Chemical studies ofr the removal of some radioactive nuclides using zirconium vanadate as acation exchanger

Soaad Mohamed Sabry Ahmed El-Ashery

The main methods currently used for the treatment of radioactive waste are chemical precipitation, absorption and ion exchange. Choice of certain techniques is governed by the radiochemical composition of the waste that will treat, as well as, the economic aspects. The potential usefulness of the inorganic ion exchangers have been proved in various areas of nuclear fuel cycle, especially in the isolation and fixation of fission products and actinides. Inorganic ion exchangers and absorber have received attention for these purposes because of their strong chemical affinity, high retention capacity and high resistance for ionizing radiation for certain radionuclides.This thesis is concerned with some fundamental studies related to the separation and preconcentration of some radionucloides, namely, cesium-137, cobalt-60, zinc-65 and europium-152+154. The main aim of this study is to prepare zirconium vanadate sample and to find optimum conditions for the separation and preconcentration of the mentioned radionuclides. In this concern, kinetic studies, distribution studies and adsorption isotherm are investigated on zirconium vanadate sample to optimize the operative conditions for removal of these radionuclides (Cs+, Co2+, Zn2+ and Eu3+) from the back end of fuel cycle.The work carried out in this thesis is summarized in to three main parts; namely, introduction, experimental and finally results and discussion.The first chapter is introduction concerning a literature survey which includes a brief account on the classification of synthetic ion exchange, zirconium vanadate as inorganic ion exchanger, Characterization and Physicochemical Properties of Inorganic Ion Exchanger, Application of ion exchange techniques for the treatment of radioactive liquids.A literature survey related to different synthetic inorganic ion exchangers and natural materials for separation of certain radionuclides of importance in nuclear technology was reviewed.The second chapter is materials and methods which include the chemicals used and their chemical purity, the method of preparation of zirconium vanadate as well as the instrumentation, the analytical techniques and the procedures used in this thesis.The third chapter deals with the results and discussion and is divided into main sections namely; preparation and characterization of adsorbent material, distribution studies, kinetic studies and sorption isotherms in the first section from third chapter is the preparation and characterization, brief account on the preparation of zirconium vanadate was required and the solubility of the prepared material was determined from H2O and

acidic solutions. The prepared zirconium vanadate matrix are stable in water and acid solutions up to 5M HNO3 and 5M HCl.. Also the I.R of the prepared material was determined at different drying temperatures, 50, 200, 400, 600 and 850oC.I.R spectra of different samples (heated at different drying temperatures) are nearly the same appearance but slightly different in details. H2O bands appear at 3500 and 1630 cm-1 where, the characteristic bands intensity decreased with increasing the drying temperatures and this may be due to loss of water with temperatures.The XRD patterns of the prepared samples was determined at different drying temperatures and results showed that, the prepared material is amorphous in nature at 50 oC and the crystallinity of the material appeared at drying temperature 850oC and there is improvement of crystallinity by increasing the drying temperature up to 850oC.Thermal analysis of the prepared material support the fact that zirconium vanadate has a good thermal stability.These results indicate that zirconium vanadate sample has a good thermal stability and chemical stability compared with the other organic resins and some inorganic exchangers.The second section from the third chapter is the distribution studies, the ion exchange properties have been studied using four cations cesium (I), cobalt (II), zinc (II) and europium (III) which represents the main different categories of the nuclear waste solution.The distribution coefficient of the studied cations (Cs+, Co2+, Zn2+ and Eu3+) was investigated in zirconium vanadate sample at different pH values at 25oC±1oC. The obtained results showed the Kd values increase with increasing the pH of the solution. from the plots of log Kd vs. pH, cesium, cobalt, zinc and europium were found to deviate from the ideal ion exchange reaction mechanism. The selectivity is decreased for amorphous zirconium vanadate sample in the order;Co2+ > Cs+ > Eu3+ > Zn2+The effect of reaction temperature on the adsorption of Cs+, Co2+, Zn2+ and Eu3+ ions (pH=4.8) on zirconium vanadate sample was carried out in the temperature range 25-60±1oC and the thermodynamic parameters (ΔH*, ΔS* and ΔG*) for the adsorption of Cs+, Co2+, Zn2+and Eu3+ ions on zirconium vanadate solid were calculated.The capacity of amorphous zirconium vanadate sample for Cs+, Co2+, Zn2+ and Eu3+ was studied. The results indicated that, zirconium vanadate show higher ion exchange capacity than other organic and inorganic ion exchangers, and the capacity of the matrix for the studied cations has the following order;Co2+ > Cs+ > Eu3+ > Zn2+The capacities of amorphous zirconium vanadate sample for Cs+, Co2+, Zn2+ and Eu3+ at different drying temperatures have been determined and showed that, zirconium vanadate sample shows decrease in its capacities by increasing the drying temperatures from 50 to 850oC.The third section from the third chapter is the kinetic studies, the kinetics of exchange of Cs+, Co2+, Zn2+ and Eu3+ on zirconium vanadate material are studied as a function of particle radius and reaction temperatures (all experiments were carried out under particle diffusion control as a limited batch techniques only).The results showed that, the rate increases with decreasing the particle size. Also, the rate of the exchange material increases with increasing the reaction temperature. The values of the effective diffusion coefficients (Di), entropy of activation (ΔS*) and energy of activation (Ea) for Cs+, Co2+ , Zn2+ and Eu3+ on amorphous zirconium vanadate sample has been determined and are compared with the values reported in literature. The

result was found that the values of diffusion coefficient (Di) inside zirconium vanadate sample follow the order; Co2+> Cs+ > Eu3+ > Zn2+. Also, the values of activation energy for all the metal ions exchanged on zirconium vanadate matrix were calculated and take the order. Eu3+ > Cs+> Co2+ > Zn2+Negative values of entropy of activation (ΔS*) were obtained for Cs+, Co2+ , Zn2+ and Eu3+ ions on zirconium vanadate sample.The last section from third chapter is the sorption isotherm, the effect of concentration on the sorption of cesium, cobalt, zinc and europium has been studied at different reaction temperatures (25, 40 and 60oC) and using concentration range 10-4–5x10-2M for Cs(I) , Co(II) and Zn(II) ions and Eu(III) concentrations investigated (10-4 to 10-2M). The results proved that the sorption of these ions is endothermic process. Also, the adsorption of all studied cations on zirconium vanadate matrix was analyzed using Langmuir adsorption isotherms