

## Acenaphthenequinone Hydrazone Derivative Based Sol-Gel In Solid-Phase Extraction of Lanthanum (III) in Aqueous

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**Abstract:** A new hydrazone based-sorbent material with excellent selectivity for lanthanum (III) was prepared by immobilizing the newly synthesized acenaphthenequinone- $[N-[(2,4\text{-dinitrophenyl})]\text{-hydrazone (ADH)}$  into sol-gel (SG) matrix. The sorbent material was characterized by FTIR, EDX, SEM, TEM and TGA. The sorption characteristics of a matrix of ten rare earth metal ions ( $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ ) using batch method was studied. Several key parameters that affected the extraction efficiency such as pH, contact time, metal ions concentration and SG size were investigated and optimized. The results showed that the sorbent material has a special selectivity and high adsorption capacity for  $\text{La}^{3+}$  from aqueous samples. Quantitative recovery of  $\text{La}^{3+}$  was achieved by stripping with 0.1M  $\text{HNO}_3$ . The maximum sorption capacity of the sorbent material was  $86.43 \text{ mg g}^{-1} \text{ La}^{3+}$ . The method has been applied to the determination of lanthanum in different water samples.

**Key words:** Hydrazone • Acenaphthenequinone • Lanthanides • Solid phase extraction • Silica

### INTRODUCTION

There are many traditional pre-concentration and separation methods for metal ions such as liquid-liquid extraction, ion-exchange, precipitation, solvent extraction, electrolysis, etc. Most of these methods have disadvantages such as noneconomic (high cost), poor removal efficiency and require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems [1-2]. Nowadays, the solid-phase extraction (SPE) is being widely utilized for pre-concentration or separation of metals, organic and inorganic species due to several advantages, such as absence of emulsion safety with respect to hazardous samples, minimal costs due to low consumption of reagents, higher enrichment factor, flexibility and environment-friendly [3-8]. Organic-inorganic hybrid materials had drawn attention of researchers as a new class of materials. One of the methods that widely used for the preparation of these hybrid materials is sol-gel process. It involves hydrolysis and condensation reactions that closely controlled by the initial synthesis condition and parameters such as temperature, concentration of alkoxide, water, acidic or basic catalyst [9,10]. Choosing a

suitable functional group for modification of the gel surface is important in order to produce solid phase with certain selectivity character [11]. Therefore, an efficient adsorbing material should possess a stable and insoluble porous matrix having suitable active groups (typically organic groups) that interact with metal ions.

Silica gel is an ideal support for organic groups because of its stability under acidic conditions and non-swelling inorganic material and has high mass exchange characteristics and very high thermal resistance [1,12]. Furthermore, the selectivity of the solid phase sorbent towards an analyte depends on the structure of the immobilized organic ligands. Immobilization of organic compounds with certain functional groups on the surface of silica gel has gained important application in different research and industrial fields [1,6,13].

Hydrazones are some of the many different types of organic compounds that have been immobilized into the sol gel matrix. They drew such of attention because of their biological and pharmaceutical activities [14-17]. These compounds can be directly complex with metal ions or immobilizing them in a matrix as a new class of materials for application in selected fields. To achieve this goal, two ways of immobilization

following either process, chemically or physically in sol-gel matrix were applied [11-13,18,19]. Sol-gel process is closely controlled by the initial synthesis conditions such as temperature, water, acid or basic. Accordingly, different range of final products such as powders, monolithic gels and thin films were produced. In the second type the ligands were covalently bonded to the silica backbone.

This paper investigates the extraction efficiency of a hydrazone derivative immobilized into sol-gel matrix and subsequently use it as adsorbent material for the removal of lanthanide metal ions. The optimum conditions for a better extraction such as pH, contact time, concentration of metal ions, sorbent particle size, foreign metal ions, mass and reusability of the sorbent also were investigated.

## MATERIAL AND METHODS

**Apparatus:** FT-IR spectra were recorded using Perkin-Elmer spectrum BX Fourier transform infrared spectrometer (FT-IR) system using KBr in the range 4000-400  $\text{cm}^{-1}$ . NMR Burkert 500MHz Ultrashield TM was used for  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis. CHN was obtained using Perkin-Elmer, Series EE, 2400. LEO supra 50vp field emission scanning electron microscope (SEM) equipped with Oxford INCA 400 energy dispersive X-ray microanalysis system (EDX) was used to study the surface morphology. The surface of the SG was visualized using a Transmission Electron Microscope (TEM), Phillips CM12 with Docu version 3.2 image analysis. TGA were recorded using TGA/SDTA851. A mechanical shaker (Stuart Scientific, UK) was used for extraction. The pH measurements were conducted by a Perkin Elmer Analyst 200. Spectroscopic measurements were recorded on A Perkin-Elmer lambda 35 (double beam) spectrophotometer equipped with a switchable holder system (solid-state and 1-cm quartz cell/liquid samples holders).

**Chemicals and Reagents:** Ten milliliters working solution ( $5\text{mg L}^{-1}$ ) for each lanthanide ( $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ ) were prepared from stock solution of lanthanides ( $100\text{mg L}^{-1}$ ) in doubled distilled water [20]. 2,4-dinitrophenylhydrazine (BDH), acenaphthenequinone (Fluka), 4-(2-pyridylazo) resorcinol (PAR) (SIGMA), ethanol (EtOH), methanol (MeOH), tetrahydrofuran (THF), nitric acid (QR&C), hydrochloric acid (HmbG), ammonia solution (SYSTEM

Chemicals), tetraethoxysilane (TEOS) (Fluka) as sol-gel precursor were used as received without any further purification. A  $4 \times 10^{-5}$  M PAR solution was prepared by dissolving 0.001g of the reagent in 1 mL methanol and the volume was topped up to 100 mL with doubly distilled water. Real water samples for analysis, namely, rain, lake and sea, all from Penang Malaysia were collected and filtered to remove suspended particles before use.

**Synthesis of Acenaphthenequinone-[N-(2,4-Dinitrophenyl)] Hydrazone (ADH):** ADH compound was prepared using reported route [11,18,19,21,22]. A mixture of 2,4-dinitrophenylhydrazine, DNH (6.93g, 0.035M), acenaphthenequinone, ANQ (6.38g, 0.035M) and a catalytic amount of acetic acid in absolute ethanol was refluxed for 24 hr. Then the reaction mixture was cooled to room temperature and the orange precipitate was filtered off, washed with fresh amount of ethanol and dried in the oven ( $60^\circ\text{C}$ ). The compound (Fig. 1) was recrystallized from chloroform. Yield 76 %; m.p;  $199-200^\circ\text{C}$ . *Anal. Calc.* for  $\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_5$  ( $362.30\text{ g.mol}^{-1}$ ): C, 59.67; H, 2.78; N, 15.46. Found: C, 59.85; H, 2.17; N, 14.76%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 7.87-7.92 (1H, q, CH), 8.16-8.18 (1H, d,  $J=8.5$  Hz, CH) 8.20-8.21 (1H, d,  $J=7$  Hz, CH), 8.24-8.26 (1H, d,  $J=8.2$  Hz, CH), 8.37-8.39 (1H, d,  $J=7.5$  Hz, CH), 8.52-8.54 (1H, q,  $J=9.5$  Hz, CH), 8.55-8.57 (1H, q,  $J=9.5$  Hz, CH), 9.25-9.26 (1H, d,  $J=0.7$  Hz, CH) and 12.31 (1H, s, br, NH) [17, 19].  $^{13}\text{C}$  (500 MHz,  $\text{CDCl}_3$ ): 118.04, 121.44, 122.91, 122.96, 126.44, 128.49, 128.82, 129.34, 130.2, 130.88, 131.22, 131.63, 132.20, 140.58, 140.70, 144.27 (16 CH), 144.57 (C=N) and 188.18 (C=O) [23,24].

**Preparation of Sol-Gel Immobilized ADH:** The sol gel immobilized was prepared according to the following procedure [13,19]. The sol solution was prepared by stirring a mixture of 20.8 g of 0.1M TEOS, 7 mL methanol and 3.6 mL of 0.03M HCl for 15 min to obtain a homogeneous sol solution. A  $1 \times 10^{-5}$  M of ADH which has been dissolved in 10 mL of THF was then added to the sol solution and stirred for further 30 min at room temperature. The resulting clear and homogeneous solution was aged in an oven at  $60^\circ\text{C}$  for 2 days. During the drying stage, shrinkage of the gel occurred causing it to crack. The gel was next ground into small pieces using mortar and pestle. Blank sorbent was prepared using the same procedure, except that no ADH was added.

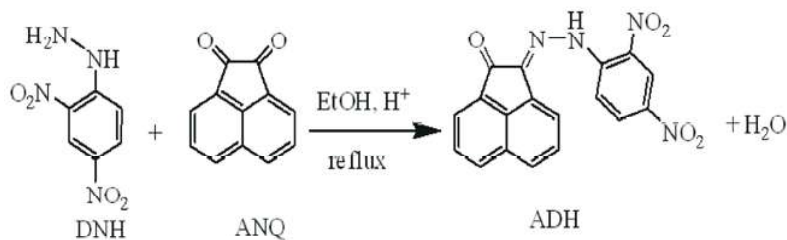


Fig. 1: Schematic diagram for synthesis of ADH.

**UV-Vis Determination of Lanthanides:** The concentration of lanthanide metal ions in aqueous was determined following the reported method by Cucinotta *et al.* [25] and Fernández-de Córdova *et al.* [26] using PAR as an indicator. A 2 mL volume of lanthanide metal ion solution was placed in a beaker and 2 mL of  $7.2 \times 10^{-6}$  M PAR solution were added. The pH of the solution was adjusted to pH 4 using 0.01M ammonia and 0.01M  $\text{HNO}_3$  solutions. The concentration of the element in the aqueous phase was determined spectrophotometrically at 410 nm.

**Extraction of Lanthanum Ion (Batch Method):** Batch method of extraction was conducted [11,13,19]. The 50 mg sorbent was placed in a 20 mL glass vial along with 10 mL of  $5 \text{ mg L}^{-1}$   $\text{La}^{3+}$  and the pH was adjusted to 4 using dropwise addition of nitric acid and ammonia solutions. The mixture was shaken mechanically at room temperature ( $25^\circ\text{C}$ ) for 1h. After the equilibrium time, the mixture was filtered and the amount of the unextracted  $\text{La}^{3+}$  ions (left in the solution after the extraction) was determined by UV-Vis spectroscopy using PAR indicator as described above. The concentration of  $\text{La}^{3+}$  ions adsorbed on the sorbent material was calculated by the difference. Once the extraction was completed, the amount of  $\text{La}^{3+}$  ions adsorbed on SG-ADH sorbent was eluted with 10 mL of 0.4 M  $\text{HNO}_3$ . The sorbent was rinsed several times with water and dried at  $60^\circ\text{C}$  before the next extraction cycle was conducted.

## RESULTS AND DISCUSSION

**FT-IR Analysis:** The formation of the ADH is suggested based on the elimination of a  $\text{H}_2\text{O}$  molecule from ANQ and DNH to form the C=N (azomethane group) bond which is confirmed by FT-IR analysis. The FT-IR analysis of ADH shows its characteristic

absorption bands at  $1643 \text{ cm}^{-1}$  and  $1631 \text{ cm}^{-1}$  which is due to C=N and C=O stretching respectively [15-17,27]. The >NH and  $\text{NO}_2$  stretching bands appear at  $3327 \text{ cm}^{-1}$  and  $1320 \text{ cm}^{-1}$ , respectively [27-29]. The blank and immobilized gels exhibited almost similar spectra. The broad and intense band between  $1350$  and  $1000 \text{ cm}^{-1}$  with maximum peak at  $1078 \text{ cm}^{-1}$  is assigned to the siloxane bond (Si-O-Si) band. A symmetric stretching and bending modes of bulk Si-O-Si bond is indicated by the band at  $796\text{-}798 \text{ cm}^{-1}$  and  $459\text{-}477 \text{ cm}^{-1}$ , respectively. The Si-OH stretching vibration of surface silanol groups is assigned at  $954\text{-}959 \text{ cm}^{-1}$  [1, 4, 30-32]. Meanwhile, the broad band at  $3454\text{-}3515 \text{ cm}^{-1}$  is due to the stretching vibration of HO-H of water molecules adsorbed on the silica surface [33]. The band at  $1639\text{-}1647 \text{ cm}^{-1}$  is attributed to the bending vibration of trapped water molecules [13]. The IR spectrum of SG-ADH after extraction of  $\text{La}^{3+}$  shows extra band at  $1381 \text{ cm}^{-1}$  which is due to  $\text{NO}_3$  group [34].

**EDX and Solid UV-Vis Analysis:** Further analysis on the immobilization of ADH in the silica matrix was conducted using EDX and solid-state UV-Vis analysis. EDX analysis confirmed the immobilization of ADH in the silica matrix. A comparison between the blank SG and immobilized SG-ADH is summarized in Table 1. For the blank SG, the main elements are Si (29.89%) and O (63.92%). No nitrogen was detected. Further analysis on the immobilized sorbent confirmed the presence of nitrogen (3.90%), indicating the presence of ADH ligand in the sorbent matrix. This finding is also confirmed by the UV-Vis analysis. Figure 2 shows a comparison between the free ligand (ADH) and its corresponding sorbent (SG-ADH). The free ligand experiences red shift with maximum absorption between 486-490 nm. This range is comparable with our previous findings [19] and Uchiyama *et al.*, [35] reports on 2,4-dinitrophenylhydrazone derivatives. There is

Table 1: EDX results for the blank and immobilized SG.

Element	Composition (%)	
	Blank-SG	2-DPHA-SG
C	6.193	4.28
O	63.92	66.73
Si	29.89	25.09
N	—	3.90

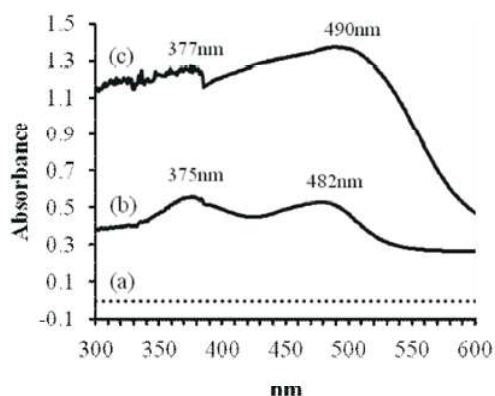
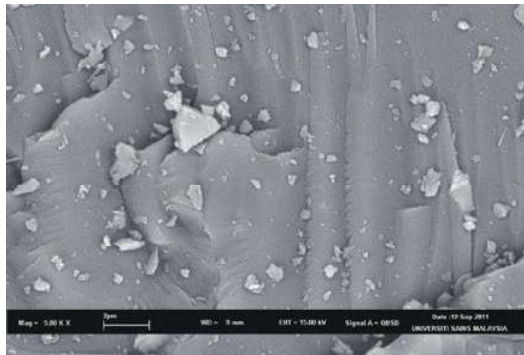
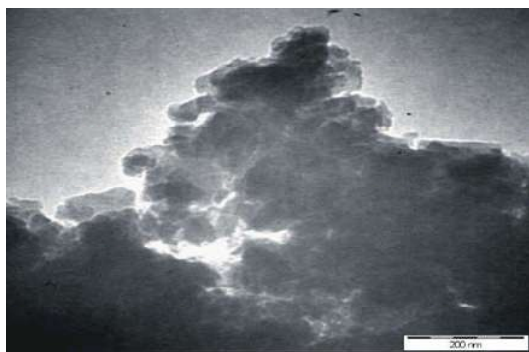


Fig. 2: UV-Vis spectra of (a) blank gel, (b) SG-ADH and (c) Free Ligand (ADH).



(a)



(b)

Fig. 3: The SEM (a) and TEM (b) of SG-ADH.

no significant absorbance for the blank SG at this range. The SG-ADH sorbent material exhibited similar phenomenon at wavelength range from 472–485 nm. The difference between the blank and immobilized gels is a strong evidence that indicates the successful incorporation of ADH into the gel network. The slight shift in the wavelength of the ligand could be due to intermolecular interaction between the ligand and the silicat, which causes the change in the characteristics of the spectrum [36].

**SEM and TEM Analysis:** Figure 3a shows the surface of the SG-ADH obtained from the SEM analysis. The surface of SG-ADH was consisting of rough layers. Further analysis to visualize the surface of the gel sorbent was conducted using the transmission electron microscope (TEM). Pores can be easily seen as white and tiny dots with a diameter less than 2 nm (Fig 3b). This reflects the porosity and the distribution of ligand (ADH) particles on the sorbent.

**Thermogravimetric Analysis:** The thermal stability of the sorbent material was investigated using thermogravimetric analysis (TGA) over the heating range from 30–900°C under nitrogen atmosphere at a constant heating rate of 20°C min<sup>-1</sup>. The thermal analysis of the free ligand, ADH shows that the maximum loss of weight (41.6%) of the ligand upon heating was recorded at 340°C. The immobilized SG generally produced similar thermal profile with the plank SG. The thermal analysis of the sorbent material inferred that the SG produced is thermally stable material since 76.6% of the total mass was retained when heated up to 900°C under nitrogen atmosphere. Slight decrease in the initial decomposition range of the sorbent was observed upon the decomposition of metal ion observed during the extraction.

#### Metal Extraction Studies by Batch Method

**Effect of pH:** In order to evaluate the effect of pH on the extraction efficiency of the sorbent material, the pH of the sample solution containing 10 mL of 5 mg L<sup>-1</sup> Ln<sup>3+</sup> was adjusted in the range of 2–8. The metal ion was then extracted with 50 mg sorbent material, SG-ADH. The extracted Ln<sup>3+</sup> concentration was calculated from the amount of the metal ions left in the supernatant which was analyzed spectrophotometrically as described earlier. The metal ion removal efficiency (%E) was calculated using the following expression (equation 1).

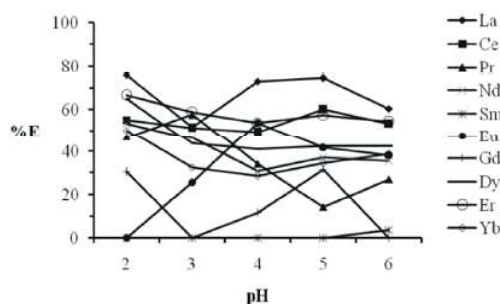


Fig. 4: Effect of pH on the extraction of  $5 \text{ mg L}^{-1}$   $\text{Ln}^{3+}$  ions, using 50 mg of SG-ADH sorbent. Contact time; one hour.

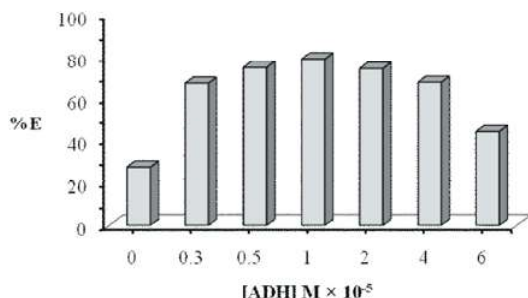


Fig. 5: Effect of ADH concentration on the extraction of  $\text{La}^{3+}$  ( $5 \text{ mg L}^{-1}$ ) from aqueous (pH 4), contact time 1 hr.

$$\%E = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium metal ion concentration ( $\text{mg L}^{-1}$ ) in solution, respectively. Figure 4 shows that the most uptakes of  $\text{Ln}^{3+}$  occur in the pH range from 2 to 5. Among the studied lanthanide metal ions, the sorbent material shows better selectivity towards  $\text{La}^{3+}$  at pH 4. Therefore, pH 4 was chosen for the subsequent studies.

**Effect of Contact Time:** The time required for the extraction is of considerable importance. The extraction was carried out by shaking mechanically the sorbent material with  $\text{La}^{3+}$  ions (pH 4) several times, ranging from 5 to 240 min at room temperature. Over 70% of  $\text{La}^{3+}$  was extracted within 1 hour. The longer equilibrium time found in the present study could be due to the steric hindrance of the ADH within the matrix. Increasing the contact time beyond one hours resulted in a decrease in the extraction of  $\text{La}^{3+}$  ions. Therefore, 60 min of extraction time was chosen for subsequent studies.

**Effect of ADH Concentration:** The effect of ADH concentration immobilized in the sol-gel matrix on the extraction efficiency towards  $\text{La}^{3+}$  was studied by varying of the concentration of the ADH ( $0.3 \times 10^{-5}$  to  $6 \times 10^{-5} \text{ M}$ ). From our previous study [13,19], it was found that the blank gel had an efficiency to extract metal ion from slightly acidic medium. Accordingly, the extraction was firstly examined in the absence of the ADH (blank gel). Results show that the extraction efficiency of the silica sorbent was enhanced upon the addition of ADH. The best result is at  $1 \times 10^{-5} \text{ M}$ , where more than 80 % of the  $\text{La}^{3+}$  are extracted (Fig. 5). Slight decrease in the extraction is observed after this concentration. Thus  $1 \times 10^{-5} \text{ M}$  of ADH is selected and used for further studies.

**Effect of Sorbent size and Amount:** Four different sizes of the sorbent material, viz. 150, 200, 250 and  $300 \mu\text{m}$  were used to study the effect of particle size on the extraction efficiency of the SG-ADH towards  $\text{La}^{3+}$ . It was observed that the smaller size of the gel sorbent ( $150 \mu\text{m}$ ) exhibits better extraction (>80%) than the bigger particle size gel ( $300 \mu\text{m}$ ) with extraction efficiency (%E) equals to 16%. This can be attributed to the larger surface area of the smaller gel [10]. Therefore,  $150 \mu\text{m}$  size of the gel sorbent was adopted for subsequent experiments. To study the effect of sorbent amount on the extraction, different amounts of the sorbent material ranging from 10 to 90 mg were studied. 50 mg sorbent exhibited the highest extraction. Therefore, this amount of sorbent material was adopted for further studies.

**Effect of  $\text{La}^{3+}$  Concentration:** At a fixed ADH concentration ( $1 \times 10^{-5} \text{ M}$ ) in the sol-gel matrix, the percentage extraction profile as a function of  $\text{La}^{3+}$  concentration was investigated. The effect of  $\text{La}^{3+}$  ions concentration on the extraction efficiency was tested by shaking different concentrations of  $\text{La}^{3+}$  (5 to  $500 \text{ mg L}^{-1}$ ) with 50 mg of SG-ADH at pH 4. Almost, 98 % of  $\text{La}^{3+}$  was extracted by the sorbent (Fig. 6). A slight decrease in the sol-gel efficiency with the increase of  $\text{La}^{3+}$  concentration was observed after  $50 \text{ mg L}^{-1}$  (not shown). However, the sorbent still performs well (>90%E) for  $\text{La}^{3+}$  concentration up to  $300 \text{ mg L}^{-1}$  (Table 2). A decrease (~88%E) was observed when the  $\text{La}^{3+}$  concentration reached  $500 \text{ mg L}^{-1}$ .

This shows the high efficiency of the present SG sorbent material towards  $\text{La}^{3+}$  extraction even at high concentration. Accordingly, the sorption capacity

Table 2: Effect of  $\text{La}^{3+}$  concentration on the extraction efficiency of SG sorbent (Capacity) and distribution ratio,  $n=4$ . 50 mg SG-ADH sorbent contains  $1 \times 10^{-5}$  M ADH.

Used ( $\text{mgL}^{-1}$ )	Extracted ( $\text{mgL}^{-1}$ )	%E	Capacity ( $Q$ , $\text{mg g}^{-1}$ )	D
2	0.88	44.00	0.18	0.16
3	1.58	52.67	0.32	0.22
4	2.79	69.75	0.56	0.46
5	4.00	80.00	0.80	0.80
6	4.95	82.50	0.99	0.94
7	5.83	83.29	1.17	0.99
8	6.60	82.50	1.33	0.97
10	8.60	86.00	1.72	1.23
15	13.67	91.13	2.74	2.08
20	18.67	93.35	3.74	2.84
25	23.74	94.96	4.75	3.76
30	28.72	95.73	5.74	4.49
35	33.84	96.66	6.77	5.85
40	38.82	97.05	7.77	6.61
45	43.58	96.84	8.72	6.14
50	48.99	97.98	9.80	9.63
100	95.92	95.92	19.18	4.70
200	187.20	93.60	37.44	2.92
300	273.84	91.28	54.77	2.09
400	353.72	88.43	70.75	1.18
500	432.15	86.43	86.43	1.27

( $Q$ ,  $\text{mg g}^{-1}$ ) of the SG-ADH sorbent and phase distribution ratio ( $D$ ) were calculated using the following expressions (2 and 3) [1,19,37]:

$$Q = \frac{(C_0 - C_e)V}{W} \quad (2)$$

$$D = \frac{Q}{C_e} \quad (3)$$

Where  $V$  is the volume of the solution (mL) and  $W$  is the mass of the sorbent material in grams (g). The sorption capacity was performed by extracting a solution containing varying amounts of  $\text{La}^{3+}$  with 50 mg SG-ADH sorbent at pH 4 for 1h. The amount (mg) of  $\text{La}^{3+}$  adsorbed per gram of sorbent,  $Q$  is presented in Table 2. Thus, as can be seen, the sorbent capacity increases with the increase in initial  $\text{La}^{3+}$  ion concentration. The capacity of the studied sorbent material for trace amount of  $\text{La}^{3+}$  was found to be up to  $86.43 \text{ mg g}^{-1}$ . This shows that, that studied sorbent material is a good extracting material for  $\text{La}^{3+}$  from aqueous (pH 4).

**Effect Of other Lanthanide Metal Ions:** The interference of other lanthanide metal ions on the extraction of  $\text{La}^{3+}$  with the sorbent material was also investigated. The selective separation of  $\text{La}^{3+}$  from binary mixture ( $5 \text{ mg L}^{-1}$  each) with  $\text{Ce}^{+3}$ ,  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$ ,  $\text{Eu}^{+3}$ ,  $\text{Gd}^{+3}$ ,  $\text{Dy}^{+3}$ ,

Table 3: Effect of lanthanide metal ions on the extraction of  $\text{La}^{3+}$  with SG-ADH sorbent.

Mixture	$K_d$	$K$
$\text{La}^{3+}$	9637	
$\text{La}^{3+} + \text{Ce}^{3+}$	196.2	49.11
$\text{La}^{3+} + \text{Pr}^{3+}$	104.1	92.56
$\text{La}^{3+} + \text{Nd}^{3+}$	88.73	108.6
$\text{La}^{3+} + \text{Sm}^{3+}$	411.1	23.44
$\text{La}^{3+} + \text{Eu}^{3+}$	234.7	41.07
$\text{La}^{3+} + \text{Gd}^{3+}$	25.81	373.4
$\text{La}^{3+} + \text{Dy}^{3+}$	138.9	69.37
$\text{La}^{3+} + \text{Er}^{3+}$	233.5	41.27
$\text{La}^{3+} + \text{Yb}^{3+}$	80.22	120.1

Table 4: Determination of  $\text{La}^{3+}$  in different water samples ( $n=4$ ).

Samples	$\text{La}^{3+}$ spiked ( $\text{mg L}^{-1}$ )	Recovery ( $\pm \text{SD}$ )	%RSD
RW	15	93.23 (0.17)	0.18
	25	96.38 (0.05)	0.05
	35	97.33 (0.19)	0.20
RvW	15	93.56 (0.16)	0.17
	25	95.08 (0.10)	0.11
	35	96.83 (0.07)	0.07
LW	15	94.59 (0.10)	0.11
	25	96.28 (0.05)	0.05
	35	97.26 (0.01)	0.01

RW= rain water, RvW= river water, LW= lake water.

$\text{Er}^{+3}$  and  $\text{Yb}^{+3}$  was conducted under the optimum conditions of  $\text{La}^{3+}$ . The distribution coefficient ( $K_d$ ), selectivity coefficient ( $K$ ) of  $\text{La}^{3+}$  over other lanthanide metal ions and the relative selectivity coefficient ( $K'$ )

Table 5: Comparison of retention/sorption capacities and equilibration time of different SPE methods used the extraction of La<sup>3+</sup> ions from aqueous.

Ionophore (support)	Q (mg g <sup>-1</sup> )	Equilibration time (min)	Reference
N,N-DHSA (Grafted on MCM polymer)	72.9	60	[7]
Bamboo charcoal	120.0	480	[34]
CMPO (Grafted on MCM polymer)	67.8	90	[39]
Iron oxide (Grafted on calcium alginate beads)	123.5	5040	[40]
ADH (Immobilized on silica-gel)	86.0	60	This work

N,N-DHSA= N,N-di-hexayl succinamic acid. MCM= merrifield chloromethylated resin. CMPO= octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide.

which defined as the comparison of the  $K$  value of the immobilized sol-gel with the blank sol-gel, were calculated following equations (4), (5) and (6), respectively [8,10,19,38].

$$K_d = \frac{C_0 - C_e}{C_e} \cdot \frac{V}{W} \quad (4)$$

$$K = \frac{K_{d(\text{La}^{3+})}}{K_{d(\text{M}^{n+})}} \quad (5)$$

$$K' = \frac{K_{(\text{immobilized SG})}}{K_{(\text{blank SG})}} \quad (6)$$

Table 3 shows that even in the presence of other lanthanide metal ions, the sorbent material still show better selectivity towards La<sup>3+</sup>. The relative selectivity coefficient ( $K'$ ) for La<sup>3+</sup> ions is found equals to 128.19 ( $K_d$  for the blank gel, 75.18).

**Reusability of SG-ADH Sorbent:** In the test of sorbent reusability, the sorbent material was reused for the extraction through six cycles. The sorbent material still maintain its extraction ability towards La<sup>3+</sup> in all cycles of extraction (RSD < 1.0 % for 24 replicates). Slight decrease from the first cycle to the next was observed. However, this loss of reactivity of the sorbent is probably due to the strong complexation of the of the ADH ligand with La<sup>3+</sup> in the sorbent pores that cause irreversible metal adsorption [10,19].

**Application to Environmental Water Samples:** In order to evaluate the applicability of the proposed method in a practical analytical situation, the method was used for the extraction of La<sup>3+</sup> from several water samples i.e., rain water (RW), river water (RvW) and lake water (LW). The samples were first directly analyzed to determine their La<sup>3+</sup> contents. Since La<sup>3+</sup> was non detectable in all samples they were then spiked with different concentrations of La<sup>3+</sup> (15, 25 and 35 mg L<sup>-1</sup>). The results

of the extraction are shown in Table 4. From the values, it is evident that the present sorbent was selective towards La<sup>3+</sup> ions from aqueous medium (pH4). The analytical data were reproducible with an R.S.D value of less than one percent for quarterly measurements.

**Comparison with Previous Studies:** The present method was compared with the previous reported methods used for the extraction of La<sup>3+</sup> from aqueous medium. Table 5 summarized some of the early reports on the SPE extraction of La<sup>3+</sup>. As can be seen, the sorption characteristics of the studied sorbent are comparable with other SPE systems for the extraction/preconcentration of La<sup>3+</sup> ions that were previously published [7,34,39,40]. High selectivity with good capacity for La<sup>3+</sup> in a very reasonable time was achieved.

## CONCLUSION

This study demonstrated the successful immobilization of ADH hydrazone ligand into the sol-gel silica. The ligand immobilization was confirmed using FT-IR, TGA, EDX, SEM and TEM. The SG-ADH sorbent showed high extraction ability towards La<sup>3+</sup> from other lanthanide metal ions in acidic medium (pH=4). Moreover, this sorbent was found to be repeatedly used through six cycles. The proposed method has been successfully applied for the extraction of La<sup>3+</sup> from different water samples. The simplicity and friendly environment immobilizing process makes this sorbent material efficient to use in diverse applications.

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