Journal of Nuclear and Radiochemical Sciences, Vol. 9, No.1, pp. 1-6, 2008

Articles

Thermodynamics Study for the Sorption of ^{134}Cs and ^{60}Co Radionuclides from Aqueous Solutions

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Received: April 26, 2007; In Final Form: December 25, 2007

The removal of cesium and cobalt radionuclides from aqueous chloride solutions using hydrous titanium oxide was investigated. The influence of initial ion concentration, pH, and temperature has been reported. The data obtained have been correlated with Langumir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models. The effect of temperature on the equilibrium distribution values has been investigated. The thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) have been calculated. Maximum ion exchange capacity and the mean free energy of each studied ion have been determined using D-R isotherm model.

1. Introduction

A number of activities and events have caused significant radioactive contamination of different areas, these include: inadequate practices for the management and disposal of radioactive waste, the intentional or accidental discharge of radioactive material to the environment, nuclear accidents, testing of nuclear weapons, etc. Such contamination may present a hazard to human populations and the environment.[1] Cesium and cobalt radionuclides are released into radioactive waste solutions from different radioactivities. They have a relatively long half-lives and are considered as hazardous elements for the environment.[2] Large amounts of cesium and cobalt radionuclides have been released to the subsurface from the Hanford site waste storage tanks.[3, 4] New type of material is needed for the selective removal and safe storage of ^{134}Cs and ^{60}Co from nuclear waste solutions and from groundwater. The radionuclide wastes are generally present in low concentrations and are associated with an assortment of other cations.[5] The cationic radioisotopes, present in the liquid effluents of low and intermidiate level liquid wastes, can be removed by the ion exchange process. The inorganic ion exchanger materials possess high exchange capacity, possible selectivity and specificity, and good resistant to radiation and heat.[6-8] Thermodynamic modeling of metal-ligand interactions in high ionic strength NaCl solutions of Co^{2+}-oxalate system has been studied.[9] Studies of the kinetic and thermodynamic for the sorption of cesium(I) on hydrous silica has been determined.[10] Also the adsorption and thermodynamic behavior of some radionuclides as uranium(VI) on bentonite composite adsorbent has been determined.[11] Ion exchange properities of hydrous titanium oxide have been receiving great attention, specially for application in radioactive liquid waste treatment.[12-17] Adsorption of some elements such as ferous ions on porous nanocrystalline TiO_2 surface has been conducted by the oxidation of ferous ions using photoelectrochemical process.[18] Some adsorption studies of titanium oxide ion exchanger has been determined such as the adsorption of cobalt on model catalysts consisting of Pd nanoparticles on the surface of TiO_2 using a thermal molecular beam.[19] An external gelation process has been conducted for developing and preparation of TiO_2–SiO_2 mixed gel spheres suitable for strontium adsorption.[20] Also, TiO_2–SiO_2 mixed gel spheres prepared via sol–gel method was used for the sorption studies of cesium radionuclides.[21] Sorption of Cs^+ and Sr^{2+} ions on hydrous titanium dioxide from chloride medium was studied,[22] where, it showed a good ion exchange capacity for both metal cations in neutral medium. The application of this study towards column technique was tested.[22] Also, hydrous titanium oxide and sodium titanate was used for removal of cesium radionuclides from aqueous solution.[23] It was reported that an increase in Cs concentration, temperature and pH at the studied conditions apparently enhanced the uptake of Cs(I) on hydrous titanium oxide.[23]

The objective of this study is to evaluate the use of hydrous titanium oxide as an ion exchange material for the removal of ^{134}Cs and ^{60}Co from aqueous solution. The effect of temperature on the exchange process of each ion was studied to determine the relevant thermodynamic parameters. Freundlisch, Langmuir, and Dubinin-Radushkevich (D-R) isotherms are applied to the sorption data to calculate the different parameters and the best fitting achieved.

2. Experimental

2.1. Preparation and characterization of sorbent oxide. All the reagents used were of AR grade chemicals. Stock solutions of the reagents were prepared by dissolving CsCl and $CoCl_2 \cdot 3H_2O$ in double distilled water. Hydrous titanium oxide was prepared by adding 150 cm^3 of liquid $TiCl_4$ to 450 cm^3 of distilled water followed by adding 2.5 M NaOH dropwisely with vigorous stirring where the pH of the solution was adjusted to 7. A white precipitate was formed. The precipitate was filtered and washed several times with distilled water until it was free of chloride ions and the washings were neutral. The product was dried at 50 °C. The white precipitate of hydrous titanium oxide was sieved to a particle size diameter < 370 μm which was used in all experiments. Infrared spectra (IR), X-ray diffraction analysis (XRD) and differential thermal analysis (DTA) studies for titanium hydrous oxide sample has been determined and described in detail elsewhere.[17] Also the specific surface area of the prepared hydrous titanium oxide sample has the value 216 m^2/g, which was measured using Micrometric type 2200 surface area analyzer. Pore size distribution analysis was carried out with high pressure Poresizer 9320, Micromeritics.

IR, XRD, and DTA curves for titanium hydrous oxide sample have been sumarized in Figure 1. As it is stated in

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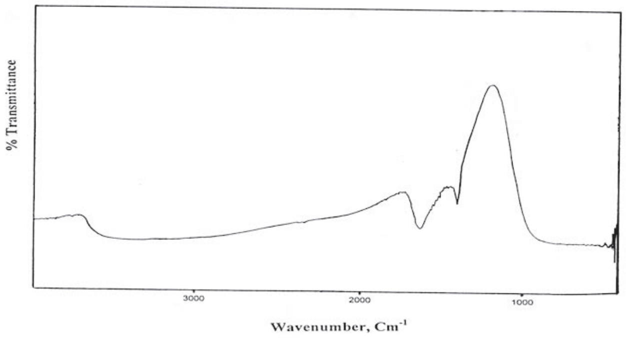

Fig. 1a

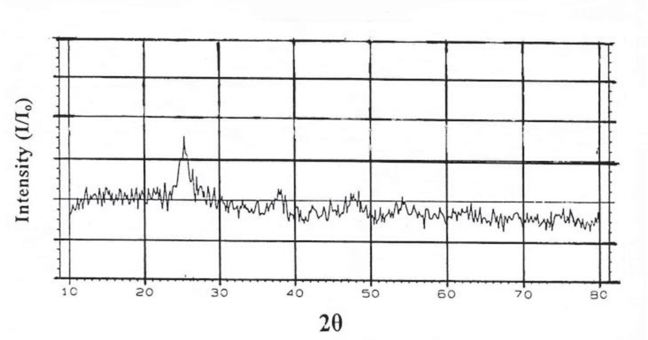

Fig. 1b

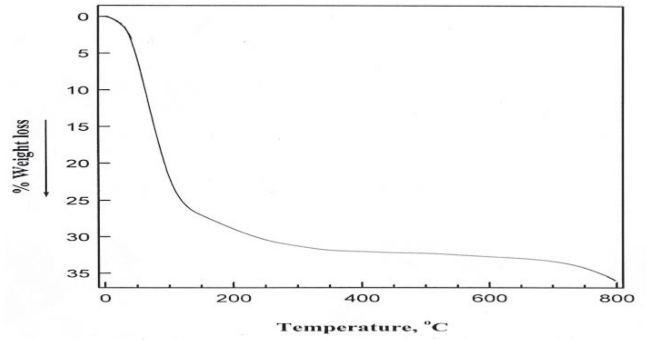

Fig. 1c

Figure 1. a) Infrared spectra, b) X-Ray diffraction pattern, c) Differential thermal analysis for titanium hydrous oxide sample.

Reference 11, IR spectrum of hydrous titanium oxide sample, Figure 1a gives broad band at about 3700 – 2500 cm^{-1}, which belongs to the stretching vibrations of water molecules and OH groups.[24] The band at 1625.9 cm^{-1} is characteristic to the bending vibration of water molecules and the band near 1400 cm^{-1} is due to the bending vibrations of hydroxyl groups bounded to titanium atoms on the surface.[24] So, the surface hydroxyl groups bonded to titanium atoms represent the adsorption active sites, as the surface hydroxyl groups increase the capacity increase. The X-ray pattern, Figure 1b shows diffuse peaks at the 2θ values 25.187, 37.936, and 62.755° corresponding to the d-spacing 35.3, 23.67, and 14.79 nm. So, the prepared hydrous titanium oxide sample seems to be largely amorphous or microcrystalline. Thermogravemetric analysis (TGA), Figure 1c shows a continuous loss in weight up to the maximum heating temperature used 800°C. The weight loss is due to dehydration and its continuous nature is indicative of the absence of definite hydrates of the prepared sample.[24] Based on these results, the chemical composition of the produced titanium oxide can be expressed as: $TiO_2 \cdot 0.82\ H_2O$ as tentative molecular formula and the percent of weight loss equal to 18.4%.[17, 25]

2.2. Ion exchange measurements. Ion exchange behavior of Cs^+ and Co^{2+} ions on hydrous titanium oxide sorbent was studied by applying batch technique. 0.1 g of the prepared powder was shaken at 298, 308, and 335 K with 40 cm^3 of different ion concentration of aqueous chloride solution in a thermostatic shaker for a specified period of contact time. Then, a fixed volume (2 cm^3) of the aliquot was withdrawn as a function of time and was applied for a radiometric measurement to determine the concentration of the studied ions. Radiometric determination was achieved using NaI scintillation detector connected to an ORTEC assembly (Nuclear Enterprises), USA. The amount of metal ion retained in the solid phase, q_e(μmol/g), was calculated from the expression:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations (M) of metal ion in solution. V is the volume (L) and W is the weight (g) of the solid. It was observed that the uptake of each ion was inhibited in the acidic medium, pH< 2.0. Where, the highest uptake for cesium and cobalt ions was observed at pH range 6.0–8.0. All sorption processs was achieved for sufficient long time up to 5 h and pH value of 6.0 for the studied ions.

3. Results and Discussion

3.1. Ion exchange isotherm. Ion exchange isotherms of Cs(I) and Co(II) ions onto hydrous titanium oxide at different temperatures are presented in Figure 2. Where a forward relation between C_e and q_e at 298, 308, and 325 K are obtained. Langmuir isotherm of Cs (I) and Co (II) onto hydrous titanium oxide at different temperatures are given in Figures 3a and 3b. The isotherms are regular, positive. The initial rapid sorption gives way to a slow approach to equilibrium at higher adsorbate concentrations. These results reflect the scavenging efficiency of hydrous titanium oxide for the removal of these metal ions from wastewater in a wide range of concentrations. The amount uptake increases with an increase in temperature for the two ions thereby indicating the process to be endothermic in nature.

Several common sorption isotherm models including Langumir, Freundlich, and D-R isotherm models were cosidered to fit the obtained isotherm data. These isotherm models which were originally derived mainly for gas-solid systems have also been used successfully to represent sorption of solutes in liquid-solid systems.

Langmuir Isotherm

The Langmuir isotherm is given by the relation:[26]

$$q_e = \frac{Q^o\, bC_e}{1 + bC_e} \qquad \text{(Non-linear form)} \tag{2}$$

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{1}{Q^o} C_e. \qquad \text{(Linear form)} \tag{3}$$

Where C_e is the equilibrium solution phase concentration (μmol/L), q_e is the equilibrium solid phase concentration(μmol/g), Q^o is the max concentration on the solid phase (μmol/g), b is the constant related to the free energy of the ion exchange ($b \propto e^{-\Delta G/RT}$).

The plot of C_e/q_e against C_e, as shown in Figures 3a and 3b, is linear in the entire range of metal ion concentration at equilibrium. The numerical value of Langmuir constants Q^o and b evaluated from slope and intercept of the plot and the correlation coefficient R^2 are given in Table 1.

The good fit of the experimental data and the correlation coefficients (R^2) higher than 0.96 indicated the applicability of the langmuir isotherm model. The Langmuir constants Q^o and b increased with temperature showing that adsorption capacity and intensity of adsorption are enhanced at higher temperatures and indicating the endothermic nature of adsorption. The increase in adsorption capacity with temperature suggested that the active, surface centers available for adsorption have increased with temperature. Another reason may be due to the change in pore size and enhanced rate of intraparticle diffusion of solute as diffusion is an endothermic process.[27] C_e/q_e values for sorption of Cs(I) and Co(II) ions using hydrous titanium

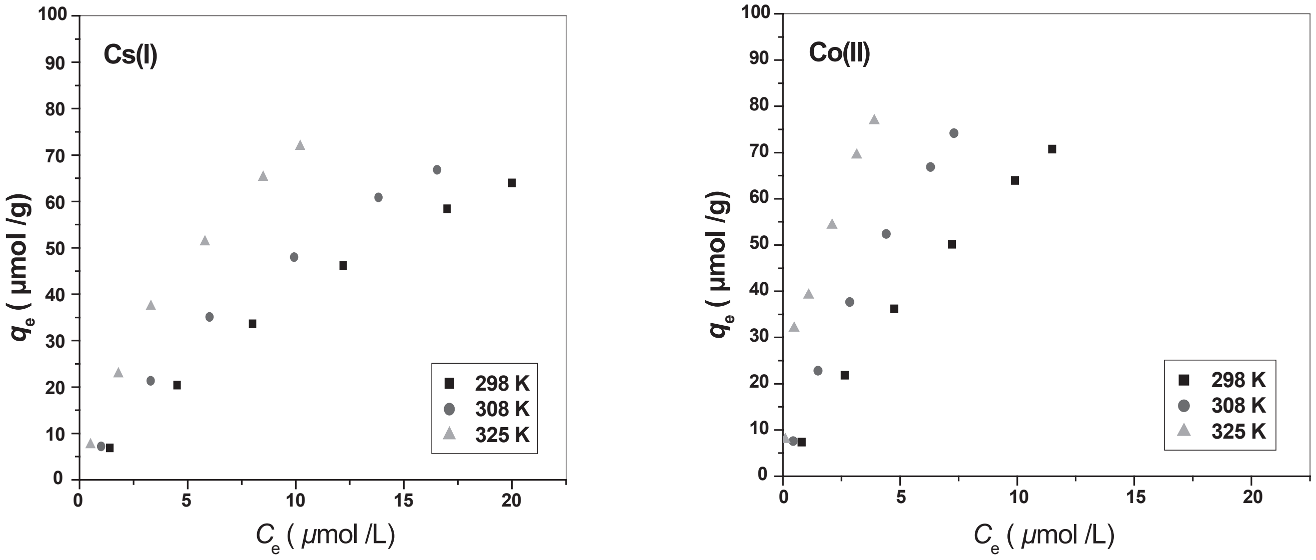

Figure 2. Ion-exchange isotherms of Cs (I) and Co (II) on Hydrous titanium oxide at different temperatures.

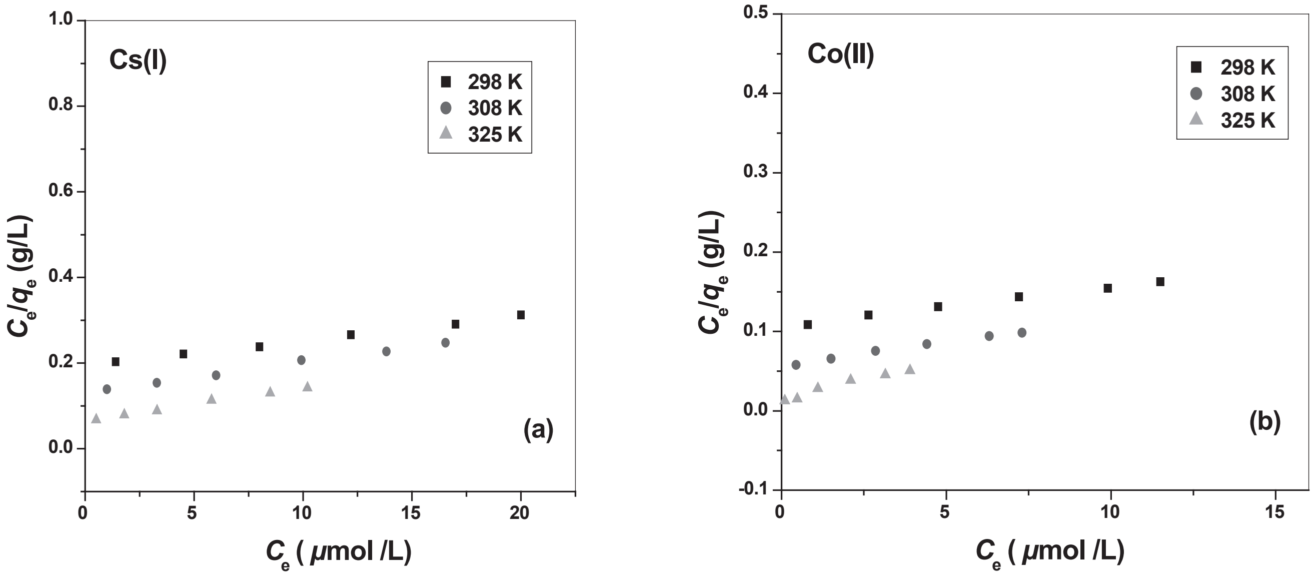

Figure 3. Langmuir isotherm of Cs (I) and Co (II) onto hydrous titanium oxide at different temperatures.

TABLE 1: Constant parameters and correlation coefficients calculated for Langmuir, Freundlisch, and D-R adsorption models at different temperatures for Cs(I) and Co(II) adsorption onto hydrous titanium oxide

Model	Parameters	Cs(I)			Co(II)		
		298 K	308 K	325 K	298 K	308 K	325 K
Langmuir	Q^o (μmol/g)	129.63	141.64	171.82	97.465	169.77	203.25
	b (L/μmol)	0.0299	0.0537	0.1196	0.0461	0.1034	0.7761
	R^2	0.9979	0.9958	0.9954	0.9950	0.9917	0.9622
Freundlich	K_F (μmol/g)	0.6237	0.4582	0.4297	1.1778	2.4593	0.1306
	$1/n$	0.8430	0.7954	0.7499	0.8710	0.8997	0.5921
	R^2	0.9960	0.9931	0.9905	0.9982	0.9818	0.9637
Dubinin-Radushkevich (D-R)	q_m (mmol/g)	0.6189	0.4436	0.4303	1.1795	1.1052	1.7461
	K (mol^2/kJ^2)	−0.00340	−0.00304	−0.00271	−0.00343	−0.00311	−0.00223
	E (kJ/mol)	12.1255	12.808	13.584	12.0636	12.6828	14.9798
	R^2	0.9959	0.9933	0.9905	0.9982	0.9972	0.9960

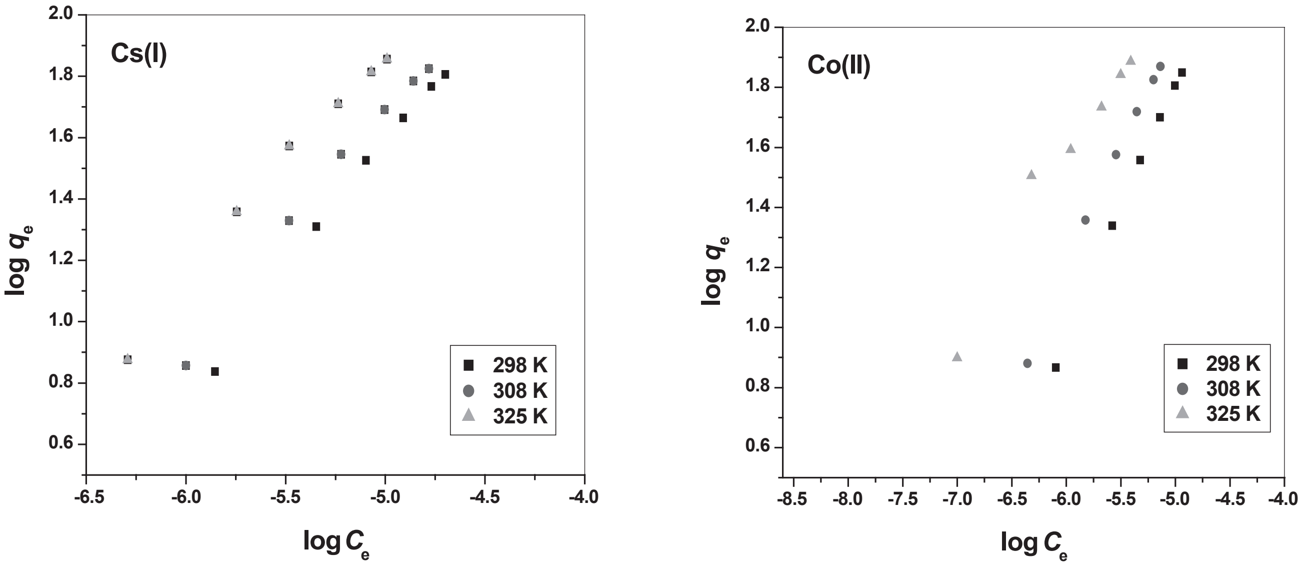

Figure 4. Freundlich isotherm of Cs (I) and Co (II) on hydrous titanium oxide at different temperatures.

oxide reach 0.3 (g/L) and 0.1 (g/L), respectively, at 298 K. These values are higher than their corresponding values 4.5 (mg/L), 2.5 (mg/L), 2.5 (mg/L), and 20 (mg/L) for sorption of Cs(I), Sr(I), Ca(II), and Mg(II) ions, repectively, using Zeolite-A sorbent.[28] Adsorption capacity Q^o for sorption of Co(II) ions using hydrous titanium oxide in the present work reachs 11.9 (mg/g), while in other work[29] it reaches 0.919 (mg/g), 1.5 (mg/g), 4.38 (mg/g), 12.34 (mg/g), and 12.82(mg/g) for dikaolinite, soil, marine bacterium, coir pith, and sluge sorbents, respectively.

Freundlich Isotherm

The Freundlich isotherm is given by the relation:[30]

$$q_e = K_F\, C_e^{1/n} \qquad \text{(Non-linear form)} \qquad (4)$$

$$\log q_e = \log K_F + 1/n \log C_e . \qquad \text{(Linear form)} \qquad (5)$$

Where K_F is the constant indicative of the relative ion exchange capacity of the adsorbent (μmol/g) and $1/n$ is the constant indicative of the intensity of the ion exchange.

Plotting log q_e versus log C_e as shown in Figures 4a and 4b gives linear relation in the entire range of concentration at equilibrium. From the slope and intercept of the plot, numerical values of the Freundlich constants K_F and $1/n$ and the correlation coefficient R^2 can be determined as shown in Table 1.

It can be seen from these data that the Freundlich intensity constant (n) are greater than unity for all studied ions. This has physicochemical significance with reference to the qualitative characteristics of the isotherms, as well as to the interactions between metal ions species and hydrous titanium oxide. In our case for all metal ion species ($n > 1$), the hydrous titanium oxide shows an increase tendency for sorption with increasing solid phase concentration. This should be attributed to the fact that with progressive surface coverage of adsorbent, the attractive forces between the metal ion species such as van der Waals forces, increases more rapidly than the repulsive forces, exemplified by short-range electronic or long-range Coulombic dipole repulsion, and consequently, the metal ions manifest a stronger tendency to bind to the hydrous titanium oxide site.[31]

Although the Freundlich and Langmuir constants K_F and Q^o have different meanings, they led to the same conclusion about the correlation of the experimental data with the sorption model. The basic difference between K_F and Q^o is that Langmuir isotherm assumes adsorption free energy independent of both the surface coverage and the formation of monolayer. Whereas the solid surface reaches saturation while the Freundlich isotherm does not predict saturation of the solid surface by the adsorbate, and therefore the surface coverage being mathematically unlimited. In conclusion, Q^o is the monolayer adsorption capacity while K_F is the relative adsorption capacity or adsorption power.[26]

Dubinin –Radshkevich Isotherm (D–R Isotherm)

In order to study the nature of the sorption processes, the D-R isotherm was also verified in the form:[32, 33]

$$q_e = q_{max}\, e^{-K' \varepsilon^2} . \qquad \text{(Non-linear form)} \qquad (6)$$

Where q_{max} is the maximum concentration on the solid phase, i.e., ion exchange capacity (mmol/g), q_e is the concentration in solid at equilibrium (mol/g), K' is the constant of the adsorption energy (mol^2/kJ^2), and ε is the Polanyi potential (kJ/mol) and it is equal to

$$\varepsilon = RT \ln(1{+}1/C_e) . \qquad (7)$$

Where R is the gas constant ($kJmol^{-1}\ K^{-1}$), T is the absolute temperature in degrees Kelvin, and C_e is the concentration in solution at equilibrium (mol/L).

The D–R isotherm can be linearized as:

$$\ln q_e = \ln q_{max} - K' \varepsilon^2 . \qquad \text{(Linear form)} \qquad (8)$$

The D-R plots of ln q_e versus ε^2 for all ions at different temperatures are given in Figures 5a and 5b. These linear plots indicate that the D-R isotherm expression is followed for both studied metal ions. The D-R parameters, evaluated for sorption of both studied ions at different temperatures, are presented in Table 1. The maximum sorption capacities (q_{max}) are in the sequence $Co^{2+} > Cs^{+}$. These values are considerably less than the theoretical exchange capacity (CEC) calculated from the chemical formula of hydrous titanium oxide (5.45 meq/g). This could be due to the size window of the hydrous titanium oxide and to the radius of all studied ions, which make difficult the ion exchange and therefore the values determined experimentally were lower.[34]

The mean sorption energy E (kJ/mol), defined as the free energy change when one mole of ion is transferred to the surface of the solid from infinity in the solution, is calculated according to the following equation:

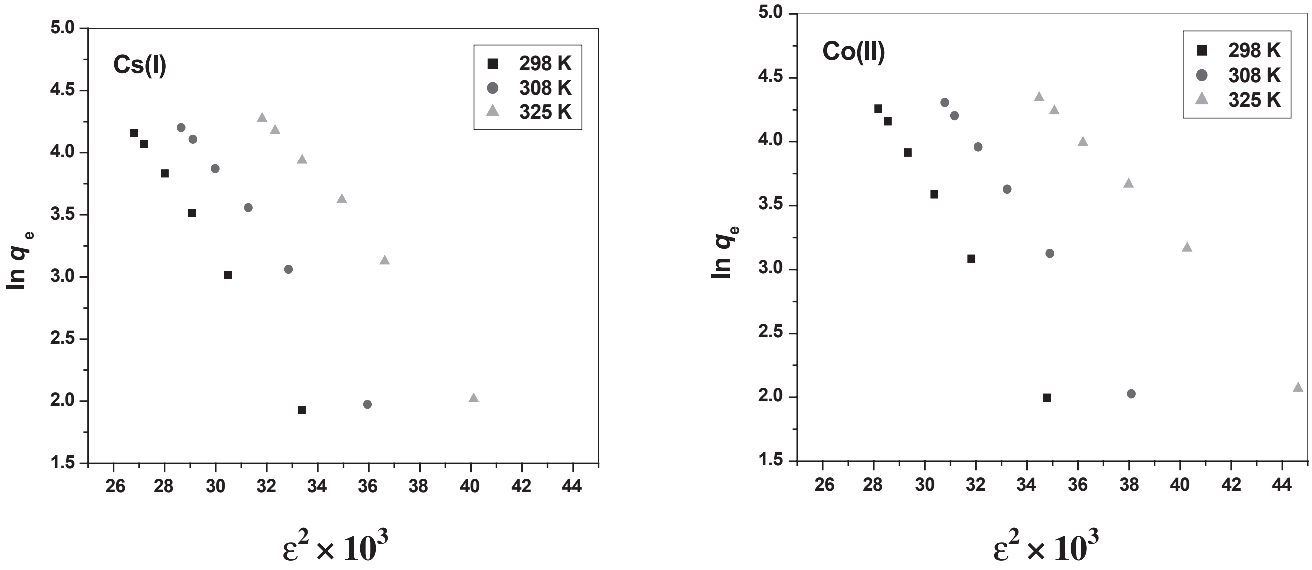

Figure 5. The D-R isotherm of Cs (I) and Co (II) on hydrous titanium oxide at different Temperatures.

$$E = 1/\sqrt{-2K'}\ . \tag{9}$$

Where, K' is calculated from the D-R equation. The values of E obtained from the slope of the D-R plots are given in Table 1. The magnitude of E is useful for estimating the type of sorption reaction occurring. Calculated mean sorption energy for the sorption of Cs^+ and Co^{2+} ions on hydrous titanium oxide has the lowest value of 12.06 kJ/mol and has the highest value of 14.97 kJ/mol, which are within the range of 8–16 kJ/mol reported by Helfferich for ion exchange reactions.[35]

Among with the isotherm models tested and based on the correlation coefficient R^2 values, the D-R approaches provided a best fit over the entire range of concentration for all systems. This suggests that some heterogenity in the surface or pores of hydrous titanium oxide will play a role in the metal ion sorption. The values of A, $B1$ and R^2 used for fitting in the linear equation $y = A + B1 \times x$, for the plots in Figures 3–5 are summarized in Table 3.

Effect of temperature

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the velocity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsobent for a particular adsorbate.[36]

Thermodynamics parameters, namely, Gibbs free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) changes for the process were also calculated using equations (10–12):

$$\Delta G^o = -RT \ln K_1, \tag{10}$$

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \tag{11}$$

TABLE 2: Thermodynamic parameters calculated for the adsorption of Cs(I) and Co(II) onto hydrous titanium oxide at 10^{-5} M ion concentration

	Cs(I)				Co(II)			
T(K)	K (L g^{-1})	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1}K^{-1})	K (L g^{-1})	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1}K^{-1})
298	K_1=5.1510	–4.061	32.961	124.0822	K_1=9.3670	–5.543	63.0511	229.5121
308	K_2=7.6138	–5.282			K_2=17.5650	–7.458		
325	K_3=15.482	–7.357			K_3=75.643	–11.617		

TABLE 3: The values of A, $B1$ and R^2 used for fitting in the linear equation $y = A + B1 \times x$ for the plots in Figures 3–5

Model	T (K)	Cs(I)			Co(II)		
		A	$B1$	R^2	A	$B1$	R^2
Langmuir	298	0.19412	0.00582	0.99799	0.10676	0.00492	0.99504
	308	0.13134	0.00706	0.99584	0.05693	0.00589	0.99177
	325	0.06459	0.00773	0.99549	0.01322	0.01026	0.96222
Freundlich	298	5.79500	0.84301	0.99601	6.07108	0.85109	0.99827
	308	5.66112	0.79540	0.99313	6.39082	0.89972	0.98186
	325	5.63318	0.74998	0.99052	5.11601	0.59216	0.96379
D-R	298	13.33583	–0.34007	0.99599	13.9809	–0.34357	0.99828
	308	13.00286	–0.30478	0.99334	13.91561	–0.31084	0.99720
	325	12.97240	–0.27095	0.99055	12.07034	–0.22282	0.99605

$$\Delta S^o = (\Delta H^o - \Delta G^o)/T. \tag{12}$$

Where K is the apparent equilibrium constant corresponding to the temperature which may be calculated from the product of the Langmuir equation parameters Q^o and b.[37] So, the values of the constants K_1, K_2, and K_3 corresponding to the temperatures of 298, 308, and 325 K, respectively, are given in Table 2. Also, the values of the corresponding thermodynamic parameters (ΔG^o, ΔH^o, and ΔS^o) are given in Table 2.

The negative free energy values (ΔG^o) as shown in Table 2, for each exchange ion, and its decrease with increasing exchange temperature is connected with the higher affinity of hydrous titanium oxide to these ions and with the change of thermodynamic stability of the hydrous titanium oxide framework during the exchange process. Also, negative free energy values indicate the feasibility of the process and its spontaneous nature. Based on the value of free energy deduced from equilibrium isotherm data, the selectivity series is $Co^{2+} > Cs^+$.

The values of enthalpy (ΔH^o) as shown in Table 2 indicate that the standard enthalpy of each exchange process does not depend on the exchange temperature in the temperature range from 298 to 325 K. The positive values of the standard enthalpy show the process to be endothermic.

The values of entropy (ΔS^o) as listed in Table 2 showed that the standard entropy of the exchange process does not depend on the exchange temperature in the temperature range from 298 to 325 K. Also, positive entropy reflects the affinity of the ion exchange material for the metal ions under consideration.

4. Conclusion

The results of this study indicate that the prepared hydrous titanium oxide sorbent can be successfully used for the recovery of cesium(I) and cobalt(II) radionuclides from aqueous solutions under investigation. Thermodynamic parameters were caculated for the adsorption process of Cs(I) and Co(II) radionuclides using hydrous titanium oxide at different temperatures. Equilibrium isotherms have been tested for different isotherm expressions and the sorption data were successfully modeled using Langumir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms. The maximum ion exchange capacity and the mean free energy of the studied cations have been determined using the D-R model expression. The obtained thermodynamic data provide valuable information about the exchange mechanisms for hazardous radionuclides from waste solutions using hydrous titanium oxide.

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