# Nano Magnesium Aluminum Layered Double Hydroxide As A base Material For Chromatographic $^{99}$Mo/$^{99m}$Tc Column Generator

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ABSTRACT

**Nano magnesium aluminum layered double hydroxide (nano MgAl LDH) sorbent, prepared via autocombustion route, was used as a base material for chromatographic $^{99}$Mo/ $^{99m}$Tc column generator. The acid–base titration curve proved the amphoteric nature of the prepared MgAl LDH (with a point of zero charge at pH 6.5). The sorbent, prepared at the optimum conditions, was characterized by IR spectroscopy and XRD. The Mo(VI) breakthrough capacity was found to be $6.54 \times 10^{-2}$ mmol Mo(VI)/g, i.e., 6.27 mg Mo(VI)/g. The prepared $^{99}$Mo/$^{99m}$Tc chromatographic column generator showed a good performance. The $^{99m}$Tc elution yield was found to be 75.0 % at flow rate of 1 ml/min, pH of the eluate ranged from 5.5 to7.5, the radionuclidic purity of the eluted $^{99m}$Tc was > 99.99 % and Al$^{3+}$ content in the eluate was < 5 ppm. The peaks that appeared in the XRD pattern resembled those in the XRD pattern of MgAl LDH, Mg$_6$Al$_2$(OH)$_{16}^{2+}$, and α-Al$_2$O$_3$ phases. The FT-IR spectrum showed the band at 681 cm$^{-1}$ which may be attributed to the translational mode of the Al-OH bond being characteristic of LDH's. In conclusion Nano magnesium aluminum layered double hydroxide (MgAl LDH) sorbent was well synthesized and characterized and used as a base material for $^{99}$Mo/$^{99m}$Tc column generator achieving higher loading capacities than that of alumina.**

## 1. INTRODUCTION

Layered double hydroxides (LDH's) or hydrotalcite-like compounds are a family of natural or synthetic materials displaying unique physical and chemical properties surprisingly close to the properties of clay minerals. The structure of the layered double hydroxide is very similar to that of brucite-like Mg(OH)$_2$ (the common name for magnesium hydroxide, with a basal distance of 4.8 Å) [1, 2, 3]. The most important group of LDHs can be expressed by the following formula [4]:

$$[M_{1-x}^{2+}M_x^{3+}(OH)_2]A^{n-}_{x/n} \cdot mH_2O$$

Where,

M$^{2+}$ = Mg$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Mn$^{2+}$ etc.

M$^{3+}$ = Al$^{3+}$, Fe$^{3+}$, Cr $^{3+}$ etc.

A$^{n--}$ = OH$^-$, CO$_3^{2-}$, SO$_4^{2-}$ , NO$_3^-$, Cl$^-$ or another anion.

LDHs have various applications in catalysis, anion exchange and medical field. The MoO$_4^{2-}$ ions present in aqueous solutions can be retained by calcined hydrotalcite samples; these ions retained either by surface adsorption or intercalation in the interlayer space.Zhang et al. and Ravindra et al. [3, 5] examined the incorporation of B, Cr, Mo, and Se oxyanions from high pH waters into hydrocalumite and ettringite. The molybdate was least preferred by ettringite following the order of:

$$B(OH)_4^- > SeO_4^{2-} > CrO_4^{2-} > MoO_4^{2-}$$
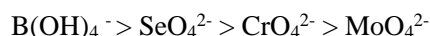
In contrast, the borate was least preferred by hydrocalumite. The thermal treatment of the hydrotalcites effect on the removal of arsenate, vanadate, and molybdate at a percentage of 90–100%. It has been illustrated that the larger molybdate anions are adsorbed preferably into the external surface of the hydrotalcite structure over intercalation [6].

The most popular $^{99m}$Tc generator is that based on an alumina column loaded with high-specific $^{99}$Mo, with a sorption capacity of 2 mg Mo(VI)/g [7, 8] On the other

hand, chromatographic gel generators, such as those based on zirconium molybdate, loaded with low-specific activity are used as an alternative to meet the shortage in the high-specific activity $^{99}$Mo [9, 10, 11].

The present work aimed at using a sorbent material for $^{99}$Mo (to be used as a base material in a chromatographic $^{99}$Mo/$^{99m}$Tc column generator) with a Mo(VI) sorption capacity higher that of alumina, as a step for future use as a base material for $^{99}$Mo/$^{99m}$Tc generators loaded with higher $^{99}$Mo radioactivities than those loaded on the commercial alumina-based generators.

## 2. EXPERIMENTAL

### 2.1. Chemical reagents

All chemicals used in this study were of AR grade. All the solutions were prepared using distilled water.

### 2.2. Instruments

Gamma-ray spectrometer (a multichannel analyzer of "Inspector 2000" model, Canberra Series, USA, with 29.4 % relative efficiency and 1.66 keV FWHM at 1332.5 keV, coupled with a high-purity germanium, HPGe, coaxial detector of GX2518 model) was used for gamma-ray activity identification and measurement.

pH-meter with a microprocessor (Hanna Instruments pH 211 model, Portugal) was used for measurement of solution pH-values.

An analytical balance (ae ADAM, PW 214, maximum capacity = 210 g, readability = 0.1 mg, Pneutrol International Ltd., Northern Ireland) was used for different weighing processes.

A centrifuge (REMI Laboratory, R32A model, India) was used for effective separation of the precipitated materials from different mixtures via centrifugation.

A FT-IR spectrometer (Bomem, model MB157S, Canada) was used for studying IR spectra of the synthesized sorbent materials (in the wavenumber range of 4000 - 400 cm$^{-1}$ at room temperature).

The X-ray diffractometer (PANalytical X'Pert PRO MRD, Netherlands) was used for X-ray diffraction (XRD) analysis of the synthesized sorbent materials using the monochromatic Cu Kα radiation (λ=1.54178 Å).

An inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy high dispersion ICP, Leeman, USA) was used for Al$^{3+}$ determination in $^{99m}$Tc eluates from $^{99}$Mo/$^{99m}$Tc chromatographic column generators.

### 2.3. Molybdenum-99 radiotracer

Molybdenum-99 was obtained by eluting commercial $^{99}$Mo/$^{99m}$Tc chromatographic column generators based on alumina (Mon-Tek Generator, Monrol Nuclear Products Industry and Trade Inc., Turkey, loaded with 20 GBq on calibration date). Each column was eluted with 20 ml of 2 M NH$_3$ solution 20 days after the calibration date. Then, few drops of H$_2$O$_2$ were added to the eluted no-carrier added (NCA) $^{99}$Mo solution, which was then evaporated to dryness. The residual $^{99}$Mo was redissolved in 5 ml of 0.1 M NaOH. Each Mo(VI) carrier stock solution (0.02 M) was prepared by dissolution of 0.3 g of MoO$_3$ in 50 ml of 0.1 M NaOH, spiked with suitable volume of the NCA $^{99}$Mo solution and containing few drops of H$_2$O$_2$, boiling for 5 min (to expel the excess H$_2$O$_2$), cooling to room temperature and completing the volume with 0.1 M NaOH to 100 ml. The addition of H$_2$O$_2$ in both cases was done to guarantee the presence of molybdenum in the hexavalent oxidation state. Suitable dilutions were conducted to prepare (i) $1\times10^{-4}$ M Mo(VI) for batch distribution coefficient and kinetic studies, (ii) $1\times10^{-3}$ M Mo(VI) solutions for breakthrough loading capacity studies and $^{99}$Mo/$^{99m}$Tc generator loading and (iii) $5\times10^{-5}$ – 0.01 M Mo(VI) solutions for thermodynamic studies. HCl, HNO$_3$ or H$_2$SO$_4$ solutions were used along with NaOH solution for pH-value adjustment

### 2.4. Synthesis of nano magnesium aluminum layered double hydroxides (MgAl LDH) sorbent material

Nano MgAl LDH was synthesized via auto combustion process. 1.25 M Al$^{3+}$ solution was prepared by dissolving about 3.33 g of AlCl$_3$ in 20 ml of distilled water. 2.5 M Mg$^{2+}$ solution was prepared by dissolving 15.25 g of MgCl$_2$.6H$_2$O g in 30 ml H$_2$O. 2.5 M NO$_3^-$ solution was prepared by dissolving 2.12 g of NaNO$_3$ in 10 ml distilled water. 2.5 M urea solution was prepared by dissolving 3.00 g of CO(NH$_2$)$_2$ in 20 ml distilled water. 0.12 M dextrose solution was prepared by dissolving 0.45 g of C$_6$H$_{12}$O$_6$ in 20 ml distilled water. To the AlCl$_3$ solution the following solutions were subsequently added dropwise: (1) MgCl$_2$, (2) NaNO$_3$, (3) urea and (4) dextrose. The molar concentration values of urea, NO$_3^-$, Al$^{3+}$, Mg$^{2+}$, dextrose in the final mixture solution (100 ml) were 0.5, 0.25, 0.25, 0.75 and 0.025 M, respectively. Thus, in the final mixture, urea: NO$_3^-$: Al$^{3+}$: Mg$^{2+}$: dextrose molar ratio was 1: 0.5: 0.5: 1.5: 0.05. The mixture was heated in a beaker at 350 °C for

1 h on a hotplate. Initially, the mixture was boiled with continuous evaporation nearly reaching dryness. Then, the residue was swelled forming a dark brown colored foam. The product material of combustion was voluminous and foamy. The resultant combustion residue (a pale brown tenuous material) was washed many times with distilled water, by mixing it with 20 ml distilled water aliquots, centrifugation and decantation. The washed material was optionally dried in the muffle furnace at 50, 100, 150, 200 and 500 °C for 24 h.

In addition, nano MgAl LDH sorbent material was further synthesized via the hydrothermal route. In such route, after passing the autocombustion process, washing and centrifugation as mentioned above, the remining solid residue was suspended in 75 ml of 1 M NH$_3$ solution. The mixture was placed in the hydrothermal reactor, heated at 150 °C for 24 h, then, the mixture was centrifugated. The NH$_3$ solution was decanted, then, the solid material was mixed with distilled water, centrifugated and decanted for water disposal for several times. Thereafter, the finally solid residual was dried at 150 °C for 24 h [12, 13].

## 2.5. Batch distribution coefficient studies of $^{99}$Mo on nano MgAl LDH sorbent

To study the effect of nano MgAl LDH drying temperature on the batch distribution coefficient of $^{99}$Mo as a function of pH, 10 ml fractions of $1\times10^{-4}$ M molybdate(VI)-$^{99}$Mo solution (in Cl$^-$ media of different pH-values) were equilibrated with 0.1 g MgAl LDH (dried at 150 and 500°C) for 24 h.

To study the effect of aqueous media on the batch distribution coefficient of $^{99}$Mo as a function of pH, 10 ml fractions of $1\times10^{-4}$ M molybdate(VI)-$^{99}$Mo solution (in Cl$^-$ and NO$_3^-$ media of different pH-values) were equilibrated with 0.1 g MgAl LDH (dried at 150°C) for 24 h.

## 2.6. pH-metric titration

Acid-base titration of nano MgAl LDH sorbent material was carried out. Samples of 0.1 g of MgAl-LDH sorbent material were placed in 20-ml glass vials and equilibrated with different volume ratios of 0.1 M NaCl / 0.1 M HCl and 0.1 M NaCl / 0.1 M NaOH (for 24 h in water bath thermostat shaker at 25°C±1) in such a way that the total volume of the solution in each vial was 10 ml with a constant ionic strength (0.1 M). The pH-value of each solution was measured after 24 h and plotted against the added meq H$^+$/g and meq OH$^-$/g to obtain the acid-base titration curve. In the same way, the blank titration curve was plotted for the solutions of

the same ratios (but without contact with MgAl LDH sorbent). The intersection point of the two curves determined the point of zero charge (PZC) of the MgAl LDH sorbent material.

## 2.7. Breakthrough loading capacity studies of $^{99}$Mo on nano MgAl LDH sorbent

To perform such study, $1\times10^{-3}$ M molybdate(VI)-$^{99}$Mo was loaded from Cl$^-$ medium (pH 5.5), rate was 0.25 ml/min, on a pre-conditioned glass chromatographic columns (ID 0.7 cm) based on 0.5 g of: (i) MgAl LDH dried at 50, 100, 150 and 200 °C and (ii) MgAl LDH synthesized via hydrothermal route (at 150 °C for 24 h) and dried at 150 °C.

## 2.8. $^{99}$Mo/$^{99m}$Tc chromatographic column generator based on nano MgAl LDH sorbent

### 2.8.1. Preparation of 99Mo/99mTc generator

Fractions (each of 10 ml) of $1\times10^{-3}$ M molybdate(VI)-$^{99}$Mo (Cl$^-$ medium - pH 5.5) were loaded (at a flow rate of 0.25 ml/min) on pre-conditioned chromatographic columns (0.7 ID) based on 0.5 g of: (i) non-hydrothermal MgAl LDH sorbents (dried at 50, 100, 150 and 200 °C) and (ii) hydrothermal MgAl LDH sorbent dried at 150°C. Then, these columns were washed with 10 ml of 0.9 % NaCl solution before starting $^{99m}$Tc elution.

### 2.8.2. Quality control specifications of the eluted $^{99m}$Tc

#### 2.8.2.1. Elution yield

$^{99m}$Tc was eluted from each column at a flow rate of 1 ml/min to compare the elution yield obtained in each case. Then, $^{99m}$Tc was eluted from the column based on the non-hydrothermal MgAl LDH dried at 150 °C, at flow rates of 0.2, 0.3 0.5 0.6 and 1 ml/min, to detect the optimum flow rate achieving the highest elution yield.

#### 2.8.2.2. Other specifications

Radionuclidic and radiochemical purities of the eluted $^{99m}$Tc were calculated. The pH-value of the eluted $^{99m}$Tc was measured. Al$^{3+}$ concentration in $^{99m}$Tc eluates was determined by ICP-OES spectrometer.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of MgAl LDH sorbent

MgAl LDH sorbent prepared via non-hydrothermal route and dried at 150 °C was chosen for characterization based on the distribution coefficient studies as mentioned below. It is a light brown material. The acid–base titration curve (Figure1) shows that the

MgAl LDH sorbent is an amphoteric material with a point of zero charge (PZC) at pH 6.5 (the intersection point of the two curves) [14].

FT-IR spectrum of MgAl LDH sorbent is represented in Figure ( 2). The band at 681 cm$^{-1}$ may be attributed to the translational mode of the Al-OH bond being a characteristic of LDH's [15]. The band at 1384 cm$^{-1}$ may be assigned to the antisymmetric stretching mode of $NO_3^-$ [16,17]. The band at 1637 cm$^{-1}$ may be related to deformation vibration of the intercalated $H_2O$ molecules, while the broad band at 3423 cm$^{-1}$ may be attributed to OH stretching mode of the hydroxide layer and the intercalated (or sorbed) $H_2O$ molecules [15, 16, 17].

XRD pattern of MgAl LDH sorbent (Figure 3), indicates the crystallinity of the synthesized sorbent. The peaks that appear in the XRD pattern resembles those in the XRD pattern of MgAl LDH, $Mg_6Al_2(OH)_{16}^{2+}$, and α-$Al_2O_3$ phases [18, 19, 20].

The crystallite size, $D_{cry}$, was calculated using the Debye-Scherrer equation [21]

$$D_{cry} = \frac{0.9\lambda}{W Cos\theta} \qquad (1)$$

Where,

$\lambda$: X-ray wavelength (1.54178 Å).

$W$: full width at half maximum (FWHM) of the diffraction peak.

$\theta$: Bragg diffraction angle. By using Equation 1, the crystallite size of MgAl LDH was found to be 28 nm.
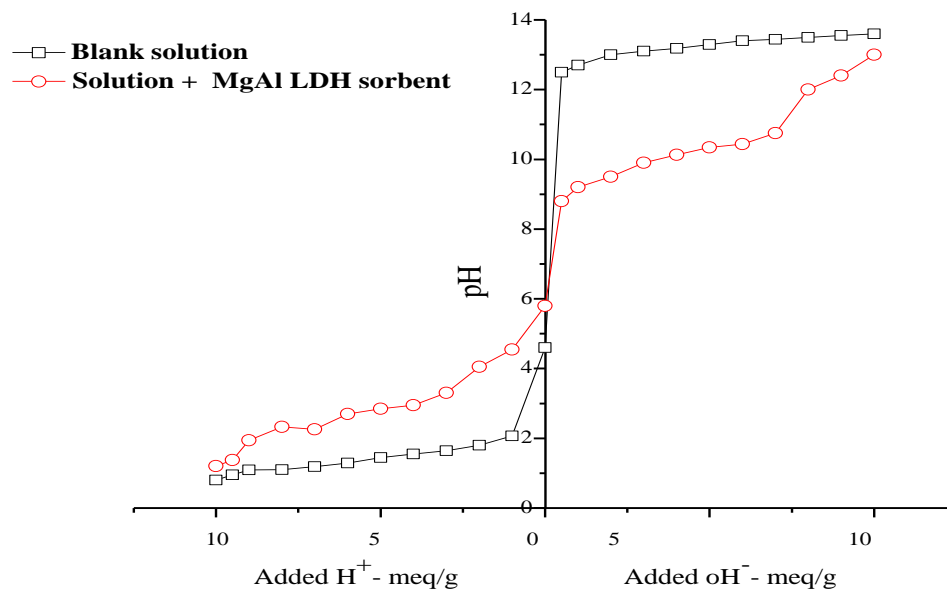


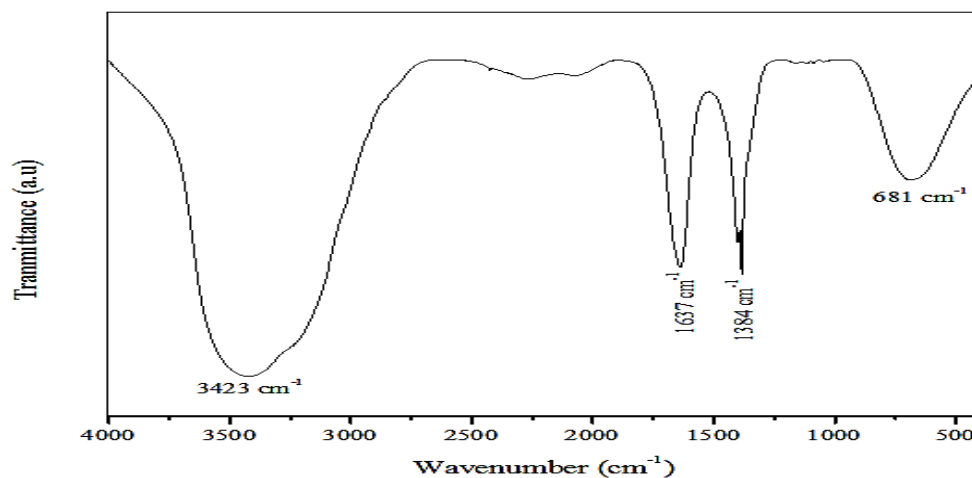**Fig (1): pH-metric titration curve of MgAl LDH sorbent dried at 150 °C**



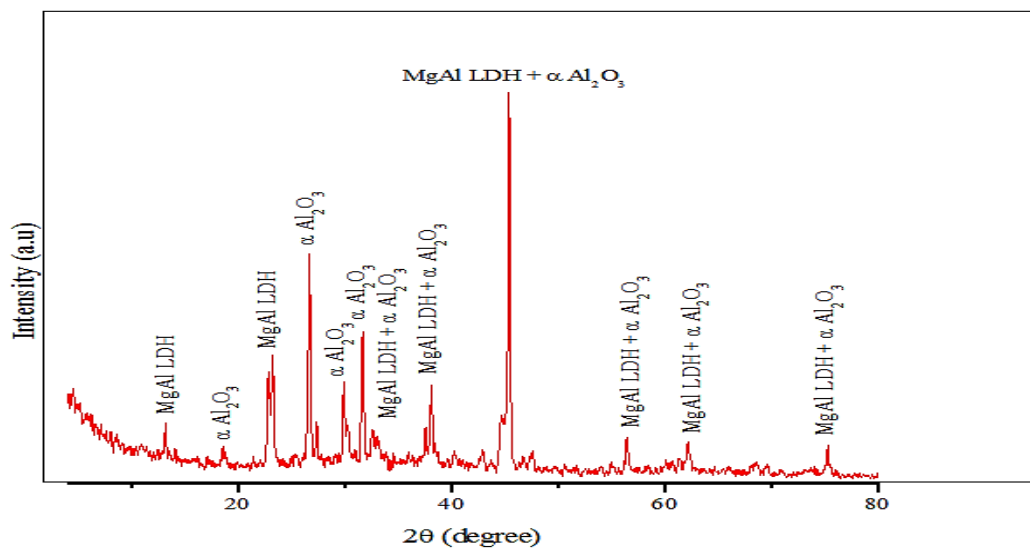**Fig. (2): FT-IR spectrum of MgAl LDH sorbent (dried at 150 °C)**
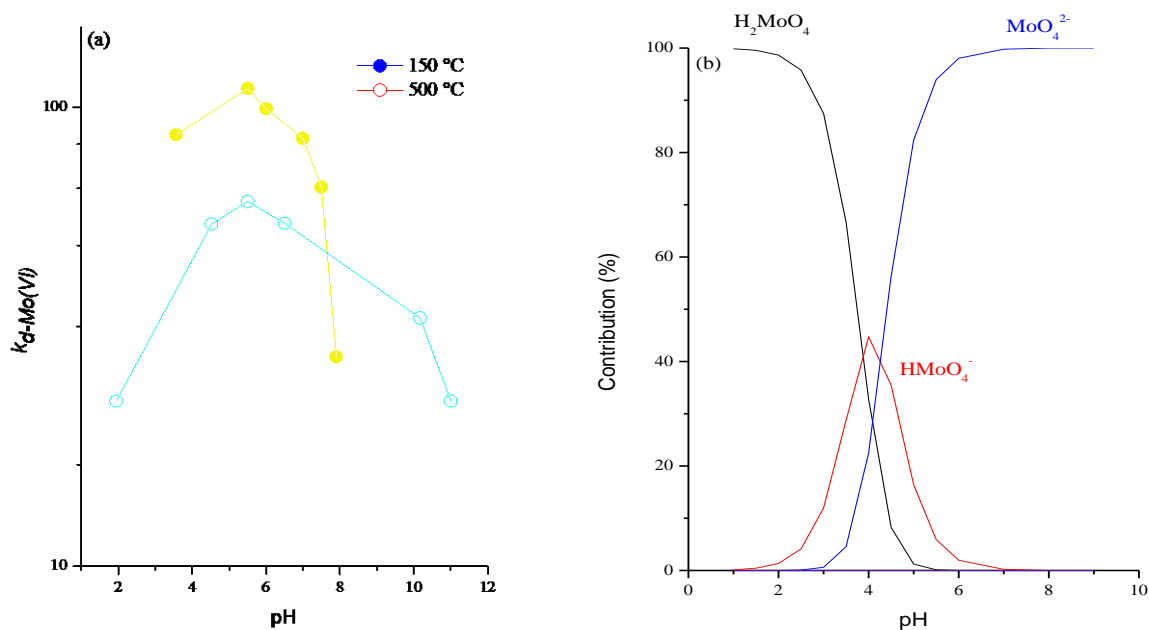
**Fig. (3) XRD pattern of MgAl LDH sorbent**



**Fig. (4) Distribution coefficient of (a) $1 \times 10^{-4}$ M molybdate(VI)-$^{99}$Mo between Cl$^-$ aqueous media and MgAl LDH (dried at different temperatures) as a function of pH and (b) $1 \times 10^{-4}$ M of Mo(VI) species contribution as a function of pH**

## 3.2.   Batch distribution coefficient studies

Distribution coefficient of a radionuclide *x*, $k_{d-Mo}$, on a definite sorbent can be represented as:

$$k_{d-Mo} = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (ml/g) \quad (2)$$

Where,

$C_0$: initial count rate of $^{99}$Mo in solution (before batch contact with the sorbent).

$C_e$: count rate of $^{99}$Mo in solution at equilibrium (after batch contact with the sorbent).

*m*: mass of the sorbent (0.1 g).

*V*: volume of the $^{99}$Mo solution (10 ml).

Figure 4 (a) shows the distribution coefficient of $1 \times 10^{-4}$ M molybdate(VI)- $^{99}$Mo between Cl$^-$ aqueous media and MgAl LDH (dried at different temperatures) as a function of pH. According to Figure 4 (a), the

highest $k_{d-Mo(VI)}$ values (110 and 62.4 ml /g) were achieved at pH-value of 5.5 for both MgAl LDH sorbents dried at 150 and 500 °C, respectively. Figure 4 (b) shows species contribution of $1\times10^{-4}$ M Mo(VI) species as a function of pH. The study of species contribution was performed by using the data given in [22] with Minteq. V4 database. According to Figure 4 (b), it is clear that at pH 5.5, the contribution of $MoO_4^{2-}$ is ~ 94 %, while that of $HMO_4^-$ is ~ 6 %. As mentioned above, MgAl LDH sorbent is an amphoteric material (PZC of 6.5). Thus, below pH 6.5, the surface of MgAl LDH sorbent is positively charged, which means that electrostatic attraction between molybdate(VI)-$^{99}$Mo and MgAl LDH sorbent may be involved in the sorption process. It is worth mentioning that at higher concentration of Mo(VI), the contribution of polyisomolybdates at low pH-values become noticeable, e.g., for $1\times10^{-3}$ M Mo(VI), the contributions of $H_3Mo_7O_{24}^{3-}$ and $H_2Mo_7O_{24}^{4-}$ are ~ 6 and 3.5 % (respectively) at pH 3, while the contribution of $H_2Mo_7O_{24}^{4-}$, $H_3Mo_7O_{24}^{3-}$ and $HMo_7O_{24}^{5-}$ are ~ 8.5, ~ 1.5 and ~ 1.4 % (respectively) at pH 4.

### 3.3. Breakthrough loading capacity treatment studies

#### 3.3.1 Effect of temperature on LDH breakthrough capacity treatment

The breakthrough capacity of species $X$, $Q_{50\%-Mo}$, of a chromatographic column bed can be calculated as [23]

$$Q_{50\%-X} = M_X \times \frac{V_{50\%-X}}{m_b} \qquad \text{(mmol/g)} \qquad (3)$$

Where,

$M_{Mo}$: the molar concentration of molybdate(VI)-$^{99}$Mo.

$V_{50\%-Mo}$: the volume of the loaded solution of species $X$ at which $C_{eff}/C_{feed} = 50$ %; $C_{feed}$ and $C_{eff}$ count rates of the $^{99}$Mo in the feed and effluent solutions (ml), respectively.

$m_b$: the weight of chromatographic column bed (g).

Figure (5) shows the breakthrough curves of $1\times10^{-3}$ M molybdate(VI)- $^{99}$Mo loading from $Cl^-$ medium (pH 5.5) on chromatographic columns based on 0.5 MgAl LDH sorbents dried at (a) 50 °C, (b) 100 °C, (c) 150 °C and (d) 200 °C. According to Figure (5), $Q_{50\%-Mo}$ values for MgAl LDH sorbents dried at 50, 100, 150 and 200 °C were found to be $1.95\times10^{-2}$, $3.71\times10^{-2}$, $6.54\times10^{-2}$ and $7.46\times10^{-2}$ mmol/g (i.e., 1.87, 3.56, 6.27 and 7.16 mg/g), respectively. It is worth mentioning that the breakthrough capacities of the sorbents dried at 100, 150 and 200 °C (3.56, 6.27 and 7.16 mg/g) are higher than the capacity of alumina (2 mg/g) [7]. Since the alumina chromatographic columns are the most famous and reliable for $^{99}$Mo/$^{99m}$Tc commercial generators, MgAl LDH sorbents dried at 100, 150 and 200 °C can be used as column beds for chromatographic columns of $^{99}$Mo/$^{99m}$Tc generators.
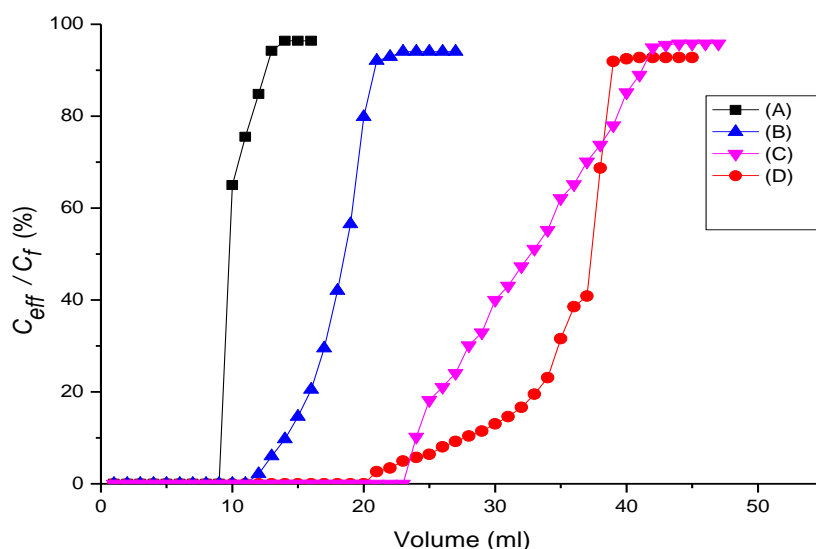


**Fig. (5): Breakthrough curves of $1\times10^{-3}$ M molybdate(VI)- $^{99}$Mo loading from $Cl^-$ medium (pH 5.5) on chromatographic columns (0.7 ID) based on 0.5 MgAl LDH sorbents dried at (A) [50 °C, Q50%-Mo= 1.87 mg/g], (B) [100 °C, Q50%Mo= 3.56 mg/g], (C)[ 150 °C Q50%-Mo= 6.27 mg/g] and (D) [200 °C Q50%-Mo= 7.16 mg/g]**

### 3.3.2. Effect of hydrothermal route on LDH breakthrough capacity treatment

It is worth mentioning that the breakthrough capacity of the sorbent dried at 150 °C (6.27 mg/g) is higher than the capacity of alumina (2 mg/g). The effect of hydrothermal route on the breakthrough capacity was studied.

Figure (6) shows the breakthrough curves of $1\times10^{-3}$ M molybdate(VI)- $^{99}$Mo loading from Cl$^-$ medium (pH 5.5) on 0.5 MgAl LDH sorbents (a) using hydrothermal route (at 150 °C for 24 h) and (b) without using hydrothermal route, both dried at 150 °C. As shown in Figure 6, for the hydrothermal-route MgAl LDH sorbent, the $Q_{50\%\text{-}Mo}$ value was found to be $3.87\times10^{-2}$ mmol/g (3.71 mg/g), while it was $6.54\times10^{-2}$ mmol/g (6.27 mg/g) for the non-hydrothermal route MgAl LDH sorbent dried at the same temperature (150 °C). Thus, the hydrothermal process adversely affected the breakthrough capacity of Mo.

It is worth mentioning that using Phreeqc Interactive Software with Minteq. V4 database, for $1\times10^{-3}$ M Mo(VI) at pH 5.5, the contributions of $MoO_4^{2-}$, $HMoO_4^-$ and $H_2MoO_4$ species are ~ 94, 5.9 and ~ 0.1 %, respectively.

### 3.4. $^{99}$Mo/$^{99m}$Tc generator

#### 3.4.1. Loading of $^{99}$Mo/$^{99m}$Tc generator

Loading efficiency, $L_{eff}$, of $^{99}$Mo on MgAl LDH sorbents prepared at different conditions was calculated according to the following equation:

$$L_{eff} = \frac{C_f - (C_{Leff} + C_{Weff})}{C_f} \times 100 \quad (4)$$

Where,

$C_f$: count rate of the feeding $^{99}$Mo solution.

$C_{Leff}$: count rate of loading effluent.

$C_{Weff}$: count rate of the washing effluent.

The sorbed amount of molybdate(VI)-$^{99}$Mo on each chromatographic column after washing with NaCl solution (pH 5.5) was calculated according to the equation:

$$m_{Mo} = \frac{M_{Mo} \times V_{Mo} \times L_{eff}}{m_b} \quad \text{(mmol/g)} \quad (5)$$

Where,

$M_{Mo}$: molarity of the molybdate(VI)-$^{99}$Mo feeding solution ($1\times10^{-3}$ M).

$V_{Mo}$: volume of the molybdate(VI)-$^{99}$Mo feeding solution (ml).

$m_b$: weight of chromatographic column bed (g).

Table 1 shows the $^{99}$Mo loading efficiency and molybdate(VI)-$^{99}$Mo sorbed amount on chromatographic columns (0.7 cm ID) based on 0.5 g MgAl LDH sorbents dried at different temperatures. $^{99}$Mo loading efficiencies were found to be 27.4, 44.6, 92.9, 74.4 % on chromatographic columns based on 0.5 g MgAl LDH sorbents dried at 50, 100, 150 and 200 °C, respectively, while it was found to be 67.3 % for MgAl LDH sorbent prepared via the hydrothermal route (at hydrothermal temperature of 150 °C for 24 h) and dried at 150 °C. It is worth mentioning that the molybdate(VI)-$^{99}$Mo solution ($1\times10^{-3}$ M) volumes were 5 and 10 ml for column sorbents dried at 50 and 100 °C, respectively, while it was 20 ml for column sorbents dried at 150 °C (using hydrothermal and non-hydrothermal routes) and 200 °C. Subsequently, the loaded amounts of molybdate(VI)-$^{99}$Mo were found to be $2.74\times10^{-3}$, $8.92\times10^{-3}$, $3.72\times10^{-2}$ and $2.98\times10^{-2}$ mmol/g for the non-hydrothermal MgAl LDH sorbents dried at 50, 100, 150 and 200 °C, respectively, while it was $2.69\times10^{-3}$ mmol/g for the hydrothermal MgAl LDH sorbent dried at 150 °C.
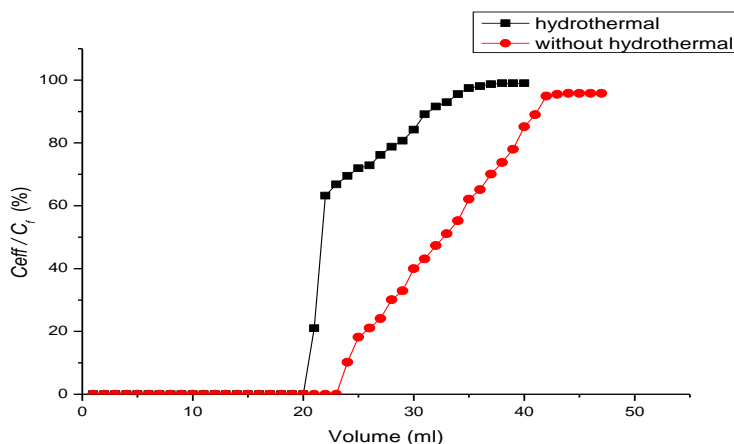


**Fig. (6): Breakthrough curves of $1\times10^{-3}$ M molybdate(VI)- $^{99}$Mo loading from Cl$^-$ medium (pH 5.5), at a flow rate of 0.25 ml/min, on chromatographic columns (0.7 cm ID) based on 0.5 MgAl LDH sorbents (a) using hydrothermal route [Q50%-Mo = 3.71 mg/g] and (b) without using hydrothermal route [Q50%-Mo= 6.27 mg/g]**

**Table (1):** $^{99}$Mo loading efficiency and sorbed amount for $1\times10^{-3}$ M molybdate(VI)- $^{99}$Mo (pH 5.5, Cl$^-$ solution) on chromatographic columns (0.7 cm ID, based on MgAl LDH sorbents dried at different temperatures) after washing with 10 ml of 0.9 % NaCl solution (pH 5.5)

| Drying temperature of MgAl LDH sorbent | Synthesis route | Loading efficiency ($L_{eff}$), % | Feeding molybdate-$^{99}$Mo solution (M) | | Real sorbed molybdate(VI)-$^{99}$Mo amount on the column after washing with NaCl, mmol/g |
|---|---|---|---|---|---|
| | | | Molybdate(VI) concentration, M | Volume, ml | |
| 50 | Non-hydrothermal route | 27.4 | | 5 | $2.74\times10^{-3}$ |
| 100 | | 44.6 | $1\times10^{-3}$ | 10 | $8.92\times10^{-3}$ |
| 150 | | 92.9 | | 20 | $3.72\times10^{-2}$ |
| 200 | | 74.4 | | 20 | $2.98\times10^{-2}$ |
| 150 | Hydrothermal route | 67.3 | | 20 | $2.69\times10^{-2}$ |
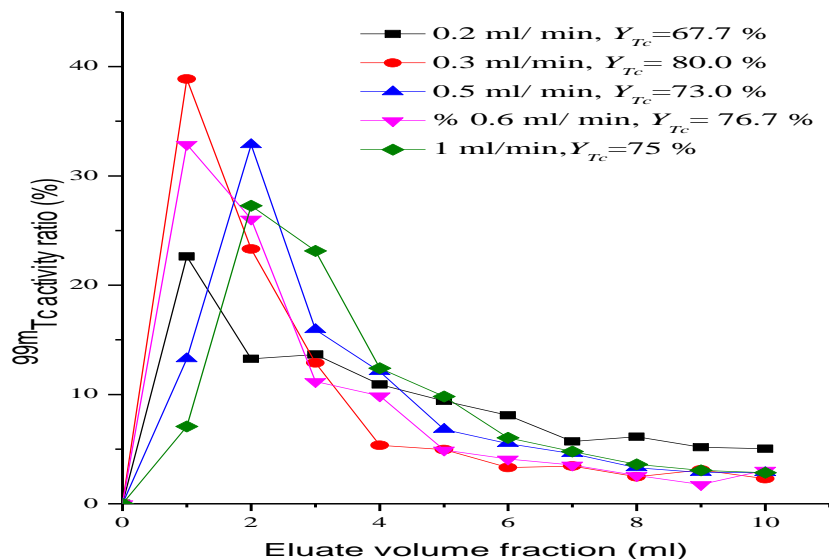


**Fig. (7):** $^{99m}$Tc elution profiles of $^{99}$Mo/$^{99m}$Tc chromatographic column generators (based on 0.5 g of non-hydrothermal MgAl LDH sorbent dried at 150 °C) with 10 ml of 0.9 % NaCl solution

Thus, to prepare $^{99}$Mo/$^{99m}$Tc generators for further studies, 10 ml fractions of $1\times10^{-3}$ M molybdate(VI)-$^{99}$Mo (from Cl$^-$ medium of pH 5.5) were loaded at a flow rate of 0.25 ml/min on pre-conditioned chromatographic columns (0.7 ID) based on 0.5 g of: (i) non-hydrothermal MgAl LDH sorbents (dried at 50, 100, 150 and 200 °C) and (ii) hydrothermal MgAl LDH sorbent dried at 150°C. Then, each column was further washed with 10 ml of 0.9 % NaCl solution before first elution of $^{99m}$Tc after 23 h.

$^{99m}$Tc elution yield, $Y_{Tc}$, can be calculated according to the following equation:

$$Y_{Tc} = \frac{Col_{Tc}^{0} - Col_{Tc}^{f}}{Col_{Tc}^{0}} \times 100 \quad (\%) \qquad (6)$$

Where,

$Col_{Tc}^{0}$: count rate of $^{99m}$Tc on the column loaded with molybdate(VI)-$^{99}$Mo before elution.

$Col_{Tc}^{f}$: count rate of $^{99m}$Tc on the column loaded with molybdate(VI)-$^{99}$Mo after elution with 10 ml of 0.9 % NaCl solution.

It was found that the average elution yields were found to be 9.3, 23.6, 75.0 and 31.6 % with the non-hydrothermal column beds dried at 50, 100, 150 and 200 °C, while it was found to be 32.7 % with the

hydrothermal column dried at 150 °C using the same flow rate for all (1 ml/min). Thus, the non-hydrothermal MgAl LDH column bed dried at 150 °C (achieving the highest $^{99}$Mo loading capacity, Table 1, and the highest $^{99m}$Tc elution yield) was chosen to study the rest of the performance aspects.

### 3.4.2. Effect of different flow rates on the elution profile

Elution profiles of the $^{99}$Mo/$^{99m}$Tc chromatographic column generator based on the non-hydrothermal MgAl LDH sorbent at different elution flow rates are shown in Figure 7. According to Figure 7, it was found that 84.9, 85.4, 79.7, 80.9 and 69.9 % of $^{99m}$Tc activities was collected in the 1$^{st}$ 5 ml fraction of the $^{99m}$Tc eluates with the elution flow rates of 0.2, 0.3, 0.5 0.6 and 1 ml/min, respectively.

### 3.4.3. Radionuclidic and chemical purity of the eluted $^{99m}$Tc

Radionuclidic purity, *RNP*, can be calculated according to:

$$RNP = \frac{Elu_{Tc}}{Elu_T} \times 100 \quad (\%) \quad (7)$$

Where,

$Elu_{Tc}$: count rate of $^{99m}$Tc in the eluate.

$Elu_T$: total count rate of eluate (sum of $^{99m}$Tc and $^{99}$Mo, if present).

*RNP* of the $^{99m}$Tc eluates was found to be > 99.9 %.

Radiochemical purity of $^{99m}$Tc eluate, *RCP*, can be calculated according to:

$$RCP = \frac{^{99m}Tc\ activity\ under\ R_f\ peak}{Total\ eluted\ ^{99m}Tc} \times 100 \quad (\%) \quad (8)$$

Where,

$R_f$: retardation factor.

$$R_f = \frac{D_{Tc}}{D_{solv}} \quad (9)$$

Where,

$D_{Tc}$: distance travelled by $^{99m}$Tc activity.

$D_{solv}$: distance travelled by the developing solvent.

It is known that for $^{99m}$TcO$_4^-$ anion, $R_f$ -value (in ascending paper chromatographic method using Whatman no. 1 paper and 85 % methanol as a developing solvent) is 0.55-0.7 [24].

Figure (8): shows a typical radiochromatogram of $^{99m}$Tc eluate containing one peak with $R_f$ -value of 0.6 and *RCP* of 96.4 %. However, *RCP* of the $^{99m}$Tc eluates along the generator performance study time was > 95 %.

$^{99m}$Tc eluates were found to have a high chemical purity along the generator performance study period, since Al$^{3+}$ content in the eluates < 5 µg/ml. Al$^{3+}$ was measured at a wavelength of 396.2 nm using inductively coupled plasma optical emission spectrometer [25]. Table (2) shows the performance parameters of $^{99}$Mo/$^{99m}$Tc chromatographic column generator based on non-hydrothermal MgAl LDH sorbent dried at 150 °C.
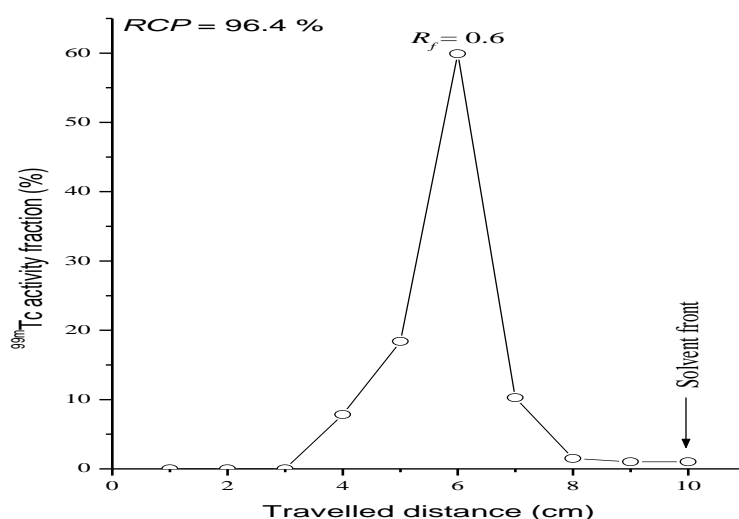


**Fig. (8): A typical radiochromatogram of $^{99m}$Tc eluted from $^{99}$Mo/$^{99m}$Tc chromatographic column generator (based on 0.5 g of non-hydrothermal MgAl LDH sorbent dried at 150 °C), using Whatman no. 1 ascending paper chromatographic method and 85 % methanol as a developing solvent**

## CONCLUSION

Nano magnesium aluminum layered double hydroxide (MgAl LDH) sorbent was synthesized via the autocombustion approach, characterized and used successfully as a base material for $^{99}Mo/^{99m}Tc$ column generator achieving higher loading capacities than that of alumina.

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