

**Evaluation of Nano Material with Magnetic
Properties as a Potential Sorbent in Radioactive
Waste Management**

By

Eng. Ola Abdel-Ghany Abdel-Moamen Ibrahim

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in partial fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
in
CHEMICAL ENGINEERING

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2015

**Evaluation of Nano Material with Magnetic
Properties as a Potential Sorbent in Radioactive
Waste Management**

By

Eng. Ola Abdel-Ghany Abdel-Moamen Ibrahim

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in partial fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
in
CHEMICAL ENGINEERING

Under the Supervision of

Prof. Dr. Nabil M. Abdel-Moniem
Prof. of Chemical Engineering
Faculty of Engineering
Cairo University

Prof. Dr. Ibrahim Ismail
Prof. of Chemical Engineering
Faculty of Engineering
Zewail University

Prof. Dr. Rehab.O. Abdel Rahman
Associate Prof. of Chemical Nuclear Engineering
Hot laboratory center
Atomic Energy Authority

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2015

**Evaluation of Nano Material with Magnetic
Properties as a Potential Sorbent in Radioactive
Waste Management**

By

Eng. Ola Abdel-Ghany Abdel-Moamen Ibrahim

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in partial fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
in
CHEMICAL ENGINEERING

Approved by the Examining committee:

Prof. Dr. Nabil M. Abdel-Moniem	Thesis main advisor
Prof. Dr. Ahmed Nasr	Member
Prof. Dr. Ahmed Amin zaatot	Member
Prof. Dr. Ibrahim Ismail	Thesis advisor

**FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2015**

Acknowledgement

I am mightily thankful to ALLAH, by the grace of advancement and prosperity of this work was possible.

First I am most deeply indebted, to Prof. Dr. Nabil M. Abdel-Moniem, Prof. of Chemical Engineering, Faculty of Engineering, Cairo University, for his supervision, motivation, guidance and continual supports in final presentation of the work.

I wish to express my gratitude and sincere thanks to Prof. Dr. Ibrahim Ismail, Prof. of Chemical Engineering, Faculty of Engineering, Zewail University, for his supervision in this work, encouragement and immense assist.

I would like to express my deep honest thanks and appreciation to Prof. Dr. Rehab O. Abdel Rahman, Associate Prof. of Nuclear Engineering, Hot Laboratories Center, Egyptian Atomic Energy Authority, for effective supervision in addition to fruitful discussion during the progress of this work.

I would like to express my gratitude and sincere appreciation to Dr. Haneen Abdel salam, Lecturer of chemical Engineering, Hot Laboratories Center, Egyptian Atomic Energy Authority, for her internal supervision, beneficial advice and aid to complete this work.

Finally, my thanks to all the staff members of waste management department, Hot Laboratories and Waste Management Center.

Table of Contents

	Page
ACKNOWLEDGEMENT	
LIST OF TABLES	iii
LIST OF FIGURES	v
NOMENCLATURE	vii
ABSTRACT	ix
1. INTRODUCTION	1
2. REVIEW OF LITERATURE	3
2.1. Background on Radioactive waste	3
2.2 Toxicity and fate of cesium and strontium	3
2.3 Aqueous radioactive waste treatment techniques	4
2.3.1. Membrane technology	4
2.3.2. Evaporation	5
2.3.3. Chemical precipitation	8
2.3.4. Combined Methods	9
2.3.5. Sorption and Ion Exchange	10
2.3.5.1. Radioactive waste treatment using nano-sized magnetic sorbents	14
2.3.5.2. Gap analysis of using magnetic nano particles in radioactive waste treatment	19
3. THEORITICAL BACKGROUND	21
3.1. Alumino-silicates description	21
3.1.1. From "boiling stone" to alumino-silicates types	21
3.1.1.1. Natural alumino-silicates	21
3.1.1.2. Synthetic alumino-silicates	22
3.1.2. Chemical and Physical Properties of alumino-silicates	23
3.2. Environmental impact and the proposed solution for treatment of liquid radioactive wastes	23
3.3. Types of sorption process and its governing equations	24
3.3.1. Physical sorption	24
3.3.2. Chemical sorption	24
3.3.2.1. Kinetic studies	24
3.3.2.2. Equilibrium studies	25
3.4. Statistical design of experiments	26
3.4.1. Main and Interaction effects plots	27
3.4.2. Normal probability of the residues plot	27
3.4.3. Pareto plot	28

4. EXPERIMENTAL	29
4.1. Chemicals and Materials	29
4.2. Preparation	29
4.3. Characterization Techniques	30
4.3.1. X-Ray Diffraction Analysis (XRD)	30
4.3.2. Energy dispersive X-ray analysis (EDX)	32
4.3.3. Transmission Electron Microscopy (TEM)	32
4.3.4. FTIR Spectroscopy of Framework Vibrations	32
4.3.5. Surface area measurements	33
4.3.6. Stability studies	33
4.3.6.1. Chemical stability	33
4.3.6.2. Thermal stability	33
4.4. Sorption studies	33
4.4.1. Sorption kinetics	34
4.4.2. Effect of sorbent dose	34
4.4.3. Effect of proton concentration	34
4.4.4. Sorption isotherms	34
4.5. Statistical design of experiments	36
5. RESULTS AND DISCUSSION	37
5.1. Characterization	37
5.2. Sorption Experimental investigations	44
5.2.1. Kinetic studies	47
5.2.2. Effect of sorbent dose	53
5.2.3. Effect of proton concentration	53
5.2.4. Sorption isotherms	55
5.2.5. Estimation of thermodynamic parameters	62
5.3. Experimental design and analysis statistic	62
5.3.1. Main and interaction effects	69
5.3.2. Analysis of the variance (ANOVA)	71
5.3.3. The Pareto chart and normal probability plot	76
5.3.4. Residual analysis	81
SUMMARY AND CONCLUSIONS	85
REFERENCES	89
ARABIC SUMMARY	

LIST OF TABLES

	Page
Table (4.1) Chemicals and reagents used	29
Table (4.2) Values of operating variables used in the designed set of experiments	36
Table (5.1) The calculated parameters of pseudo-first and pseudo-second order kinetic models for Cs^+ and Sr^{2+} ions sorbed onto the prepared materials at 298 K	50
Table (5.2) The calculated parameters of pseudo-first and pseudo-second order kinetic models for Cs^+ and Sr^{2+} ions sorbed onto the prepared materials at 303 K	50
Table (5.3) The calculated parameters of pseudo-first and pseudo-second order kinetic models for Cs^+ and Sr^{2+} ions sorbed onto the prepared materials at 313 K	50
Table (5.4) The calculated parameters of langmiur and freundlish isotherm models for Cs^+ and Sr^{2+} ions sorbed onto the prepared materials at 298 K	61
Table (5.5) The calculated parameters of langmiur and freundlish isotherm models for Cs^+ and Sr^{2+} ions sorbed onto the prepared materials at 303 K	61
Table (5.6) The calculated parameters of langmiur and freundlish isotherm models for Cs^+ and Sr^{2+} ions sorbed onto the prepared materials at 313 K	61
Table (5.7) Values of thermodynamic parameters for sorption of Cs^+ and Sr^{2+} ions onto the prepared materials	63
Table (5.8) Experimental results of 2^4 designs for both cesium and strontium ions sorbed onto nano alumino silicate material in a single system	65
Table (5.9) Experimental results of 2^4 designs for both cesium and strontium ions sorbed onto magnetic alumino silicate material in a single system	65
Table (5.10) Experimental results of 2^4 designs for mixture of cesium and strontium ions sorbed onto nano and magnetic alumino silicate material in a binary system	65
Table (5.11) Statistical parameters for 2^4 designs for the sorption of Cs^+ and Sr^{2+} ions onto the prepared nano alumino-silicate material in a single system	67
Table (5.12) Statistical parameters for 2^4 designs for the sorption of Cs^+ and Sr^{2+} ions onto the prepared magnetic alumino-silicate material in a single system	68

Table (5.13) Statistical parameters for 2^4 designs for the sorption of Cs^+ and Sr^{2+} ions onto the prepared nano alumino-silicate material in a binary system	68
Table (5.14) Statistical parameters for 2^4 designs for the sorption of Cs^+ and Sr^{2+} ions onto the prepared magnetic alumino-silicate material in a binary system	69
Table (5.15) Analysis of variance-reduced model fit for cesium and strontium ions sorbed onto the prepared nano and magnetic materials in a single system	77
Table (5.16) Analysis of variance-reduced model fit for cesium and strontium ions sorbed onto the prepared nano and magnetic materials in a binary system	78

LIST OF FIGURES

	Page
Fig. (2.1): Environmental passage of radionuclides	6
Fig.(2.2): Schematic of the treatment of aqueous radioactive waste	6
Fig.(2.3): Membrane decontamination processes	7
Fig.(2.4): Schematic of a thin film evaporator type	7
Fig.(2.5): Flow diagram of a typical aqueous waste treatment facility	12
Fig. (3.1): A 'Black Box' Process Model Schematic	26
Fig. (4.1): Synthesis procedure of nano-sized and magnetic nano-sized alumino-silicate materials	31
Fig. (5.1): X-ray diffraction pattern of (A) nano-sized alumino-silicate and (B) magnetic nano-sized alumino-silicate materials	39
Fig. (5.2): EDX of (A) nano-sized alumino-silicate and (B) magnetic nano-sized alumino-silicate materials	40
Fig. (5.3): FTIR spectrum of (A) nano-sized alumino-silicate (free metal ion) ; (B) magnetic nano-sized alumino-silicate materials silicate (free metal ion); (C) Cs^+ and Sr^{2+} ions loaded onto nano-sized alumino-silicate ; (D) Cs^+ and Sr^{2+} ions loaded onto magnetic nano-sized alumino-silicate materials	42
Fig. (5.4): TEM image of the prepared (A) nano-sized alumino-silicate and (B) magnetic nano-sized alumino-silicate materials	43
Fig. (5.5): The effect of PH on the weight loss of (A) nano-sized alumino-silicate and (B) magnetic nano-sized alumino-silicate materials	45
Fig. (5.6): TGA/DTA of the prepared (A) nano-sized alumino-silicate and (B) magnetic nano-sized alumino-silicate materials	46
Fig. (5.7): Effect of contact time on the amount sorbed onto the prepared alumino-silicate materials at (A, B) 298 K; (C, D) 303 K and (E, F) 313K	48
Fig. (5.8): Kinetic plots of pseudo first-order for the sorption of Cs^+ and Sr^{2+} ions onto the prepared materials at (A,B) 298 K ; (C,D) 303 K and (E,F) 313 K	51
Fig. (5.9): Kinetic plots of pseudo second-order for the sorption of Cs^+ and Sr^{2+} ions onto the prepared materials at (A,B) 298 K ; (C,D) 303 K and(E,F) 313 K	52
Fig. (5.10): Effect of sorbent dose onto the prepared alumino-silicate materials at 298 K	54
Fig. (5.11): Effect of pH on the sorption of Cs^+ and Sr^{2+} ions sorbed onto (A) nano alumino-silicate material and (B) magnetic alumino-silicate material	56
Fig. (5.12): Relation between the initial concentration and the removal percent (A,B) and the initial concentration and sorbed amount (C,D) of the prepared materials at 298 K	58
Fig. (5.13): Comparison of experimental and predicted sorption isotherms of the synthesized materials according to Langmuir (single system) and extended Langmuir (binary system) model at (A, B) 298 K; (C, D) 303 K and (E, F) 313 K	59
Fig. (5.14): Comparison of experimental and predicted sorption isotherms of the synthesized materials according to Freundlich (single system) and	60

extended Freundlich (binary system) model at (A, B) 298K; (C, D) 303K and (E, F) 313K

Fig. (5.15): Relationship between Gibbs free energy change and temperature of sorption of Cs^+ and Sr^{2+} ions onto the prepared materials in single and binary system	63
Fig. (5.16): Experimental results at the center point of the experimental domain for both Cs^+ and Sr^{2+} ions sorbed onto the prepared magnetic and nano alumino silicate materials in single and binary systems	70
Fig. (5.17): The main effect plots of (A)Cs; (B) Sr sorbed onto the prepared nano material ;(C) Cs and (D)Sr sorbed onto the prepared magnetic material in a single system	72
Fig. (5.18): The main effect plots of (E)Cs; (F) Sr sorbed onto the prepared nano material; (G) Cs and (H)Sr sorbed onto the prepared magnetic material in a binary system	73
Fig. (5.19): Interaction effect plots of (A) Cs ; (B) Sr sorbed onto the prepared nano material; (C) Cs and (D)Sr sorbed onto the prepared magnetic material in a single system	74
Fig. (5.20): Interaction effect plots of (E) Cs; (F) Sr sorbed onto the prepared nano material;(G) Cs and (H)Sr sorbed onto the prepared magnetic material in a binary system	75
Fig. (5.21): The significant main and interaction terms of Cs (A); Sr (B) sorbed onto nano material and Cs (C); Sr (D) sorbed onto magnetic material in a single system at a significance of 0.05	79
Fig. (5.22): The significant main and interaction terms of Cs (E); Sr (F) sorbed onto nano material and Cs (G); Sr (H) sorbed onto magnetic material in a binary system at significance of 0.05	80
Fig. (5.23): Residuals versus predicted response for % removal of (A)Cs; (B)Sr sorbed onto the prepared nano material ; (C) Cs and (D) Sr sorbed onto the prepared magnetic material in a single system	82
Fig. (5.24): Residuals versus predicted response for % removal of (E) Cs; (F)Sr sorbed onto the prepared nano material ; (G) Cs and (H) Sr sorbed onto the prepared magnetic material in a binary system	83

NOMENCLATURE

C_i : Initial concentration of metal ion in solution (mg/l)

C_e : Equilibrium concentration of metal ion in solution at equilibrium (mg/l)

C_t : Concentration of metal ion in solution at time t (mg/l)

E : Mean free energy of sorption (kJ/mol)

k_1 : First order rate constant (min^{-1})

k_2 : Second order rate constant (g/mg.min)

K_f : Freundlich constant indicative of the relative adsorption capacity (mmol/kg)

m : Weight of the sorbent (g)

n : Freundlich constant indicative of the relative sorption capacity

%R: Removal percent

Q^0 : Maximum concentration on the solid phase (Langmuir saturation capacity) (mmol/kg)

q_e : Amount of metal ions sorbed onto the prepared materials at equilibrium (mg/g)

q_m : Maximum amount sorbed onto unit weight of sorbent i.e sorption capacity (mmol/kg)

q_t : Amount of metal ions sorbed onto the prepared materials at time t (mg/g)

R : Gas constant =8.314 J/mol. K

T : Absolute temperature (K)

V : Volume of solution (ml)

ΔG° : Gibbs free energy (kJ/mol)

ΔH° : Enthalpy change (kJ/mol)

ΔS° : Entropy change (J/mol.K)

E_i :The effect of the variable

R_{exp} : The measured response

N : Number of experiments at each level

t_j : Student's t-test

m : number of experiment at the central point

R_0 : observed value of sorption percent at the i central point

R_{0mean} : mean percent sorption at the central point

Nano: Abbreviation of the synthesized nano alumino-silicate material

Mag.: Abbreviation of the synthesized magnetic nano alumino-silicate material

SST: Total sum of squared

SSR: Sum of squares for regression

SSE: Sum of squared errors

MSE : the mean-square-error

F : The F-ratios

l : Number of the significance parameters

ε : Observed residuals

ABSTRACT

The long half life and high fission yield of cesium and strontium ions make them two of the most high risk products from nuclear fission consequently; their removal from radioactive wastes is a significant step in mitigating their harmful effects. Nano-sized alumino-silicate material, owing to its high radiation resistance, selectivity and thermal stability, was considered as an efficient sorbent for this purpose. To enhance the separation of sorbent-sorbate complex from aqueous solution after the sorption process, the material was prepared as a magnetized composite with magnetite. This magnetically modified alumino-silicate material enabled efficient and quick separation of the sorbent from solution using magnetic separation. Comparison between the capability of nano-sized alumino-silicate and the magnetic composite to eliminate Cs^+ and Sr^{2+} ions from aqueous solution was assessed and characterized using different characterization techniques. Effect of different variables such as initial ion concentration, sorbent dose, contact time, temperature and pH in the sorption process in single and binary system were studied and optimized. Pseudo first- and second-order rate constants were calculated from the graphical representation of the suggested models. The equilibrium sorption data were dissected using non-linear Langmuir and Freundlich models to assess the sorption characteristics and thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS). The experimental factors influencing the removal of cesium and strontium ions from aqueous solutions onto synthesized magnetic and nano alumino-silicate materials and their respective levels were studied, i.e. the initial Cs^+ and/or Sr^{2+} ion concentration in solution, C_i , ($50 \leq C_i \leq 1500$ mg/l), contact time, t , ($10 \leq t \leq 120$ min), power of hydrogen, pH, ($5 \leq \text{pH} \leq 11$) and temperature, T , ($298 \leq T \leq 303\text{K}$). These sorption factors were statistically investigated via means of analysis of variance and factorial design using Minitab software.

Within this context, the following investigations were executed:

- i. Review the most commonly used techniques for the treatment of aqueous radioactive waste and the main benefit of using sorption and particularly magnetic sorbents for removal of radionuclides from radioactive liquid wastes.
- ii. Synthesis of both nano- and magnetic nano-sized alumino-silicate from sodium aluminosilicate solution and using tetra methyl ammonium hydroxide as a template.
- iii. Examination and comparison characteristics of nano-sized and magnetic nano-sized alumino-silicate material.
- iv. Assessment of the sorption capability of the prepared materials for removal of cesium and strontium ions from single (non-competitive) and binary (competitive) aqueous systems and the effective factors such as temperature, initial Cs^+ and/or Sr^{2+} ion concentration, sorbent dose, pH and contact time on the sorption process were studied and optimized.
- v. Factorial design analysis was used to optimize the factors affecting the sorption of cesium and strontium ions. The interactions between affecting factors were also studied.

Based on the obtained results, the following were concluded:

- i. Magnetic nano-sized alumino-silicate material was successfully synthesized and characterized using different characterization techniques.
- ii. The sorption studies indicated the feasibility of using the prepared magnetic material for removal of Cs^+ and Sr^{2+} ions from liquid solution in both single and binary system due to its chemical stability, selectivity and high capacity for the concerned ions. The mean free energy in magnetic and nano materials was in the range corresponding to the chemisorptions type.

iii. A factorial design was employed to assess the quantitative removal of Cs^+ and Sr^{2+} cations from aqueous solution onto the synthesized magnetic and nano alumino-silicate. The studied experimental factors and their respective levels were the initial metal ion concentration in solution, contact time, power of hydrogen value and temperature.

1. INTRODUCTION

The incorporation of fast population growth and intensive industrial progress all over the world has led to several environmental issues [1]. Researchers are continuously looking for new ways to solve these environmental problems and as a result, many operational processes including treatment of radioactive waste have been proposed and improved.

Radioactive wastes originate from different sources such as the generation of electricity by nuclear fission, nuclear research centers and different uses of radioactive material for human requirements such as medicine. Radioactive waste may also developed from the processing of raw materials that enclose Naturally Occurring Radionuclides Materials (NORMs) such as in fertilizer manufacture [2]. ^{137}Cs and ^{90}Sr ions are two of the most important fission products owing to their high fission yield and long half life [3]. Evaporation, chemical precipitation and ion exchange/sorption are commonly used techniques for treatment of liquid radioactive wastes. Ion exchange/sorption process appears to be the most commonly used treatment technique for aqueous waste stream owing to its preference, efficiency and simplicity [4]. A wide variety of materials possessed different physical and chemical characteristics, that can be occur naturally or synthetic, is accessible for this technique. Inorganic synthetic ion exchange materials have germinated as an increasingly significant substitution or supplement for traditional organic ion exchangers, mainly in treatment of liquid radioactive waste because of their stability towards radiation and greater preference towards certain radionuclides such as cesium and strontium ions. Numerous inorganic ion exchangers such as sodium titanates, silicotitanates, hexacyanoferrates and alumino-silicates are in use in nuclear sites for the treatment of aqueous radioactive wastes [5]. The unique properties of alumino-silicates i.e. high ion exchange capacity, high radiation resistance, chemical and thermal stability and potential selectivity have been received considerable attention, especially for application in liquid radioactive waste treatment [5, 6].

Nano-sized alumino-silicates have higher ion exchange capability, higher surface area, faster exchange kinetic and amenable porosity compared to micron size alumino-silicates. However, despite these benefits, the major essential challenge with nano-sized alumino-silicates is their separation from the medium using conventional separation methods such as sedimentation and filtration as the sorbents may block filters or be lost. In addition, the sorbents might be discarded with the process sludge which produces secondary waste. To conquer the problems related to the separation and regeneration of sorbents, recent research has been focused on magnetic separation technology [7]. Separation technologies utilizing magnetic sorbents are an alternative method for treating radioactive waste that has received substantial attention in recent years [8]. The main benefit of this technology is that a large volume of radioactive waste can be purified in a very short time using less energy [8-12].

In order to assess the efficiency of the prepared material for elimination of cesium and strontium cations from aqueous solutions, a series of experiments were carried out under batch mode in single and binary contaminant system. The pertinent data, with respect to kinetic and equilibrium exchange studies, was obtained using simple kinetic and thermodynamic models.

Statistical design of experiment was performed to decrease the total number of experiments required to attain the optimal conditions for the sorption of chosen metallic ions onto the prepared materials using batch sorption system and to model a