Diffusion Rate Effect Study On Kinetic Of Controlled Release Of Insecticide Chlorpyrifos From Hybrid Nanocompund

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Abstract*: insecticide chlorpyrifos Mg/Fe –LDHs was prepared by indirect and direct ion exchange. description of this compound Mg/Fe–LDHs and hybrid nanocompound done by FT –IR spectrophotometer before and after intercalation formation of hybrid nano compound , then cooperation to ensure the form hybrid nanocompound and the two and three dimensional image of the above compound in (AFM) for the layer and hybridnanocompound. The aim of this study is the synthesis hybrid nanocompounds for limited of environment pollution and study the effect of diffusion rate caused by insecticide chlorpyrifos released from the hybrid nanocompound layers by the diffusion rate anion that effect on kinetics of different aqueous solution. The results study of effect all aqueous solution on diffusion rate anionin same time fromhybrid nanocompound layer, appeared that thediffusion rate of hybrids to liquids in different carbonate, phosphate and sulfate concentration0.5Mthe diffusion rate release in to aqueous solution carbonate>phosphate>sulfate. The results of the study number of active sites of hybrid nanocompound in the aqueous and alcoholic medium by direct and indirect ion exchange process showed that is better for preparation in alcoholic medium and that the number active sites is higher in hybrid nano compound prepared by indirect ion exchange fromprepared by direct ion exchange.

Keywords: LDHs; Chlorpyrifos; Hybrid nanocompound

INTRODUCTION

Insecticides can be biological activity molecules that have extrusive use in agriculture, leading to direct contact by uses, it is also possible that these particles seep into soil and groundwater one of the problems experienced by this sector,it also has effects on human health which affects the human nervous system as well as the growth and immunity of children, adding to the risk of causing lung cancer. in order to reduce the phenomenon of pollution by these materials it is possible to use a method to control release of these molecules in the form of ions and applying the technique of Nano particles represented by the layered double hydroxides LDHs[1] are a class of compounds carry positively charged layers with anions and water molecules intercalated in the interlayer and call anionic clay compare with the more conventional cationic clay[2]. Is the most often investigated anionic clay and is hardly ever found in nature[3]. The chemical composition of LDHs is represented by general formula [4, 5]$[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2x}^{+}][A^{n-}_{x/n-}.YH_2O]^{x-}$
Divalent cation such as $M^{2+} = Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}$

Trivalent cation such as$M^{3+}= Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, V^{3+}$.The M^{II}/M^{III}molar ratio usually lies between (2 and 5),The layers, as a result, take a positive charge[6]. This rate is attributed to the charge density of the hydroxide basal layer, namely, anion exchange ability (AEC). LDHs layer have positive charge diffusion on the surface of them due to the M^{+3} substituted for the M^{+2}, and the interlayer space is neutralized by the intercalation of anions with water molecules. The intercalation of various anions into LDHs has been classify by the following methods: calcination- rehydration(reconstruction), ion exchange, co-precipitation , thermal reaction and hydrothermal reactions[7], (A^{n-}) is an ion exchangeable anion such as OH^-, Cl^-, NO^{3-}, CO_3^{2-}, SO_4^{2-} and various organic anions[8,9,10,11,12], but also organic anions ,complex anions , herbicides[13], vitamins[14]Insecticides[15,16], pharmaceuticals[17].These layers have the capability to capture active molecular such as phosphorus organic insecticide chlorpyrifose , in the form anion bonded between the layer to form Nano crystalline hybrid organic – inorganic , where the layer represent the host part but the packed anion represent the guest .

MATERIAL AND METHOD

Production of layer by co-precipitation method

The normal layer was synthesized via a Co-precipitation method. A mixed dissolved weight of 2.5 gof $Mg(NO_3)_2$. $6H_2O$and 2.01g of Fe $(NO_3)_3.9H_2O$ when R=2/1 in 100 mLethanol, solution at 44 C^O with stirring and the postponement for 18 hours . The solution pH was adjusted at 10 for theMg/Fe-LDHs bydrop wise addition of 2M NaOH solution during the instillation of the mixed solution. divide the precipitated the washing by water and ventilation at 40 temperature[18].

The hybrid nanocompound prepare

Indirect Ion Exchange

Dissolved 2.5g of $Mg(NO_3)_2$.$6H_2O$, 2.01g $Fe(NO_3)$.$9H_2O$ in 100 mL ethanol when molar ratio R = 2/1 , adjusted the PH at 10 by 2M NaOH ,step by step addition 500ppm of chlorpyrifose dissolved in 100 mL ethanol .incubate the solution in water bath with shaking at 44^0C for 18 hours , divide the precipitated the washing by water and ventilation at 40^0C , and the same condition the hybrid nano compound in aqueous medium[19] .

Direct ion exchange

Dissolve 0.4g of layers which plan by Co-precipitation method.In 100mL ethanol, step by step addition 500ppm of chlorpyrifose dissolved in 100 mLethanol, adjusted the PH at 5.5 by 2M NaOH. keep warm the solution in water bath with shaking at 44^0C for 18 hours, divide the precipitated the washing by water and ventilation at 40 temperatures, and the same condition the hybrid nano compound in aqueous medium[19].Where the layer represent the host part but the packed anion represent the guest as shown in fig1

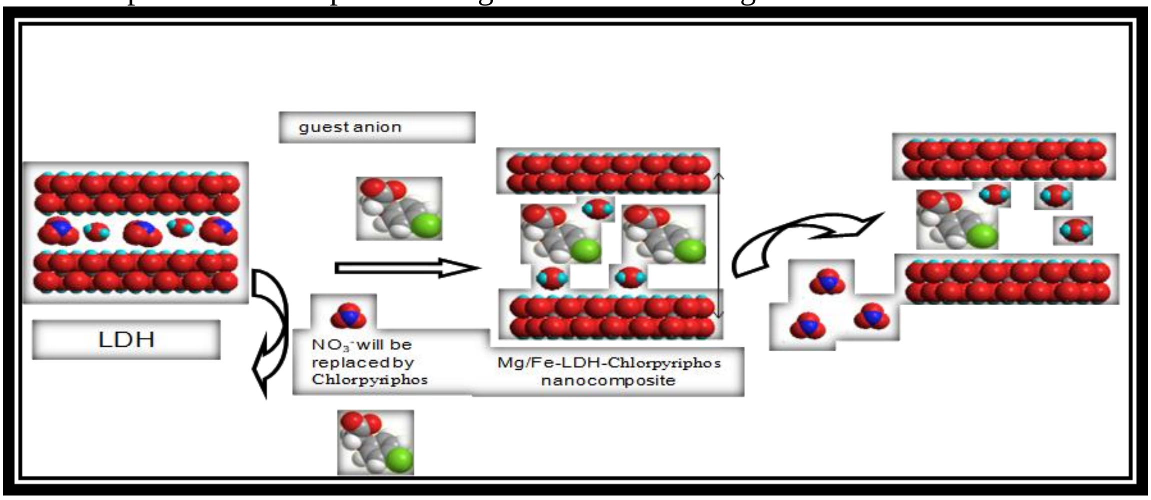


Fig 1. demonstrates the intercalation anion chlorpyrifose in Mg/Fe–LDHs

Effect diffusion rateon the kinetic Controlled Release of chlorpyrifose

The study effect diffusion rate aniononControlled release chlorpyrifose from host Mg/Fe-LDHs to dilute solution 0.5M from Na_2CO_3 , Na2SO4and Na_2PO_4 then measure the release concentration of anion ion by U.V ray at the λ_{max}= 260 nm bythefollowing Bhaskarequation[20]

$$-\ln\left(1 - \frac{Ct}{Cf}\right) = K_d t^{0.5} \quad \ldots\ldots (1)$$

Study the active sites of the hybrid nanocompounds

Thestudy the active sites of all the hybrid nano compounds ready by Direct and indirect ion exchange method in ethanol medium and aqueous medium.

RESULT AND DISCUSSION

The observation of the values of the active sites of hybrid nanocompound prepared by direct ion exchange method and indirect ion exchange method in aqueous and alcoholic mediums, it is clear to us the anionic (insecticide) is slowly entering between layer double hydroxide LDH prepared in aqueous medium in the process of composition the hybridnanocompound compared to hybrid nanocompound prepared in an alcoholic medium. The number of active site of the hybrid nanocompound prepared by indirect ion exchange methods more comparable to hybrid nanocompound prepared by direct ion exchange method.

Table 1. Active sites number for hybrid nanocompound prepared

R	x	1-x	$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n}_{(x/n)}.YH_2O]^{x-}$	Active sites number Number Molecular for the anionic(chlorpyriphose)			
				hybrid nanocompoundprepare in ethanol medium		hybrid nanocompoundpreparein aqueous medium	
				prepare by direct ion exchang	prepare by indirect ion exchang	prepare by direct ionexchang	prepare by indirect ion exchang
2	0.697	0.307	$[Mg^{2+}_{(0.697)}Fe^{3+}_{(0.307)}]^{+}$ $[\mathbf{chlorpyriphose}_{(0.307)}]^{-}$ Y H_2O	$84x10^{16}$	$120x10^{16}$	$21.08x\ 10^{16}$	$105x10^{16}$

Atomic Force Microscopy (AFM)

Figures (2,4,6) explains was characterize by (AFM) for the two and three-dimensional image to l Mg/Fe NO_3–LDH and hybridnano compound Mg/Fe –chloropyrophose – LDH

Fig. (2a) the image shows two-dimensional layer before intercalation process where molecular clusters appear whilefig.(2b) were show the three-dimensional image elevated molecular assembly which has limitsrange (0.39-0.61nm) ,shows the diameters , sizes and aggregation of the molecular in layer Mg/Fe NO_3–LDH[19,21].

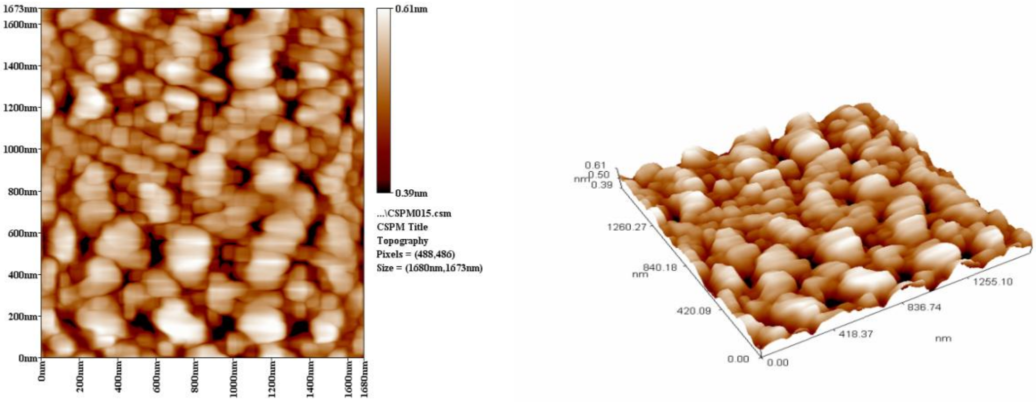


Fig 2. AFM image of layer (a) two- dimensional image(b) three- dimensional image

Table 2 and figure 3 the standard diameters of particle size 87.5nm before the intercalation process anion . The process of prepare layer to get nano compound with diameters between than (65-120)nm , and the high percentage of those nano compound is 14.29% molecules to the diameter 90nm ,between the low ratio is 4.49% molecules with a diameter of 65nm.

Table 2. Diameters, sizes and aggregation of the molecular in Mg/Fe NO_3–LDH

SPM Scanning Probe Microscope

Avg. Diameter:87.50 nm

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
65.00	4.46	4.46	85.00	9.82	41.96	105.00	6.25	84.82
70.00	10.71	15.18	90.00	14.29	56.25	110.00	8.04	92.86
75.00	8.04	23.21	95.00	13.39	69.64	115.00	6.25	99.11
80.00	8.93	32.14	100.00	8.93	78.57	120.00	0.89	100.00

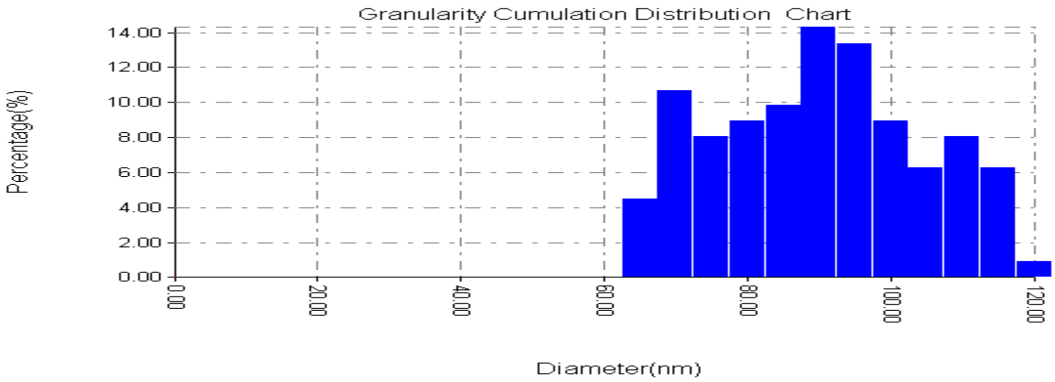


Fig 3. Percentage of diameter of LDHs.

Fig. (4a) the image shows two-dimensional of Nano compound make by indirect ion exchange method showing molecular clusters of spherical shapeswhilefig. (4b) were show the three-dimensional image for section of the surface of the Nano compound Mg/Fe –chloropyrofse -LDH showing the high of the molecular clusters that are within limits(0.28-1.35),suggesting[19,21,22]the make of Nano compound from insecticide chloropyrofse and Mg/Fe –LDH of particle size of Nano compound.

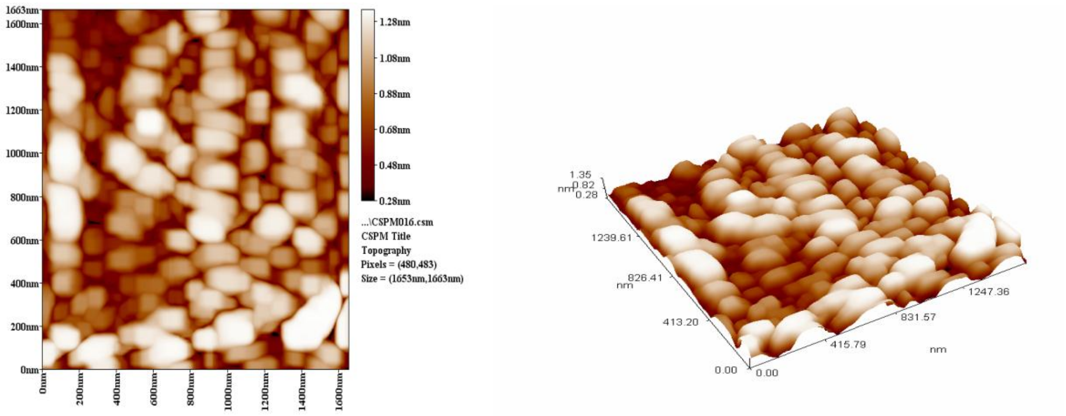


Fig 4 . AFM image of Mg/Fe –cloropyrofse-LDH (a) two- dimensional image(b) three-dimensional image

Table 3 and figure 5 the medium diameters of nanohybrid compound prepared by indirect ion exchange method 108.08nm. The method of prepare hybrid nano compound to get nanoparticles with diameters between than (60-140)nm , and the maximum percentage of those nano molecules is 26.47% molecules to the diameter 130nm ,between the lowly ratio is 2.6% molecules with a diameter of 60nm

Table 3. Diameters, sizes and aggregation of the molecular in Mg/Fe clorpyrifose –LDH.

SPM Scanning Probe Microscope

Avg. Diameter:108.08 nm

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
60.00	2.63	2.63	90.00	7.89	18.42	120.00	15.79	65.79
70.00	2.63	5.26	100.00	7.89	26.32	130.00	26.32	92.11
80.00	5.26	10.53	110.00	23.68	50.00	140.00	7.89	100.00

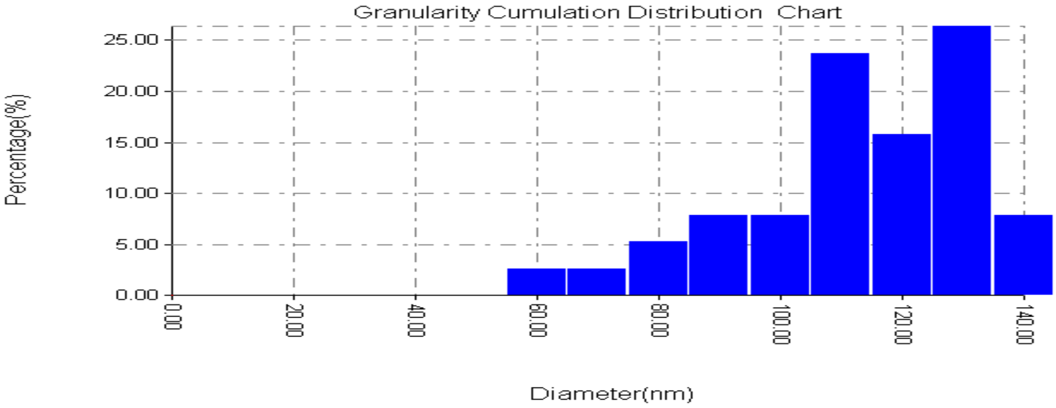
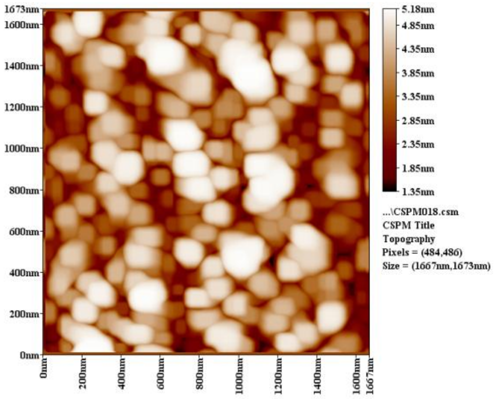


Fig 5. Percentage of diameter of hybrid nano compound make by indirect ion exchange method.

Fig. (6a) image appeared two-dimensional of hybrid nano compound ready by direct ion exchange method showing molecular clusters of spherical shapeswhilefig.(6b) were appeared the three-dimensional image for section of the surface of the hybrid nano compoundMg/Fe – chloropyrifose – LDH showing the high of themolecular clusters that are within limits (1.35-5.18),suggesting[19,21,22] the produce of nano compound from chloropyrifose and Mg/Fe –LDH particle size of hybrid nano compound.



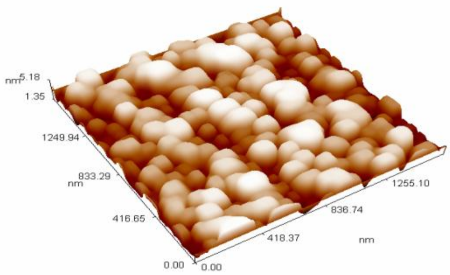


Fig 6. AFM image of(Mg/Fe –cloropyrifose-LDH) make by direct ion exchange method(a) two- dimensional image(b) three- dimensional image

Table 4 and figure 7 the medium diameters of nanohybrid compound ready by direct ion exchange method 112.05nm. The route of prepare nanohybrid compound to obtain nanoparticles with diameters between than (60-180)nm , and the maximum percentage of those nano compound is 15% molecules to the diameter 120nm ,between the lowly ratio is 1.6% molecules with a diameter of 60nm.

Table 4. Diameters , sizes and aggregation of the molecular in Mg/Fe-cloropyrifose –LDH prepared by direct ion exchange method

Avg. Diameter:112.05 nm

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
60.00	1.67	1.67	110.00	10.00	45.00	160.00	6.67	95.00
70.00	6.67	8.33	120.00	15.00	60.00	170.00	3.33	98.33
80.00	10.00	18.33	130.00	8.33	68.33	180.00	1.67	100.00
90.00	11.67	30.00	140.00	11.67	80.00			
100.00	5.00	35.00	150.00	8.33	88.33			

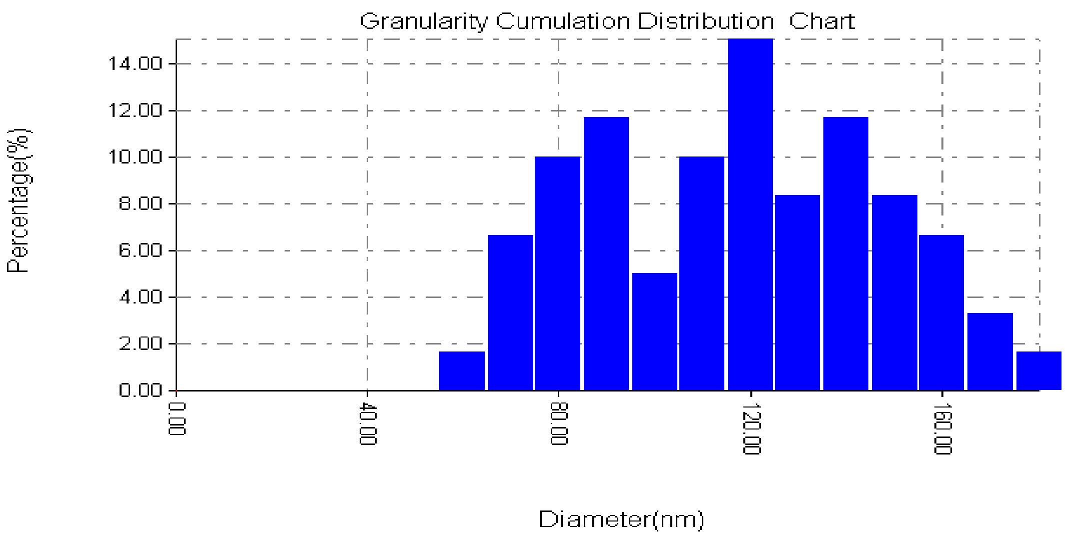


Fig 7. Percentage of diameter of hybrid nano compound make by direct ion exchange method.

Figures (8,9) explains FT-IR spectrum of layerMg/Fe –LDH and Ni/Al – chloropyrofse - LDH

Where there is a difference in location and number of peaks between layer double hydroxide and the Nano compound, this indicates the success of the process of preparing the composition of the Nano compound.

The layersMg/Fe – NO_3-LDH the peaks to υ_{O-H} stretches at 3454cm^{-1} [23] , the NO3 gives an absorption peak at 1390 cm^{-1} in the layers [24], peaks to υ_{Mg-O}at 437 cm^{-1} and , absorption peaks to υ_{Fe-O} at 578 cm^{-1}in layers[25] , see the table 5 and fig 5 .

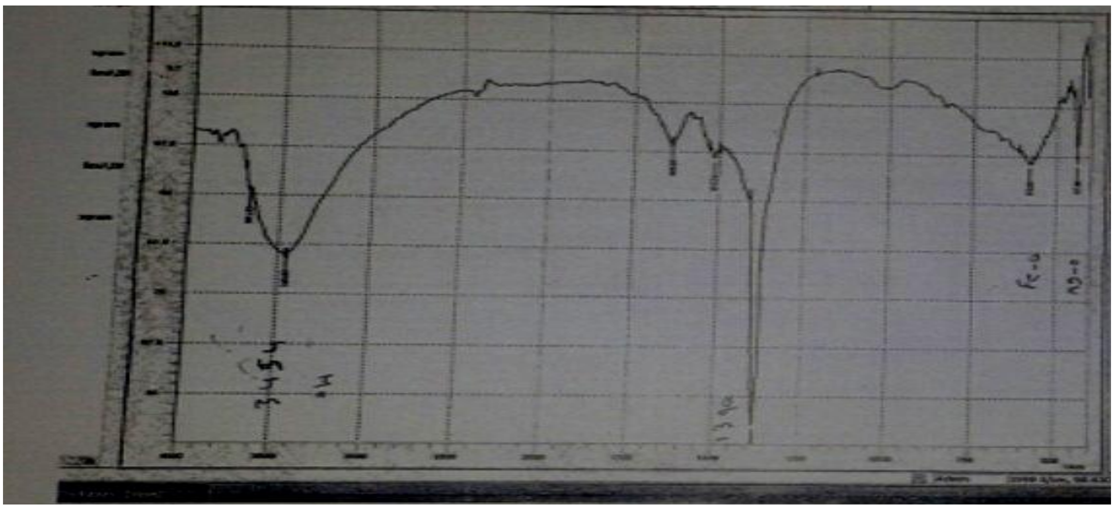


Fig 8. FT-IR spectrum of Mg/Fe– NO_3-LDH

Frequency	Hybrid compound	LDH
υ_{O-H}	3483	3454
υ_{C-H} Aliphatic	2362	------
C=N Aromatic	1690	------
C=C Aromatic	1516 , 1464	-----
υ_{NO3}	1381	1390
$\upsilon_{P-O-Aryl}$	1250	-----
$\upsilon_{p-o- Alkyl}$	1030	-----
υ_{Ar-Cl}	690	-----
υ_{Mg-O}	434	437
Fe-Oυ	586	578
$_{C-H}\delta$ Aromatic	669	-----

The Nano compound Mg/Fe-chloropyrofse –LDH appear many one more peaks this indicate success for intercalation an ion chloropyrofse between the layers, absorption peaks of υO–H stretch in the 3483cm^{-1} , The absorption peaks of aliphatic $\upsilon_{C–H}$ stretch in 2362cm^{-1}, absorption peaks of $\upsilon_{C=C}$aromatic praise at 1516cm-1,1464cm $^{-1}$[26,] absorption peaks of $\upsilon_{C=N}$ stretch ataromatic1690 cm^{-1}, The NO3 give an absorption peak at 1381cm−1 in LDHs[24] , absorption two peaks of $\upsilon_{P-O-alkyl}$ and $\upsilon_{P-O-aryl}$at 1030 cm^{-1} , 1250 cm^{-1} . [26],but peak at the 690cm^{-1} it is Cl-aryl ,the peakδ_{C-H}aromaticpaper at 669cm^{-1} , absorption peaks to $\upsilon_{Mg–O}$ at434 cm^{-1} in layers and , absorption peaks to $\upsilon_{Fe–O}$ at 586 cm^{-1}in layers[25] see the table 5 and fig 6.

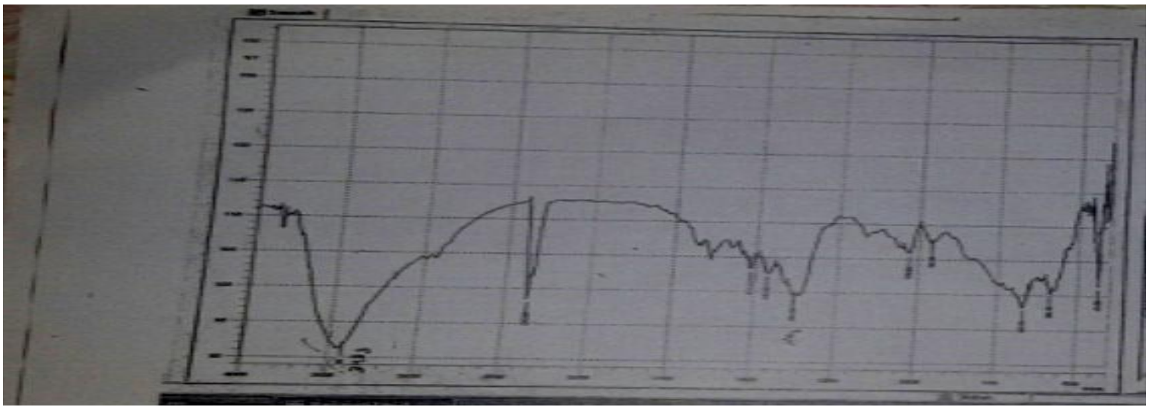


Fig 9. FT-IR spectrum of hybridnano compound

Table 5.Peaks of theMg/Fe – NO_3-LDH and the hybrid nano compound

Diffusion rate effect study chlorpyrifoseon Kinetic of controlled release

In order to study the Diffusion rate effect on Kinetic of controlled release of anionic chlorpyrifose from the layer of the hybrid Nano compound during the ion exchange process in the different aquatic for Bhaskarequation[20]:-

$-\ln(1 - \frac{Ct}{Cf}) = k_d t^{0.5}$ ….. (1)

Ct = concentration at each time by ($mg . L^{-1}$)
Cf = concentration at equilibrium by ($mg . L^{-1}$)
k_d= Diffusion rateconstant (min^{05})

Through the note figures (10) A,B and C) and (11) A ,B and C) of values $-\ln(1 - \frac{Ct}{Cf})$ for values ($t^{0.5}$) and notevalue (r^2) , (k_d) and time for Diffusion in table 6 for the resulted diapered presence of disturbance for inter and out the ion through the releases process that the effect on Kinetic of controlled release of anionic chlorpyrifose from the layer of the hybrid nano compound during the ion exchange

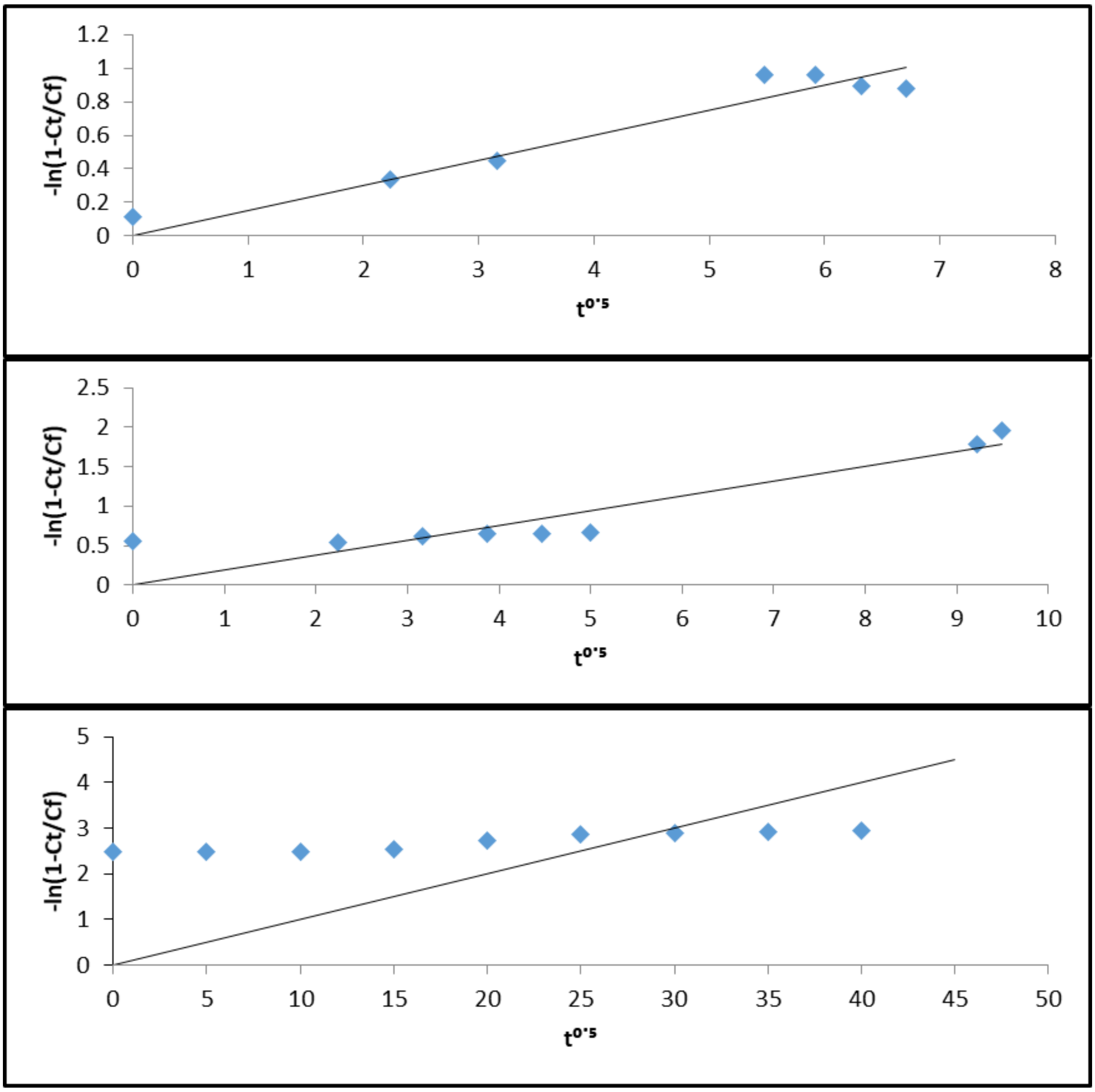


Fig10. Bhaskar equation for the Diffusion rateeffect anion on Kinetic of controlled release from nano compound prepared byindirect ion exchange indifferent mediums, (A) carbonate (B) phosphate (C) sulphate

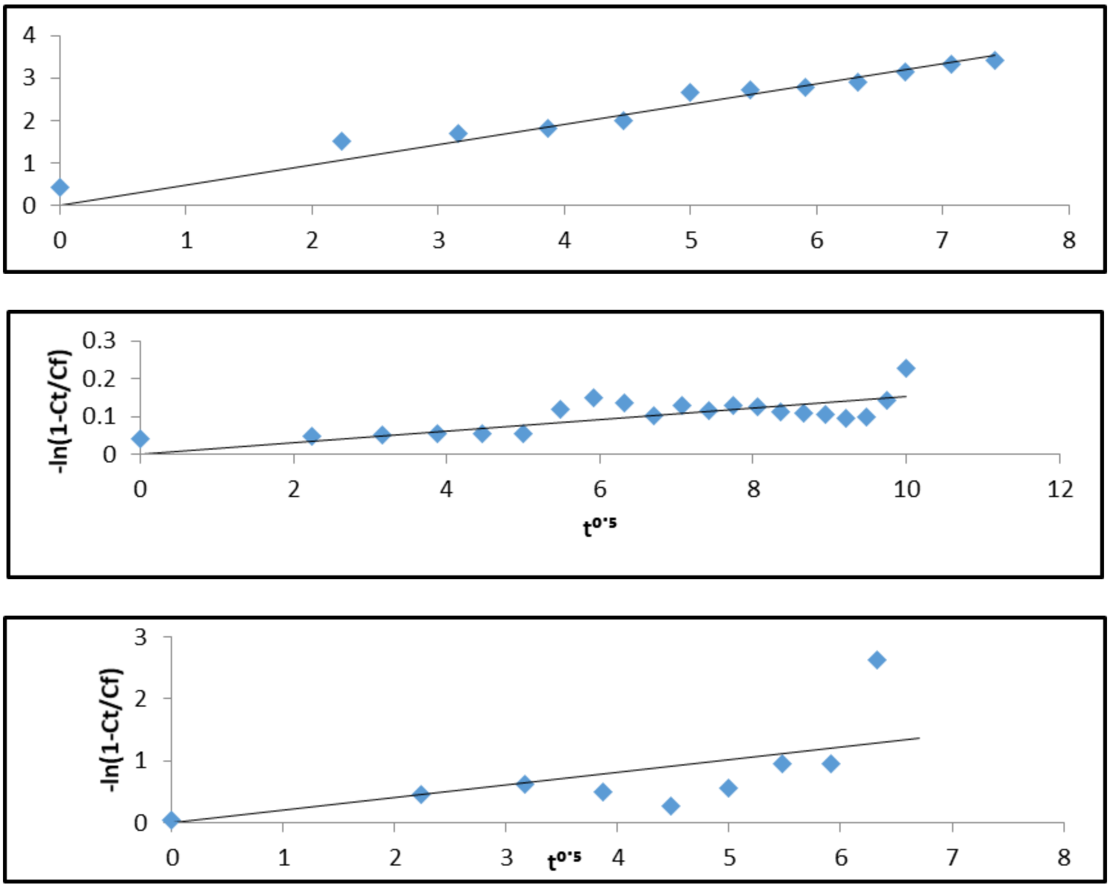


Fig11. Bhaskar equation for the Diffusion rate effect anion onKinetic of controlled release from nano compound prepared bydirect ion exchange indifferent mediums , (A) carbonate (B) phosphate (C) sulfate

Table 6. value for Diffusion rateconstant by ion exchange method from the nano compound layer prepare in ethanol by direct and in direct ion exchange in (0.5M) sodium carbonate ,sodium phosphate and sodium sulfate **Nano compound prepare by indirect ion exchange**					
k_d ($min^{-0.5}$)	**Time for Diffusion (min)**	**r^2**	**Concentration Mol . L^{-1}**	**Sample**	**R**
0.180	**45**	**0.922**	**0.5**	**Na_2CO_3**	**2**
0.173	**90**	**0.802**		**Na_2PO_4**	
0.100	**100**	**-0.419**		**Na_2SO_4**	
Nano compound prepare bydirect ion exchange					
0.488	**40**	**0.935**	**0.5**	**Na_2CO_3**	**2**
0.180	**85**	**0.874**		**Na_2PO_4**	
0.170	**90**	**0.43**		**Na_2SO_4**	

When we note the value for the Diffusion rateconstant (k_d) and (r^2) at figure (7 ,8) result in different medial is as the following
Na_2CO_3> Na_2PO_4> Na_2SO_4.

The causes is that carbonate ion more electro file compare with sulfate ion and the figure of carbonate is triangular so is easily intercalation with LDH than phosphate and sulfate ion which is tetragonal. The Diffusion rate effect for hybrid nano compound prepare bydirect ion exchange method be more comparable to hybrid nano compound ready by indirect ion exchange method, and the Diffusion rate effect for hybrid nano compound prepare in alcoholic medium ofless disturbance comparable to hybrid nano compound prepared in aqueous medium because of the nature of the ion bond between the nano compound layer.

CONCLUSION

The result appear can be synthesis hybrid nano compound by intercalation of insecticide chlorpyriphosas anion between Mg /Fe double layer hydroxide by two method direct ion exchange and indirect ion exchange.Study control release by direct ion exchange process to limit the problem of environment pollution that effect onhealthy human. Where the Diffusion rate effect on kinetic control release at 0.5M from sodium carbonate, sodium phosphate and sodium sulfate, the highly Diffusion rate effect for hybrid nano compound prepare bydirect ion exchange method in aqueous medium. The study number of active sites of hybrid nano compound in the aqueous and alcoholic medium by direct and indirect ion exchange process showed that is better for preparation in alcoholic medium and that the number active sites is higher in hybrid nano compound prepared by indirect ion exchange fromprepared by direct ion exchange.

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