

## Synthesis of Zinc-Aluminum Layered Double Hydroxides and Their Applications in Removal of Technetium from Aqueous Solutions.

Gh.M. Rashad and H.H. Sameda

Nuclear Chemistry Department, Hot Laboratories and Waste Management Center, Atomic Energy Authority, Cairo, Egypt

Received: 1/11/2014

Accepted: 25/12/2014

### ABSTRACT

Zinc-aluminium layered double hydroxide was synthesized by coprecipitation method in molar ratios Zn : Al 2:1 and 3:1. The prepared layered double hydroxides were characterized by Fourier-transform infrared spectra (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The synthesized layered double hydroxides were used to study the removal of pertechnetate anion ( $\text{TcO}_4^-$ ) from aqueous solution. The influence of some parameters on pertechnetate adsorption, including pH of aqueous solution, contact time and temperature were investigated. The results showed that the sorption process is most effective at a pH of about 3 in the acidic solution. The thermodynamic parameters, such as  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  clarified that the sorption is an endothermic process accompanied with an increase in the disorder of the system.

*Key words: Layered double hydroxide, pertechnetate, sorption.*

### INTRODUCTION

In recent days, the progress in science and technology has contributed to the improvement of various types of materials. As one type of these materials, layered double hydroxide (LDH) has attracted a great interest in the field of material science due to its favorable properties. These include thermal, mechanical and optical behavior. These properties have facilitated the application of LDH in many potential fields, as ion exchanger, catalysis, additive, polymer stabilizer, drug delivery, absorbent and contaminant remover<sup>(1-8)</sup>.

Layered double hydroxides (LDHs) are known as anionic clays or hydrotalcite-like materials. They are a group of clay minerals with a similar structure to the mineral brucite ( $\text{Mg}(\text{OH})_2$ ), which consist of divalent magnesium ions occupying octahedral positions surrounded by OH groups in a complex layered structure. LDHs represent a class of layered materials with general chemical composition  $[\text{M}^{+2}_{1-x}\text{M}^{+3}_x(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$  in which  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are the di and trivalent cations respectively, x is a ratio of  $\text{M}_2/(\text{M}_2+\text{M}_3)$   $0.2 < x < 0.33$ , m is the number of water molecules participated in the double layered<sup>(9)</sup>. The positive charge can be compensated by a variety of inorganic anions (A) as (often carbonate, chloride or nitrate) and different organic anions can be intercalated into layered double hydroxide through various methods. Their large interlayer space and high concentrations of active sites have allowed a series of multifunctional LDH materials to be used as anion exchangers<sup>(10)</sup> absorbents<sup>(11,12)</sup> and magnetic materials<sup>(13,14)</sup>.

In recent years, growing attention has been directed to anionic species found in water streams from industrial, medical and active waste) due to their hazardous effect on the environment and human beings. Various researches were carried out on the application of layered double hydroxide in removal of anionic species from aqueous solutions. Many oxyanions as arsenate ( $\text{AsO}_4^{3-}$ ), selenite ( $\text{SeO}_3^{2-}$ ) and molybdate ( $\text{MoO}_4^{2-}$ ) are removed from aqueous solution using of calcined and uncalcined layered double hydroxides<sup>(15)</sup>. The reported data clarify that LDH is a promising adsorbent for removal of

such species even in presence of other competing anions such as:  $\text{CO}_3^{2-}$  and  $\text{HPO}_4^{2-}$ . Also, the adsorption of chromate ( $\text{CrO}_4^{2-}$ ) from aqueous solution was studied using aluminum-magnesium mixed hydroxide with various Mg/Al molar ratios. It was found that LDH capacity for Cr (VI) ranged from (105.3 to 112.0) mg/g at 20 to 40 °C. Therefore, LDH is considered an effective sorbent for Cr(VI) removal with higher sorption capacity and fast rate at pH values close to which pollutants are found in the environment<sup>(16)</sup>. Also, super paramagnetic microparticles modified with LDH were studied as phosphate absorbers<sup>(17,18)</sup>.

Pertechnetate is considered one of the most hazardous anionic species found in aqueous waste which is released from the medical field.  $\text{Tc}^{99m}$  has been extensively used in nuclear medicine for diagnostic purpose due to its favorable decay properties. Since its half life is ~ 6.1h and its  $\gamma$  energy reached 140 KeV. These properties are sufficiently safe for the medical application which encourages the usage of  $\text{Tc}^{99m}$  on wide scale.  $\text{Tc}^{99m}$  decays to long life  $\text{Tc}^{99}$  which is a low  $\beta$  emitter and has a long half life of  $2.1 \times 10^5$  years, this together with its high solubility and mobility at neutral and basic mediums. Also,  $\text{Tc}^{99}$  is produced as a fission product during irradiation of uranium nuclear fuels and its ratio reached to 6%. Thus,  $\text{Tc}^{99}$  must be preconcentrated and removed from aqueous waste solution before the disposal process takes place .

Therefore this work aims to prepare Zn-Al  $\text{CO}_3$  layered double hydroxides (ZAC-LDH) in different molar ratios of Zn: Al equal 2:1 and 3:1 and study their use in removing pertechnetate species from aqueous solutions.

## EXPERIMENTAL

### Materials

The chemical materials used in this work were analytically graded and used without further purification.  $\text{Tc}^{99m}$  is obtained from  $\text{Mo}^{99}/\text{Tc}^{99m}$  generator (Mansoura University's Hospital).

### Synthesis of LDH

Zn-Al- $\text{CO}_3$  LDH was synthesized by coprecipitation technique as described by Reichle 1986<sup>(19)</sup>. Zn/Al ratios close to 2 and 3 were chosen since these ratios produce samples of good crystallinity. A solution containing 0.6 M of  $\text{ZnCl}_2$  and 0.3 or 0.2 M of  $\text{AlCl}_3$  was added with vigorous stirring to a solution of 0.1 M of NaOH and 0.2 M of  $\text{Na}_2\text{CO}_3$ . The addition occurred at room temperature maintaining the pH of the aqueous solution close to 10. The resulting slurry was then crystallized at 60 °C for 24 h followed by cooling and washing several times with distilled water. The material was dried at 60 °C in the oven for 24 h. The precipitate was filtered and washed with distilled water till the solution reached pH nearly 7, followed by drying at 60 °C. All of the obtained products were then ground into fine powder and kept in sample bottles for further use.

### Characterization of Adsorbents

The synthesized ZAC-LDHs were characterized by XRD spectrophotometer of type Philips PW 1800 diffractometer, using Cu-K $\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) at 40 kV, 20 mA. The Fourier transform infrared (FTIR) spectra of the solids were obtained, in the 400- 4000  $\text{cm}^{-1}$  range, using KBr pellet technique and scan electron microscopy (SEM) coupled with energy- dispersive x- ray spectroscopy (EDX) , Jeol 6510A from Jeol, Japan was used for a surface scan of the prepared layered double hydroxide and to determine its elemental constituents.

### Preparation of $\text{Tc}^{99m}$ Sample

2ml of  $\text{H}_2\text{O}_2$  in percent 30% were added to Tc sample and were gently heated for 15 minutes to completely convert all Tc species to pertechnetate form.

### Sorption Process

A batch technique was applied to study the sorption of  $Tc^{99m}$  by the two prepared layered double hydroxides. In this technique, 0.05 g of LDH in molar ratio either of 2:1 and 3:1 were vigorously shaken with 5 ml of aqueous solution containing active  $Tc^{99m}$ . At different time intervals, 1 ml of the sorption matrix was withdrawn, filtered and subjected for radiometrical assay. A decay curve was constructed for each experiment and the count activity was compared with its corresponding one at the same time in decay curve. The distribution coefficient was calculated from the relation

$$K_d = (A_i - A_f/A_f) \times V/m$$

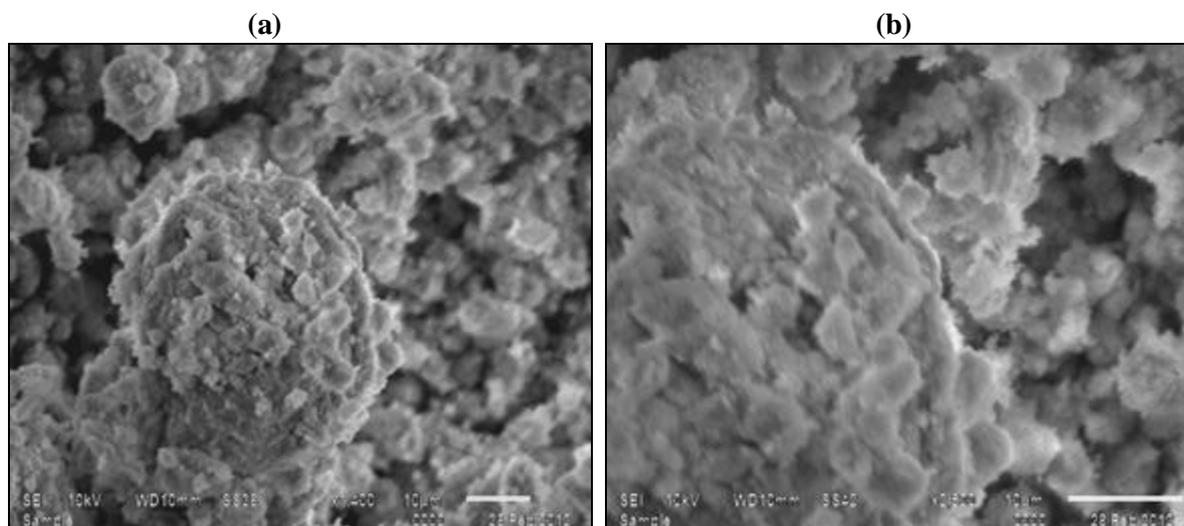
Where  $A_i$  and  $A_f$  refer to initial and final activities in aqueous solution,  $V$  is the volume of aqueous solution in liter and  $m$  is the weight of layered double hydroxide in milligram.

## RESULTS AND DISCUSSION

### Characterization of Prepared LDHs

#### Scanning Electron Microscopy

The SEM images of Zn/Al layered double hydroxide are shown in figure. (1).The pictures indicate that the prepared Zn/Al LDH consists principally of large aggregate particles. The elemental constituents of the prepared samples are determined qualitatively by EDX in figure (2) and the spectra showed bands that are characterized for Zinc, Aluminium, Oxygen and Carbon.



**Fig. (1):** The SEM images of Zn/Al-LDH prepared at different molar ratios Zn:Al of a) 2:1 and b) 3:1

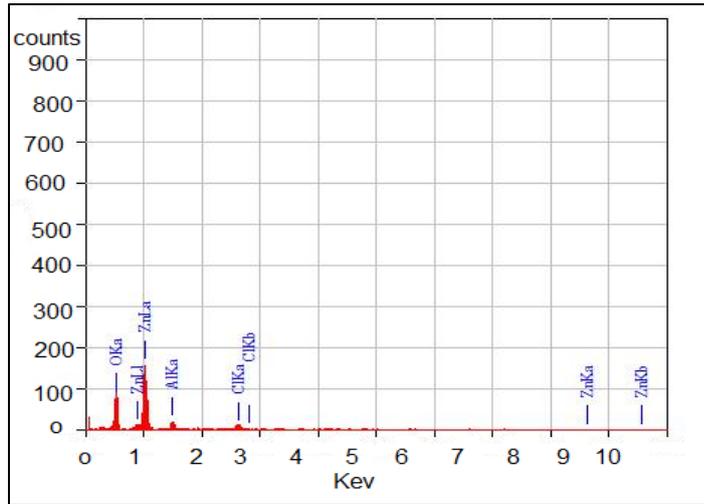


Fig. (2): The SEM images of Zn/Al-LDH prepared at molar ratio of Zn:Al is 2:1

**XRD Patterns**

The XRD patterns of Zn/Al-LDH prepared at different molar ratios are given in figure (3). From this figure, one can observe sharp and strong signals in  $2\theta$  range  $2-70^\circ$ . These peaks indicate that the prepared LDHs are characterized by high crystallinity and consistent to great extent, with the peaks of hydroxalite structure. So, it indicates that the prepared LDHs are hexagonal lattice compounds<sup>(20, 21)</sup>. Various researches mentioned that the lattice parameters (c, a) which refer to interlayer and cation-cation distances can be calculated from XRD signals<sup>(22-24)</sup>. The strong signals (003), (006) and (110) with d-spacing basal distances 7.78, 3.97 and 1.05Å for Zn:Al ratio 2:1 and 7.82, 3.88 and 1.04 Å for Zn:Al in molar ratio 3:1 allow to calculate interlamellar distance (c) which equals 3d (003) and found to be 23.34, 23.46 Å for ratio 2:1 and 3:1, respectively. Cation-cation distance (a) is calculated from 2d (110) and found to be 2.1 and 2.08 Å for molar ratios 2:1 and 3:1, respectively. The recorded data show the similarity between the interlamellar and cation- cation distance with respect to the synthesized layered hydroxides that means the increase of zinc concentration in this range does not affect the hexagonal lattice parameters of Zn-Al LDH.

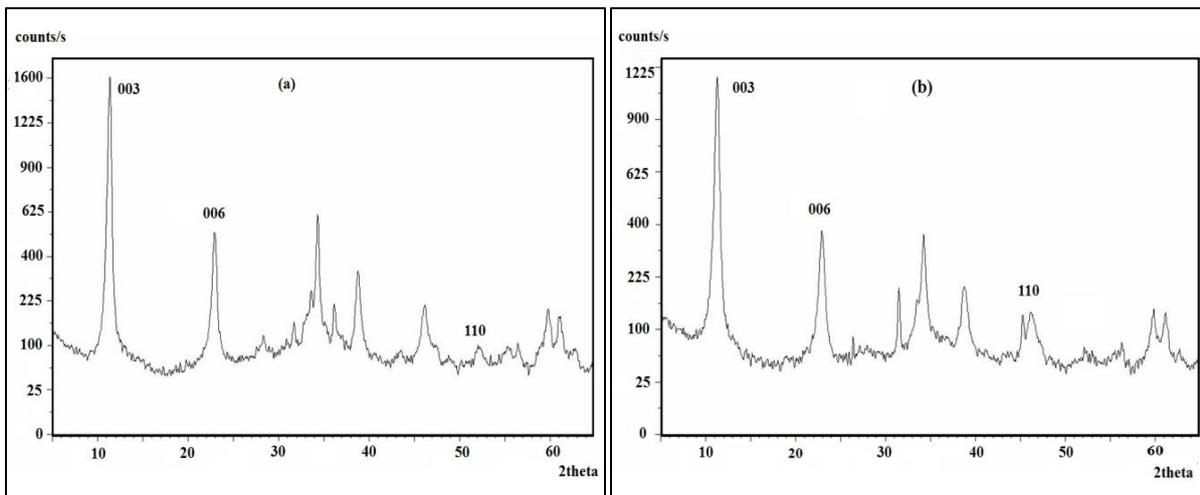
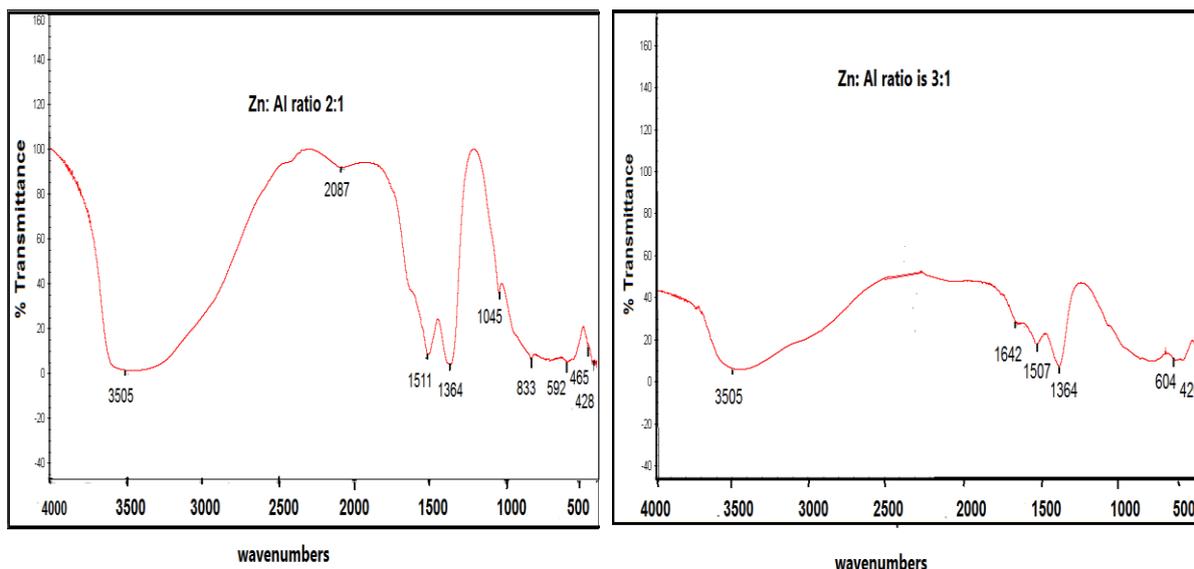


Fig. (3): XRD patterns for Zn/Al-LDH prepared at different molar ratios Zn:Al of a) 2:1 and b) 3:1  
The FTIR spectra

The FTIR spectra of the prepared Zn/Al-LDHs are represented in figure (4). The spectra showed a broad absorption band in the 4000-3000  $\text{cm}^{-1}$  region centered at around 3500  $\text{cm}^{-1}$  which is referred to O-H stretching mode of the hydroxyl group in the layers and physo-sorbed water molecules on the surface of LDH. These bands are commonly observed in the LDHs materials <sup>(2,25,26)</sup>. At about 1364  $\text{cm}^{-1}$ , there is a characteristic signal of  $\text{CO}_3^{2-}$  stretching vibrations <sup>(27)</sup>. Also, the absorption band that was detected at 1515  $\text{cm}^{-1}$  could be ascribed to H-O-H bending vibration of the interlayer water <sup>(28)</sup>. The intense absorption peaks in the low frequency region, 400 – 800  $\text{cm}^{-1}$  correspond to the lattice vibration modes of M-O and O-M-O (M= Zn, Al) <sup>(28-31)</sup>.

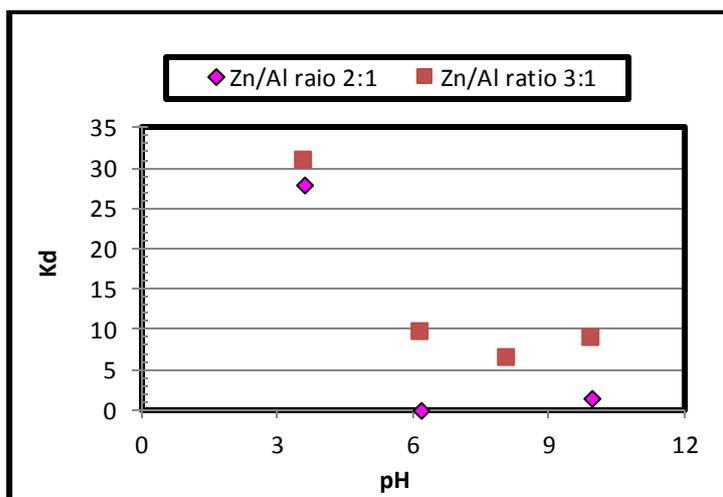


**Fig. (4):** IR spectrum for Zn/Al-LDH prepared at different molar ratios Zn:Al of 2:1 and 3:1

## Removal Study

### Effect of pH

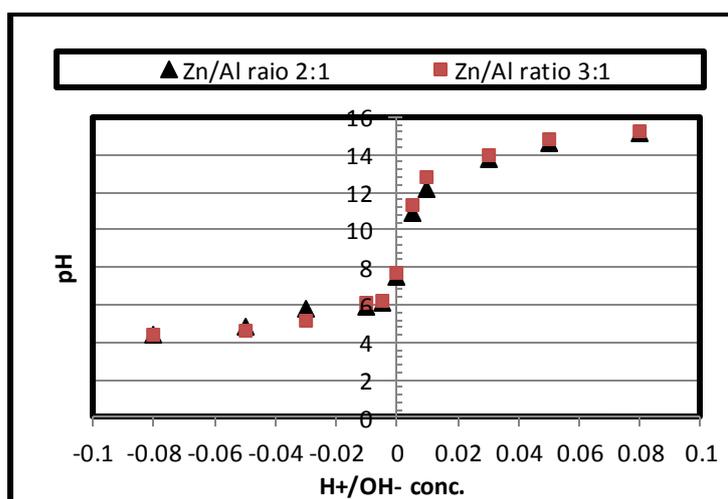
The effect of hydrogen ion concentration on the distribution coefficient of pertechnetate  $\text{TcO}_4^-$  on Zn-Al- layered double hydroxide in molar ratio 2:1 and 3:1 is shown in figure (5). The plots show that the highest distribution of  $\text{TcO}_4^-$  occurs from aqueous solution of nearly pH~3 and the LDH in both molar ratios have nearly the same removal ability of technetium, but the Zn/Al-LDH with molar ratio Zn:Al 3:1 recorded the higher sorption ability especially from aqueous of pH 3. The curve also shows that the sorption of  $\text{TcO}_4^-$  decreased by increasing pH values and this refers to the increase of competing anions as  $(\text{OH}^-)$  by increasing pH values. The plots also clarify the low removal ability of the prepared layer hydroxide for  $\text{TcO}_4^-$  anion. This low tendency of LDH may be attributed to the presence of carbonate anion which can not be easily replaced with anionic species and prevents the LDH to behave as anion exchanger <sup>(32)</sup>. So, the removal of the pertechnetate anion may take place on the surface of LDH in a manner similar to metal oxide behavior.



**Fig. (5):** The effect of hydrogen ion concentration on the distribution coefficient of pertechnetate on Zn/Al-LDH prepared at different molar ratios Zn:Al of 2:1 and 3:1 [t=25°C , V/m=100, time=1h]

### Isoelectric Point

Surface charge for Zn/Al layered double hydroxide in molar ratio of Zn: Al equals 2:1 and 3:1 was determined by contacting LDH with aqueous solution of pH values from (1 to 14) and fixed ionic strength and the obtained data represented in figure (6). The plots confirm that the pH of zero charge was detected at the values 7.74 and 7.51 for LDH of the molar ratio 3:1 and 2:1, respectively. This implies that the layered double hydroxide surface have a positive charge at pH values ranged from 1 to 7.74, and from 1 to 7.51, and a negative charge in the range from 7.74 to 14, and from 7.51 to 14 for LDH in ratios 3:1 and 2:1, respectively. This surface charge shows that LDH can behave as a traditional sorbent similar to different metal oxides in addition to its main anion exchange property.



**Fig. (6):** The titration curve of Zn/Al-LDH prepared at different molar ratios Zn:Al of 2:1 and 3:1 using 0.1 M NaNO<sub>3</sub>

### Effect of Contact Time

The sorption of pertechnetate from aqueous solution of pH nearly 3 keeping temperature at 25°C at different time intervals was carried out and the obtained results are illustrated in figure (7). The graph represents a relation between contact time and distribution coefficient of pertechnetate. The data report that the potential equilibrium was reached nearly after 40 minute and the distribution kept nearly constant for 2 hours. The distribution is calculated after 24 hours and found to be not affected and nearly fixed at the same value. This means that 40 minutes is a sufficient time to reach the equilibrium sorption of technetium.

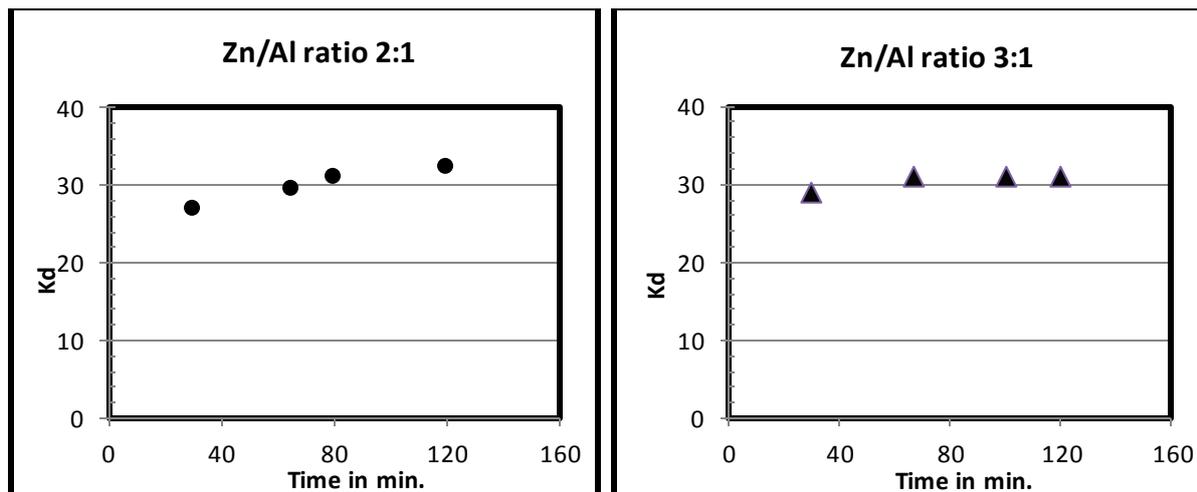


Fig. (7): The effect of contact time on the sorption of pertechnetate from aqueous solution onto Zn/Al-LDH prepared at different molar ratios Zn:Al of 2:1 and 3:1 [t=25°C, V/m=100, pH= 3]

### Effect of Temperature

The effect of temperature on the sorption of  $TcO_4^-$  by Zn/Al LDH in molar ratio 2:1 and 3:1 was investigated and represented in figure (8). It can be observed from this figure, that the sorption of  $TcO_4^-$  is increased by raising the temperature of the sorption process from 25 to 45°C and a remarkable increase in the sorption is observed at 45°C. The distribution coefficient of  $TcO_4^-$  anion is related to the enthalpy change by the equations<sup>(33)</sup>:

$$\ln K_d = -\Delta H/RT$$

and

$$\Delta G = -RT \ln K$$

The thermodynamic parameters of the sorption process were determined by plotting the relation between  $\log K_d$  (distribution coefficient) and  $1/T$  (where T is temperature in Kelvin). The plots of such relation are shown in figure (9). The different thermodynamic parameters for the sorption of technetate on Zn/Al-LDH were estimated and given in table (1). The positive value of enthalpy change ( $\Delta H$ ) indicates that the sorption is endothermic process. This means that the pertechnetate oxianion needs energy to liberate from the surrounding hydration shells to be able to interact with solid surface. The enthalpy values suggest the possibility of strong interaction between  $TcO_4^-$  and Zn-Al-LDH. The negative value of Gibbs' free energy ( $\Delta G$ ) indicates that the sorption process is spontaneous and favored by raising the temperature. The positive value of entropy change ( $\Delta S$ ) indicates that the disorder increased in the sorption process and this may be due to the liberation of water molecules surrounded pertechnetate anion, also it suggests some structure changes in the  $TcO_4^-$  and LDH.

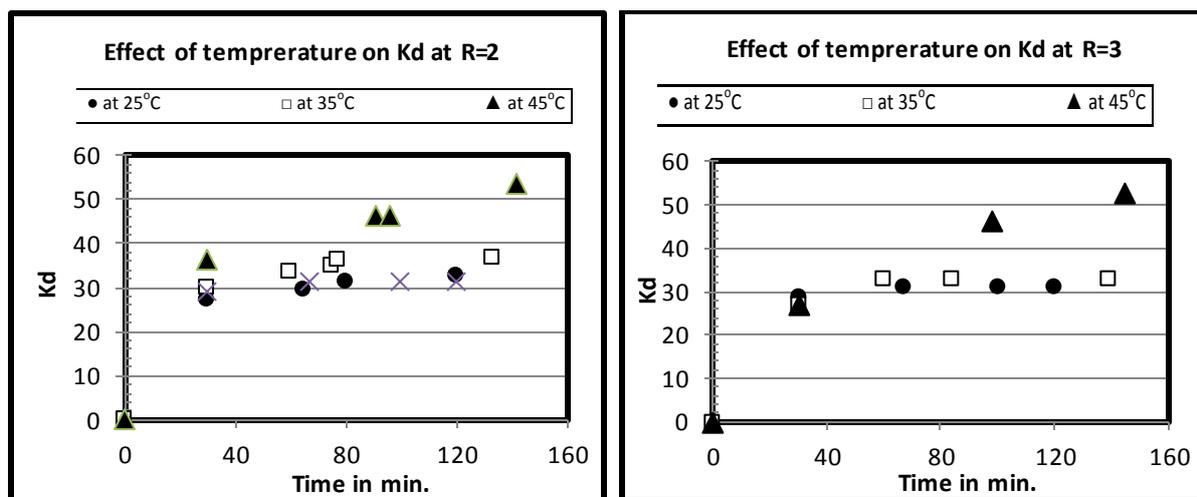


Fig. (8): The effect of temperature on the sorption of pertechnetate from aqueous solution onto Zn/Al-LDH prepared at different molar ratios Zn:Al of 2:1 and 3:1[V/m=100, pH= 3]

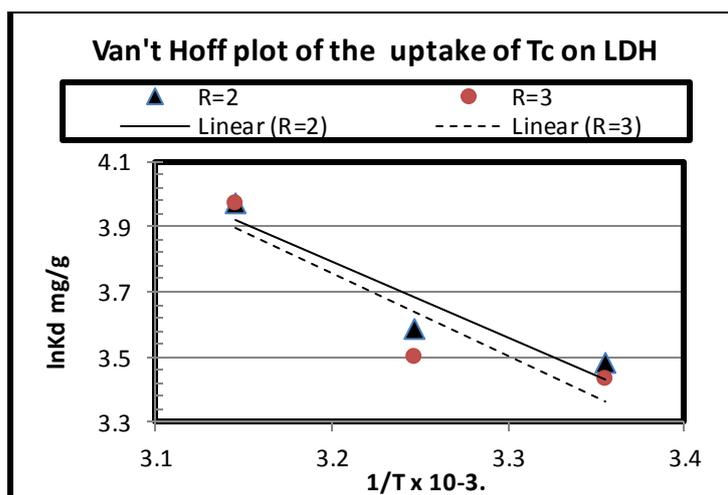


Fig. (9): Van't Hoff plot for the sorption of pertechnetate from aqueous solution onto Zn/Al-LDH prepared at different molar ratios Zn:Al of 2:1 and 3:1[V/m=100, time=1h, pH= 3]

Table (1): Thermodynamic parameters for the sorption of pertechnetate from aqueous solution onto Zn/Al-LDH prepared at different molar ratios Zn:Al of 2:1 and 3:1[V/m=100, time=1h, pH= 3]

Ratio	T	K <sub>d</sub>	slope	Δ H° (KJ/mole)	-Δ G° (KJ/mole)	Δ S (J/mole)
2:1	298	32.50	-2.30	19.13	8.63	93.14
	308	36.00			9.18	91.90
	318	53.00			10.50	93.17
3:1	298	31.00	-2.52	20.94	8.51	92.74
	308	33.00			8.95	91.18
	318	53.00			10.50	93.17

## CONCLUSION

Zn/Al layered double hydroxide was prepared with different molar ratios and characterized with IR, XRD and SEM. The analysis of the obtained data confirms the hydrotalcite compound structure of the synthesis layered double hydroxides. The synthesized layered double hydroxides consist principally of large aggregate particles and have a stretching vibration at about  $1364\text{ cm}^{-1}$  which is a characteristic signal of  $\text{CO}_3^{2-}$  and have intense peaks in the range 400-800 which corresponds to lattice vibration mode of M-O (where M = Zn, Al). The increase in Zn/Al molar ratio from 2 to 3 does not change the hexagonal lattice parameters of Zn/Al LDH and does not change the morphology of the prepared samples.

LDHs are used to study the removal of pertechnetate from aqueous solution and the results show that sorption of pertechnetate takes place from acidic solution of pH nearly 3 and the sorption on the surface of LDH may participate in the removal of technetium and the sorption is increased by raising temperature of the reaction. Different thermodynamic functions were calculated which indicate that the sorption process is endothermic, spontaneous and accompanied by increase the randomness in the system. The LDH in both molar ratios have nearly the same removal ability of technetium.

## REFERENCES

- (1) B.F. Sels, D.E. De Vos, P.A. Jacobs, "Hydrotalcite-like-anionic-clays-in-catalytic-organic-reactions" *Catal. Rev. Sci. Eng.* 43, 443 (2001).
- (2) F. Cavani, F. Trifiro, A. Vaccari, "Hydrotalcite-type anion clays: preparation, properties and applications", *Catal. Tod.* 11, 173 (1991).
- (3) F. Leroux, J.P. Besse, Layered double hydroxide/polymer nanocomposites. In: Wypych, F., Satyanarayana, K.G. (Eds.), *Clay surfaces: fundamentals and applications*. Elsevier, Amsterdam, pp. 459–495 (2004).
- (4) Z. Wang, E. Han, W. Ke, "Influence of nano-LDH on char formation and fire-resistant properties of flame-retardant coating" *Prog. Org. Coat.* 53, 29 (2005).
- (5) H. Jung, H. Mi-Kim, Y.B. Choy, S.J. Hwang, J.H. Choy, "Itraconazole-laponite: kinetics and mechanism of drug release", *Appl. Clay Sci.* 40(1–4), 99 (2008).
- (6) V. Rives, "Layered Double Hydroxides: Present and Future", Ed., Nova Science Publishers, Inc., New York (2001).
- (7) L. Lv, J. He, M. Wei, D.G. Evans, X. Duan, "Factors influencing the removal of fluoride from aqueous solution by calcined Mg-Al- $\text{CO}_3$  layered double hydroxides", *J. Hazard. Mater.* B133, 119 (2006).
- (8) M.R. Mahmoud, and H. H. Someda, "Mg-Al layered double hydroxide intercalated with sodium lauryl sulfate as a sorbent for  $^{152+154}\text{Eu}$  from aqueous solutions", *J. Radio. Nucl. Chem.* 292, 1391 (2012).
- (9) I.A. Abdullah, "Controlling the Morphology of Nano-Hybrid Materials", *J. Am. Appl. Sci.* 7(2), 171 (2010).
- (10) Z. Liu, R. Ma, M. Osada, N. Liy. Ebina, K. Takada, T. Sasaki, "Synthesis Anion Exchange and Delamination of Co-Al Layered Double Hydroxide: Assembly of the Exfoliated Nanosheet/Polyanion Composite Films and Magneto-Optical Studies", *J. Am. Chem. Soc.* 128, 4872 (2006).
- (11) Y. Guo, Z. Zhu, Y. Qiu, J. Zhao, "Enhanced adsorption of acid brown 14 dye on calcined Mg/Fe layered double hydroxide with memory effect", *Chem. Eng. J.* 219, 69 (2013).

- (12) A. Garcia-Gallastegui, D. Iruetagoiena, V. Guovea, M. Mokhtar, A.M. Asiri, S.N. Basahel, S. A. Al-Thabaiti, A. O. Alyoubi, D. Chadwick, M.S.P. Shaffer, "Graphene Oxide as Support for Layered Double Hydroxides: Enhancing the CO<sub>2</sub> Adsorption Capacity", *Chem. Mater.* 24, 4531 (2012).
- (13) J. Han, Y. Dou, M. Wei, D.G. Evans, X. Duan. "Erasable nanoporous antireflection coatings based on the reconstruction of layered double hydroxide" *Chem. Int. Ed.* 49, 2171 (2010).
- (14) J.L. Gunjekar, I.Y. Kim, J.M. Lee, N-S. Lee, S-J, "Self- assembly of layered double hydroxide 2D nanoplates with graphene nanosheets: an effective way to improve the photocatalytic activity of 2D nanostructured material for visible light-induced O<sub>2</sub> generation" *Energy Environ. Sci.* 6, 1008 (2013).
- (15) K.H. Goh, T.T. Lim, Z. Dong, *Water Res.* "Application of layered double hydroxides for removal of oxyanions: A review" 42 (6-7) 1343 (2008).
- (16) L. Yujiang, G. Baoyu, W. Tao, S. Dejun, L. Xia, W. Biao, L. Fengjuan, "Chromium remover by double layered hydroxide", *Water Research* 43(12), 3067 (2009).
- (17) A. Drenkova-Tuhtan, Karl Mandel, A. Paulus, et al. "Phosphate recovery from wastewater using engineered superparamagnetic particles modified with layered double hydroxide ion exchangers", *Water Res.* 47, 5670 (2013).
- (18) K. Mandel, A. Drenkova-Tuhtan, F. Hutter, et al. "layered double hydroxide ion exchangers on superparamagnetic microparticles for recovery of phosphate from waste water" *J. Mater. Chem. A* 1, 1840 (2013).
- (19) W.T. Reichle, "Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite", *Solid States Ionics*, 22 (1), 135 (1986).
- (20) L. Ren, J. Hu, L. Wan, C. Bai, "A simple method to synthesis layered double hydroxide nanoscrolls", *Mat. Res. Bulle.*, 42, 571 (2007).
- (21) T. Komeda, S. Saito, Y. Umetsu, "Mg-Al-layered double hydroxide intercalated anion: synthesis and application to the uptake of heavy metal ions from an aqueous solution, with ethylene-diaminetetraacetate" *Sep. purif. technol.* 47, 20 (2005).
- (22) P. Beaudot, M.E. De Roy, J.P. Besse, "Preparation and Characterization of Intercalation Compounds of Layered Double Hydroxides with Metallic Oxalato Complexes", *Chem. Mater.* 16, 935 (2004).
- (23) J. Carpentier, J.F. Lamonier, S. Siffert, E.A. Zhilinskaya, A. Aboukais, "Characterization of Mg/Al hydrotalcite with interlayer palladium complex for catalytic oxidation of toluene", *Appl. Catal. A: Gen.* 234, 91 (2002).
- (24) M. Intissar, J.C. Jumas, J. P. Besse, F. Leroux, "Reinvestigation of the layered double hydroxide containing tetravalent cations: unambiguous response provided by XAS and Mossbauer spectroscopies" *Chem. Mater.* 15, 4625 (2003).
- (25) B.J. Zaemah, Z.H. Mohd, H.Y. Asmah, Z. Zulkarnain, H.S. Siti, Halimah Sarijo, "Development of controlled drug release formulation based on pamoate-zinc-aluminium-layered double hydroxide nanocomposite", *Malays. J. Anal. Scie.* 2, 491 (2008).
- (26) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", fifth ed. Wiley, New York (1997).
- (27) L.F. Zhang, D.G. Evan, C. Forano, X. Duan, "Structure and thermal evolution of Mg-Al layered double hydroxides containing interlayer organic glyphosate anion", *Thermochim. Acta.* 424, 15 (2004).

- (28) T. Tanaka, S. Nishimoto, Y. Kameshima, J. Matsukawa, Y. Fujita, Y. Takaguchi, M. Matsuda, M. Miyake, " A novel nanocomposite material prepared by intercalating photoresponsive dendrimers into a layered double hydroxide", *J. Soli. State Chem.* 183, 479 (2010).
- (29) Y. Feng, D. Li, Y. Wang, D.G. Evans, X. Duan, "Synthesis and characterization of a UV absorbentintercalated Zn-Al layered double hydroxide", *Poly. Degr & Stab*, 91, 789 (2006).
- (30) P. Ding, B. Qu, "Synthesis and characterization of exfoliated polystyrene/Zn/Al layered double hydroxide nanocomposite via emulsion polymerization", *Coll. and Interfa. Sci*, 291, 13, (2005).
- (31) B. Li, J. He, D.G. Evans, X. Duan, "Inorganic layered double hydroxides as a drug delivery system-intercalation and in vitro release of fenbufen " *Appl. Clay. Sci.* 27, 199 (2004).
- (32) N.K. Lazaridis, D.D. Asouhidou, "Kinetics of sorptive removal removal of chromium (VI) from aqueous solution by calcined Mg-Al-CO<sub>3</sub> hydrotalcite" *Wat. Res.*, 37, 2875 (2003).
- (33) Q. Wang, J. Li, C. Chen, X. Ren, J. Hu, X.Wang, "Removal of cobalt from aqueous solutions by magnetic multiwalled carbon nanotube/ iron oxide composites", *Chem. Engin. J.*, 174, 126-133, (2011).