies were carried out at the ratio S:L=0.1g XAD7-Val:25 mL In(III) solution.

- It was found that with the increase in contact time the adsorption capacity of the material increases, establishing that after 90 minutes, equilibrium is reached. At the same time, it was observed that simultaneously with the increase in temperature, in the range of 298-328 K, the adsorption capacity increases, but insignificantly.

- The maximum concentration of 140 mg In(III)/L leads to a maximum adsorption capacity of 25.14 mg/g.

Kinetic, thermodynamic and equilibrium studies were carried out to establish the adsorption mechanism of In(III) on the XAD7-Val material. Thus:

- It was found that the adsorption processes accurately follow the pseudo-second-order kinetic model, as a result of the close value of the regression coefficient, R^2 , to 1.

- Based on the obtained activation energy, it can be stated that the adsorption processes are physical processes.

- Based on the study of the three adsorption isotherms, Langmuir, Freundlich and Sips, it was found that most of the studied materials accurately follow the Sips isotherm model, confirmation being the regression coefficient, $R^2 \sim 1$, as well as the value of the maximum adsorption capacity established by calculation ($q_{e,calc}$), which is close to the value established experimentally ($q_{e,exp}$).

In the case of Ga(III) recovery by adsorption, specific process parameters were determined, establishing the following:

- the optimal S:L ratio is 0.1 g : 25 mL;
- the optimal pH is at pH values > 2 ;
- the contact time is 90 minutes and the temperature is 298 K;
- a maximum concentration of 100 mg Ga(III)/L allows to obtain the maximum adsorption capacity of the XAD7-Val material, $q_{max} = 19.6$ mg/g.

Under these conditions, the mechanism of the adsorption process of Ga(III) ions on the XAD7-Val material was found to be spontaneous and endothermic, the process being of a physical nature.

Adsorption-desorption studies are important in the complete characterization of an adsorbent material and its performance in separation or purification processes. They provide information about how well a material can retain a certain compound (adsorption) and how easily and efficiently the compound can be released later (desorption).

It was observed in the experimental studies that after indium adsorption, the XAD7-Val adsorbent material was reused 6 times, and after gallium adsorption, the material was reused 5 times.

In **Chapter 6**, starting from experimental data and with the aim of facilitating the scaling of the process at an industrial level, the doctoral thesis proposes the optimization of the adsorption process through factorial design, which is an extremely efficient statistical method to achieve this, allowing the simultaneous investigation of the influence of several variables (factors) and the interactions between them, with a minimum number of experiments.

The factorial design is applied, following a series of steps such as:

(i) identification of factors and levels (S:L ratio; solution pH; initial metal ion concentration; contact time and temperature);

(ii) choosing the type of factorial design (Full Factorial Design; Fractional Factorial Design or Response Surface Methodology (RSM));

(iii) conducting experiments (experiments were performed according to the matrix generated by the chosen design, each experiment being a specific combination of levels for all factors);

(iv) data analysis (data were statistically analyzed, usually using specialized software (e.g. Minitab, Design-Expert, R, Python with libraries such as statsmodels or scipy)

(v) interpretation of results and optimization (based on the analysis, the most influential factors will be identified; the interactions between factors will be understood (e.g. the optimal pH depends on the S:L ratio); the optimal conditions for maximum metal ion recovery and the prediction of process performance under various conditions).

The experimental and optimized data are in agreement, suggesting that optimizing the indium(III) recovery process by adsorption on MgFe_2O_4 spinel is a viable and credible strategy.

Analysis of the experimental data, using Response Surface Methodology (RSM) and Response Surface Design (RSD), demonstrated that the In(III) adsorption process depends largely on the contact time and initial concentration. In contrast, temperature and pH had a much smaller influence on this process.

By optimizing the adsorption process response, it is observed that at contact time values of ~106 min and an initial In(III) concentration of ~264 mg/L, the adsorption capacity is ~ 48 mg/g with a probability of 80%.

In the case of the Ga(III) adsorption recovery process, by optimizing the response of the adsorption process, it is observed that at contact time values of ~106 min and at an initial Ga(III) concentration of ~124 mg/L, the adsorption capacity is ~25.8 mg/g with a probability of 58%.

These contributions to the design of new materials are crucial for optimizing recovery processes and implementing efficient recycling protocols, thus contributing to a circular economy and sustainable resource use for indium and gallium.

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The original research presented in this doctoral thesis resulted in:

- the publication of 3 scientific papers in journals indexed in Web of Science, Clarivate, 2 of which were classified as Q2 and 1 as Q1. Thus:

1. Cosmin Vancea, **Loredana Ciocarlie**, Adina Negrea, Giannin Mosoarca, Mihaela Ciopec, Narcis Duteanu, Petru Negrea, Bogdan Pascu, Nicoleta Nemes, Evaluation of Functionalized Amberlite Type XAD7 Polymeric Resin with L-Valine Amino Acid Performance for Gallium Recovery, **Polymers**, 2024, 16, 837. <https://doi.org/10.3390/polym16060837> (Q1); FI=4,9

2. **Loredana Ciocărlie**, Adina Negrea, Mihaela Ciopec, Narcis Duțeanu, Petru Negrea, Paula Svera, Cătălin Ianăși, Adsorption performances and mechanisms of MgFe₂O₄ spinel toward gallium(III) from aqueous solution, 2024, **Materials**, 2024, 17, 5740. <https://doi.org/10.3390/ma17235740> (Q2); FI=3,2

3. **Loredana Ciocărlie**, Adina Negrea, Mihaela Ciopec, Narcis Duteanu, Petru Negrea, Paula Ianasi, Catalin Ianasi, Nicoleta Sorina Nemes, Indium Recovery by Adsorption on MgFe₂O₄ Adsorbents, **Materials**, 15, 7054, 2022, <https://doi.org/10.3390/ma15207054> (Q2); FI=3,2

- **4 papers presented** at national scientific events;
- **4 dissertation papers**;
- **H-index = 3**;
- **Cumulative factor, FIC=11.3.**

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