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Extraction of Cerium (III) by a Solvent Extraction Technique Using Diaminododecylphosphonic Acid (DADTMTPA): Experimental, Density Functional Theory and Molecular Dynamic Studies

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Abstract :

This paper aims to present the recent results progress on diaminododecylphosphonic acid (DADTMTPA) as an extractant of cerium (III) from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution medium. Different parameters including pH, temperature, extractant concentration, and foreign ions present in the aqueous phase were examined to investigate the extractational mechanism. The optimum conditions of solvent extraction of Ce(III) are as follows: under experimental conditions of 298 K and the initial concentration of Ce(III) being kept at 10^{-4} M at pH 3.50. The agitation duration of 5 min for a volume ratio equal to 2, and the best yield is 77 % in one-step. An increase in the temperature reduced the extraction process. The DADTMTPA extracts Ce(III) after the second cycle with a yield of 95 %. The extraction thermodynamic parameters such as ΔG , ΔH and ΔS are also determined and reported. On the other hand, density functional theory (DFT) based on B97D3 functional with 6-311++G(d,p) basis set analysis and molecular dynamics simulations were used to extremely fast methods at calculating the non-bonded interactions and to understand its properties of molecular interactions, which have proved to be an adopted and useful tool to predict and describe the chemical behavior of the evolution of the system.

Introduction

In recent years, rare earths play an important role in modern life and have attracted much attention.[1] The rare earth elements (REEs), are a set of 17 elements including 15 lanthanides (Ln), scandium (Sc) and yttrium (Y), which are generally categorized into two groups based on their electron configuration; the light rare earth elements (La, Ce, Pr, Nd, Pm, Sm, Eu) and the heavy rare earth elements (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y).[2,3] The separation and purification of trivalent rare-earth elements has recently received significant attention due to the ever-increasing demand for these elements and their compounds.[4] Rare earth metals (REMs), which are the elements that have become extremely important to our world of technology due to their unique physical and chemical properties, have wide uses in different industries such as catalysts and alloys which are used in magnets, metallurgy, cell phonesoptics, lasers, phosphors, solar panels and wind turbines.[2,5–7] One of these rare metals and the most abundant member of the lanthanide series is Cerium whose abundance in the upper earth crust is 64 ppm. It belongs to group 15 of the periodic table with electronic configuration of $4f^{15}d^16s^2$. It is chemically characterized by having two stable valence states,

Ce^{3+} (cerous), and Ce^{4+} (ceric), for which the ionic radii are respectively 114 pm and 97 pm. Many of the uses of cerium and cerium compounds center on the redox chemistry of the Ce (IV)/Ce (III) couple.[3,8,9] Given their unique physicochemical properties, cerium compounds have been widely used in phosphorus for cathode ray tubes, luminescence, in optical coatings, in automobile exhaust catalysts and in paints. It is used in carbon-arc lighting with other rare earths, especially in the motion picture industry. It is also used to produce permanent magnets, used as an effective catalyst for petroleum refining, as well as for metallurgical and nuclear applications.[3,8–11] It has a lot of significance in high-tech fields, which is why high purity cerium is desired.[12] The unique physicochemical properties of Ce (III) show that this metal has attracted a large number of researchers to use different techniques for the cerium (III) extraction from aqueous solutions. Several techniques for the extraction of Cerium (III) from aqueous solutions such as membrane separation, solvent extraction, ion exchange, and adsorption.[13] Solvent extraction is the most common process used for recovery, and removal of metal ions from aqueous solutions[14] field over other adopted methods. It is one of the most significant extractions and recovery methods for precious metals such as indium, molybdenum, vanadium, rare-earth metals, and other heavy metal ions. Organophosphorus compounds tend to be the most promising to extract rare earth metal ions from various media by means of solvent extraction.[14–18] The advantages of organophosphorus extractants in liquid-liquid extraction processing are including their chemical stability, good extraction kinetics, good loading and stripping characteristics. In recent years, the potential applications of phosphinic and phosphonic acids in the recovery of REEs from different aqueous solutions have received considerable attention.[6] As a significant group of extractants (cationic, anionic, solvating) for the extraction of rare earth elements, several extractants such as neutral organophosphorus esters, organophosphorus acid, and amines have been investigated; likewise, Diaminododecylphosphonic acid

(DADTMTPA), Cyanex 572, Di(2-ethylhexyl) phosphoric acid (P204), di(1-methyl-heptyl) methyl phosphonate (P350), Cyanex 272, TBP, Cyanex 923, Cyanex 921, Cyanex 302, PC-88A and di(2-ethylhexyl)-phosphoric acid (D2EHPA).[19–29]

The purpose of this study is to cast light upon the best conditions for cerium (III) extraction. Extraction tests are performed using diaminododecylphosphonic acid as an extracting agent. The molecular formula of (DADTMTPA) is $C_{16}H_{40}N_2O_{12}P_4$ and has been undertaken by varying several parameters such as contact time, extractant concentration, and initial cerium (III) ion concentration, pH of aqueous solutions, ion strength, and temperature. In addition, the values of thermodynamic parameters for this mixture were calculated. Finally, the stoichiometry is of the extracted Ce (III) complexes, the equilibrium extraction constants, and the extraction mechanism were experimentally evaluated and discussed. The extraction method is based on complex formation between cerium (III) and diaminododecylphosphonic acid. This extractant is composed of several groups of phosphoric acid and amine function. This may explain its high extraction efficiency and affinity with rare earth cations and reflect the chelating behaviour of the acid.

Experimental Section

Materials and Reagents

The necessary information of all chemicals used in this study and which are listed in Table 1. UV/Vis spectra were obtained using a (Optizen 3220 UV), a digital pH meter.

Extraction Experiments

The extraction experiments were conducted with DADTMTPA dissolved in chloroform to the desired concentration. After various preliminary tests with different solvents, chloroform has been chosen because it dissolves the extractant without trouble or emulsion, then the Ce^{3+} in aqueous solution was prepared by dissolving the $Ce(NO_3)_3 \cdot 6H_2O$ into distilled water to the desired concentration. Different volumes ($V_{aq}=2 V_{org}$) of aqueous and organic solutions were mixed in a glass beaker and stirred using a

mechanical stirrer to achieve complete equilibrium. All procedures of the extraction were performed at room temperature of 298 ± 2 K and contact time 5 min. A dilute nitric acid (HNO_3) solution was used to adjust the solution acidity to the desired value. After equilibration, the mixture of organic and aqueous solutions was transferred to a separator funnel, where the phases were allowed to separate. The determination of Cerium (III) ion concentration in the aqueous phases before and after extraction was carried out by spectrophotometrically using Arsenazo III. It is one of the most frequently used azo-dyes in spectrophotometry, especially for the determination of a lanthanide and actinide ions.[31] In spectrophotometric method, the cerium (III) ions react with Arsenazo (III) at pH 3.5 to form a colored chelate absorbing at λ_{max} of 652 nm.

Theoretical Background

In this section, the DFT calculations and molecular dynamics simulations are used to study non-covalent interactions. At first, the 2-D chemical structure of the acid compound was drawn using Chemdraw software.[32] The optimization of the geometry and frequency calculations were performed with density functional theory[33] using the B97D3[34–36] functional and 6–311+ +G(d,p) basis set level of theory implemented in Gaussian 16 software package,[37] The frequency calculations revealed that there was no imaginary value in the spectrum, indicating the optimized geometries were true energy minima. The effect of the solvent environment has been studied using the SMD model (Solvation Model based on density)[38] to improve the precision of the calculations and to be as coherent as possible with the experimental environment,

On the other hand, the obtained optimized structures have been used in the molecular dynamics simulation as the initial coordinates of the system. All molecular dynamics simulations were performed in Gromacs/2020.4-GPU software package[39] using Charmm36 force field,[40] which is used to describe the interaction between atoms. Further, to perform the MD simulations, the size of number of particles, volume/pressure, and temperature) were selected in simulations for equilibration with 20 ns, and 500 ns

were used for dynamics simulation. A time step of 0.002 ps was used for all simulations. All the visualization tasks of the MD model were performed in Pymol software.[41]

Table 1. The Chemical name, Supplier and Purity of the Chemicals Used.				
Chemical Name	Chemical Formula	M _w (g.mol ⁻¹)	Mass Purity	Supplier
Potassium nitrate	KNO ₃	101.1	≥ 99.5	BIOCHEM hemopharma
Sodium Acetate	CH ₃ COONa	82.03	≥ 99	PANREAC
Cerium (III) nitrate hexahydrate	Ce(NO ₃) ₃ .6H ₂ O	434.22	≥ 99	BIOCHEM Chemopharma
Arsenazoll disodium salt	C ₂₂ H ₁₆ As ₂ N ₄ Na ₂ O ₁₄ S ₂	820.34	100	Alfa Aesar
Nitric acid	HNO ₃	63.01	≥ 65	Riedel De Haen
Acetic acid	CH ₃ COOH	60.05	≥ 99.8	Riedel De Haen
Chloroform	CHCl ₃	119.369	≥ 99	BIOCHEM Chemopharma
Diaminododecyl-phosphonic acid (DADTMTPA)	C ₁₈ H ₄₀ N ₂ O ₁₂ P ₄	576	≥ 93	Synthesized ^[39]

Results and Discussion

Results of the extraction experiments will be discussed in terms of extraction yield (R) and distribution coefficient (D) defined by Equations (1) and (2):[42–44]

$$R = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

$$D = \frac{R}{100 - R} \times \frac{V_{aq}}{V_{org}} \quad (2)$$

Where A_i is the original metal absorbance in the aqueous phase before extraction and A_f is the metal absorbance in the aqueous phase after extraction, while V_{aq} is the volume of the aqueous phase and V_{org} is the volume of the organic phase.

Volume Ratio

In solvent extraction process, volume ratio (V_{aq}/V_{org}) is an Important parameter that influences the extraction ability of the chelating extractants. The effect of the volume ratio was investigated by varying the V_{aq}/V_{org} ratio from 1 to 5 keeping the total volume of the phase constant and initial pH 3.5. The DADTMTPA and cerium(III) concentrations remained constant at 10⁻³ M and 10⁻⁴ M, respectively. According to the results obtained, the best efficiency is 72.50% with a volume ratio equals to 2, Figure 1. The latter was chosen for the rest of the experiment. We noticed that the transport of Ce (III) cations to the organic phase containing the extractant DADTMTPA is

easier and favourable when $V_{aq}=2 V_{org}$.

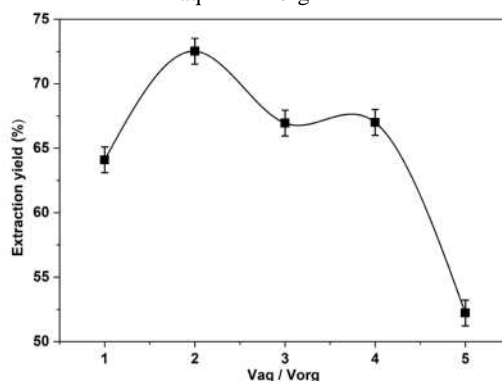


Figure 1. Effect of the volume Ratio. $[Ce^{3+}] = 10^{-4}$ M, $[DADTMTPA] = 10^{-3}$ M, $T = 25^{\circ}C$.

To determine the optimal time of agitation, a series of experiments were carried out at different contact time of aqueous and organic phases and at fixed value of volume ratio. The effectiveness of time was studied in the range of 0 to 35 min at $25^{\circ}C$. The results show that the contact time was fast, and under the given experimental conditions, the cerium extraction was proceeding rapidly from the first minute of contact (44.5 %). The best efficiency (77%) is obtained after 5 min of agitation, which is sufficient to reach the extraction equilibrium. The results were represented in Figure 2. This rapid contact time has also been observed in the elimination of Sm (III) by the same extractant.[42]

Effect of the Organic Phase Concentration

To determine the effect of extractant concentration on the extraction of Ce (III), a series of experiments were performed in which the concentration of DADTMTPA was varied over the range of 10^{-6} M to 10^{-3} M. Figure 3 clearly shows the significant evolution of the extraction efficiency as a function of the extractant concentration from $5 \cdot 10^{-5}$ M.

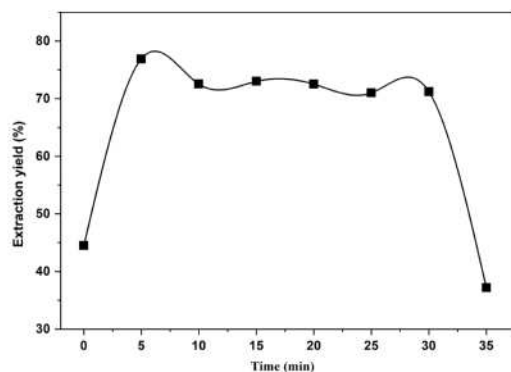


Figure 2. Influence of contact time of aqueous and organic phases on the Cerium (III) Extraction. [DADTMTPA] = 10^{-3} M, $[Ce^{3+}] = 10^{-4}$ M, Vaq/Vorg = 2.

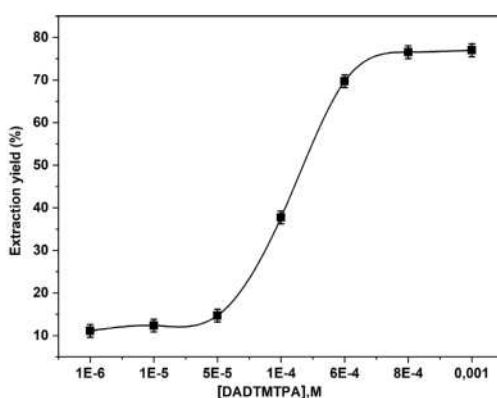


Figure 3. Yield of the Extraction in Function of the DADTMTPA. $[Ce^{3+}] = 10^{-4}$ M, Vaq/Vorg = 2, $t = 5$ min, $T = 25$ °C.

from 15% to 77% by increasing the DADTMTPA concentration from $5 \cdot 10^{-5}$ M to 10^{-3} M in the presence of chloroform.

As a significant parameter, which plays a determining role in the extraction of metal extraction, the molar ratio (Q) in the cerium extraction should be provided. The molar ratio (Q) in the Equation (3) is defined as the ratio of the number of moles of the extractant in the organic phase versus the number of moles of metal in the aqueous phase before extraction.[42–45]

$$Q = \frac{n_{\text{extractant}}}{n_{\text{metal}}} \quad (3)$$

The variation of the extraction efficiency test of 10^{-4} M cerium (III) from aqueous solutions as a function of Q is shown in Figure 4. The extraction of Ce(III) was found to increase by increasing the concentration of DADTMTPA.

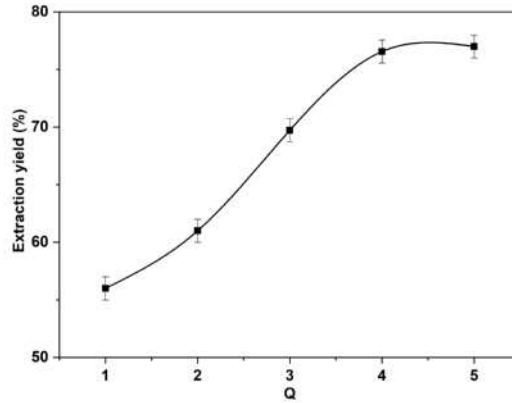


Figure 4. Effect of the Molar Ratio on the Extraction Efficiency of Ce(III). $[Ce^{3+}] = 10^{-4}M$, $V_{aq}/V_{org} = 2$, $t = 5$ min, $T = 25^{\circ}C$.

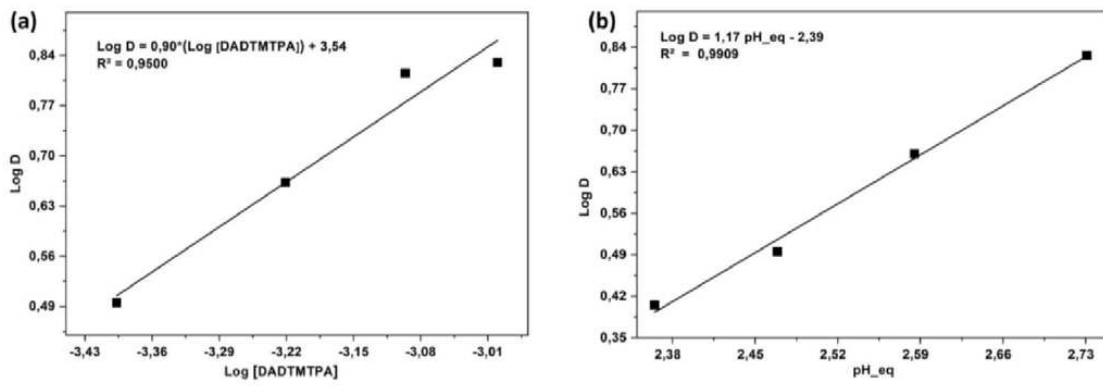
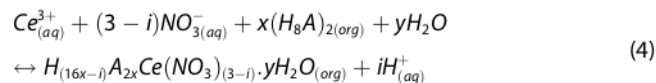


Figure 5. (a) Evolution of the Distribution Ratio in Function $\log[DADTMTPA]$. $[Ce^{3+}] = 10^{-4}M$, $V_{aq}/V_{org} = 2$, $t = 5$ min, $T = 25^{\circ}C$. (b) Effect of the Equilibrium pH on the Distribution Ratio of Cerium. $[Ce^{3+}] = 10^{-4}M$, $V_{aq}/V_{org} = 2$, $t = 5$ min, $pH_{3,5}$, $T = 25^{\circ}C$.

The stoichiometric coefficients obtained from the plots $\log D$ versus $\log [DADTMTPA]$ and $\log D$ versus pH_{eq} (the pH of aqueous solution in an equilibrium state) was determined by slope analysis. [13,26] The obtained results are shown in Figures 5. The process of extraction of Cerium (III) cation from aqueous solutions with an extractant of DADTMTPA can be presented in the following general reaction, Equation (4): [26,46,47]



Further, the distribution ratio and equilibrium constant for the above reaction can be presented as follows, Equations (5) and (6):

$$K_{eq} = \frac{[H_{(16x-i)A_2xCe(NO_3)_{(3-i)} \cdot yH_2O}_{(org)}] \cdot [H^+]^i_{(aq)}}{[Ce^{3+}]_{(aq)} \cdot [NO_3^-]_{(aq)}^{3-i} \cdot [(H_8A)_2]_{(org)}^x} \quad (5)$$

$$D_{Ce} = \frac{[H_{(16x-i)A_2xCe(NO_3)_{(3-i)} \cdot yH_2O}_{(org)}]}{[Ce^{3+}]_{(aq)}} \quad (6)$$

Where $H_{(16x-i)A_2xCe(NO_3)_{(3-i)} \cdot yH_2O_{(org)}}$ is the only extractable species.

By combining Equations (5) and (6), the dependence between the equilibrium constant K_{eq} and the distribution ratio D could be presented in Equations (7) and (8):

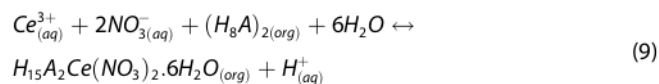
$$K_{eq} = \frac{[H^+]^i_{(aq)} \cdot D_{Ce}}{[NO_3^-]_{(aq)}^{3-i} \cdot [(H_8A)_2]_{(org)}^x} \quad (7)$$

$$\log D_{Ce} = \log K_{eq} + (3-i) \log [NO_3^-]_{(aq)} + x \log [(H_8A)_2]_{(org)} + ipH \quad (8)$$

To obtain the extraction reaction stoichiometry, the above studies were used to determine (x) and (i) values by analyzing the experimental data. As shown in Figure 5(a), the plots of $\log D$ versus $\log [DADTMTPA]$ giving one straight line with good correlation coefficient 0.95 and slope equal to 0.90, which is close to 1. The influence of the equilibrium pH on the distribution ratio of cerium (Figure 5(b)). The plots of $\log D$ versus pH_{eq} which also gave one straight line with a good correlation coefficient 0,99 and slope equal to 1.17, which is close to 1. This result suggests that one molecule of extractant reacted with one cerium ion (Ce^{3+}).

DADTMTPA is an acidic organophosphorus extractant and in the organic solvent it is present generally as a dimer $(H_8A)_2$ [23,45,48–50] as shown in Figure 6.

The equation of the extraction equilibrium can therefore be written as the following Equation (9):



Based on the above results and discussion, the extracted complex of Ce (III) by DADTMTPA is presented as $H_{15}A_2Ce(NO_3)_2 \cdot 6H_2O$.

FTIR analysis

The I.R spectra in the range of 4000–400 cm^{-1} were recorded as potassium bromide discs on a Shimadzu FTIR-8300 Fourier Transform infrared spectrophotometer. This provides information regarding the coordination mode in the complexes were analyzed by comparison with the data for the free extractant shown in Table S1 (Supporting Information), The IR spectra of the extractant revealed some characteristic stretching bands, a P- O- H stretching band around 943.1 cm^{-1} , (O=)POH of phosphonic acid were observed at around 2362.6 cm^{-1} ; however, it was absent in the infrared spectra of complexes, indicating the deprotonation and coordination of the phosphonic acid groups to the metal atom moiety as well as the formation of Ce□ O bond via deprotonation at 873.7 cm^{-1} .and P=O absorption band was observed at around 1170.7 cm^{-1} . In fact, Ce(III) substituted the hydrogen atom in the P- O- H group, thus confirming the cation exchange mechanism proposed, and P=O absorption band was observed at around 1170.7 cm^{-1} .(See Table S1, Figures S1 and S2 in supporting information).

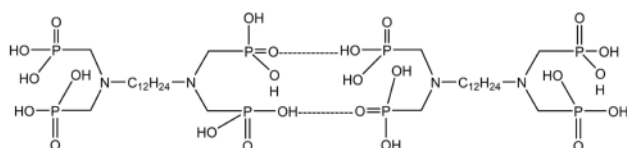


Figure 6. Structure of Dimeric Form of DADTMTPA.

Ionic strength is a size that measures the tension of the electric field in the solution. To verify the effect of the ionic strength on the output of the extraction of 10^{-4} M Ce^{3+} , the aqueous phase is changed by adding KNO_3 and CH_3COONa that have been added to the aqueous phase with different concentrations (0.1–0.5 M).

Influences of the Addition of KNO_3

According to these results, the concentrations of the KNO_3 addition would have the effect of reducing the extraction yield. The efficiency of extraction decreases with the increase in the concentration of nitrate anions. In this case, the extraction yield does not benefit from the addition of a common ion, the extraction yield reaches a maximum value of 69% for the quantity of KNO_3 0.3 M see Figure 7.

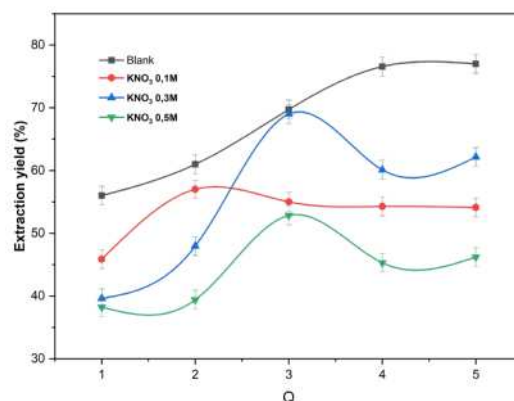


Figure 7. Evolution of the Yield According to the Reports Molar Q after the Addition of KNO_3 .

Influence of the Addition of CH_3COONa

In general, the addition of sodium acetate, whatever the concentration, leads to a decrease in the extraction efficiency (Figure 8). This can be explained by the increase in the solution pH, which affects the extractability of the cations; in addition, competition in extraction between Na^+ and cations in solution (Ce^{3+}) explains the poor results after adding the acetates.[42,51]

The Effect of Solution pH

The acidity of the aqueous phase is another critical variable influencing the recovery of cerium. This survey requires the addition of an acid to a given pH. The influences of pH on the extraction of cerium (III) by DADTMTPA was investigated at different initial pH of aqueous solutions ranging from 1 to 3. The results are shown in Figure 9. Based on these results, the addition of the nitric acid has the effect of reducing the extraction yield. It is clear from the figure that percent extraction of Ce(III) increases continuously with decreasing aqueous phase nitric acid concentrations.[42,13] This can be attributed to competitive extraction between Ce(III) and HNO_3 . [12] This phenomenon had been reported in the Ce(IV)

extraction by TBP.[52] When the acid concentration increases the percent extraction decreases, confirming that the metal transfer mechanisms.[11,53–54]

To accomplish this survey, we investigated successively the effect of the following parameters: The temperature and second cycle.

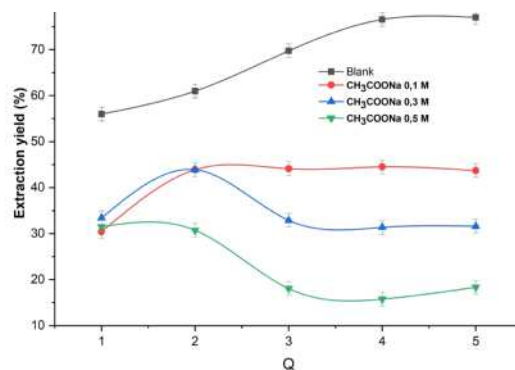


Figure 8. Evolution of the Efficiency According to the Reports Molar Q after the Addition of CH₃COONa.

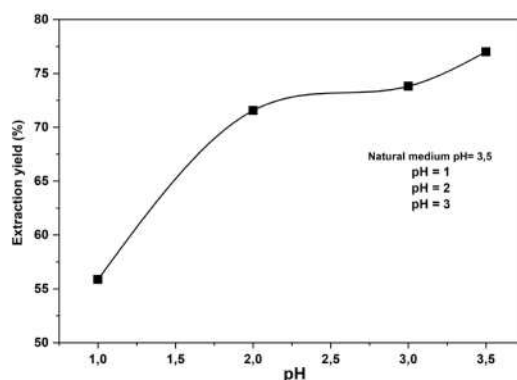


Figure 9. Variation of the Percentage Extraction of Ce(III) as a Function of the Initial pH of the Aqueous Phase. [Ce³⁺] = 10⁻⁴ M, [DADTMTPA] = 10⁻³ M, Vaq/Vorg = 2, t = 5 min, T = 25 °C.

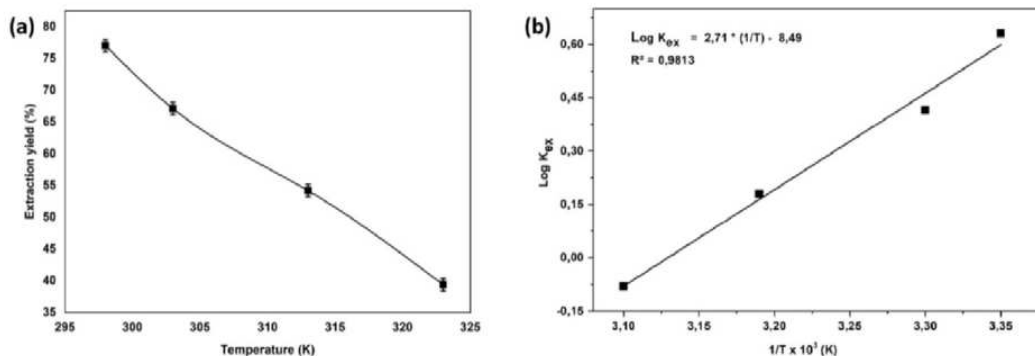


Figure 10. (a) Effect of Temperature on the Percentage Extraction of Ce(III). [Ce³⁺] = 10⁻⁴ M, [DADTMTPA] = 10⁻³ M, Vaq/Vorg = 2, t = 5 min, (b) Variation in log K_{ex} with 1/T for Ce(III) with DADTMTPA.

Effect of the Temperature

The extraction efficiency of certain extracting agents depends significantly on temperature. Therefore, the extraction of 10^{-4} Ce(III) was investigated at different temperatures ranging from (298 to 323 K), shown in Figure 10(a). The extraction yield of Ce(III) has an inverse relation with increasing temperature. The results show that the increase of temperature in the range 298–323 K decreased the extraction of cerium (III) .[55]

The Van't Hoff equation used to calculate the enthalpy and entropic changes (ΔH° and ΔS°) associated with the extraction of this metal, is thus expressed Equation (10) .[42,56]

$$\text{Log}k_{ex} = \left(\frac{-\Delta H^\circ}{2.303RT} \right) + \left(\frac{\Delta S^\circ}{2.303R} \right) \quad (10)$$

The values of enthalpy (ΔH°) and entropy (ΔS°) changes are calculated from the slope and the intercepting of the plot of $\log K_{ex}$ versus $1/T$, respectively. For the extraction of the metal gave a straight line (Figure10(b)). The following thermodynamic formulas were employed to calculate thermodynamic functions.

ΔH° can be calculated by plotting $\log K_{ex}$ against $1/T$ as the following Equation 11, in which the slope equals to:

$$\text{Slope} = \frac{\Delta \log k_{ex}}{\Delta(1/T)} = \frac{-\Delta H^\circ}{2.303R} \quad (11)$$

Further, the changes in standard free energy (ΔG°) and entropy (ΔS°) have also been determined using the following Equations 12 and 13:[42,57–59]

$$\Delta G^\circ = -2.303RT \log k_{ex} \quad (12)$$

Where R ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$) is the ideal gas constant, T (K) is the temperature.

The effect of temperature on the equilibrium constants (K_{ex}) varying from 298 to 323 K is given in Figure 10(b).

The thermodynamic parameters (ΔH° , ΔG° and ΔS°) derived from the plots and formulas are presented in Table 2. From the data in Table 2, our results show that while the

extraction of cerium is of an exothermic nature. The negative value of ΔG° for the extraction of cerium (III) by DADTMTPA means that the extraction reaction occurs spontaneously, the entropy change ΔS° is negative, indicating that the system is more orderly. In addition, an increase in ΔG° values (from -3.60 kJmol^{-1} at 298 K to -2.41 kJmol^{-1} at 303 K) with an increase in temperature showed that the extraction is disfavoured.

Second Extraction Step

To enhance the yield of cerium extraction, we studied the cycle effect of extracting the same aqueous solution, twice in succession with the same concentration of extractant. The operating conditions were set as before (the concentration of the aqueous phase, the volume ratio, the stirring time and the temperature).

After one-step, the yield obtained was of 77%. Figure 11 illustrates that the yield of extraction of Ce(III) was fully recovered (95%) after the second cycle.

Table 2. The Thermodynamic Parameters (ΔH° , ΔG° and ΔS°) Associated with the Extraction of Ce(III).				
Temperature (K)	$\log K_{ex}$	ΔG° (kJmol^{-1})	ΔH° (kJmol^{-1})	ΔS° ($\text{Jmol}^{-1}\text{K}^{-1}$)
298	0.631	-3.60	-51.88	-162.56
303	0.416	-2.41		
313	0.18	-1.078		
323	-0.079	+0.49		

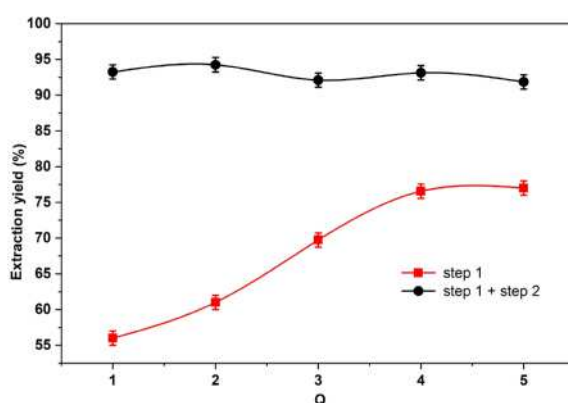


Figure 11. Evolution of the Efficiency According to the Second Cycle. $[\text{Ce}^{3+}] = 10^{-4}\text{M}$, $V_{aq}/V_{org} = 2$, $t = 5 \text{ min}$, $T = 25^\circ\text{C}$.

published results with the current work, the results showed that a good efficiency for lower acid concentrations.

DFT and Molecular Dynamic Simulations

Frontier Molecular Orbitals (FMOs) based on the density functional theory (DFT) provides chemists to further analyze the stabilities the complexes that contribute to understanding the quantitative prediction of chemical reactivity. The optimized geometry (Figure 12(a)) and the Frontier Molecular Orbitals (FMOs) are presented in Figure 12(b,c). In the FMOs plot, two colored regions represent two types of interactions. The red color region explains the positive phase (the repulsive interactions) which located over amine group, while the green color region referred to the negative phase. (Strong attraction) which is presenting the most preferred site for a nucleophilic attack. The initial point for molecular dynamics simulations was defined as follows; ten complexes (Ce(III) @DADTMTPA) have been added randomly in a cubic simulation box with the size of the cell at 50 Å. The box is solvated with the TIP4P water model Figure 13(a,b) which was used to fill the entire simulation box. The initial system was subjected to steepest descent energy minimization to eliminate the possible conformational overlap. The isovolumetric-isothermal (NVT) and isobaric-isothermal (NPT) equilibrations that stabilized the temperature and the pressure of the system were performed for 20 ns which most closely resembles experimental. After the thermodynamic balance, a 500 ns (250,000,000 Steps) MD simulations were performed. Further, all MD simulations were performed with system temperature at 298.15 K and pressure of 1.013 bars. The stability of the system is explored through the calculations of the RMSD (root mean square deviation), and Rg (radii of gyration) with respect to a reference structure, the RMSD and RMSF calculations indicates that the structure is very stable (see Figure 13(c,d)). The trajectories were stored every 2 ps and visualized using VMD.[67]

Extractant-biosorbent	Extraction Yields %	Experimental conditions	References
Cyanex 572	93.12 %	0.04 M Ce(III) 0.5 M Cyanex 572 0.05 M NO ₃ ⁻ pH 5 t = 10 min	[7]
Cyphos IL 104	99 %	0.01 M Ce(III) 0.1 M Cyphos IL 104 pH 4.8 t = 20 min T = 21 °C	[60]
Cyanex 923	100 %	0.001 M Ce (III) 0.4 M Cyanex 923 0.1 M HCl and 0.6 M H ₂ SO ₄	[61]
PC 88A and Cyanex 921	96.6 %	0.001 M Ce(III) 0.7 M PC 88 A and 0.1 M Cyanex 921.	[62]
Hexaacetato Calix (6) arene	99.63 %	0.001 M HNO ₃ 10 ⁻⁴ M Hexaacetato Calix (6) arene pH 7 1 N NHO ₃ t = 10 min	[63]
2-ethylhexyl phosphoric acid-2-ethylhexyl ester (EHEHPA)	99.92 %	t = 2.98 seconds	[64]
Chelating polymeric sorbent	97.38 %	pH 5 the residence time is 210 min $\mu = 0.6$	[65]
Loquat leaves	60 %	0.1 M HNO ₃	[66]
Diaminododecylphosphonic Acid DADTMTPA	54 mgg ⁻¹ 95 %	[DADTMTPA] = 10 ⁻³ M pH 3.5 [Ce ³⁺] = 10 ⁻⁴ M Vaq/Vorg = 2 t = 5 min	Present work

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Conclusion

The present study has been polarized on the solvent extraction of Cerium (III) from Ce(NO₃)₃.6H₂O solution medium using

Diaminododecylphosphonic acid (DADTMTPA) as an extractant. Further, in the light of the obtained results, the following key findings can be summarized as:

The present investigations clearly highlight that DADTMTPA has proven to be a good extractant and more selective for the recovery of Ce(III) cations from the solution with K^+ and Na^+ cations. They can completely be recovered to 95% after the second extraction step.

Maximum extraction efficiency is attained by a volume ratio of 2, and 10 \square 3M DADTMTPA in chloroform at an initial concentration of Ce^{3+} 10 \square 4 M, pH 3.5. DADTMTPA extracts Ce^{3+}

very rapidly. The best efficiency is obtained after 5 minutes of agitation. The extraction reaction of cerium with DADTMTPA was found to be cation-exchange mechanism releasing one H^+ ion during the extraction. From results of the slope analysis, the composition of the extracted species has been presented to be $H_{15}A_2Ce(NO_3)_2 \cdot 6H_2O$. Thermodynamic extraction functions (ΔG° , ΔH° and ΔS°) were calculated. Negative enthalpy indicates that the extraction phenomenon follows the exothermic type, and the reaction of extracting cerium (III) was found to be spontaneous.

The Molecular dynamics simulations and the DFT calculations evinced the formation of the complexes in the vacuum and in the aqueous solution.

Supporting Information Summary

The supporting information contains FTIR spectroscopy.

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for Functional.

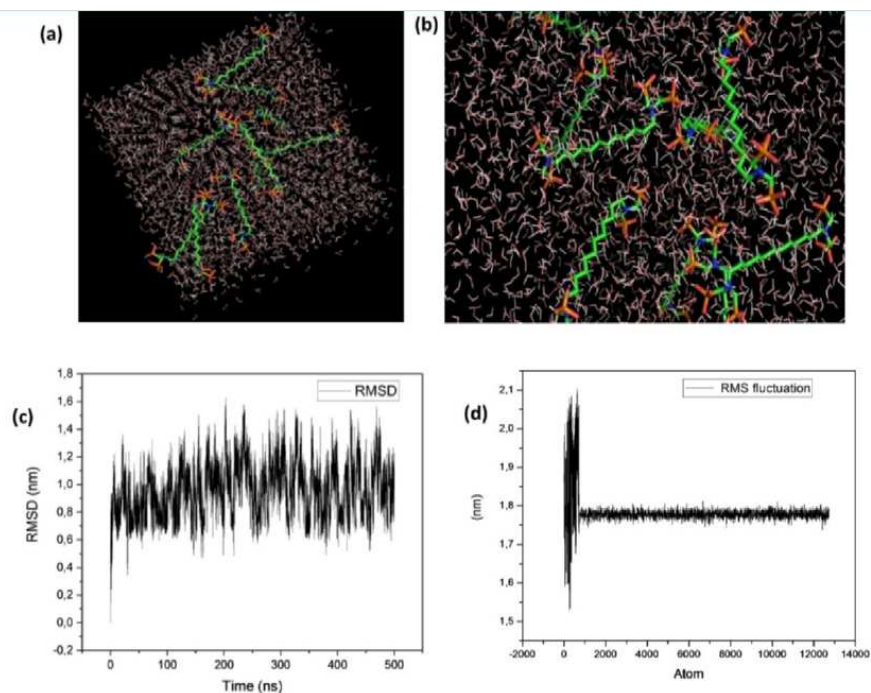


Figure 13. (a) and (b) Interactions of [DADTMTPA] [Ce] in the Solvation Shell. (c) and (d) Results Obtained by MD Simulations with 500 ns. Root Mean Square Deviation (RMSD) and Root Mean Square Fluctuation (RMSF) in Mixed Hydrophobic Solvent, respectively.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: Cerium · DFT · Diaminododecylphosphonic · DM · Extractant

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