Sorption of rare-earth erbium from aqueous solution onto sol–gel-derived zirconia

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Abstract
Zirconia powder was synthesized via sol gel method and used for erbium sorption. The adsorption is strongly dependent on pH of the medium where the removal efficiency increases as the pH turns to alkaline range. The process was very fast initially and maximum adsorption was attained within 60 min of contact. Pseudo-second-order model and homogeneous particle diffusion model (HPDM) was found to be the best to correlate the diffusion of erbium into zirconia particles. Adsorption thermodynamic parameters were calculated. Erbium adsorption is an endothermic (ΔH > 0) and good affinity of erbium ions towards the zirconia (ΔS > 0).

Keywords: erbium, zirconia, sol–gel; kinetics; thermodynamics.

Rare earth elements (REE) are gaining increasing importance, both in terms of research activity, and in terms of commercial products. The REE elements are being widely used in industry due to their metallurgical, optical and electronic properties. They are used in glass additives, fluorescent materials, catalysts, ceramics, lighters, supra-conductors and magnets or condensers [1]. They are also reported to be used as diagnosis reagents of magnetic resonance imaging (MRI) in medicine and some fertilizers in agriculture [2]. Among REE, erbium is used as a neutron-absorbing control rods. It is commonly used as a photographic filter, and due to its resilience it is useful as a metallurgical additive and in nuclear technology as nuclear poison, as neutron-absorbing control rods [3]. Anthropogenic activities may thus end up with REE metals in the hydrosphere and eventually in the food cycle and biosystem [4]. Therefore, the isolation of these elements from the environment is an important preventive measure against harmful exposure.

A good deal of interest has grown in the last decades in the application of inorganic ion-exchangers in nuclear technology due to their high mechanical, chemical and radiation stabilities, granulometric properties suitable for column operation and high ion-exchange capacity and adsorption efficiency [5]. Among these materials, metal oxides are a group of inorganic ion exchangers that has been investigated extensively in the treatment of radioactive waste [6]. Preparation method affects the crystallinity of the metal oxides and its ion exchange properties [7–14]. Sol–gel process is an attractive alternative to other methods for synthesis of inorganic ion-exchangers for many reasons: for example, low temperature synthesis, simple equipment that is used, thin film formability and so on. Adsorbent powders of metal oxide origin, synthesized by the sol-gel process in this work, have not previously been used in removing erbium from aqueous solutions.

In the present study, zirconia was successfully prepared by a sol–gel technique and used as an adsorbent for the removal of erbium ions from aqueous solution. Adsorption kinetics and thermodynamics of erbium adsorption by sol–gel-derived zirconia from aqueous solutions were studied.

METHODOLOGY

Chemicals and reagents
All chemicals used were of analytical reagent grade. An accurately weighed quantity of the erbium nitrate (purchased from Merck Company) was dissolved in deionized water to prepare a stock solution. Experimental solutions of the desired concentrations were obtained by successive dilutions. All sample bottles and glassware were cleaned; rinsed with deionized water and oven dried at 60 °C.

Preparation and characterization of zirconia
In the present work, the synthesis of zirconia was carried out using sol–gel polymeric route. Briefly polymerization reaction between urea and formaldehyde was carried out at 70–80 °C with stirring for 1 h in an alkaline medium (pH 8–9) to form the respective resin. Zirconium nitrate was added during the resin form-
Ethylene glycol was used to terminate the polymerization reaction. The produced gel was slowly dried at 120 °C and then calcined at 900 °C for 2 h to produce the zirconia powder [15].

The X-ray powder diffraction patterns of the prepared material were recorded on film at room temperature in a Philips XRG3100 X-ray diffractometer using CuKα X-ray operated at 30 kV and 30 mA with a fixed slit. FTIR analysis was investigated by a Fourier transform infrared spectrometer (IRPrestige-21, Japan). The thermogravimetric analysis (TGA) was carried out using Shimadzu TGA-50 analyzer, Japan.

Sorption studies

100 mg of zirconia powder in 25 ml conical flasks containing 10 ml of erbium solution (10^{-2} M) were mixed. The conical flasks then covered with aluminum foil and were then placed in a thermostatic shaker at room temperature for different time intervals. The adsorbent was finally removed by filtration, erbium concentration was determined radiometrically, using a NaI crystal using a pulse height multi-channel analyzer (McA) model 800 obtained from USA. Influence of solution pH on the sorption of erbium (30 ppm) was studied in the pH range of 2.0 to 10.0 under similar experimental conditions. Before each experiment, the solution pH was initially adjusted using HCl and/or NaOH depending on the required pH value. The thermodynamic studies were investigated by carrying out batch study at different temperatures. The temperatures chosen for study were 298, 313 and 333 K. The temperature of the erbium solution was adjusted using a thermostatic water bath (Memmert WB29 Model). The erbium uptake \( q_t \) (mg/g) at any time \( t \) was calculated from the mass balance as follows:

\[
q_t = \frac{(A_0 - A_t)}{A_0} c_0 \frac{V}{m}
\]

where \( A_0 \) and \( A_t \) are the initial and time interval activities of metal ion in solution, \( V \) is the volume of the solution (L) and \( m \) is the weight of the adsorbent (g) and \( c_0 \) is the initial concentration (mmol/l) of the metal ion used.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis

X-ray diffraction is one of the techniques commonly used for the structural characterization of inorganic ion-exchangers. The X-ray diffraction (XRD) patterns using CuKα of sol–gel-derived zirconia are shown in Fig. 1. By analyzing the XRD patterns of the synthesized materials, it was observed that X-ray pattern showed the monoclinic zirconium phase at 900 °C. It was observed that the three strongest peaks \( (2\theta \approx 30, 50, \text{and } 60°) \) could be assigned to zirconia [16]. The peak at \( 2\theta \approx 28° \) is considered due to the monoclinic phase. The sharp peak at \( 2\theta \approx 30° \) corresponds to tetragonal phase [17].

FTIR characterization

Infrared spectra of the prepared zirconia were carried out in the range of 200–4000 cm⁻¹ and shown in Fig. 2. The broad absorption band in the range 3396–2950 cm⁻¹ is due to the stretching vibrations of the water molecule OH groups [18], whereas the absorption band which appears at 1624.5 cm⁻¹ is characteristic of the bending vibration of water molecules. It is uncertain whether the water observed in these spectra reflects the composition of the surface resulting from the heating process, or water which had rapidly reached to the surface during cooling. The peaks at 1124.8 and 800 cm⁻¹ are due to the bending vibration of hydroxyl groups bound to zirconia.

Effect of pH

It is known that pH is important factor for the adsorption of metal ions on the adsorbents. Specifically it affects the solution chemistry of the solute as well as the functional groups present in the sorbent. Results of the effect of solution pH on adsorption of erbium ions on the zirconia are shown in Fig. 3. The plot shows a

![Figure 1. X-ray diffraction pattern of prepared zirconia at 900 °C.](image-url)
marked influence with a gradual rise in the uptake with increase in pH from 2 to 5 and thereafter it remained constant. The variation in the removal of the erbium with respect to pH can be elucidated by considering the functional groups present on the surface of the zirconia and the nature of the physicochemical interaction of the species in solution. Zirconia contains hydroxyl groups which can act good role in ion-exchange reaction through the substitution of its protons by erbium ion, according to the following reactions [19]:

$$\text{M}^{n+} + m(\text{OH}) \rightleftharpoons \text{M(OOC)}^{n-m} + m\text{H}^+$$  \hspace{1cm} (2)

Where $\text{M}^{n+}$ = metal ion with $n+$ charge, $\text{OH} = \text{hydroxyl group}$, and $m\text{H}^+ = \text{number of protons released}$. In such a system, for low pH, because of the high concentration of $\text{H}^+$, there is competition of excess $\text{H}^+$ with erbium ions for binding onto the biomass surface. Then Eq. (2) lies to the left. At the same time the predominant charges on Zirconia are positive, which results in the lower uptake of positively charged erbium ions on Zirconia. By increased pH, active sorption sites available for erbium ions increase as results of deprotonating of ion exchange sites and then negative charge on the sorbent increases. Therefore, electrostatic attraction between the negatively charged sorbent surface and the positively charged erbium ions will occur. This means that Eq. (2) precedes further to the right and metal ion removal is increased. Within this pH range, the ion exchange process is the major mechanism for removal of metal ion from solution. In the subsequent studies, experiments were performed in the solution pH value of 5 to avoid any possible hydroxide precipitation. Further, a decrease in the solution pH was observed after equilibration as compared to the initial solution pH. The drop in equilibrium pH suggests that $\text{H}^+$ ions are liberated from the solid surface into the aqueous phase as a result of the exchange with metal cations.

**Effect of contact time and temperature**

The adsorption profile of erbium uptake with time at different temperature is shown in Fig. 4. The removal curves are single, smooth and continuous leading to saturation, suggesting possible monolayer coverage of erbium ions on the surface of the zirconia and typically 80–90 % adsorption of the equilibrium value for each ion occurred within 30 min. Erbium removal increases with time and attained equilibrium at 60 min. Short equilibrium time is one of the important considerations for economical wastewater treatment applications. The initial rapid adsorption of erbium ions on zirconia is due to the availability of larger number of vacant adsorption sites for the erbium of the bulk solution. The subsequent slower adsorption is likely because of the competition among the erbium ions for the limited number of vacant adsorption sites. Thus the driving concentration gradient between the bulk sol-
ution and the solid surface is the main factor controlling the kinetics of the system.

![Figure 4](image-url)  
*Figure 4. Effect of contact time on erbium ions adsorption onto prepared zirconia at 298, 313 and 333 K.*

The equilibrium sorption capacity of erbium onto zirconia was found to increase with increasing temperature, increasing indicating that the erbium ion sorption on the adsorbent was favored at higher temperatures. The sorption of erbium is endothermic, thus the extent of sorption increased with increasing temperature. The sorption of erbium by zirconia involves not only physical, but also chemical sorption. At high temperature, ions are readily dehydrated, and therefore their sorption becomes more favorable.

**Kinetic study**

Analysis of experimental date at various time make possible to calculate the kinetic parameters, and take some information for designing and modeling the adsorption processes. To understand the adsorption mechanism of zirconia for erbium, the adsorption kinetics was investigated using pseudo first order [20] and pseudo second order [21], with Eq. (3) and Eq. (4) respectively:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{pseudo-first order} \quad (3)
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{pseudo second order} \quad (4)
\]

where \( q_t \) and \( q_e \) are the amount adsorbed (mmol g\(^{-1}\)) at time \( t \) and at equilibrium time, respectively and \( K_1 \) and \( K_2 \) are the first and second rate adsorption constants, respectively. By testing the two plots of \( \log(q_e - q_t) \) versus \( t \) (Fig. 5), and \( (t/q_t) \) versus \( t \) (Fig. 6), the rate constants, \( k_1 \) and \( k_2 \), can be calculated. The conformity between experimental data and each model predicted values was expressed by the correlation coefficient \( R^2 \) in Table 1.

![Figure 5](image-url)  
*Figure 5. Pseudo first order plots for the sorption of erbium ions onto prepared zirconia at 298, 313 and 333 K.*

![Figure 6](image-url)  
*Figure 6. Pseudo second order plots for the sorption of erbium ions onto prepared zirconia at 298, 313 and 333 K.*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( q_e ) mmol/g</th>
<th>( h ) mmol/(g min)</th>
<th>( K_2 ) g/(mmol min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>8.8</td>
<td>2.5</td>
<td>0.03</td>
</tr>
<tr>
<td>313</td>
<td>9.9</td>
<td>4.3</td>
<td>0.04</td>
</tr>
<tr>
<td>333</td>
<td>11.9</td>
<td>10.7</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The result indicates that the pseudo-second-order model \( (R^2 = 0.98) \) is more suitable than the pseudo-first-order kinetic model \( (R^2 = 0.92) \) for erbium adsorption on zirconia, and that the adsorption complies with the pseudo-second-order reaction. The calculated \( q_e \) values obtained from the first-order kinetic model do not give responsible values, which are too low compared with experimental \( q_e \) values. Estimated \( q_e \) values of pseudo-second-order model accurately predict the
adsorption kinetics over the entire working times and temperatures. Therefore, this model has enough suffi-
ciency for acceptable accurate prediction of the kin-
etics of erbium adsorption onto zirconia. This sug-
gested the overall rate of the adsorption process is
most likely to be controlled by the chemisorption pro-
cess [22] and rate of reaction is directly proportional
to the number of active sites on the surface of adsorbent.
From Table 1, it can be shown that the values of
the initial sorption rate \( h = k_o q_e^2 \) increased with the in-
crease in temperature. According to pseudo second
order model, the adsorption rate \( dq_r/dt \) is proportional
to the second order of \( q_r - q_e \). Since zirconia has rela-
tively high equilibrium adsorption density \( q_e \), the ad-
sorption rates become very fast and the equilibrium
times are short. Such short equilibrium times coupled
with high adsorption capacity indicate high degree of
affinity between adsorbate molecules and carbon sur-
face [23]. These results explain that the pseudo second
order sorption mechanism is predominant and that the
overall rate constant of each ion exchange process
appears to be controlled by the chemical sorption
process [24–26].

One of the most widely models describe the kinetic
of ion exchange data and can predict the actual slowest
step is the homogeneous particle diffusion model
(HPDM). In this model, the rate-determining step of
sorption normally involves two mainly steps of film
diffusion that involve diffusion of ions through the
liquid film surrounding the adsorbent and/or particle
diffusion that involve diffusion of ions into the adsorb-
ent beads. If film diffusion is rate-determining step, the
following expression can be utilized to calculate the
diffusion coefficient:

\[
- \ln(1 - X) = \frac{3DC_c}{r_o D_c}t 
\]  

(5)

where \( c \) and \( c_e \) are the equilibrium concentra-
tions of the ion in solution and solid phases, respec-
tively, \( D \) is the diffusion coefficient in the liquid phase, \( X \) is the
fraction attainment of equilibrium or extent of ads-
orbent conversion, \( r_o \) is the radius of the adsorbent
particle, \( \delta \) is the thickness of the liquid film. If film
diffusion was involved in erbium adsorption, then the
plot of \( - \ln(1 - X) \) vs. time would be the straight line
through the origin.

If the diffusion of erbium ions through the ads-
orbent beads is the slowest step, the particle diffusion
will be the rate determining step and the particle dif-
fusion model can be apply to calculate the diffusion
coefficients. Then, the rate equation is expressed as:

\[
- \ln(1 - X^2) = \frac{2D_{p} \pi^2}{r_o^2}t 
\]  

(6)

where \( D_p \) is the particle diffusion coefficient. If particle
diffusion was involved in erbium adsorption, then the
plot of \( - \ln(1 - X^2) \) vs. time would be the straight line
through the origin.

The kinetic rate data of erbium ions sorbed onto
zirconia powder were tested using Eqs. (4) and (5). The
kinetic plots of \( \ln(1 - X) \) vs. time exhibit straight lines
that do not pass through the origin for all studied tem-
peratures. This indicating that the film diffusion model
does not control the rate of the sorption processes.
When adsorption starts, reacted layer thickness is still
very small and film resistance to erbium ions diffusion
is therefore comparable to adsorbent outer shell resis-
tance. Moreover, \( \ln(1 - X^2) \) vs. \( t \) plots is given in Fig. 7.
Straight line with zero intercept would suggest erbium
adsorption to be controlled by its diffusion within the
particles of zirconia.

![Figure 7. Plots of –ln(1 – X) as a function of time for the dif-
fusion of erbium ions onto prepared zirconia at 298, 313 and
333 K.](image)

**Thermodynamic studies**

In any sorption process, both energy and entropy
considerations must be taken into account in order to
determine what process will occur spontaneously.
Values of thermodynamic parameters are the actual
indicators for practical application of a process. Diffusion
coefficient of erbium sorption is expressed as a
function of temperature by the following Arrhenius
type relationship:

\[
\ln D_r = \ln D_0 - \frac{E_a}{RT} 
\]  

(7)

where \( D_0 \) is a pre-exponential constant analogous to
Arrhenius frequency factor.

A plot of \( \ln D_r \) vs. \( 1/T \) was found to be linear (Fig. 8).
The \( E_a \) value calculated from the slope of the plot is
equal to 9.95 kJ mol\(^{-1}\). The relatively low activation
energy (less than 42 kJ/mol) suggested that erbium
sorption is a diffusion-controlled process [27].
The other thermodynamic parameters, change in the free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), were determined by using following equations [28, 29]:

\[
D_0 = 2.72(kTd^2 / h) \exp(\Delta S / R)
\]

(8)

\[
\Delta G = \Delta H - T\Delta S = E_a - RT - T\Delta S
\]

(9)

where k is the Boltzmann constant, h is the Plank constant, d is the average distance between two successive positions, R is the gas constant and T is the absolute temperature. Assuming that the value of d is equal to 5×10^{-8} cm [30], the values of thermodynamic parameters were calculated and presented in Table 2. The positive values ΔH indicate the presence of an energy barrier in the sorption and endothermic process [31]. The positive value of entropy change reflects good affinity of erbium ions towards the sorbent and the increasing or increasing randomness at the solid-solution interface during the sorption process [32]. The positive ΔG values suggest the existence of an energy barrier and that the reaction is non-spontaneous process [33].

**Table 2. Thermodynamic parameters of the sorption of erbium ions onto zirconia**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>D_0 × 10^{11} m^2/s</th>
<th>D_0 × 10^{12} m^2/s</th>
<th>E_a (kJ/mol)</th>
<th>ΔS (kJ/mol K)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>11.1</td>
<td>8.9</td>
<td>9.95</td>
<td>439.0</td>
<td>127.1</td>
<td>7.3</td>
</tr>
<tr>
<td>313</td>
<td></td>
<td></td>
<td>44.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td></td>
<td></td>
<td>49.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

Using of zirconia for erbium ion removal from aqueous solution was studied. The highest removal efficiency of zirconia for erbium ion was obtained at pH 5.0. The adsorption can be explained as ion exchange mechanism between erbium ion and hydroxyl groups. The kinetics studies showed that most of the erbium ion uptake rapidly occurred in the first 30 min, and the adsorption equilibrium was obtained within one hour. The adsorption kinetics was well described by pseudo-second-order and homogeneous particle diffusion models implied that chemisorption is a predominant mechanism and particle diffusion control erbium adsorption. Based on the values obtained from some adsorption thermodynamic parameters such as ΔH, ΔS and ΔG, it was found that erbium adsorption on zirconia is an endothermic and good affinity of erbium ions towards the sorbent.

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**REFERENCES**


IZVOD

SORPCIJA ERBIJUMA IZ VODENIH RASTVORA NA SOL–GEL DOBIJENOM CIRKONIJUM–OKSIDU

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(Naučni rad)

Prah cirkonijum-oksida je sintetisan sol–gel postupkom i korišćen za sorpciju erbijuma. Adsorpcija uveliko zavisi od pH vrednosti medijuma gde efikasnost otklanjanja raste u odnosu povratka pH u alkalni spektar. Proces je prvobitno veoma brz i maksimalna adsorpcija je postignuta u 60 min nakon kontakta. model Pseudo-drugi reda reakcije i model difuzije homogenih čestica (HPDM) su najbolji u korelaciji difuzije erbijuma na čestice cirkonijuma. Izračunata je adsorpcija termodinamičkih parametara. Adsorpcija erbijuma je endotermička ($\Delta H > 0$) i dobrog je afiniteta erbijumovih jona u odnosu na cirkonijum ($\Delta S > 0$).

Ključne reči: Erbijum • Cirkonijum • Sol–gel • Kinetika • Termodinamika