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

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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 sorpion (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: Feundlich 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, ($5 \leq pH \leq 11$) and temperature, T, ($298 \leq T \leq 303K$). 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