Spectrophotometric Study on the Solvent Extraction of Gadolinium (III) with N-Acetylcysteine

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ABSTRACT

One of the famous solvent extraction type known as LLE (liquid-liquid extraction) was used to study extraction of Gadolinium (III) ion by using N-acetylcysteine as derivative of amino acid. Extraction efficiency is measured based on the ratio and percent of extraction, for that, some parameters affect both of them were studied. These parameters are effects of acidic function, equilibrium time, temperature, addition of some cations and anions, metal and reagent concentrations and addition of some oxidation and reduction agents. Thermodynamic study of some thermodynamic functions (ΔH, ΔG and ΔS) improved that the reaction was endothermic and spontaneous. Job's and mole ratio methods have been studied for the purpose of knowing the chelating ratio between metal and ligand, it was found that the ratio was (1:3) M:L, moreover, mole ratio method was used to calculate Stability constant.

INTRODUCTION

Gadolinium (Gd) is one of the rare earth (RE) elements. Many industrial processes use these elements as raw materials. They are widely utilized as a part of astro navigation, photograph electronic and metallurgical enterprises. These components are likewise imperative in nuclear energy program, subsequently, the separation and purification of rare earth are requested. Solvent extraction was effectively teachings to separate most of metals including rare earth metals. Efficiency of this method depends on extractant and ligand used in complexation [1]. Gadolinium progressively aggregate in soils and water soils and this will, in the long run, lead to expanding accumulation in people, creatures and soil particles. Gadolinium salts chafe skin and eyes and are suspected to be tumorigens [2].

N-Acetyl-Cysteine (NAC) (Acetylcysteine) is one of the amino acid derivatives which produced from acetylation of cysteine. It has free thiol group on one side and protected α-amino group by acetyl group on the other side, this fact made (NAC) formed simple peptide bond in protein and give him interesting in many studies as a fact that binary and ternary metals can form many complexes with these types of derivatives [3].

Fig. (1) Structure of (NAC)

Numerous studies to determine gadolinium were created, solvent extraction [4-6], selective redox reaction and ion exchange chromatography [7-11], spectrophotometric determination [12-13], online cloud-point [14-15], (CCC) Chromatography [16], ICP-MS [17-19], XRF [20]. In this study (NAC) was used to extract gadolinium (III) and studying the best condition to make this method fast and efficient.

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MATERIALS AND METHODS

Preparation

Stock solution of gadolinium (III) 1.00 mg/ml was prepared by dissolving 0.115 gm of gadolinium oxide in 2.00 mL of HCl and completing the volume to 100 mL with distilled water.

Series solutions of gadolinium (III) have been prepared by diluting the stock solution with specific volume of distilled water.

0.2 gm of NAC was dissolved in 100 mL of ethanol to prepare 0.2% solution of the reagent NAC.

1.00 gm of ascorbic acid was dissolved in 100 mL distilled water to prepare 1% w/v solution of ascorbic acid.

0.05 gm of arsenazo (III) was dissolved in 100 mL distilled water to prepare 0.05% w/v solution of arsenazo (III).

60 mL of formic acid was used to dissolved 28 gm of sodium hydroxide in order to prepare 1.00 L of formate buffer solution (pH=3.5)

A series of alkaline solution of sodium hydroxide ranged from 0.1 to 1.0 M were prepared from stock solution of sodium hydroxide.

Chloride salt solutions of [K(I), Cd(II), Ni(II), Cr(III)] were prepared by dissolving calculated weight for each of them and dissolved in 25 mL of distilled water.

Potassium salt solutions of (I^{-1}, Br^{-1}, $SO_4^{=}$, NO_3^{-}, ClO_3^{-1}) were prepared by dissolving calculated weight in 25 mL distilled water.

0.564 gm of tin chloride was dissolved in 1.0 mL of hydrochloric acid and then diluted to 25 mL of distilled water to prepare 0.1 M of tin chloride solution.

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EXPERIMENTAL

Calibration curve of Gd (III)

A series of different concentrations (0.063×10^{-4} – 0.953×10^{-4}) M were prepared from stock solution, then from each 5 ml of this solution, 1 mL of 1% ascorbic acid solution was added, after 1-2 minute 1mL of formate buffer and 2 mL of Arsenazo solution was added , then diluting to 20 mL with distilled water, by using dilute HCL/NaOH solution, the pH was adjusted to 2-2.6 and complete the volume to 25 mL with distilled water. The absorbances of all solutions were measured at λ_{max} 650 nm, finally, the relation between absorbance and concentration was drowned to obtain calibration curve as shown in figure (2).

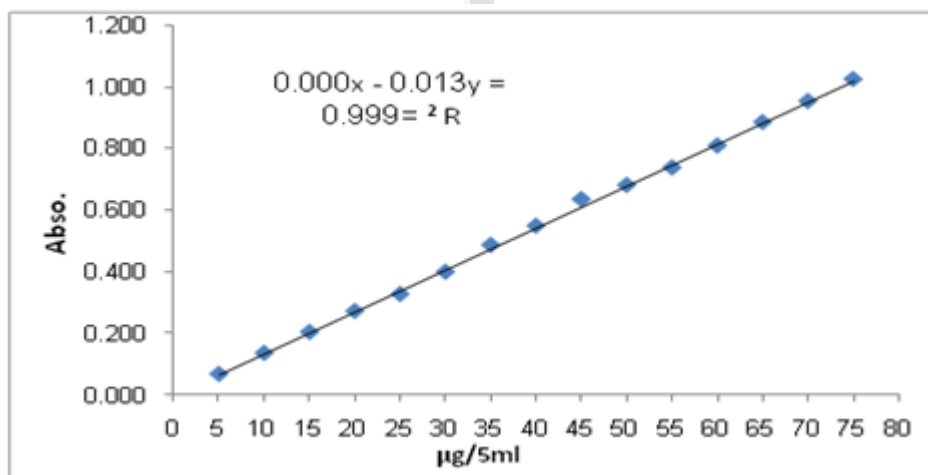**Fig. (2) Calibration curve for gadolinium (III)**

Extraction of Gd (III) ion by using reagent (NAC)

"The aqueous phase was composed of (2.5 ml) (1.4398×10^{-3}M) (500 µg) of Gd (III) (2.5ml) (0.2%) of ligand (NAC) in ethanol which poured into a separating funnel. The pH of the solution is which is equal to 7 was adjusted with diluted HCl and NaOH solutions. 5mL of chloroform was used to equilibrate with aqueous phase for (60) minutes. The two phases allowed to still and separate. Gd (III) ion determined spectrophotometrically after extraction in aqueous phase with arsenazo (III)"[21]. An aliquot of the aqueous phase in the cells for absorbance measurements at (λ_{max}= 650 nm).

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RESULTS AND DISCUSSION

Effect of pH

Acidic function of Gadolinium (III) solution was adjusted from 1.0 to 10.0 to study the effect of pH by using solution of NAC as organic phase, the results were shown in table (1).

Table (1): Effect of pH in the extraction of Gd (III)

pH	D	E%
1	0.731	42.290
2	0.779	43.788
3	0.898	47.310
4	1.882	65.301
5	2.061	67.330
6	2.289	69.595
7	3.045	75.278
8	1.727	63.329
9	0.911	47.671
10	0.875	46.666

Results in table (1) explained that there is increasing in distribution ratio (D) and (E %) up to 7 and then reduced. Thus could be because of the property of organic reagent utilized as a part of solvent extraction procedure and its effect on pH. Most of amino acid derivatives coordinate as di dentate ligand in acidic and basic solution, for that Gd (III) give high E% in acidic media. These results were consistent with the results of other studies [22].

Effect of shaking time (time equilibrium)

Time for shaking was relevant with the activity of extraction and the value of distribution ratio results in table 2 explained that shaking time of equilibrium between two layers was 30 min. at optimum conditions which give the best value of distribution ratio while down and above this

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point distribution values were minimized by decreasing the dissociation distribution. These results agreed with other studied [23-24].

Table (2): Effect of time of equilibrium in the extraction of Gd (III)

Time	D	E%
10	1.490	59.170
20	1.564	60.160
30	3.045	75.278
40	2.474	71.140
50	2.140	68.390
60	1.425	58.490
70	1.138	51.720
80	1.001	50.200

Effect of organic solvents

Table (3): Effect of polar organic solvent to extract Gd (III)

Organic Solvent	ε	1/ε	D	Log D	E%
Nitrobenzene	35.600	0.028	1.144	0.059	53.440
Benzaldehyde	17.800	0.056	1.123	0.050	56.710
1,2-dichloroethane	10.420	0.095	5.636	0.750	85.320
chloroform	4.810	0.207	3.045	0.483	75.278
Toluene	2.380	0.420	6.980	0.843	87.520
Benzene	2.280	0.438	2.999	0.477	74.160

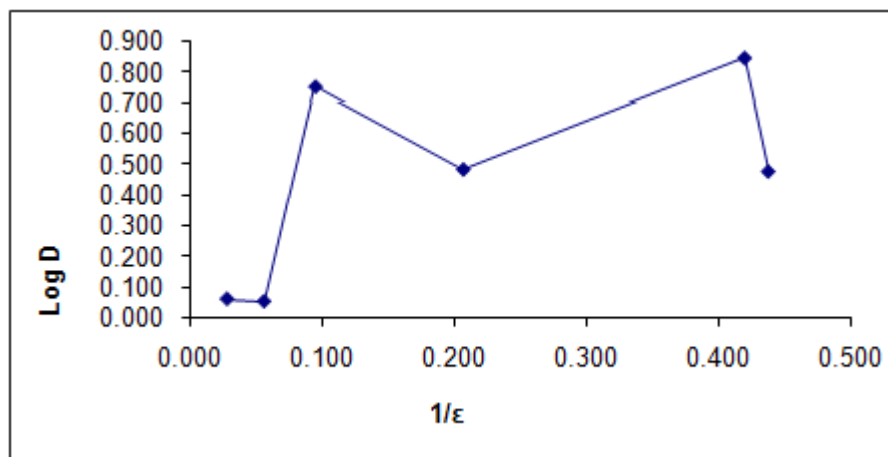*Citation: Ihsan Mahdi Shaheed et al. Ijppr.Human, 2016; Vol. 7 (3): 181-198.*

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Fig. (3) The effect of polar organic solvent to extract Gd (III)

Lack of linearity between distribution ratio and dielectric constant (ε) at optimum conditions improved that the complex has no charge chelate and the extraction system cannot be controlled by the values of (ε). These uncharged complexes affect by several factors, including solubility of complex or geometrical structure of organic solvent. This is upheld the role of organic solvent composition to accomplish the best extraction far from the polar organic solvent that utilized as to have a part in making the best extraction, yet its part was not a noteworthy, it's not bar the probability of involvement of organic solvent during the time of extraction, chloroform was chosen as being less toxic and expensive and gives acceptable D and E% .The results of this study are consistent with earlier studies [25].

Effect of anions on the extraction

The results in the table (4) at optimum conditions demonstrates that the presence of anions causes irregular influence during the time of extrication of Gd (III) ion relying upon the nature of the anions included. Some anions greatly affected diminishing the value of D and hence on the (% E) to extract Gd (III) by utilizing (NAC), these ions were (NO^{3-}, CLO^{3-}, and Br^{-1}) which forms undissolved compounds in aqueous solution contains lanthanides elements [26] and accordingly they carry on as masking agents attempting to decrease the coordination of cations with reagents [27], while some other anions like ($SO_4^{=}$) greatly affected increasing the D values and subsequently on the (% E) to extricate Gd (III). This ion decreased the energy of hydration for

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ions and afterward stimulates formation of complex in organic phase. These results are in concurrence with other studies [28].

Table (4): Effect of adding some anions on extraction Gd (III)

Anions	0.2%(w/v)		0.4%(w/v)	
	D	E%	D	E%
	3.042	75.275	3.891	79.570
I^{-1}	2.337	70.032	0.650	39.393
Br^{-1}	1.203	5460.7	1.948	66.078
$SO_4^{=}$	4.333	81.248	1.769	63.885
NO_3^{-}	1.103	52.448	2.248	69.211
ClO_3^{-1}	1.532	60.505	1.004	50.099

Effect of cations on the extraction

Numerous cations were chosen around Gd (III) ion in periodic table to study its influence on extraction of Gd (III) at optimum conditions. Results were illustrated in table (5).

Table (5): Effect of adding some cations on the extraction of Gd (III)

Cations	1000 µgm/2.5mL		2000 µgm/2.5mL	
	D	E%	D	E%
-----	3.042	75.275	3.084	75.514
K^{+1}	3.900	79.591	2.000	66.666
Cd^{+2}	5.934	85.578	5.170	83.792
Ni^{+2}	1.070	51.960	5.701	85.076
Cr^{+3}	1.910	65.635	1.510	60.159

Results in table (5) explained that addition of some cations like (Ni^{+2} and Cr^{+3}) reduced the values of D due to the competition of this cations to coordinate with (NAC) to produced complexes. These results improved in some studies [22].

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Effect of oxidation and reduction on extraction

The effects of oxidation were studied by adding (1mL) solution of hydrogen peroxide with concentration (35%) as an oxidant agent in extraction of Gd (III) ion with (NAC) under the experimental conditions. Distribution values of Gd (III) ion with (NAC) was calculated after separating aqueous phase from organic phase. The amount of remained ion was calculated in aqueous phase by using colorimetric method. To study the influence of reducing agent on (D) value to extract Gd (III) ion with (NAC) , (1mL) of SnCl$_2$.2H$_2$O solution (1M) had been added to the aqueous phase and by following the same method used with the studying the influence of oxidizing agent. Results had been obtained in the table (6).

Table (6): The effect of oxidation-reduction factors in the extraction of La(III) with (NAC)

Extraction	D	E%
Gd (III) with (NAC) In absence of oxidation- reduction factors	3.045	75.275
Gd (III) with (NAC) In presence of oxidation factors	5.023	85.761
Gd (III) with (NAC) In presence of reduction factors	10.424	91.246

Temperature: - (20±3) ^{o}C

The results of this study show that the extraction processes are inefficient in presence of oxidizing agents because of its effect on the reagent. It probably works on the oxidation and changing nature of chelating reagent. As well as the oxidation of Gd (III) ion is also expected. This oxidation distorts the system of complex formation extracted. The result of reducing agent shows that distribution ratio was increased because of increasing in stability of trivalent oxidation state of Gd (III). So Gd (III) ion do not reduce by using SnCl$_2$ .2H$_2$O.

Effect of metal ion concentration

Different concentration of Gd (III) solutions ranged from (50μg/2.5 mL to 1000μg/2.5mL), (0.128x10^{-3} to 2.543x10^{-3}) was prepared, then Gd (III) ion was extracted from these aqueous

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solutions by using 2.5 mL of 0.2% NAC as reagent at optimum condition obtained. Figure (4) illustrate the results obtained from this study.
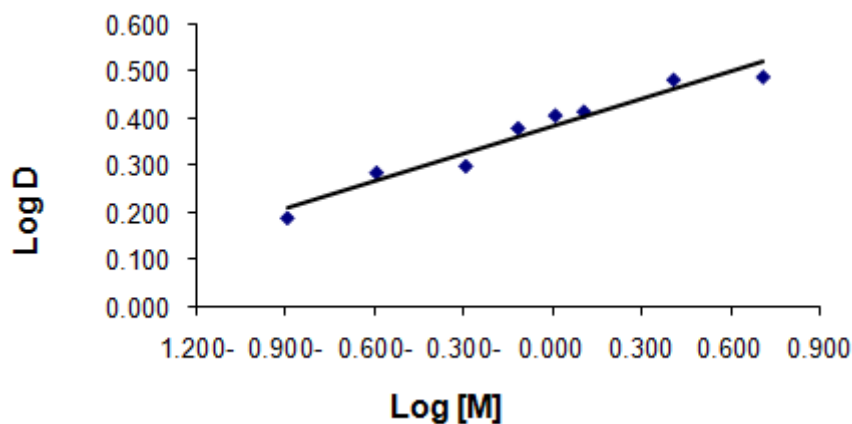

Figure (4) Effect of different concentration of Gd (III)

It`s noticed that increasing in concentration of Gd (III) solution leads to enhanced the extraction and consequently increased the values of D by using NAC as a reagent at optimum conditions . This can be explained on the basis of increasing the interaction between the ion and reagent with no adducts that promote deviation from the linearity. These results improved in other studies [29].

Effect of reagent (NAC) concentration on the extraction

A known amount of Gd (III) solution (1000 μg/2.5 ml) was prepared and extracted by using variable concentration of (NAC) under optimum conditions. Results are drowned in figure (5).
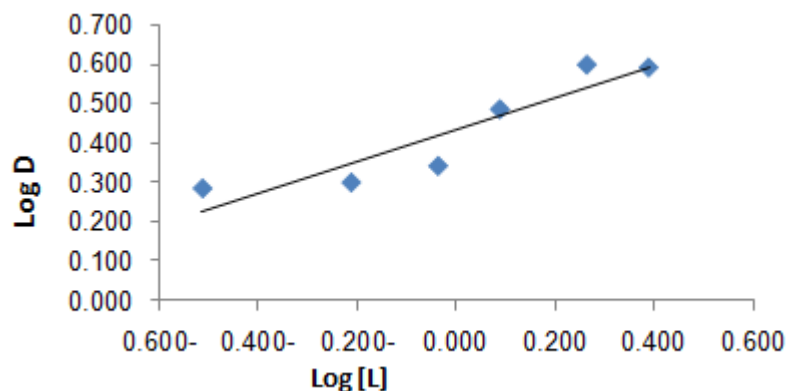

Fig. (5) Effect of different concentration of reagent (NAC)

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Straight line obtained by plotting Log D against Log NAC explained that there is increasing in extraction of Gd (III) ion by using different concentration of reagent (NAC). Results are in agreements with recent study [30].

Effect of temperature

Effect of different temperatures (20–45) °C on extraction of Gd (III) was studied, results are shown in table (7) and figure (6).

Table (7): Effect of temperature on extraction of Gd (III)

T(K)	$1/T*10^{-3}$	D
293	0.0034	0.955
298	0.0034	2.11
303	0.0033	3.22
313	0.0032	3.999
318	0.0031	4.545

Thermodynamic functions (ΔH, ΔG and ΔS) were studied from figure (6) and equations of Vant-Hoff and Gibbs [31]. Calculations illustrated in table (8).

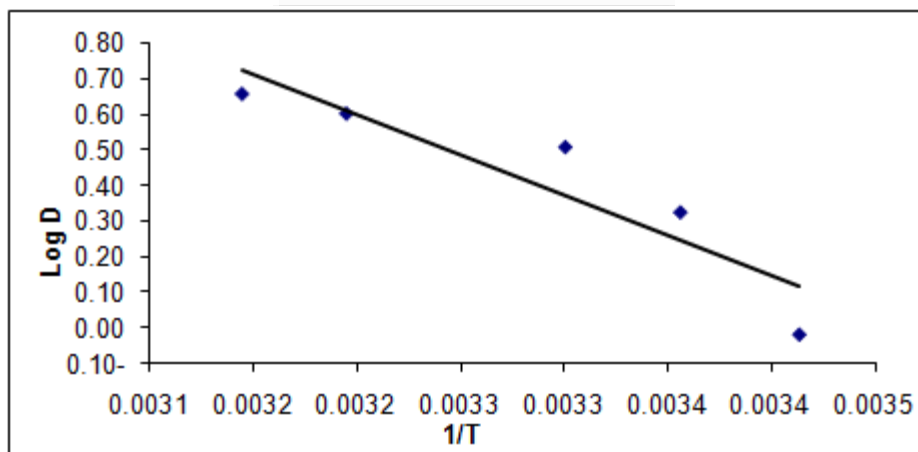**Fig. (6) The effect of temperature to extract Gd (III) by (NAC)**

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Table (8): Thermodynamic functions

T (K)	ΔH (Kj.Mol^{-1})	ΔG (Kj.Mol^{-1})	ΔS (Kj.Mol^{-1}K^{-1})x10^{-4}
293	-43.261	0.112	-1.48031
298	-43.261	-1.850	-1.38963
303	-43.261	-2.946	-1.33054
313	-43.261	-3.607	-1.26691
318	-43.261	-4.003	-1.23453

From the results obtained and organized in Table (8) can be concluded that the thermodynamic functions were favorites for reaction between Gd (III) and NAC. Positive enthalpy improved that the reaction was endothermic, thus increase the complex formation, and negative energy explained that the reaction was spontaneous which facilitate the transmission of ion from aqueous to organic phase. A lot of studied agreed with this results [32-34].

Stoichiometry

Job's method (continuous variables)

Under optimum conditions Known constant concentration of Gd (III) ion with increasing concentration of ligand (NAC) was mixed. For each solution, extraction was done by using chloroform and absorption were measured for organic layer at maximum wavelength, finally, the ratio of (M/L) was obtained by plotting absorption against mole ratio.
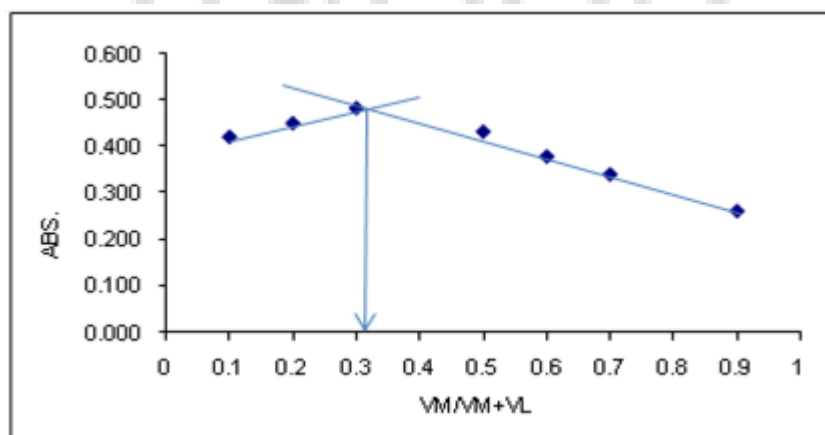

Fig. (7) Job's method for the Gd (III) ion .

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Related to the results explained in figure (7) can be concluded that chelating ratio between metal and reagent M:L was (1:3).

Mole ratio method

Various volumes of solutions having equal concentrations of Gd (III) with ligand (NAC) were mixed under optimum conditions, and then these solutions transferred to 10 ml conical flask. Volumes were completed with water and extractions of organic layer were done by using chloroform. Absorptions of extracted organic layers for each solution were plotted against (V_L/V_M) at greatest wavelength.
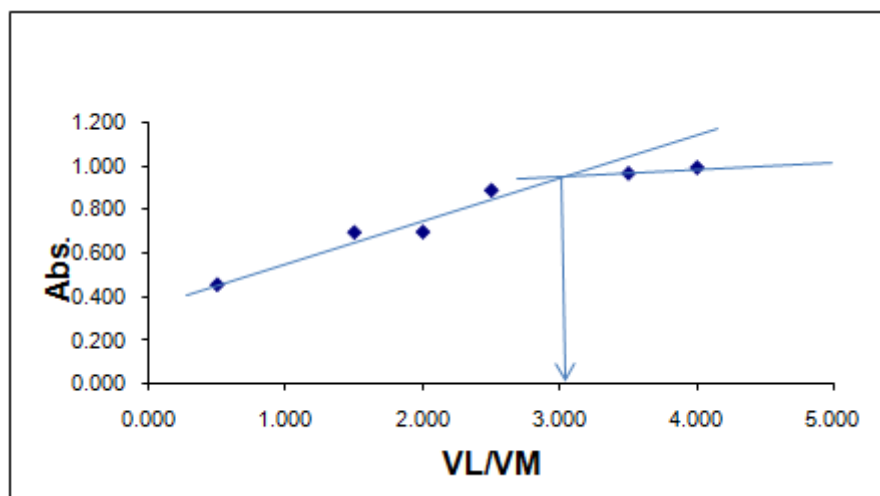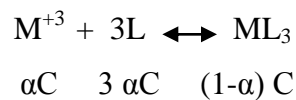

Fig. (8) The molar ratios method to extract Gd (III)

Results obtained and illustrate in figure (8) improved that the more likely structure of complex chelating between M:L was (1:3). Job's method results were in agreements with results obtained from mole ratio method.

Study the stability for the extracted complex in organic Phase

Table (9): Data of dissociation constant and stability constant for extracted complex

Complex	A_m	A_s	α	$K_{sta.}$
Gd (NAC)^3	0.991	0.897	0.105	2.728×10^{17}

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$$M^{+3} + 3L \longleftrightarrow ML_3$$
$$\alpha C \quad 3\,\alpha C \quad (1-\alpha)\,C$$

$$K = (1-\alpha)\,C \,/\, \alpha C \,(3\alpha C)^{\,3}$$
$$\alpha = A_m - A_s / A_m$$

Where (α, C, K, A_m and A_s) are the degree of dissociation, concentration of metal, stability constant, the greatest absorption and absorption at the end point, respectively.

Spectrophotometric studies

UV-Visible spectra for Gd (III) ion , the ligand NAC and the complex of Gd (III) with NAC at pH=7 were illustrated in figures (9,10 and 11).
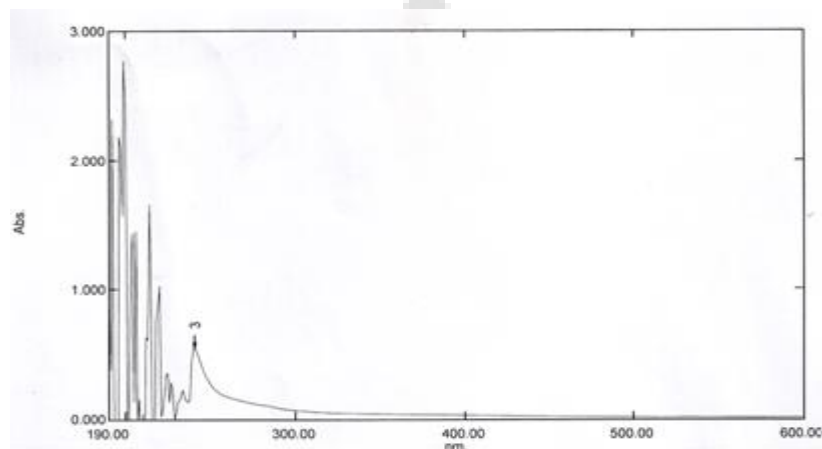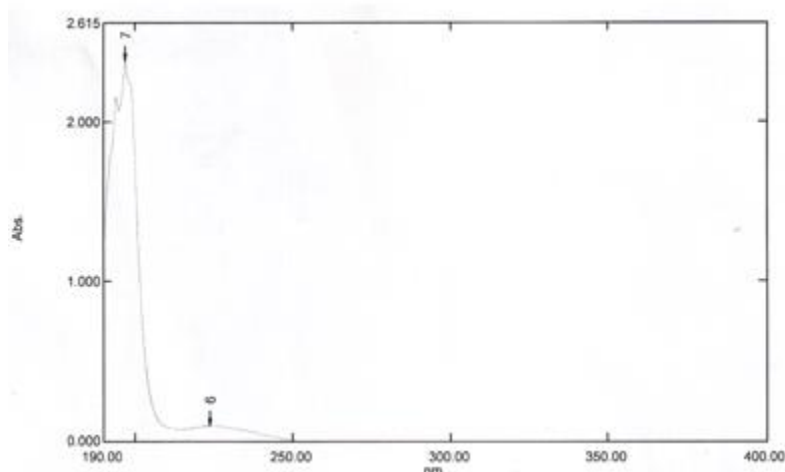

Figure (9) UV-Visible spectrum of ligand (NAC)

Figure (10) UV-Visible spectrum of ligand (NAC)

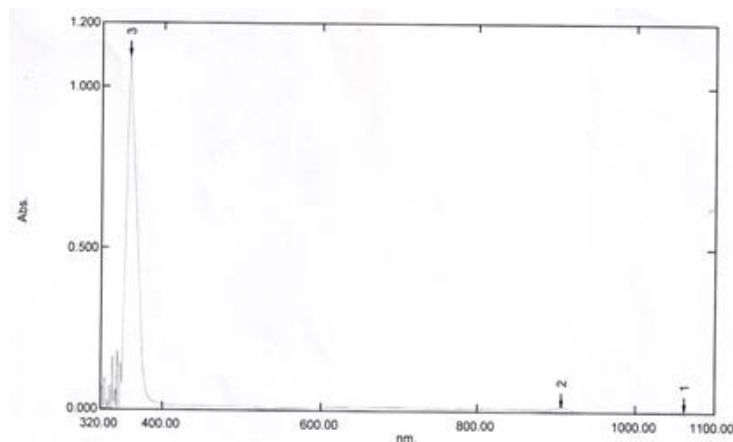*Citation: Ihsan Mahdi Shaheed et al. Ijppr.Human, 2016; Vol. 7 (3): 181-198.*

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Figure (11) UV-Visible spectrum of the complex [Gd(NAC)₃]

Figure (9) explained there is intense peak at 197nm for Gd (III) ion, figure (10) explained there is intense peak for ligand NAC at 241nm and figure (11) explained there is intense peak for complex at 356nm. By comparison between these three figures, there was red shift for the complex.
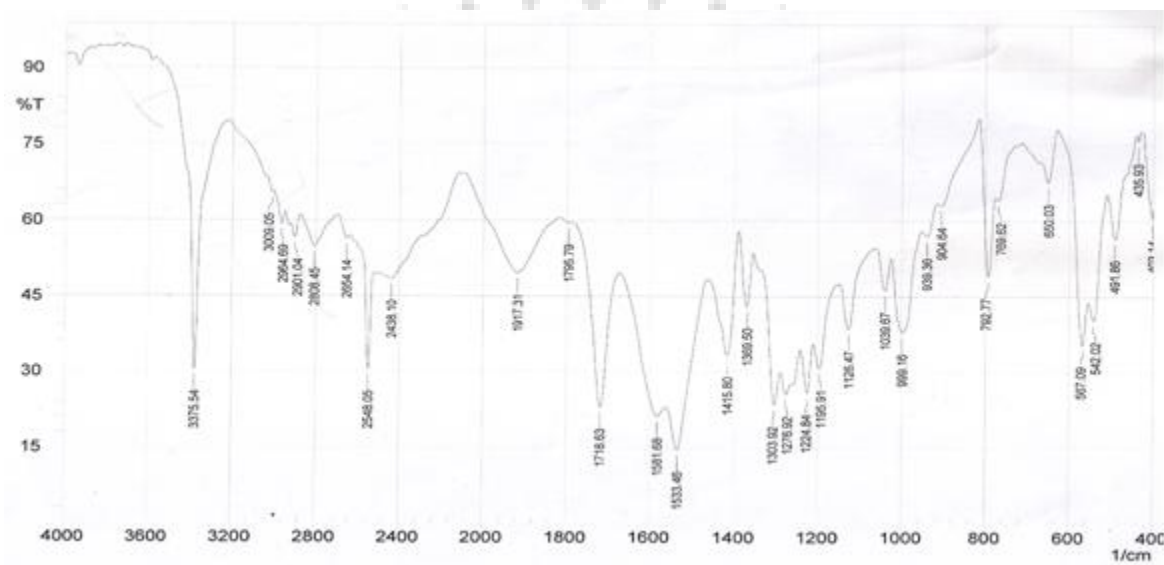
FT-IR Spectra

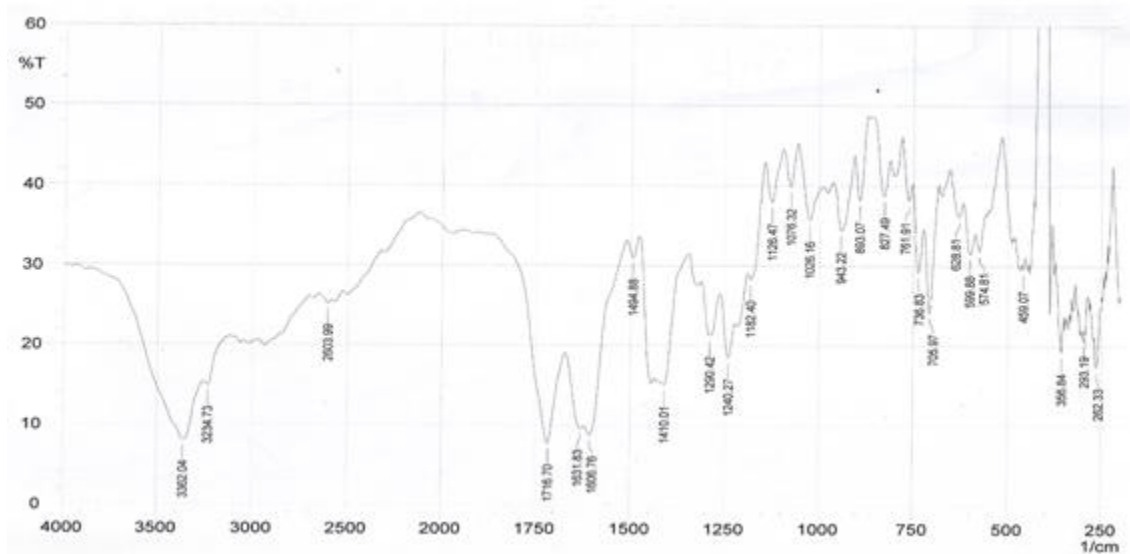**Figure (12) Infrared spectrum of ligand**

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Figure (13) Infrared spectrum of complex

Table (10): Results of FT-IR spectra of ligand and complex

Compound	Stretching vibration ν N-H	Amide group ν C=O	Acidity ν C=O	Bending Vibration ν O-H	δN-H	δO-H	νS-H	νM-O	νM-N
Ligand	3375.54	1605-1581	1728.63	3009.05-28808.45	1581.68-1533.64	1369.50-1276.92	2548.05	--------	--------
complex	3234.73	1631.83	1716.70	--------	1606	--------	2500	510	356.84

Some physical properties of the complex

Table (11): Some physical properties of complex

Melting point (^{o}C)		Electrical conductivity μS.cm^{-1}	
Complex	65-77	Chloroform	0.000
ligand	160-163	Complex (in chloroform)	0.020

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CONCLUSIONS

Results obtained in this study can be used in future to extract Gd (III) ion from some materials and soil or separation of Gd (III) from other rare earth metals by controlling the conditions of extraction and separation.

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