



Ain Shams University  
Faculty of Science  
Chemistry Department



# **Development and performance evaluation of hybrid magnetic composites as solid phase extractants for some lanthanides**

*A Thesis Submitted by*

***Mohamed Abd El-Hameed Attia Mohamed***

*M. Sc. of science in chemistry (2015)*

*Assistant Lecturer*

*Nuclear Chemistry Department – Hot Laboratories Center*

*Atomic Energy Authority*

*For the Ph. D. Degree of Science in Chemistry*

*(Inorganic Chemistry)*

*To*

*Chemistry Department*

*Faculty of Science*

*Ain Shams University*

2019



Ain Shams University  
Faculty of Science  
Chemistry Department



# Development and performance evaluation of hybrid magnetic composites as solid phase extractants for some lanthanides

*A Thesis Submitted by*

***Mohamed Abd El-Hameed Attia Mohamed***

*M. Sc. of science in chemistry (2015)*

*Assistant Lecturer*

*Nuclear Chemistry Department – Hot Laboratories Center*

*Atomic Energy Authority*

*Under Supervision of*

**Prof. Dr. Ebtisam Ahmed Saad**

*Prof. of Inorganic and Radiation  
Chemistry, Chemistry Dept.,  
Faculty of Science,  
Ain Shams University*

**Prof. Dr. Hanan Hussien Someda**

*Prof. of Radiochemistry, Head of  
Radioisotopes Production Division,  
Hot Laboratories Center,  
Atomic Energy Authority*

**Prof. Dr. Reda Rashad Sheha**

*Prof. of Inorganic and Radiochemistry,  
Head of Nuclear Chemistry Dept.,  
Hot Laboratories Center,  
Atomic Energy Authority*

**Dr. Saber Ibrahim Moussa**

*Lecturer of Radiochemistry,  
Nuclear Chemistry Dept.,  
Hot Laboratories Center,  
Atomic Energy Authority*

2019



Ain Shams University  
Faculty of Science  
Chemistry Department



Approval Sheet

**Thesis Title:**

"Development and performance evaluation of hybrid magnetic composites as solid phase extractants for some lanthanides"

*Submitted by*

***Mohamed Abd El-Hameed Attia Mohamed***

*M. Sc. Chemistry, 2015*

*For the Ph.D. Degree of Science in Chemistry*

*(Inorganic Chemistry)*

*To*

*Chemistry Department, Faculty of Science, Ain Shams University*

**This thesis for Ph.D. Degree has been approved by:**

**1- Prof. Dr. Ebtisam Ahmed Saad**

Prof. of Inorganic and Radiation Chemistry,  
Faculty of Science, Ain Shams University.

**2- Prof. Dr. Hanan Hussien Someda**

Prof. of Radiochemistry,  
Hot Laboratories Center, Atomic Energy Authority.

**3- Prof. Dr. Reda Rashad Sheha**

Prof. of Inorganic and Radiochemistry,  
Hot Laboratories Center, Atomic Energy Authority.

**4- Dr. Saber Ibrahim Moussa**

Lecturer of Radiochemistry,  
Hot Laboratories Center, Atomic Energy Authority.

**Head of Chemistry Department**

Prof. Dr. Ibrahim Hussieny Ali Badr



Ain Shams University  
Faculty of Science  
Chemistry Department



Approval Sheet

**Thesis Title:**

"Development and performance evaluation of hybrid magnetic composites as solid phase extractants for some lanthanides"

*Submitted by*

***Mohamed Abd El-Hameed Attia Mohamed***

*M. Sc. Chemistry, 2015*

*For the Ph.D. Degree of Science in Chemistry*

*(Inorganic Chemistry)*

*To*

*Chemistry Department, Faculty of Science, Ain Shams University*

**This thesis for Ph.D. Degree has been approved by:**

**1- Prof. Dr. Abdelhakim Taha Kandil**

Prof. of Inorganic and Nuclear Chemistry,  
Faculty of Science, Helwan University.

**2- Prof. Dr. Sadeek Atia Sadeek**

Prof. of Inorganic Chemistry,  
Faculty of Science, Zagazig University.

**3- Prof. Dr. Ebtisam Ahmed Saad**

Prof. of Inorganic and Radiation Chemistry,  
Faculty of Science, Ain Shams University.

**4- Prof. Dr. Hanan Hussien Sameda**

Prof. of Radiochemistry,  
Hot Laboratories Center, Atomic Energy Authority.

**Date of discussion**

23/4/2019

**Head of Chemistry Department**

Prof. Dr. Ibrahim Hussieny Ali Badr



بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

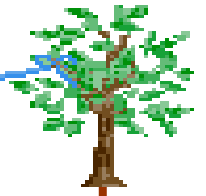
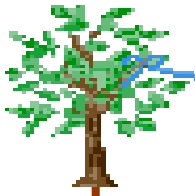
قَالُوا سُبْحَانَكَ

لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا

إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ

صَدَقَ اللَّهُ الْعَظِيمُ

سورة البقرة: آية ٣٢



Dedicated to

*(The Spirit of My Father)*

To

*My Dear Mother, My Lovely Wife, My Children,  
My Brother and My Sisters*

All of those who

Love me

Mohamed A. Attia



## Acknowledgement

First, I would like to thank **ALLAH**, most merciful, who blesses my effort, shows me the way and enables me to present this work in an acceptable style. On the top, **my parents, my wife, my children and the rest of my family**. None of the things I have done would be done without their endless support, patience and encouragement throughout my years of study.

I would like to express my deeply heart thanks to **Prof. Dr. Ebtisam Ahmed Saad** (Prof. of Inorganic and Radiation Chemistry, Faculty of Science, Ain Shams University) for giving me the honor of working under her supervision, and her unforgettable sincere encouragement.

I would like to express my deeply heart thanks to **Prof. Dr. Hanan Hussien Sameda** (Prof. of Radiochemistry, Atomic Energy Authority) for giving me the honor of working under her supervision, and her unforgettable sincere encouragement.

No words can express my feeling and respect to **Prof. Dr. Reda Rashad Sheha** (Prof. of Inorganic and Radiochemistry, Atomic Energy Authority) for giving me the honor of working under his supervision, his backing and encouragement gave me a push to this work.

I wish also to express my deep thanks to **Dr. Saber Ibrahim Moussa** (Lecturer of Radiochemistry, Atomic Energy Authority) who supported me during the study and the investigations of all the stages of the experimental work.

Mohamed A. Attia





## **Publications**

## Publications

Applied Radiation and Isotopes 145 (2019) 85–94



Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: [www.elsevier.com/locate/apradiso](http://www.elsevier.com/locate/apradiso)Hydroxyapatite/NiFe<sub>2</sub>O<sub>4</sub> superparamagnetic composite: Facile synthesis and adsorption of rare elementsMohamed A. Attia<sup>a,\*</sup>, Saber I. Moussa<sup>a,\*</sup>, Reda R. Sheha<sup>a</sup>, Hanan H. Someda<sup>a</sup>, Ebtsam A. Saad<sup>b</sup><sup>a</sup> Nuclear Chemistry Dept., Hot Lab Center, Atomic Energy Authority, P.O. 13759, Cairo, Egypt<sup>b</sup> Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

## HIGHLIGHTS

- A superparamagnetic hydroxyapatite composite (CaHAP/NF) was successfully synthesized.
- The composite is a crystalline in nature, possesses a high porous structure and chemically stable at pH > 3.5.
- <sup>152+154</sup>Eu and <sup>160</sup>Tb radionuclides were effectively removed using the synthesized magnetic composite.
- REEs were sufficiently recovered using FeCl<sub>3</sub> and EDTA as eluents.
- The chromatographic separation of Eu(III) from Tb(III) was significantly attained using EDTA.

## ARTICLE INFO

## Keywords:

Hydroxyapatite  
Ferrite  
Superparamagnetic  
Eu(III)  
Tb(III)

## ABSTRACT

A magnetic hydroxyapatite composite (CaHAP/NF) derived from calcium hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] and nickel ferrite [NiFe<sub>2</sub>O<sub>4</sub>] was successfully synthesized by a coprecipitation method. The synthesized composite was characterized using Fourier transform infrared spectroscopy (FT-IR), X-Ray diffractometer (XRD), thermogravimetric differential thermal analysis (TG-DTA), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). Results clarify that the composite is a crystalline in nature, thermally stable up to 800 °C and possesses a high porous structure. The synthesized CaHAP/NF composite is a superparamagnetic material easily separated from aqueous solutions and would dissociate to some extent in strongly acidic conditions. The synthesized material was successfully applied as a solid phase for separation of Eu(III) and Tb(III) ions from aqueous solutions. The effect of various parameters (e.g. solution pH, equilibrium time and ionic strength) on sorption process was studied in static conditions. The synthesized sorbent could be considered as an efficient candidate for separation and recovery of Eu(III) and Tb(III). The sorption process was very fast initially, reached equilibrium within 6 h of contact and independent of ionic strength. The maximum sorption capacity values were 137.35 and 130.43 mg g<sup>-1</sup> for Eu(III) and Tb(III), respectively. Desorption of Eu(III) and Tb(III) from loaded sample was studied using various eluents and maximum recovery was obtained using FeCl<sub>3</sub> and EDTA solutions. More importantly, both FeCl<sub>3</sub> and EDTA were individually applied as eluents in chromatographic separation of Eu(III) and Tb(III) in CaHAP/NF packed column and the best separation results were obtained by EDTA.

## 1. Introduction

Rare earth elements (REEs) consist of 17 elements of the periodic table including 15 lanthanides along with yttrium and scandium (Liatsou et al., 2015; Anastopoulos et al., 2016; Jacinto et al., 2018). They are further subdivided into light and heavy rare earth elements on the basis of their atomic number. REEs have unique properties and often termed as "seeds of technology" (Ponou et al., 2014). They are

widely used in different applications such as metallurgy, electronics, alloys, fertilizers, lasers, magnets, superconductors, catalysis, chemical reagents and nuclear energy (Smith et al., 2016; Rychkov et al., 2018). The total demand for REEs was increased from 128,000 t in 2011 to 170,000 t in 2015, while it is expected to rise to 255,000 t in 2020 with a growth rate about 6–10%/year (Fernandez, 2017). Such expected great demand for rare earth elements is resulted mainly from their widespread applications in many fields of human life. With ever-

\* Corresponding author.

E-mail addresses: [mohamed.attia@eaea.org.eg](mailto:mohamed.attia@eaea.org.eg) (M.A. Attia), [saber.moussa@eaea.org.eg](mailto:saber.moussa@eaea.org.eg) (S.I. Moussa), [reda.sheha@eaea.org.eg](mailto:reda.sheha@eaea.org.eg) (R.R. Sheha).<https://doi.org/10.1016/j.apradiso.2018.12.003>

Available online 05 December 2018

0969-8043/ © 2018 Published by Elsevier Ltd.



# **Contents**

## **Contents**

<b><i>Contents</i></b>	<b><i>Page</i></b>
<b>List of Tables.</b>	v
<b>List of Figures.</b>	x
<b>List of Abbreviations.</b>	xix
<b>Aim of the work.</b>	xx
<b>Abstract.</b>	xxi

### ***CHAPTER 1***

#### **INTRODUCTION**

<b>1. Introduction.</b>	1
<b>1.1. Characteristics of the lanthanides.</b>	1
<b>1.2. Occurrence and abundance of lanthanides.</b>	3
<b>1.3. Lanthanide ores.</b>	4
<b>1.4. Extraction of lanthanides from ores.</b>	4
<b>1.5. Separation of lanthanides.</b>	5
1.5.1. Precipitation.	5
1.5.2. Chemical separation.	6
1.5.3. Fractional crystallization.	6
1.5.4. Solvent extraction.	7
1.5.5. Ion exchange chromatography.	8
<b>1.6. Application of lanthanides.</b>	11
<b>1.7. The studied lanthanides.</b>	13
1.7.1. Samarium.	13
1.7.2. Europium.	14
1.7.3. Terbium.	15
<b>1.8. Nano–materials.</b>	15
<b>1.9. Literature survey.</b>	17

### ***CHAPTER 2***

---

## EXPERIMENTAL

<b>2. Experimental.</b>	18
<b>2.1. Chemicals and reagents.</b>	18
<b>2.2. Apparatus.</b>	19
<b>2.3. Synthesis of sorbents.</b>	20
2.3.1. Nickel ferrite.	20
2.3.2. Calcium hydroxyapatite.	21
2.3.3. Calcium hydroxyapatite/Nickel ferrite.	21
2.3.4. Nickel ferrite/Calcium hydroxyapatite.	22
2.3.5. Calcium hydroxyapatite–Nickel ferrite.	23
<b>2.4. Characterization techniques.</b>	24
2.4.1. Brunauer–Emmett–Teller (BET) surface area.	24
2.4.2. Fourier transform infrared spectroscopy (FT–IR).	24
2.4.3. X–Ray diffraction (XRD).	24
2.4.4. Thermal analysis.	24
2.4.5. Scanning electron microscope (SEM).	25
2.4.6. Magnetic properties.	25
<b>2.5. Radiotracers preparation.</b>	25
<b>2.6. Batch experiments.</b>	25
2.6.1. Chemical stability.	25
2.6.2. Sorption procedures.	27
2.6.2.1. Effect of contact time.	27
2.6.2.2. Effect of pH.	27
2.6.2.3. Maximum sorption capacity.	29
2.6.2.4. Effect of sample mass.	30
2.6.2.5. Effect of ionic strength.	30
2.6.2.6. Ion exchange behavior.	30
2.6.2.7. Effect of initial concentration.	31
2.6.2.8. Effect of temperature.	31
2.6.2.9. Effect of competing cations.	31
2.6.3. Desorption procedures.	32
2.6.4. Regeneration procedures.	33

<b>2.7. Column experiments.</b>	33
2.7.1. Individual system.	33
2.7.2. Binary system.	35

## ***CHAPTER 3***

### **RESULTS AND DISCUSSION**

<b>3. Results and discussion.</b>	36
<b>3.1. Characterization.</b>	36
3.1.1. Surface area measurements.	36
3.1.2. FT–IR spectroscopy.	37
3.1.3. X–ray diffraction.	39
3.1.4. Thermal analysis.	41
3.1.5. Scanning electron microscope.	44
3.1.6. Magnetic properties.	47
<b>3.2. Stability assessment.</b>	52
<b>3.3. Static studies.</b>	61
3.3.1. Equilibrium study.	61
3.3.1.1. Equilibrium time.	61
3.3.1.2. Effect of pH.	64
3.3.1.3. Maximum sorption capacity.	66
3.3.1.4. Effect of sample mass.	68
3.3.1.5. Effect of ionic strength.	71
3.3.1.6. Ion exchange behavior.	73
3.3.1.7. Effect of initial concentration.	77
3.3.1.8. Effect of temperature.	79
3.3.1.9. Effect of competing cations.	81
3.3.2. Desorption study.	84
3.3.3. Recycling study.	87
<b>3.4. Mathematical models.</b>	94
3.4.1. Validation of kinetic and isotherm models.	95
3.4.1.1. Reduced Chi–square (Reduced $\chi^2$ ).	96
3.4.1.2. Residual Sum of Squares Error (SSE).	96
3.4.1.3. Adjusted R–square ( $R^2$ ).	96
3.4.1.4. Root mean square of the error (Root–MSE).	97

3.4.2. Sorption kinetics.	97
3.4.2.1. Pseudo–first order model.	97
3.4.2.2. Pseudo–second order model.	102
3.4.2.3. Elovich model.	106
3.4.2.4. Intra–particle diffusion model.	109
3.4.3. Sorption isotherms.	114
3.4.3.1. Two–parameter isotherm models.	114
3.4.3.1.1. Langmuir model.	114
3.4.3.1.2. Freundlich model.	120
3.4.3.1.3. Dubinin–Radushkevich model.	124
3.4.3.1.4. Temkin model.	129
3.4.3.2. Three–parameter isotherm models.	134
3.4.3.2.1. Redlich–Peterson model.	134
3.4.3.2.2. Langmuir–Freundlich model.	141
3.4.3.2.3. Sips model.	147
3.4.3.2.4. Khan model.	153
3.4.3.3. Four–parameter isotherm models.	158
3.4.3.3.1. Marczewski–Jaroniec model.	158
3.4.3.3.2. Baudu model.	165
3.4.3.4. Five–parameter isotherm models.	171
3.4.3.4.1. Fritz–Schlunder model.	171
3.4.3.5. Final remarks on sorption isotherms.	178
3.4.4. Sorption thermodynamics.	181
<b>3.5. Dynamic studies.</b>	188
3.5.1. Individual system.	188
3.5.1.1. Eu(III) sorption.	188
3.5.1.2. Tb(III) sorption.	190
3.5.2. Binary system.	193
<b>SUMMARY AND CONCLUSIONS.</b>	199
<b>REFERENCES.</b>	209
<b>ARABIC SUMMARY.</b>	i