



Thermodynamic analysis for the sorptive removal of cesium and strontium ions onto synthesized magnetic nano zeolite



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ABSTRACT

The present study aims at examining the feasibility of using synthesized magnetic nano zeolite for the sorptive removal of cesium and strontium ions existing in the liquid radwaste stream. Cs⁺/Na⁺ and Sr²⁺/Na⁺ binary ion exchange experiments were performed in the batch mode at different three temperatures (298, 303 and 313 K), optimized proton concentration (pH), equilibrium time and constant total normality. The thermodynamic analysis of both binary systems was performed using four types of model equations: Langmuir; Freundlich; Radlisch-Peterson and thermodynamic equilibrium models. The extended Debye–Huckel relation and the Wilson equation were used to estimate the solution and the solid phase activity coefficients, respectively. The results obtained during this study demonstrated the correlation of the four examined models with the experimental equilibrium data, which proved to be satisfactory. On the other hand, the thermodynamic non-idealities was found to give the best results. Thermodynamic parameters such as enthalpy change, Gibbs free energy change and entropy change were also calculated. The obtained affirmative results demonstrated that the synthesized magnetic nano zeolite can be used as an efficient sorbent for the removal of Cs⁺ and Sr²⁺ ions from the contaminated solutions.

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1. Introduction

Similar to several peaceful activities in modern civilization, the utilization of radio-isotopes in numerous fields and the generation of byproducts from several industries can produce large volumes of aqueous radioactive waste [1,2]. In several cases, this radioactive waste overrides the maximum permissible limits and require to be decontaminated before being discharged into the environment. Amongst the existing radioactive contaminants in the waste are cesium (Cs⁺) and strontium (Sr²⁺) ions, which have a hazardous effect on human health. The seriousness of these elements lies in their long half life time and their poisonous effect, which is a major concern from an environmental point of view [3]. Decontamination techniques such as evaporation and/or membrane, precipitation and sorption can be used for the treatment of radioactive waste streams containing these concerned ions [4,5]. Sorption has become one of the most commonly utilized treatment methods for

such aqueous streams owing to its simplicity, preference and efficiency. The management of radioactive waste grants the validity of using inorganic exchangers such as zeolites to reach a discerning removal of contaminants from the waste stream [6]. Zeolite Y contains a sole property as it has the most open framework of all known zeolite structures [7,8].

Recently, considerable attention has been paid on the synthesis of nanocrystalline materials to increase their industrial applications, owing to their large surface area and shorter diffusion paths compared to the micro-sized crystals [9]. In spite of its benefits, there is a problem related to the separation of spent nanomaterials from the aqueous medium. The technique for former's separation involves the use of centrifugation process, which is very costly and time consuming. Lately, researchers proceeded to use the magnetic separation technique since it is efficient, simple and fast. This work is an extension of our former study on a synthetic nano-sized zeolite Y, which was chemically prepared, totally characterized and tested as an inorganic ion exchanger for application in radioactive waste treatment [10].

The present study deals with strategies for improving the efficiency of sorbent-sorbate complex separation of the previously

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prepared nano material [10] by converting this material into a magnetized composite that could be easily eliminated from the aqueous medium using a strong magnet. The synthesized magnetic nano-sized zeolite (MNZ) was chemically prepared, characterized and sequences of experiments were performed to assess the utility of the synthesized exchanger for the elimination of cesium and strontium ions from liquid solutions. The characteristics of the sorption process were defined taking into account the interaction energy of the ionic solutes contained in a factor called activity coefficient. This coefficient deals with the non-ideality behavior of the solute in an aqueous phase using the Debye–Hückel equation and in the solid phase addressed using the Wilson model. The thermodynamic models were employed to predict the ion exchange equilibrium in the binary systems for gaining insight into the interaction energy between the two solutes in the solution.

2. Experimental and characterization details

2.1. Materials

All chemicals and reagents used in this work were of analytical grade and were used without further purification. Sodium aluminate (Sigma–Aldrich); fumed silica (Aldrich); sodium hydroxide (Winlab); cesium and strontium chloride (Koch light) were used as alumina; silica; sodium; cesium and strontium sources in the (MNZ) synthesis, respectively. Tetra methyl ammonium hydroxide (Merck) was used as a template.

2.2. Experimental and characterization procedure

MNZ was synthesized via two main steps. The first step involved the preparation of nano-sized zeolite [10,11] and the second step included the incorporation of iron particles onto the prepared nano-sized zeolite through precipitation technique.

The MNZ composite was prepared under deoxygenated atmosphere using N_2 gas and its pH value was adjusted at 11. After that, a mixture of 1 M aqueous $FeCl_3$ solution and 2 M $FeCl_2$ solution of 4:1 volume ratio were added drop wise to the nano-zeolite mixture under vigorously stirring with mechanical agitation. A magnet was used to separate the prepared material. Finally, the product was washed with bidistilled deoxygenated water and dried at 50 °C. The organic template (used in the first step) was removed by contacting the composite with 1 M sodium nitrate solution at 70 °C for 24 h. The procedure for synthesis of MNZ is illustrated in Fig. 1.

Spectroscopic and microscopic analyses were used to characterize the synthesized material. The used spectroscopy techniques include X-ray diffraction (XRD), Energy dispersive X-ray analysis (EDX) and Fourier transformed infrared spectroscopy (FTIR). The utilized microscopic method was transmission electron microscopy (TEM).

2.3. Sorption experiments

Preliminary kinetic experiments were carried out at different time intervals. The sorbed amount of each metal ions sharply increases in the initial stage (5–30 min range) then slowly increases until reaching equilibrium at approximately 120 min. A further increase in contact time had a negligible effect on the amount of ion sorption. According to these results, the equilibrium time was fixed at two hours for all sorption experiments.

Proton concentration (pH) is a significant controlling parameter in the sorption process as it influences the sorbent surface charge; the degree of ionization and the speciation of sorbate [12]. To determine the pH range at which the maximum Cs^+ and Sr^{2+} uptake onto the prepared material would take place, a series of 50 ml

test tubes each containing 0.02 g of the sorbent was filled with 10 ml of the desired concentration (775 mg/l). The pH was adjusted to values ranging from 4.0 to 8.0 using diluted hydrochloric acid or sodium hydroxide solution. The tubes were shaken for 2 h to reach equilibrium.

The obtained suspension was subjected to a strong magnet to separate the solid from the liquid phase. The obtained clear liquid phases were diluted to an appropriate concentration to be analyzed by Atomic Absorption Spectrophotometer (Buck scientific model VGP 210).

The construction of ion exchange isotherms was performed by mixing 0.02 g of MNZ with 10 ml of varying metal ions concentration solution ranging from 50 to 1000 mg/l at various temperatures (298, 303 and 313 K) and constant optimum pH. After the established contact time (2 h) was reached, the equilibrated samples were chemically analyzed and amount of metal ions maintained in the prepared material's phase (mg/g) was estimated using the following equation:

$$q_e = (C_i - C_e) \cdot \left(\frac{V}{m}\right) \quad (1)$$

The percentage of the removal of both Cs^+ and Sr^{2+} onto the synthesized material can be calculated as:

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where, C_i and C_e are concentrations of Cs^+ and Sr^{2+} in solution initially and at equilibrium, respectively. V is the solution volume (l), m is the weight of sorbent (g) and q_e (mg/g) is the amount of sorbed metal ion at equilibrium.

2.4. Modeling

The ion exchange between the cations in solution phase, Cs^+ or Sr^{2+} , (stand for ingoing ions), and Na^+ ions (stand for outgoing ions) in the solid phase, a magnetic material, can be written according to the following ion exchange process:



where, A represents Cs^+ or Sr^{2+} in solution; B represents Na^+ in the zeolite; Z_A , Z_B represent the charge of the ingoing ions ($Z = 1$ for Cs^+ and $Z = 2$ for Sr^{2+}) and the symbols s and z refer to the solution phase and zeolite phase, respectively. The stoichiometric reactions at different proportions of the ingoing and counter cations can be used for construction of an ion exchange isotherm. This is a pictorial representation of the relative preference of Cs^+ and Sr^{2+} for MNZ or solution phase at equilibrium. The isotherms of the ion exchange process were obtained by plotting the ionic equivalent fraction of Cs^+ and Sr^{2+} in magnetic material (A_z), Eq. (4), in the y-axis against their equivalent ionic fraction in solution (A_s), Eq. (5), in the x axis [13].

$$A_z = \frac{Z_A M_A}{Z_A M_A + Z_B M_B} \quad (4)$$

$$A_s = \frac{Z_A C_A}{Z_A C_A + Z_B C_B} \quad (5)$$

where, C_A and C_B are the concentrations of A and B in the solution phase; M_A and M_B are the concentration of A and B in the sorbent phase.

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