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Preparation of Ni(II)Fe(III)-layered double oxide and its application for the removal of methyl orange dye: Adsorption isotherm and thermodynamic study

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ABSTRACT

The Ni(II)Fe(III)-LDO has been synthesized by calcination of Ni(II)Fe(III)-LDH at 500 ℃. The prepared LDO is applied in the treatment of Methyl Orange (MO) dye from a synthetic solution. A batch of experiments is conducted to examine the effects of varying adsorption parameters, i.e. initial dye concentrations and temperature. The results indicate that the adsorption of MO increases with rising dye concentration and solution temperature. Temkin, Freundlich, and Langmuir isotherms are analyzed to investigate the adsorption process at different pH levels. Various thermodynamic parameters such as ΔS, ΔH and ΔG^o have also been calculated. The adsorption of MO dyes on the Ni(II)Fe(III)-LDO is found endothermic and non-spontaneous in nature. The findings reveal the adsorption process is physical sorption.

1. Introduction

The textile industry faces a major challenge in treating wastewater contaminated with highly visible colored effluents from textile production [1-3]. While dyes may not always be harmful, they can have a noticeable negative impact on the appearance of our surroundings. The increasing levels of dye pollutants in the environment pose a threat to public health and the ecosystem. Among all the dyes, methyl Orange is an azo dye that finds extensive usage across diverse industries and research facilities. Its applications span the paper manufacturing, printing, textile, pharmaceutical, and food sectors. Furthermore, the dye is often utilized as an acid-base indicator in a laboratory focusing on Analytical Chemistry [4, 5]. When consumed, Methyl Orange undergoes a metabolic process catalyzed by intestinal microorganisms, producing aromatic amines. This is a commonly observed phenomenon among dyes of the same classification. The toxicity of this dye is still uncertain, but its high concentration has harmful effects in living bodies.

It is of utmost importance to ensure that industrial effluents are treated properly prior to being discharged into the environment. However, treating these effluents can significantly reduce their negative impact on the planet. The most effective method for removing color effluents from water is adsorption. Compared to other techniques such as ion-exchange, reverse osmosis, solvent extraction, ozonation, membrane filtration, and chemical precipitation, the adsorption technique is superior [6-8].

Various types of synthetic dyes have been attempted to be removed from wastewater using various adsorbents Numerous types of synthetic dyes have been attempted to be removed using a variety of adsorbents [9-12]. However, these adsorbents are costly and require high resources for the activation method [13]. Therefore, development of a cost-effective novel adsorbent materials having high adsorption capability is important for the removal of synthetic dye from wastewater.

Layered double hydroxides (LDHs) have gained significant attention as potential adsorbents due to their low synthesis cost, high specific surface area, and high anion exchange capacity [14]. LDH is a type of two-dimensional anionic mineral with the general formula: $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$ $(A^{n-})_{x/n}.mH_2O$, where M^{2+} represents a divalent metal (Mn^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, etc.) and M^{3+} represents a trivalent metal cation (Fe^{3+}, Al^{3+}, etc.). The A^{n-} is an interlayer anion (OH^-, Cl^-, SO_4^{2-}, etc.) [15]. LDHs have the ability to be transformed into LDOs through calcination treatment at a specific temperature. LDO has been identified as an attractive candidate for the adsorption of different dyes.

This investigation aims to study the adsorption isotherm and thermodynamic parameters for removing methyl orange dye from a synthetic solution. The adsorption process is accomplished by newly fabricated Ni(II)Fe(III)-LDO.

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2. Materials and methods

2.1. Materials

Methyl Orange, also known as Sodium p-dimethylamino azobenzene sulphonate, with the molecular formula $C_{14}H_{14}N_3NaO_3S$ (molecular weight 327.33) was purchased from Merck, India. During the studies, Deionized water and A.R grade reagents were utilized.

A microprocessor-based pH meter (Model HI 2002 (Edge pH meter, Henna Instruments, UK)) was used for all pH readings. An UV/visible spectrophotometer (T60UV-Visble Spectrophotometer, PG Instruments Limited, UK) was used to measure absorbance.

2.2. Preparation of Ni(II)Fe(III)-LDH (layered double hydroxide) and Ni(II)Fe(III)-LDO (layered double oxide)

The Ni(II)Fe(III)-LDH precursor used in the present investigation was synthesized through homogeneous co-precipitation method. The molar ratio for di and trivalent metal was 1:1. A 500 mL solution was prepared by dissolving 0.50 mol/L $NiCl_2$ and $FeCl_3$ in the deionized water to obtain the salt solution. A 500 mL of mixed alkali solution containing 1.0 mol/L NaOH and 1.0 mol/L Na_2CO_3 was prepared. The salt solution was slowly mixed with the alkali solution drop by drop maintaining the pH at 8.0. The resulting clayey material was stirred vigorously for another 3h. The clayey material was then filtered and washed with deionized water. The obtained Ni(II)Fe(III)-LDH was put into an oven at 60 ℃ for 7h to dry it. The LDH was then put into the muffle furnace at 500 ℃ for 3h. The material that was obtained is referred to as Ni(II)Fe(III)-LDO.

2.3. Adsorption studies

The adsorption studies were conducted using the batch technique. The flask shaking instrument (Model Oscillating laboratory shaker EW-51900-01, Stuart Equipment, UK) was utilized for the purpose of shaking. A 25 mL volume of dye solution, with varying concentrations, was taken in a different 50 mL glass stoppered reagent bottle. The desired pH was adjusted before the experiment.

For this investigation, a shaking time of 60 minutes was predetermined and used. The solutions were centrifuged with a centrifuged machine and then filtered with Whattman filter paper (number 42). The dye solution is analyzed spectrophotometrically at λ_{max} 502 nm [4, 5, 11, 16]. The following formula was used to get the percentage of dye elimination.

$$\% \text{ dye removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad \textbf{(1)}$$

where C_o and C_e (mg/L) are the initial dye concentration and concentration at equilibrium, respectively.

The mean MO adsorbed by the LDO at each temperature was determined using a mass balance equation as follows:

$$q_e = \frac{(C_o - C_e)v}{m} \quad \textbf{(2)}$$

where q_e = equilibrium MO adsorption per unit weight of LDO (mg/g), C_o = initial dye concentration, C_e = concentration of dues at equilibrium, v = volume of initial MO solution used (L), and m = mass of LDO used (g).

3. Result and discussion

3.1. Methyl orange(MO) concentration variation effect on the adsorption of MO onto Ni(II)-Fe(III) LDO

The extent to which dye is removed is largely affected by the initial concentration of the dye. The effect of the initial dye

concentration factor is determined by the relationship between dye concentration and accessible binding sites on an adsorbent surface. **Figure 1** illustrates the log (C_i, mg/L) vs log (C_e, mg/L) and adsorption %. The experiment is conducted at pH 4.5 and 6.5. The temperature is adjusted at 303 K for this experiment. It is clear that the percentage of MO adsorption increases as the initial dye concentration increases. Increasing the initial concentration of the dye improves the bonding between the dye and the adsorbent material [17, 18]. Additionally, as the initial dye concentrations rise, so does the driving power needed to overcome the mass transfer barrier of the dye between the solution and the adsorbent surface.

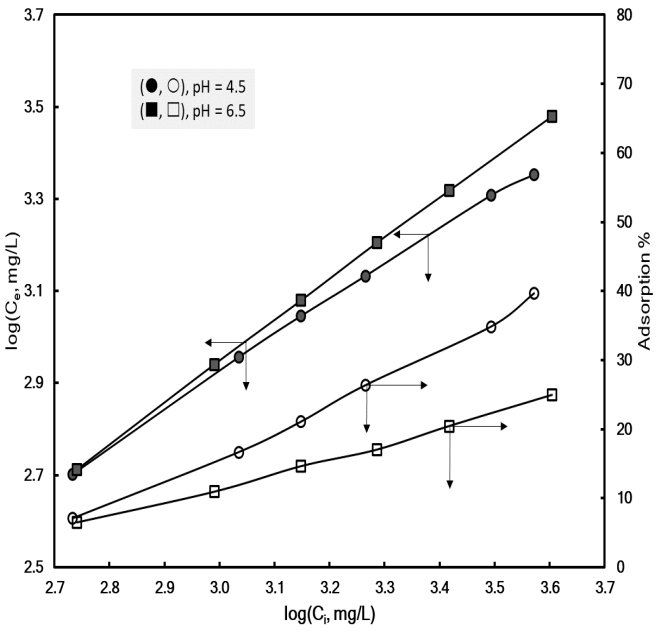


Figure 1. Effect of initial dye concentration for the adsorption of MO on to Ni(II)Fe(III)-LDO. Vol. of aqueous phase = 25 mL, wt. of adsorbent = 25 mg, equilibration time = 60 min.

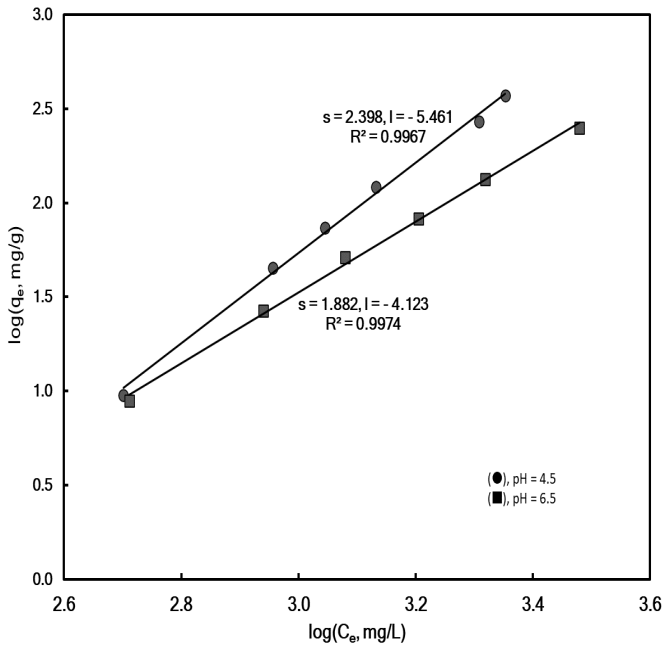


Figure 2. Freundlich adsorption isotherm for the adsorption of MO on to Ni(II)Fe(III)-LDO.

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Table 1. Langmuir, Freundlich and Tempkin isotherm parameters and correlation coefficients for the adsorption of MO in aqueous solution onto Ni(II)-Fe(III) LDO at different pH

pH	Langmuir isotherm			Freundlich isotherm			Tempkin isotherm		
	q_{max} (mg/g)	K_L (L/mg)	R^2	K_F(mg/g)	n	R^2	b_T(J/mol)	A(L/mg)	R^2
4.5	-26.954	-5.57×10^{-4}	0.926	4.25×10^{-3}	0.417	0.996	11	1.56×10^{-3}	0.827
6.5	-34.843	-4.21×10^{-4}	0.951	1.62×10^{-2}	0.531	0.997	20	1.54×10^{-3}	0.833

Higher dye concentrations cause the accessible active sites to become blocked and the adsorption rate to increase, resulting in this phenomenon.

3.2. Adsorption isotherms study

Adsorption isotherms describe the balance between the adsorbent and adsorbate in an equilibrium relationship. In the present study, three adsorption isotherm equations were utilized, namely, Langmuir [19], Freundlich [20] and Tempkin [21]. In this adsorption investigation, the applicability of isotherm models was compared using the correlation coefficient values. The Freundlich, Langmuir, and Tempkin isotherms represented by the following equations:

$$\frac{C_e}{q_e}=\frac{1}{q_{max}K_L}+\frac{C_e}{q_o} \quad \textbf{(3)}$$

where C_e is the equilibrium concentration of MO (mg/L), q_e is the amount of MO dye adsorbed onto the adsorbent at equilibrium, q_{max} is the theoretical maximum adsorption capacity (mg/g) at equilibrium, and K_L is the constant related to the free adsorption energy (Langmuir constant, L/mg). The plots of $1/C_e$ vs. $1/q_e$ give a straight line with a slope and intercept of $1/(K_Lq_{max})$ and $1/q_{max}$, respectively.

$$\log q_e=\log K_F+\frac{1}{n}\log C_e \quad \textbf{(4)}$$

where C_e is the equilibrium concentration (mg/L) of MO, q_e represents the amount of MO adsorbed at equilibrium (mg/g), and K_F is a constant that indicates the adsorption capacity of the adsorbent (mg/g).

The term "1/n" represents the adsorption intensity. The plots of log q_e against log C_e (**Fig. 2**) give a linear graph. The values of n and K_F was calculated from the slope (1/n) and intercept (log K_F) of this graph.

$$q_e=\left(\frac{RT}{b_T}\right)\ln A+\left(\frac{RT}{b_T}\right)\ln C_e \quad \textbf{(5)}$$

At equilibrium, q_e represents the amount of adsorption per unit mass of LDHs (mg/g), while C_e represents the adsorbate concentration and equilibrium (mg/L), T represents the absolute temperature (K), R is the molar gas constant (8.341 J/mol K). A (L/g) and b_T (J/mol) are the Temkin constants. Calculation of b_T and A can be obtained from the slopes (RT/b_T) and intercepts ((RT/b_T)lnA) of the plot of q_e vs. lnC_e. The relationship between the concentration of dye in the solution and the concentration of dye adsorbed is demonstrated at equilibrium by the adsorption isotherm. **Table 1** presents the theoretical adsorption isotherm parameters and their corresponding regression coefficients.

From the regression coefficients values at two different pH it is clear that the present investigation follows the Freundlich isotherm **(Fig. 2).**

3.3. Temperature Effect on the adsorption of MO onto Ni(II)-Fe(III) LDO

Temperature is one of the crucial parameters in adsorption reactions. Figure 3 shows the effect of temperature on the adsorption of MO removal by Ni(II)Fe(III)-LDO. The studies are conducted at two pH values (4.5 and 6.5) and at temperatures of 293, 298, 303, 308, 313, and 318 K. The MO adsorption is increased with the increase in temperature. The percentage of adsorption at pH 4.5 and 6.5, at a temperature of 308 K, are 17.98 and 12.42, respectively.

3.4. Thermodynamic study

Thermodynamic parameters (ΔG^o, ΔS and ΔH) were determined for the Ni(II)Fe(III)-LDO adsorbents using the following relations [22-24]:

$$K_d=\frac{q_e}{C_e} \quad \textbf{(6)}$$

$$\Delta G^o=-RT\ln K_d \quad \textbf{(7)}$$

$$\ln K_d=\frac{\Delta S}{R}-\frac{\Delta H}{RT} \quad \textbf{(8)}$$

Table 2 contains a list of the thermodynamic parameters. The positive ΔG^o values confirmed that the adsorption was nonspontaneous. The ΔG^o values decreased with the increase

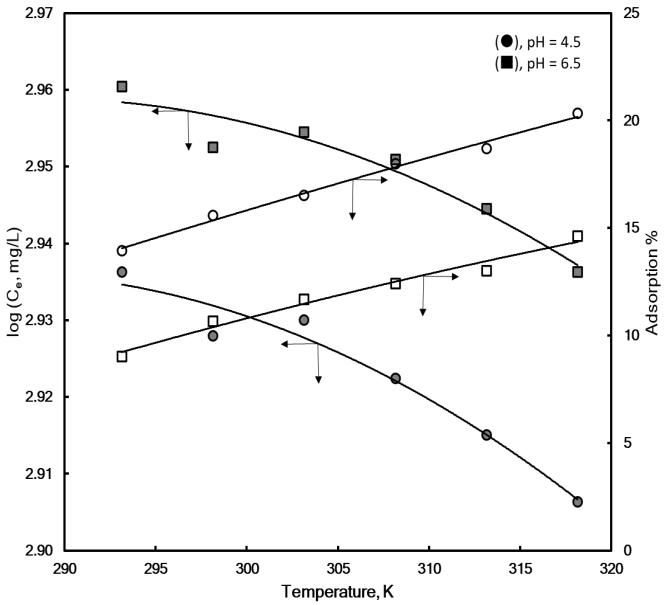


Figure 3. Effect of temperature for the adsorption of MO on to Ni(II)Fe(III)-LDO. Vol. of aqueous phase = 25 mL, wt. of adsorbent = 25 mg, equilibration time = 60 min.

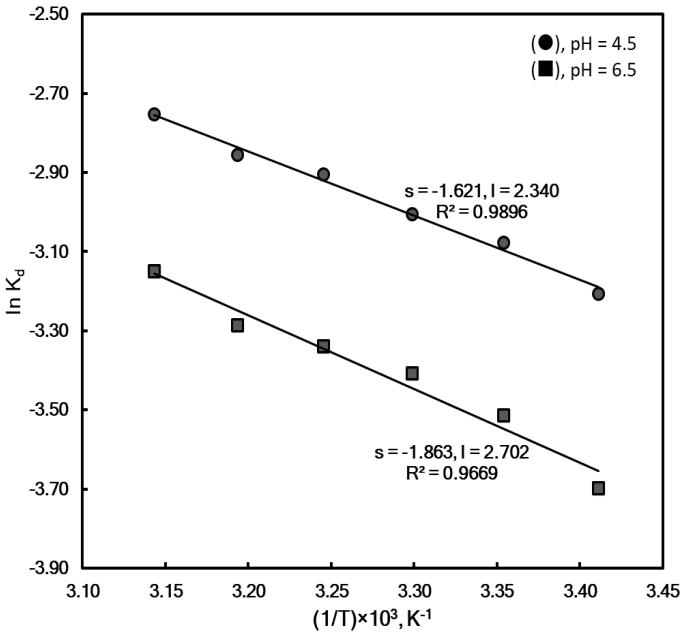


Figure 4. Van't Hoff plot for the adsorption of MO on to Ni(II)Fe(III)-LDO.

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Table 2. Thermodynamic parameters for the adsorption of methyl orange (MO) onto the Ni(II)-Fe(III) layered double oxide.

pH	Temp (K)	ΔG°, kJ/mol K	ΔS°, J/mol K	ΔH°, kJ/mol
4.5	293	7.82	19.45	13.48
	298	7.63		
	303	7.57		
	308	7.44		
	313	7.44		
	318	7.28		
6.5	293	9.01	22.45	15.49
	298	8.71		
	303	8.59		
	308	8.56		
	313	8.56		
	318	8.33		

in temperature. This phenomenon illustrated that adsorption was a physical process. The other parameter values are calculated from the Van't Hoff equation (Eq. (8)). The ΔS and ΔH were calculated from the intercept and slope of the Van't Hoff plot ($\ln K_d$ vs. 1/T) (Fig. 4). The ΔH values at pH 4.5 and 6.5 are 13.48 and 15.49 kJ/mol, respectively. The value of ΔH was found to be positive, indicating the endothermic nature of the adsorption. The obtained ΔS values are 19.45, and 22.45 J/molK at pH 4.5 and 6.5, respectively. Consequently, positive values of ΔS signify an increase in randomness during dye adsorption at the solid-liquid interface [25].

4. Conclusion

The Ni(II)Fe(III)- LDH was synthesized using the coprecipitation process, and Ni(II)Fe(III)-LDO was synthesized by high-temperature calcination. With an increase in MO dye content in the aqueous phase, the adsorption percentage grew steadily. Greater concentrations of adsorption at all accessible active sites led to this occurrence. From the isotherm study, it was observed that the system followed the Freundlich isotherm. The temperature study shows that the adsorption percentage is increased with the increase in temperature. From the thermodynamic study ΔGº, ΔH, and ΔS values are obtained. The investigated ΔGº value was positive at all temperatures, confirming the adsorption process's nonspontaneous nature and non-feasibility. The ΔH value was found to be positive. Hence, the adsorption was endothermic in nature. The positive value of ΔS indicated that randomness at the interface between solid and liquid increased during the process of adsorption.

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