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SORPTION OF METHYLENE BLUE DYE THROUGH SYNTHESIZED AND MODIFIED PHENYL PYRUVATE ZN AL LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

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Abstract
Water pollution has been a major threat to our lives for a long time. This prevalent problem has become the cause that is jeopardizing the marine life as well as our health. It occurs when hazard and toxic substances spilt into river, lake, ocean or stream that degrade the water quality and rendering it lethal to the life. To mitigate of this challenging issue, a biocompatible compound, Zn Al Layered Double Hydroxide (LDH), has been designed and modified through the co-precipitation method. This synthesized compound was modified with phenyl pyruvate to improve its functionality. This synthesized and PPA-modified Zn Al LDH was subjected to characterization *via* FTIR, SEM, EDX, and XRD, which endorsed the intercalation of guest ions. Moreover, PPA-modified Zn Al LDH was applied for the sorption of organic dye Methyl Blue from water and optimized various parameters, including pH, dosage, volume, time, and temperature, and found that the best sorption was found at pH 10 with a dosage amount of 0.25g and a volume of 30 ml at 40 ^{o}C within 100 min. The adsorbent capacity was calculated at 92 mg/g. In addition, it was perceived through kinetic study and sorption isotherm that the pseudo-second-order equation is more applicable, which indicated that the sorption might be physio-sorption. Conclusively, the studied parameters and various isotherm models explained that PPA-modified Zn Al LDH has the ability to sorp the organic dye and can be utilized industrially.

Key words: Synthesized, Modified. Phenyl pyruvate, Layered Double Hydroxide (LDH), Water pollution

1.0. Introduction
Nanotechnology is comparatively a new field of science and technology studies tiny objects range from (0.1–100 nm). This technology has various positive qualities including biogenic synthesis of nanoparticles (NPs), it is cost effective, minimal threat to environment as well. There are numerous therapeutic applications of such nano composites which have impartial overview of present understanding of NPs [1]. The materials that have at least one dimensional externally and have the size range between 1-100nm are termed as nano materials. These materials are naturally occurring, but can be achieved by different methods [2]. Layered double hydroxide are also termed as anionic clays resemble to a natural compound hydrotalcites (Mg_6Al_2 $(OH)_{16}CO_3$)**.** The standard formula for these compounds can be explained as M^{2+}_{1-x} M^{3+}_{x} $(OH)_2](A^{n-})_{x/n}$ yH_2O where,M^{2+} represents the *di-*

valent cation like (Zn, Mg, Fe, Ni, Co.) ,M^{3+}shows the *tri*-valent including **(**Al, Ga, Fe so on) and A^{-n} describes the intercalated anion which can be , nitrates, carbonates, chloride [3]. These are also as the positive charged layers having OH on the edges sharing octahedral geometry akin to brucite Zn $(OH)_2$ in which the neutralized hydrated anions occupied between the interlayer space [4]. These compounds having properties like interlayer anion portability and high surface area can be implemented as catalysts, anion exchangers, in sorption process, in the application of medicines, pharmaceuticals, polymerization and in environmental cleaning by ion exchange [5,6].

Pollution has been a serious life threating issue for the living organisms since long. Especially organic dyes, toxic metals and other chemical compounds are considered dangerous water pollutants that need to be removed or at least minimized. However, they can be eliminated from the environment in a number of ways, mainly based on biological, chemical and physical techniques [7]. Most of the traditional chemical, physical and biological methods of pollutant ions contaminated water disadvantages include high costs and significant energy usage [8]. Therefore, there is a dire need to find novel and extra resourceful ways to treat contaminated wastewater. The material consistency, stability, environmental costs and current atmospheres, recyclability, selective absorbability as well as type of ions in wastewater are the factors to consider that the material can be used for removal of pollutant ions. Among various materials LDHs are reported for their significant sorption behavior towards various pollutant ions [9]. The amalgamation of Di and Trivalent cations in LDHs proofs beneficial to sorption of heavy metal and other pollutant ions, therefore the sorption studies of Zn Al-LDH is the most prevalent topic in research. The capacity of LDH containing *di* and *tri*-valent cation has also been studied earlier for instance, the intercalation of triethylenetetramine along with Li Al-LDH and its utilization to absorbed Nd^{3+} and Sr^{2+} ions [10].

Methylene blue (MB), is given **Figure-1** classified as an organic dye that has a variety of applications comprising of wools and cotton dyes, paper coloring, hair coloring as well as for coating paper stock. M. B is an exemplary compound that can remove the dyes as well as organic pollutants from aqueous solutions. Although M.B is less noxious, yet, it can cause some injurious effects on human beings. Frequent use of M.B dye and untreated discharge in fresh water is very threatening issue now a days this dye can affect the eyes of human and animals. If it is ingested, it may arouse gastrointestinal tract that cause nausea, diarrhea. It may be the reason of dyspnea, tachycardia, cyanosis and convulsions *etc* [11,12].

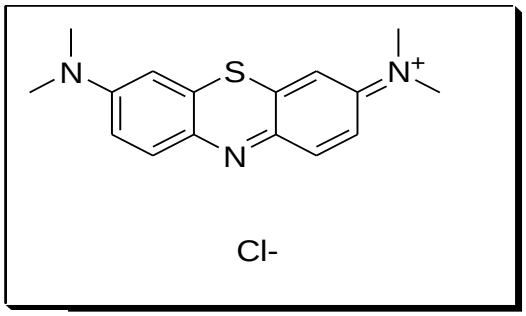


Figure 1 Chemical Structure of Methylene Blue

Being harmful for humans, it is mandatory to remove it from aqueous solutions. Various methods have been established for the decoloration process, including adsorption, reverse osmosis, precipitation and ion exchange, amid these methods, adsorption is frequently employed due to its inexpensive cost and simple technique [13].

2.0. METHODS AND MATERIALS

All the chemicals [Al $(NO_3)_3.9H_2O$] and [Zn $(NO_3)_2.6H_2O$], Phenyl pyruvic acid, NaOH, HCl and HNO_3were purchased from Sigma-Aldrich.

2.1. Procedure for the Synthesis of Zn /Al - LDH

This compound was synthesized by following the procedure in literature [14]. For that purpose, a *di*-valent cation Zn $(NO_3)_2$•$6H_2O$ (8 g, 0.03mol) and a *tri*-valent cation Al $(NO_3)_3$•$9H_2O$ (15g, 0.05mol) were mixed in a ratio of 1:2 and dissolved in deionized water for the formation of a clear solution. Consequently, aqueous sodium hydroxide was taken (16 g, 0.4 mol) and kept under constant stirring till pH 10 to complete precipitation. The acquired Zn -Al- LDH was then stirred for 24 hrs at 65°C. Finally, the obtained Zn Al-LDH filtered off and distilled water was utilized for washing several times and the leftover solid was dried in an oven at 80°C to overnight.

2.2. Procedure for the Modification Zn /Al-LDH with Phenyl pyruvate

Firstly, the amount of synthesized Zn/Al- LDH taken as 5g and then added 4g of PPA in it. Secondly, Stirred for 6h. After that filtered that compound and then dried at 65°C. Lastly, the modified Zn /Al - PPA -LDH was obtained.

3.0 Procedure for sorption of Methylene Blue Dye from Water by Using PPA Modified Zn/ Al LDH

The method for the sorption of organic dye Methylene blue (M.B) from water was developed with specific parameters that are being explained with detail in supplementary file.

4.0. Results and Discussion

4.1 Chemistry of Modified LDH

According to previous literature [1-5] LDHs have layered double structure having nitrate ions and some water molecules between the layers. Following the literature [14], we have synthesized Zn Al and modified it with the treatment of Phenyl pyruvate anions. The **Figure –2** shows that the PPA anions incorporated in between the layers with the substitution of nitrate ions as given below:

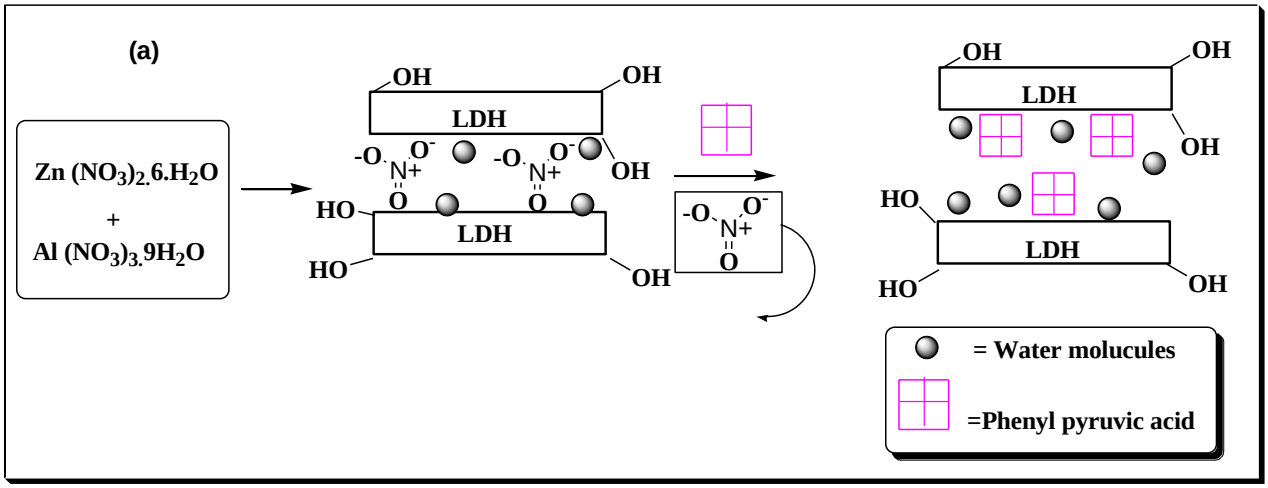


Figure -2 The mechanism of the PPA modified Zn Al LDH

4.1. CHARACTERIZATION TECHNIQUES

PPA modified Zn Al LDH was characterized *via* FTIR, SEM, EDX, XRD and TGA. All the results of characterizations have been discussed below.

4.1.1 FT-IR Spectral Analysis of Phenyl pyruvate modified Zn Al - LDH

Following in **Figure-3** (**a**) peak appeared at 3357 cm^{-1} was allocated for –OH stretching vibration due to the existence of –OH between layers or H_2O molecule. The weaker absorption band at around 2460 cm^{-1} was due to the aliphatic C-H stretching. Moreover, the peaks appeared at 1353 cm^{-1} was showing the presence of $–NO_3$ group into the layer. The band below 1000 cm^{-1} indicating the presence of M-O-H vibrations. In comparison to (**b**) the band seemed at approximately 3460 cm^{-1} was owing to the

network of layered bonded with hydrogen –OH and water molecules. The peaks appeared at 1450-cm^{-1} - 1555 cm^{-1} nominated for carbonyl group as well as due to the replacement of nitrate groups with some guest anions as stretching vibration of COO^- citrate anions. The band at the position at 1172 cm^{-1} were due to C-O-C stretching respectively.

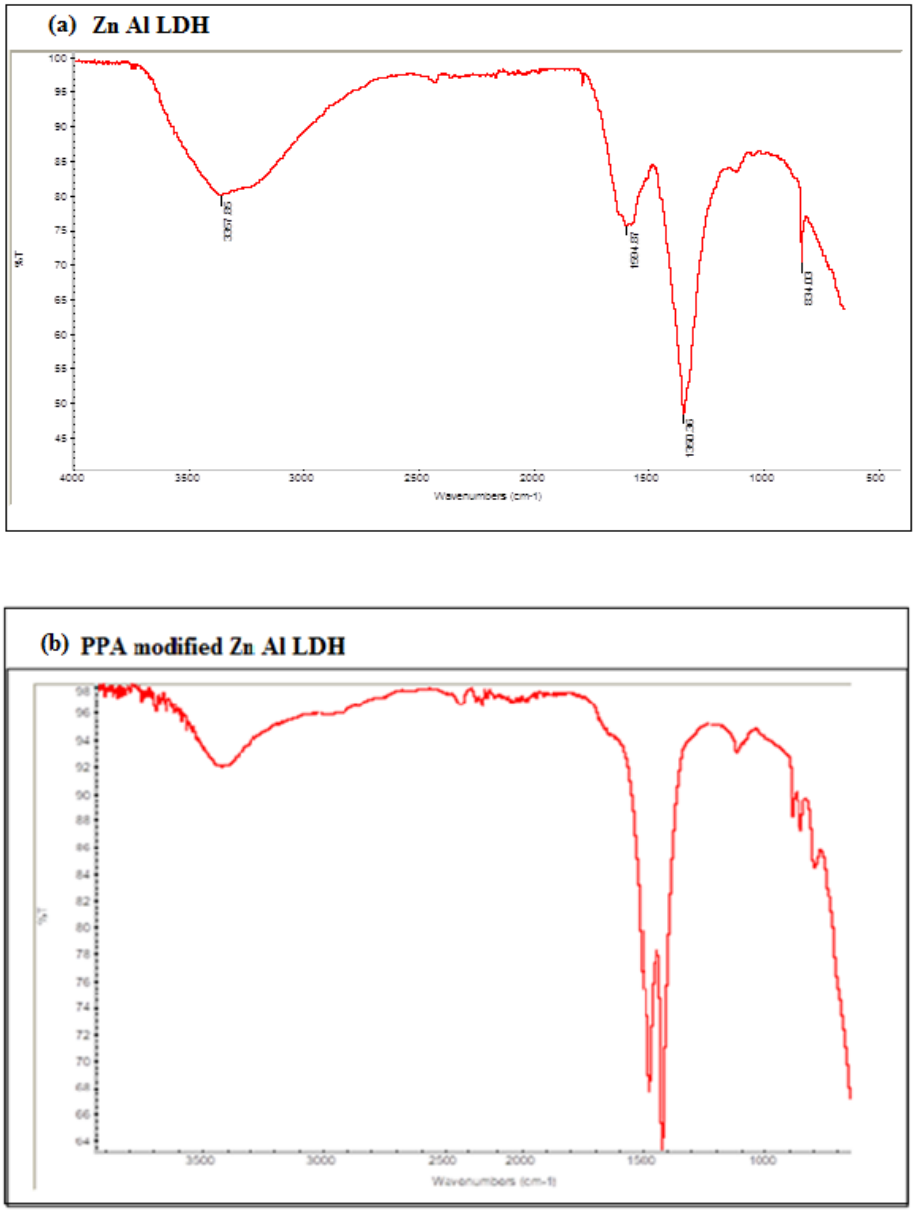


Figure 3 FT-IR of (**a**) Pure Zn-Al LDH (**b**) Phenyl pyruvate modified Zn Al-LDH

4.1.2 XRD Analysis

The XRD analysis was used to notice the crystal structure of the provided samples through Bragg's Law Eq (1) [15] which was applied for the calculation of basal spacing (d) of LDH layers:

$$n\lambda = 2dsin\theta \quad (1)$$

Where n = reflection coefficient and is equal to 1

λ = wavelength and it is akin to 1.51418 Å

θ = Bragg- Brentano geometry

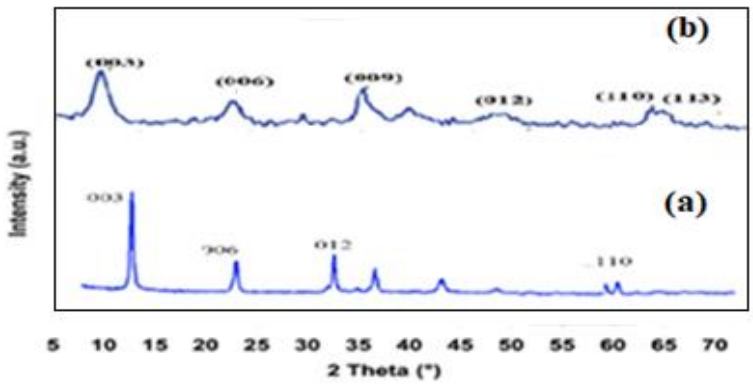


Figure 4 The XRD pattern of (a) pure Zn Al-LDH (b) Phenyl pyruvate modified Zn Al-LDH

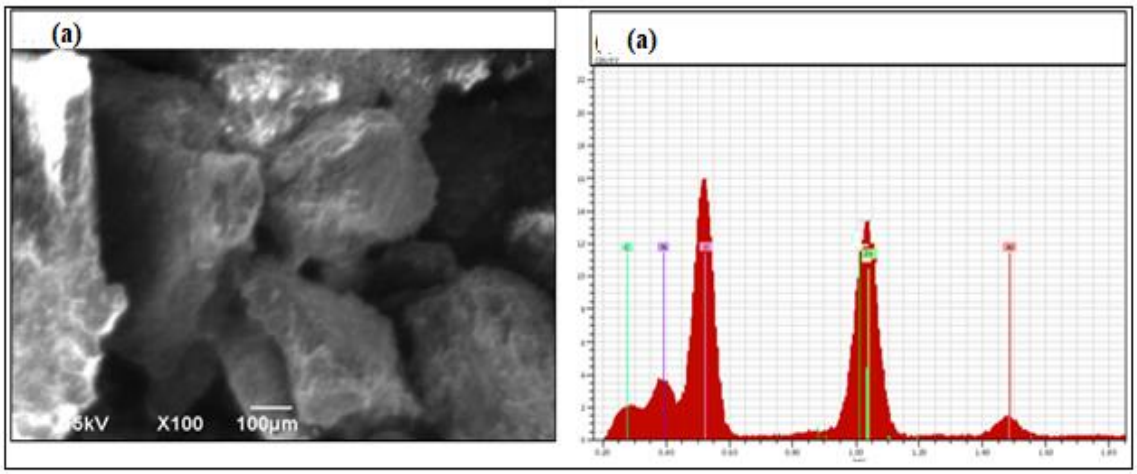
Following the equation (1) in **section-4.1.2** as mentioned above the XRD analysis for **Figure-4** (**a**) Pure Zn Al LDH at 2θ equivalent to 7.41, 3.82, 2.63, 1.54 according to peak intensity at (003),(006) and (012),(010) respectively. The d-spacing values of (**b**) PPA modified Zn Al LDH at the positions (003), (006), (009), (012) The d-spacing values were found to be 9.81, 4.23, 2.79, 3.69 and 1.93. Comparatively, 2θ values of Pure Zn Al LDH and PPA modified Zn Al LDH were shifted from lower to high value, which indicated the invasion of large size anions amid the layers consequently widened the space as shown in the **Table-1** below:

Table -1 Interlayer space values 2θ for (**a**) Pure Zn Al –LDH (**b**) Phenyl pyruvate modified Zn Al - LDH

S. No	Peak Intensity	Interlayer spaced-Spacing(nm) (a)	Interlayer spaced-Spacing(nm)(b)
1.	003	7.41	9.81
2.	006	3.82	4.23
3.	012	2.63	3.21
4.	110	1.54	1.93

4.1.3 SEM and EDX Analysis

The Surface study and elemental composition of the compounds were evaluated by Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray analysis (EDX) respectively. **Figure-5** shows the topography of (**a**) pure Zn Al-LDH (**b**) PPA modified Zn Al-LDH which has been described below.



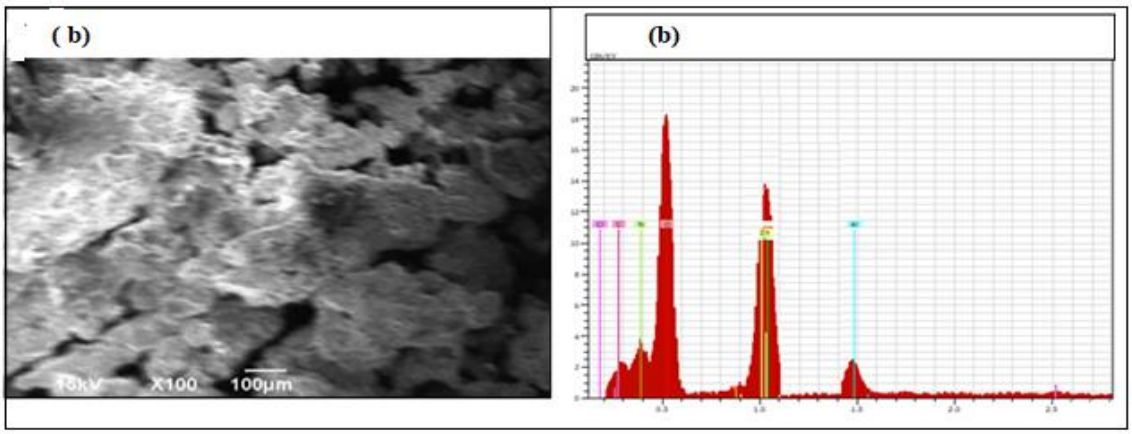


Figure 5 SEM and EDX **(a)** Zn Al -LDH **(b)** Phenyl pyruvate modified Zn Al-LDH

Here, the topographic changes were observed through SEM images in **Figure-5** (**a**) showing the plate like structure of pure Zn Al-LDH and **(b)** after the intercalation of phenyl pyruvate anions. The comparison of morphology with pure Zn Al–LDH, confirms the effect of guest ions intervention. Moreover, the elemental compositions of (**a**) and (**b**) also confirm the presence of intercalated anions. These results were also confirmed by FTIR as described earlier.

5.0 Sorption of Organic Dye Methyl Blue (M.B) from Water by Phenyl Pyruvate modified Zn Al LDH

5.1 Calibration of Methyl Blue (M.B)

Calibration of M.B **Figure -6** was studied by preparing five solutions of concentration range from 2ppm to 10 ppm. Linear calibration curved was obtained with regression equation y =0.217x + 0.0826 and $R^2 = 0.989$.

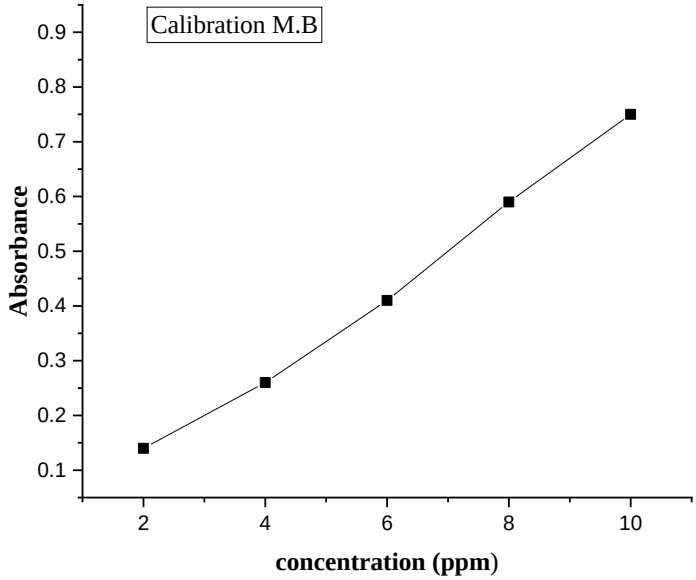


Figure 6 Calibration of Methylene blue

5.1.2 Optimized Parameters of Adsorption

Adsorption technique was used to optimize various parameters like pH, volume, dosage of sorbent, sorption kinetics, equilibrium and thermodynamics studies, which effect the sorption of dye from

water under UV radiations. The percentage sorption of the compounds was calculated by using the following equation-2 [16]:

$$\% \text{ Sorption} = C_i\text{-}C_f/C_i \times 100 \qquad \text{[Eq-2]}$$

5.1.3 pH effect

pH is supposed to crucial variable which affects the exterior activity. In the **Figure -7** the pH was studied in acidic, basic and neutral medium from range 3, 6,7,8,9 and 10. It was observed the increase in % sorption from pH 3 to 9 and then attained the equilibrium till pH 10 and pH 10 was optimized for further study. The increment in % sorption is due to increase in protonation.

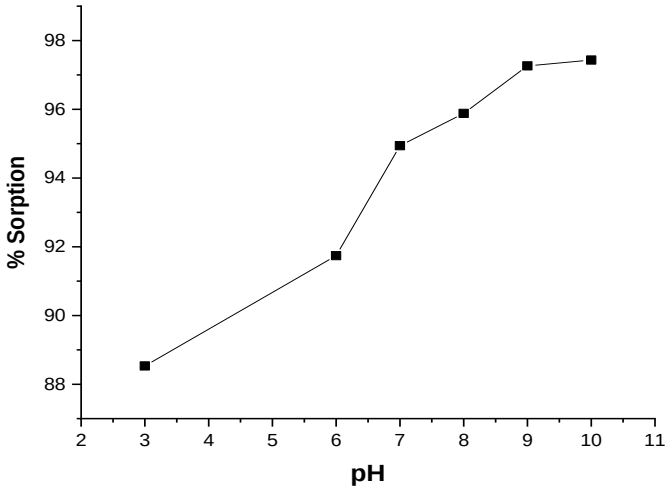


Figure 7 pH effect of M.B sorption onto PPA modified Zn Al LDH

5.1.4 Dosage effect

The LDH dosage consequence for the sorption of PPA modified Zn Al LDH was studied by taken different amount from the range of 0.1g, 0.15g, 0.2g, 0.25g and 0.3g. Sorption was augmented with the increment of LDH amount up to 0.25 and then the capacity of sorption remained constant. As shown in the **Figure -8** the reason behind is that due to the accessibility of more sorption sites and at higher sorbent amount there are not enough amount of M.B to inhabit the active positions and the sorption attained the equilibrium. Therefore 0.25g was selected as optimum dosage for further study.

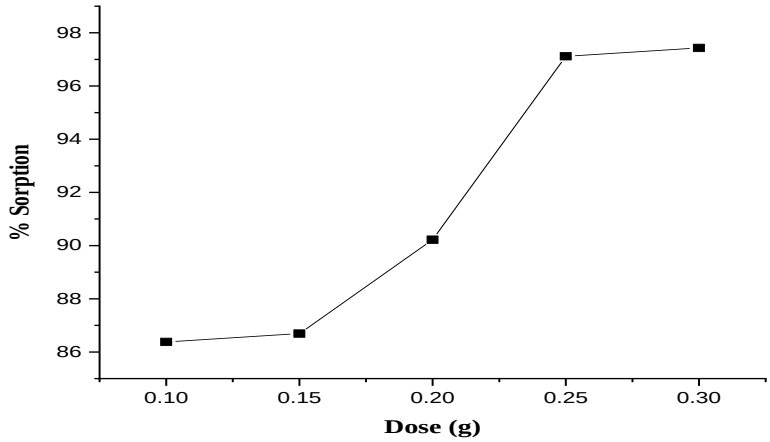


Figure 8 Dosage effect of LDH for the removal of M.B through PPA modified Zn Al LDH

5.1.5 Volume effect

The volume outcome of methylene blue on % sorption by phenyl pyruvate modified Zn Al LDH was observed and is shown in **Figure-9** the % sorption was started increasing from 10ml to 30ml and then started decreasing till 60ml and volume 30 ml was optimized for further study. The reason of inclination of % sorption that there might be more active sites on surface but as the volume increases the shortage of active sites causing declination in % sorption.

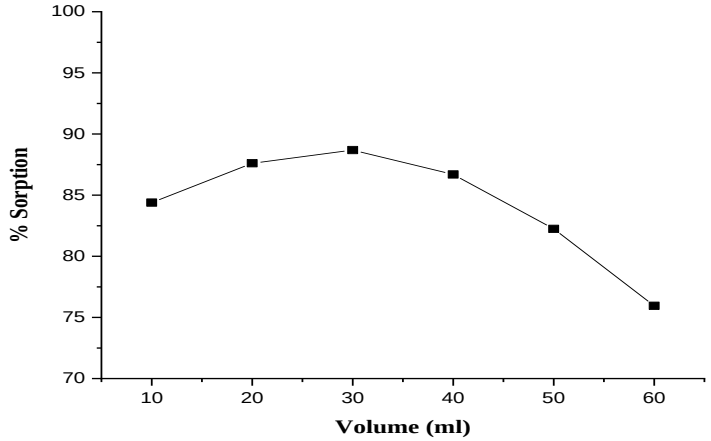
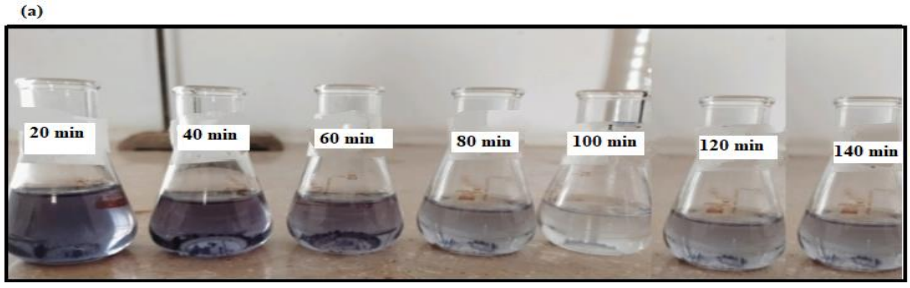


Figure 9 Volume effect of M.B sorption onto PPA modified Zn Al LDH

5.1.6 Time study

The opted % sorption of pH, dosage, and volume time was also studied from 20 min to 140 min with the interval of 20 min for sorption of M.B on to PPA modified Zn Al LDH. In the **Figure -10** the % sorption was increased from 20 min to 100 min and then started to decline. The maximum sorption was found at 100min and selected for further study. The reason of increasing of %sorption was due the more active sites for sorption and after a particular time the molecules detached from the sites and sorption leading to decrease in %sorption.



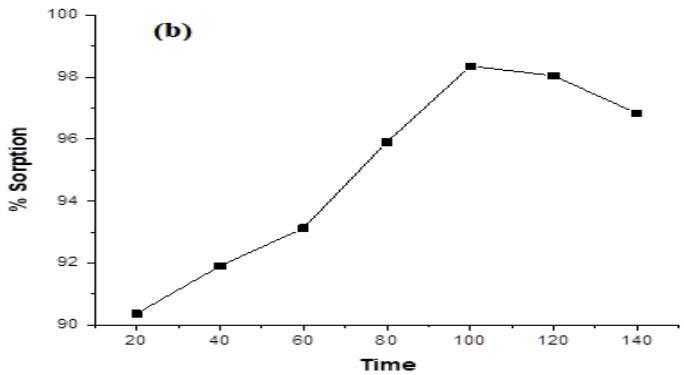


Figure 10 (**a**) and (**b**) shows Time Study of PPA modified Zn Al LDH for the removal of M.B

5.1.7 Temperature study

Temperature was studied according to the selected values of above-mentioned parameters. The range of temperature was from 20°C to 90°C with the interval of 10°C.In the **Figure -11** it is shown that the %sorption started increasing from 20°C to 40 °C and then declined afterwards and 40 °C was designated which was showing the detachment of molecules at higher temperature due to weak interaction of adsorbent and adsorbate.

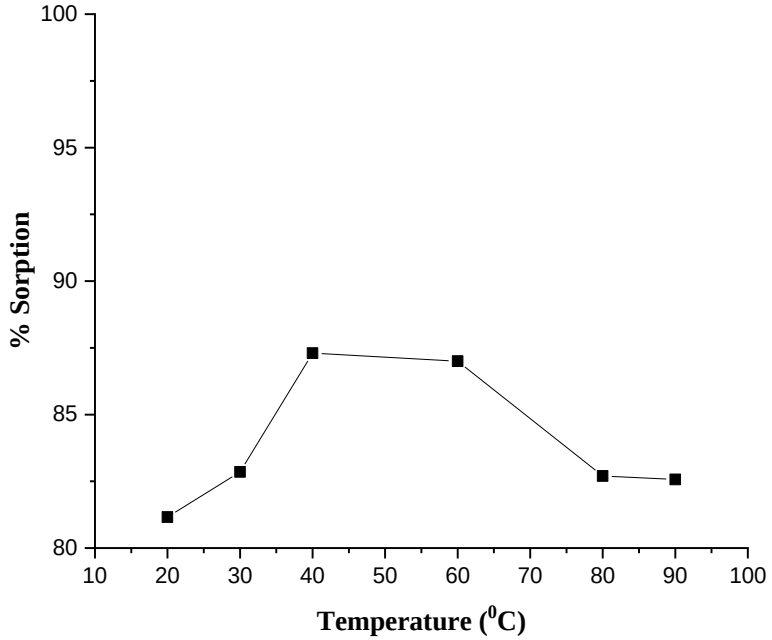


Figure 11 shows temperature effect on PPA modified Zn Al LDH for the removal of M.B

5.2 Kinetic Study

Kinetic models are crucial for evaluating kinetic data because they describe what happens throughout the sorption process and offer data on how much solute is absorbed and how much is still present in the solution at any given time during the experiment. The kinetic data was exposed to three widely used kinetic models Langergren, Ho, and McKay as well as Morris Weber models in order to determine the sorption process.

5.2.1 Langergren (pseudo- first order)

Langergren pseudo -first order values were calculated by Equation-3 [17] is given below:

$$\ln (q_e - q_t) = \ln q_e - K_1 t \qquad \text{[Eq-3]}$$

Where K_1 is the pseudo-first-order rate constant in min^{-1} the slope and intercept of the linear plot of ln (qe - qt) versus time **Figure-12** were used to calculate the amount of M.B sorbed on the sorbent at equilibrium and q_t (mg/g) is the amount of M.B ions sorbed on the sorbent at time t. Kinetic parameters were obtained in this study are given below.

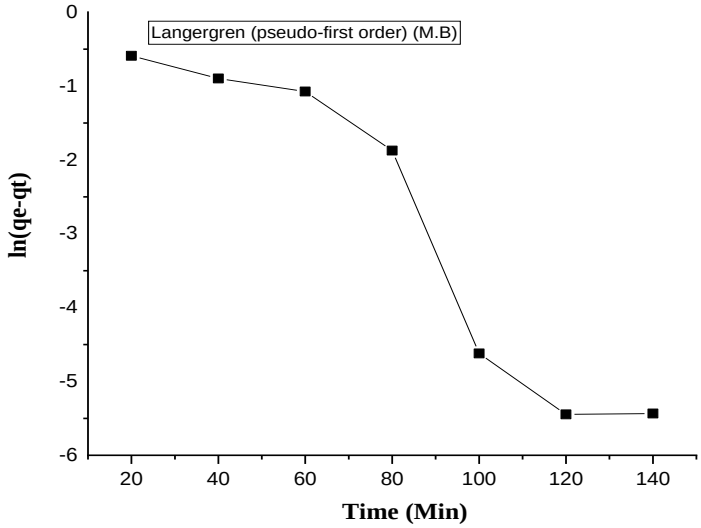


Figure 12 Langergren (pseudo-first-order for sorption of M.B onto PPA modified Zn Al LDH

5.2.2 Ho and McKay (pseudo-second order)

Ho and McKay kinetic model is presumable depend on chemisorption, in which sorption occur by the exchange of electron between sorbate and sorbent [17]. The pseudo- second –order rate Equation -4 is given below:

$$t/q_t=(t/k_2qe^{2)} +(1/q_{e)} \qquad \text{[Eq-4]}$$

Where, K_2 is rate constant in (g/µg min^{-1}) of pseudo –second order and q_e (mg/g) is the amount of sorbed M.B. The slope and intercept of a linear plot of t/qt against t were used to determine the quantity of M.B ions sorbed on the sorbent at equilibrium as described in **Figure -13** and q_t in (mg/g) is the amount of sorbate retained at time (100 min). Following in **Table -2** are kinetic parameters that were determined in this study.

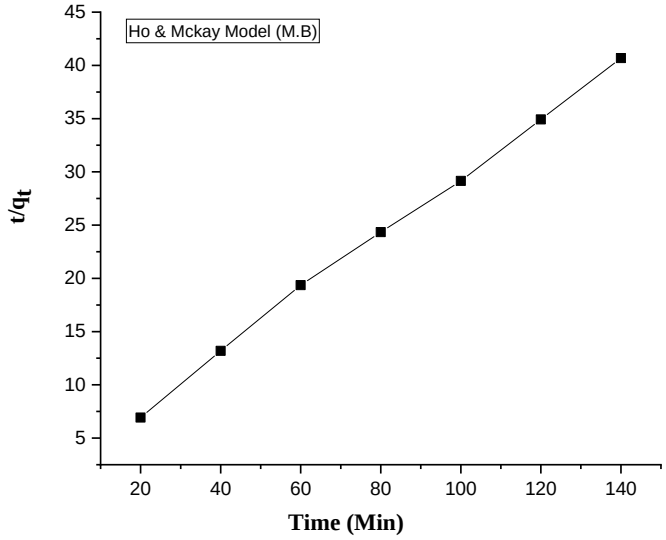


Figure 13 Ho & McKay model for the sorption of M.B onto PPA modified Zn Al LDH

The following **Table-2** shows the comparative data of pseudo-first order and pseudo-second order of M.B sorption.

Table- 2 comparison between the value of pseudo-first and pseudo-second order equation for M.B sorption

Parameters	**Pseudo-first-order equation**	**Pseudo-second-order equation**
Equation	$\ln (q_e - q_{t)} = \ln q_e - K_1 t$	$t/ q_t = (t/ k_2 qe^{2)} + (1/q_e)$
K_1 (Min^{-1})	0.0002	------
K_2 (g/ mg Min^{-1})	-------	2.0094
q_e (mg/g) Calculated	32.4	0.497
q_t (mg/g) Experimental	3.43	3.43
R^2	0.921	0.998

Table-2 has summarized the corresponding parameters of pseudo –first order and pseudo-second order kinetics that displayed the premeditated qe value 32.4mg/g of Langergren is far away to experimental value 3.43 mg/g as compared to calculated value of Ho and McKay 0.497mg/g which is a description of the kinetic process, a pseudo-second-order equation is more applicable and this is the indication that the sorption might be physio sorption.

5.2.3 Morris Weber (Intra -particular diffusion)

The Langergren, Ho, and McKay kinetic models cannot be used exclusively to study the diffusion mechanism. Therefore, the Morris-Weber model also used kinetic data. According to this model, sorption is thought to occur via intra-particle diffusion and the rate-regulating step only depends on it if the plot of qt against t is straight and passes through the origin. If it does not, however, the other kinetic phenomenon is thought to be involved. According to **Figure -14** from this work, the plot of qt *vs* t is linear but does not cross the origin, indicating that there may be other kinetic processes controlling the sorption rate [17].
Equation-5 of this model is given:

$$qt = R_d \sqrt{t} \qquad \text{[Eq- 5]}$$

Where qt is the quantity of organic dye M.B that is sorbed in µg/g at time t in min $^{-1/2}$ and R_d is the rate constant of intra-particle diffusion, which is determined from the value of slop against t.

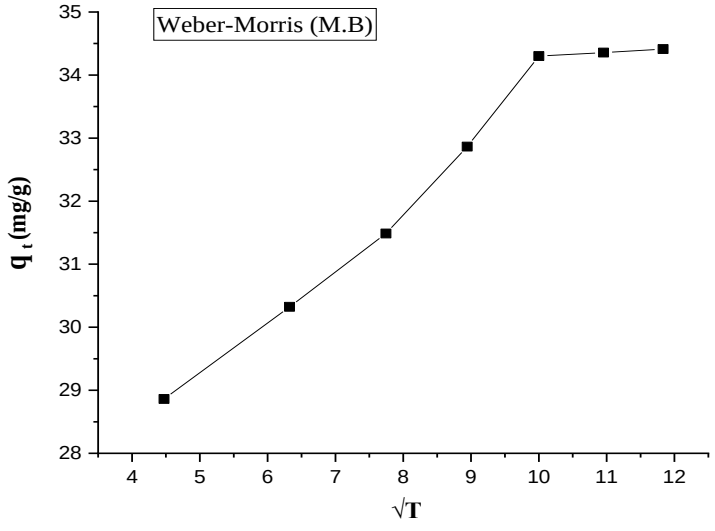


Figure 14 Morris -weber Model for M.B sorption on PPA modified Zn Al LDH

5.3 Sorption Isotherm

Sorption isotherms are essential for predicting a sorbent's ability to remove a pollutant. By using the Langmuir, Freundlich, and D-R isotherms, the sorption capacity of PPA modified Zn Al LDH for the removal of M.B ions has been examined.

5.3.1 Langmuir Isotherm

The Langmuir isotherm is utilized to infer the maximal sorption capacity of the sorbent as well as the assumption of monolayer surface coverage, which shows the equal affinities of all binding sites for sorbate molecules. The following Equation-5 [18] is used for the Langmuir calculation as shown in **Figure -15** below:

$$C_e / C_{ads} = 1/ Qb + C_e/Q \qquad \text{[Eq-5]}$$

Where Ce is the concentration of M. B in mg/L at equilibrium Cads is the adsorption capacity of modified LDH. The plot of Ce / Cads Vs Ce gives 1/Q and b as a slop and intercept from which value of Q can be obtained. In this equation b is a constant related to free energy of sorption.

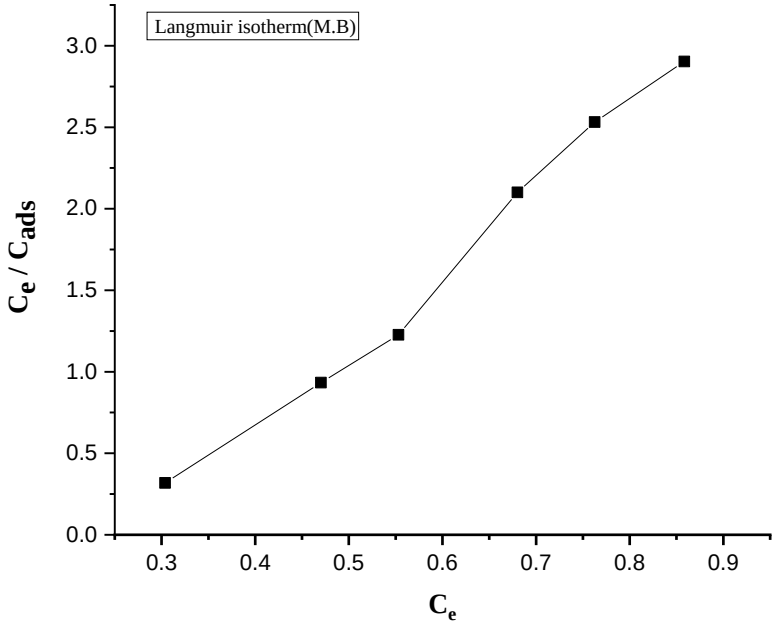


Figure 15 Langmuir isotherm for M.B sorption onto PPA modified Zn Al LDH

5.3.2 Freundlich Isotherm

According to the non-linear energy distribution of the sorption sites for the same sorbent, the Freundlich isotherm [18] is used to prediction the probability of multilayer surface coverage by using Equation-6 given below:

$$\text{Log Cads} = \log A + 1/n \log Ce \qquad \text{[Eq-6]}$$

Whereas the intercept and slop of the plot of log Cads *vs* log Ce may be used to establish the maximal sorption capacity A and heterogeneity factor 1/n, which are Freundlich constants, the obtained values are presented in **Figure -16** and linear plot, which has a regression coefficient $R^2 = 0.97$, demonstrates how well the experimental data given fits the Freundlich isotherm.

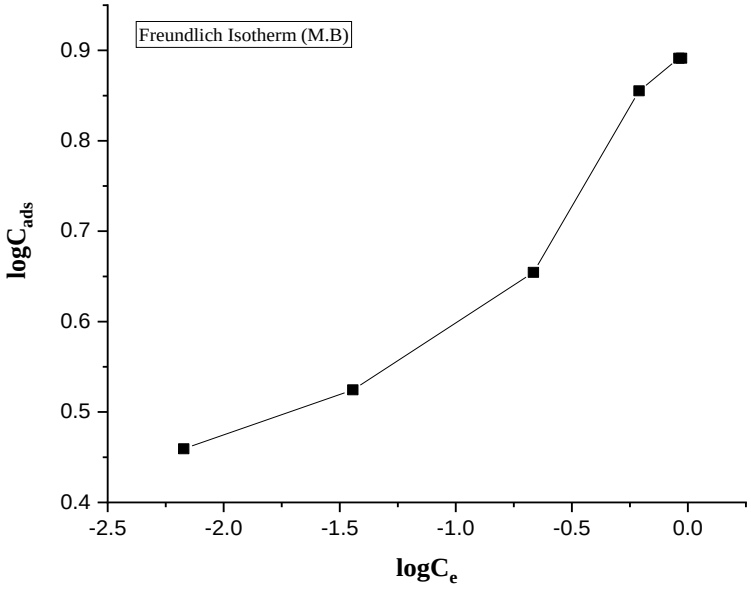


Figure 16 Freundlich isotherm for M.B sorption onto PPA modified Zn Al LDH

5.3.3 Dubinin -Radushkevich isotherm (D-R)

The porosity properties and the apparent free energy of sorption are assumed using the D-R isotherm [18] . The linearized form of the D-R is seen in the following Equation-7:

$$\ln C_{ads} = \ln X_m - \beta\varepsilon^2 \qquad [\text{Eq-7}]$$

Where, C_{ads} is the quantity of M.B ions sorbed per unit mass of sorbent, X_m, and β are D-R isotherm constant, and ε is a potential that can be found from the formula given below in Equation-8:

$$\varepsilon = RT\ln(1+1/C_e) \qquad [\text{Eq -8}]$$

Where, R is a gas constant in J/mol/K, T is the temperature in K and C_e is the equilibrium concentration. By knowing the value of slop, energy E can be calculated by using Equation-9 given below:

$$E = 1/\sqrt{-2\beta} \qquad [\text{Eq-9}]$$

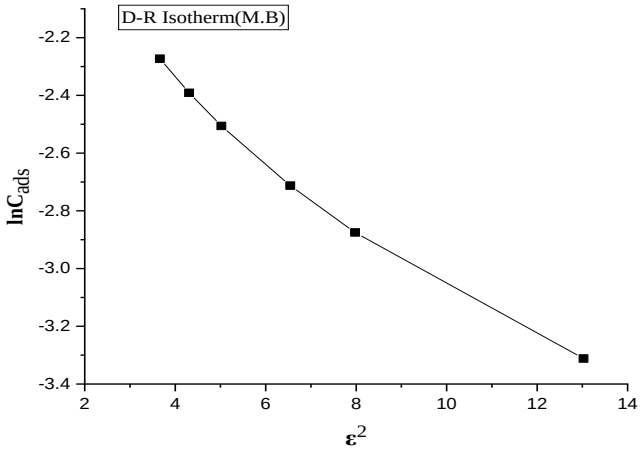


Figure 17 D-R isotherm for M.B sorption onto PPA modified Zn Al LDH

A chemical ion exchange or physisorption may be the sorption mechanism, according to the magnitude of mean free energy E (KJ/mol). If the value of E is between 0 and 8, the sorption mechanism will be deemed to be physisorption, and between 8 and 16 it will be considered to be chemisorption. In the **Figure-17** showing the calculated value of mean free path obtained from the value of slop and calculated value of E = 0.813(KJ/mol) mentioned in **Table-3** assuming that the sorption mechanism is physisorption.

Table -3 D-R isotherm parameters for M.B sorption on PPA modified Zn Al LDH

β (mol^2KJ^{-2})	Xm (mg/g)	E (KJ/mol)	R^2
0.7676	1.084	0.813	0.945

5.3.4 Thermodynamics Study

Sorption of M.B onto PPA modified Zn Al LDH was examined at different temperature from 20°C, 30°C,40°C,60°C,80°C and 100 °C. The extreme sorption was recorded at 40°C. According to [19] an exothermic process would be assumed if the sorption capacity decreased as the temperature rose and vice versa. The sorption process temperature dependency is related to a number of thermodynamic factors that include: change in Gibb's free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°). These parameters were analyzed by Van't Hoff equations that are given below:

$$\Delta G° = -RT\ln K_c \qquad \text{[Eq- 10]}$$

$$\ln K_c = \Delta S°/R - \Delta H°/RT \qquad \text{[Eq-11]}$$

Where, R is the gas constant (8.314J/mol/K), T is absolute temperature (k) and K_c is the equilibrium constant. The ratio of the sorbed quantity of M.B onto PPA Zn Al LDH was used to compute the value of Kc in **Figure-18**. The values for G°, S°, and H° provide in **Table 4**. The slop and intercept of the plot of lnKc vs 1/T were used to determine the change in enthalpy and entropy values.

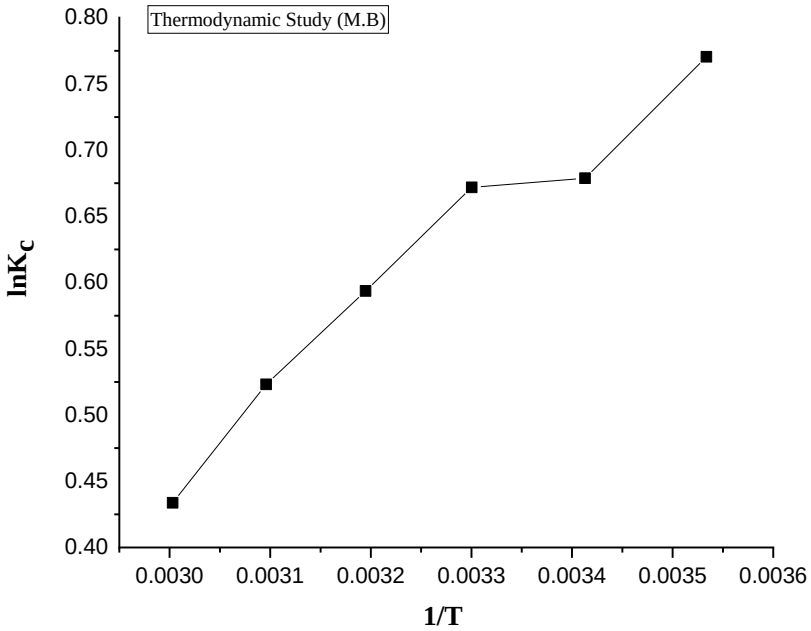


Figure 18 Thermodynamic study for M.B sorption onto PPA modified Zn Al LDH

In the current study, **Table 4** showing the negative entropy change demonstrated that M.B randomness decreased as it transitioned from its solution to sorbed state, but negative enthalpy change indicated that the sorption process was exothermic. The positive change free energy indicating that

endothermic nature of sorption process whereas the positive entropy change showing the increase in the randomness as it conceded from the solution to sorbed state. These positive change value showing the reaction is non-spontaneous.

Table 4. Thermodynamic parameters for M.B sorption onto PPA modified Zn Al LDH

T in° C	ΔG=(RTlnKc)	ΔH° (KJ/mol)	ΔS°(KJ/mol)
10	**-1.81**	**182.3**	**-0.014**
20	**-1.65**		
30	**-1.69**		
40	**-1.54**		
50	**-1.40**		
60	**-1.20**		

6.0 Chemistry of Sorption Mechanism

The chemistry of sorption has been discussed in **Figure – 19**, given above, it is depicted that the PPA modified Zn Al LDH having guest anions and some water molecules in between the layers, as well as a hydroxide ion on the edges of the layers. This modified LDH interacted with organic dye and has the ability to sorb the dye particle which is physically bonded with anions and hydroxide ions with the removal of some water molecules as shown in the mechanism below.

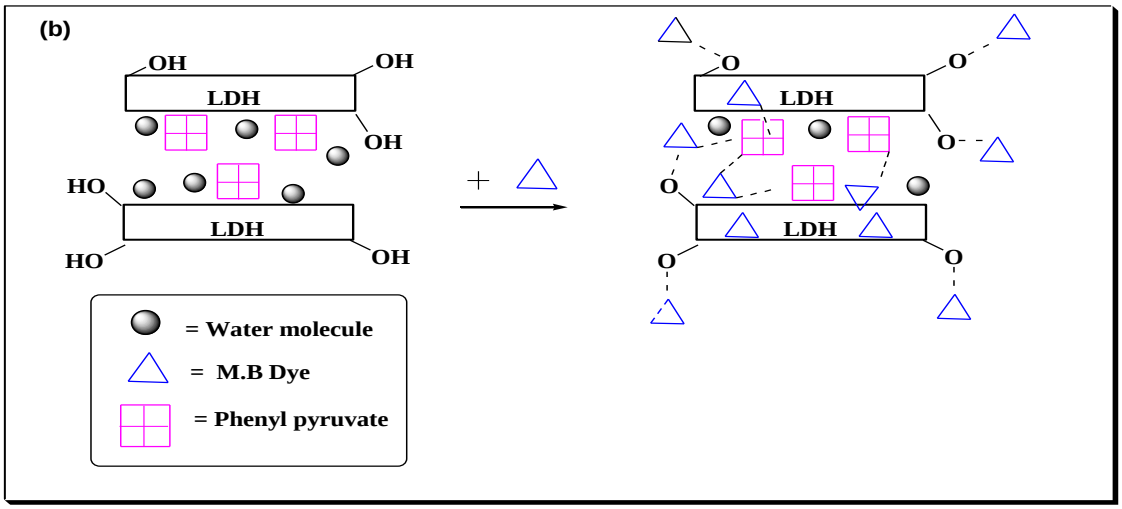


Figure 19 The sorption mechanism of M.B by using PPA modified Zn Al LDH

6.1 Desorption study

To ensure the longstanding usage of repeated removal recovery cycles, the removal efficiency of loaded ions upon PPA modified Zn Al LDH must be investigated [20]. The PPA modified Zn Al LDHs reinstatement can be used as a gauge for determining its suitability for commercial use. Three consecutive cycles of sorption-desorption tests were used to investigate the mechanical stability and M.B ion sorption capacity of PPA modified Zn Al LDH. Desorbing agents included 0.1M solutions of HNO_3, NaOH, and HCl. It was discovered that the 0.1M NaOH worked well as an eluent to desorb M.B from PPA modified Zn Al LDH. For at least three cycles, the overall sorption efficiency was lowered by 65%. From the obtained results, it can be inferred that the PPA modified Zn Al LDH has a sizable capacity to sorbed M.B species from water.

7.0 Comparative Study

The developed methodology has compared with reported studies for sorption of M.B is mentioned below in **Table -5**:

Table -5 Comparative study for sorption of Methylene blue (M.B)

S. No	Adsorbent	Dye	Equilibrium conditions	Adsorbent capacity (mg/g)	Reference No
1.	Rice husk	Methylene blue	pH 8, 32°C, 40min	40	21
2.	Cellulose–chitosan composite beads	Methylene blue	pH 6, 90 min, 20°C	55	22
3.	Magnesium ferrite spinel ($MgFe_2O_4$)	Methylene blue	pH 11, 120 min, 25 °C,	78	23
4.	Oxone treated hydrochar (OHC)	Methylene blue	pH 7, 240 min, 45 °C,	86	24
5.	Phenyl pyruvate modified Zn Al LDH	Methylene blue	pH10, 100min, 40 °C,	92	**This Study**

8.0 CONCLUSION

It is concluded from the aforementioned work that the phenylpyruvate modified Zn Al LDHs molecules with high potential that can be utilized in industries for the removal of water pollutants. In current study we have used co-precipitation method for the intercalation of phenylpyruvate ions with Layered Double Hydroxide (LDH) in basic condition. The guest ions phenylpyruvate accommodated in nano LDH by increasing the interlayer distance for PPA modified LDH. The sorption of methylene blue dye from water was observed and witnessed by applying kinetic study, isotherm models as well as thermodynamics study. Hence, it is concluded that the modified LDHs of such type have the admirable capability of sorption and can be utilized industrially for the organic dye removal.

9 .0 Statements and Declarations

There is no conflict of interest

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