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# **Research Article**

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# Nanocores Magnetic Humic Acid on Montmorillonite Nanoneedles for Adsorption Dye Via RSM: Adsorption Isotherm, Kinetic Modelling and Thermodynamic Studies

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#### Abstract

The current inquiry aimed at using core-shell Fe<sub>3</sub>O<sub>4</sub>@Humic acid/montmorillonite nanocomposites for removing methyl orange dye from an aqueous solution. The samples were characterized by FT-IR, TEM, SEM, XRD, BJH, and BET analytical methods. The efficiency removal has been utilized for 300 min reaction time using the response surface methodology by a design of five-factor-three-level central composite. The adsorption kinetics followed the pseudo-second-order rate kinetic model, showing an acceptable correlation ( $R^2 > 0.99$ ). Langmuir, Freundlich, Temkin, Dubinin–RadushKevich, and Harkins–Jura isotherms were utilized for the analysis of the equilibrium data. Also, we have estimated standard Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ), and the activation energy (E<sub>a</sub>). The findings of this investigation suggest that the absorption of methyl orange on the adsorbent pursues the Frondelich isothermal formulation. The  $\Delta G^\circ$  values obtained showed physical

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absorption in this adsorption process.  $\Delta H^{\circ}$  showed that the dye adsorption mechanism was endothermic, and  $\Delta S^{\circ}$  indicated an increase in irregularity and the probability of contact between methyl orange molecules and the adsorbent surface in the dye adsorption process. Positive Ea values pointed out the nature of the endothermic absorption process. S\* value was minimal and close to zero, which established the process of physical absorption.

**Keywords:** Core-Shell structure; Reusable adsorbent; Standard enthalpy; Kinetic; Mathematical modeling

#### 1. Introduction

Textile manufacturing holds a major role in the realm of economy of various nations across the world. Such a process results in the emergence of relatively colored wastewater, which varies with the rate of fixation of the dyestuffs on the lower layers. This could be different with reference to the quality of the matters, the optimal anount of coloration, and the treatment technique [1]. The vast amounts of wastewater produced by dye-manufacturing and dyeconsuming industries act as hazardous environmental challenges. The entire making of world dyes and pigments across the world is supposed to come by 800,000 tons each year, 10% of which enters the environment at least. Researchers have recently delved into a range of methods for removing contaminants in wastewater, such as adsorption [2, 3], biodegradation [4, 5], photocatalysis [6, 7], and biocatalytic oxidation [8, 9]. Of such approaches, adsorption has been the generally utilized and shown as effective method in treating wastewater. Surface adsorption occurs in both physical and chemical forms. Physical adsorption, which happens due to van der Waals forces between pollutant molecules and the adsorbent surface, is one of the most common types of adsorptions and has reversible properties. On the other hand, Chemical adsorption occurs due to a chemical reaction between pollutant and adsorbent surface. This adsorption type has a low velocity and is irreversible, unlike physical adsorption [10]. So far, various adsorbent has been studied to remove organic dyes and contaminants. The use of cheap and eco-friendly adsorbents increases the value of adsorption operation. Numerous type of adsorbents has been utilized to remove the dye in wastewater. The use of Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) as a very effective adsorbent has drawn substantial attention by the researchers owing to the merits of being economical, big particular surface area, and great adsorption capacity.

In this study, a magnetic adsorbent was synthesized using inexpensive, natural material, and methyl orange dye adsorption kinetic was investigated. As a coating agent, different weight percentages of Humic acid were added to iron oxide, and the weight percentage of sodium montmorillonite to the synthesized adsorbent structure was investigated. Different methods were employed to characterize synthesized samples. Afterward, synthesized adsorbent has been used by considering five parameters and examining the effect of these parameters on the maximum efficiency of methyl orange dye removal, using Design-Expert software. By the result of the software, the best percentages of sodium montmorillonite (MMT) and humic acid (HA) were selected to synthesize adsorbent. Finally, using this optimum condition, the kinetic and thermodynamic of the adsorption mechanism have been scrutinized.

#### 2. Materials and Methods

#### 2.1. Materials

FeCl<sub>3</sub>.6H<sub>2</sub>O, FeCl<sub>2</sub>.4H<sub>2</sub>O, NH<sub>3</sub>, Humic acid ( $C_{187}H_{186}O_{89}N_9S_1$ ), NaOH, and HCl were prepared from Merck, Germany. NaCl and methyl orange ( $C_{14}H_{14}N_3NaO_3$ ) were bought from Sigma Company. Sodium montmorillonite (Cloisite Na<sup>+</sup> with a cation exchange capacity (CEC) of 92.6 mequiv. 100 g clay was prepared by Nanocor Inc. The whole reagents had analytical grade and were applied with no further purification.

#### 2.2. Preparation of Fe<sub>3</sub>O<sub>4</sub>@HA/MMT

To synthesize  $Fe_3O_4$ @HA composite, 1:2 ratio of FeCl<sub>3</sub>.6H<sub>2</sub>O and FeCl<sub>2</sub>.4H<sub>2</sub>O dissolved in 50 ml of distilled water in a three-neck round-bottom flask attached to a reflux condenser and with using magnetic stirring were provided homogeneous solutions until the temperature turned 80 °C, followed by adding 10% humic acid (HA) (30 and 50 wt% for another ratio) to this mixture accompenaied by steady stirring. It was followed by the addition of 50 mL of 25% ammonium hydroxide to the mixture accompenaied by steady stirring and kept at 80 °C for an additional 120 min. A magnet was applied to separate the synthesized  $Fe_3O_4$ @HA composites, they then were washed with distilled water several times. Ultimately, we collected a powder product and dried it at 80 °C for 8 h. To prepare  $Fe_3O_4$ @HA/MMT, the 1.8 g of the  $Fe_3O_4$ @HA composite was dispersed in 100 mL ethanol under ultrasound for 40 min. In the separate dishes, 450 mg MMT (94.7 and 257 mg for another ratio) were scattered in the 20 mL water under ultrasound for 60 min. Then, MMT and  $Fe_3O_4$ @HA solutions were augmented slowly. At room temperature, the mixture was stirred mechanically for 24 h. The output  $Fe_3O_4$ @HA/MMT obtained was washed with water and ethanol. Finally, the sample was dried at 80 °C overnight [11, 12].

#### 2.3. Investigation of Adsorbent Activity on Removal of Methyl Orange Solution

The methyl orange dye solution was used to study the laboratory effectiveness of the synthesized adsorbent. The number and design of the experiments were performed using design expert software and the CCD method. In this research, five independent parameters were used that include adsorbent content (1-5 g.L<sup>-1</sup>), pH (3-9), the humic acid weight percentage (10%-50%), sodium montmorillonite weight percentage (5%-20%), and the initial concentration of methyl orange dye solution (5-25 mg.L<sup>-1</sup>). Each of these five independent parameters was determined in high- and low-level values and considering the  $\alpha = 1$ .

#### 2.4. Design of Experiment and Data Analysis

Response surface methodology (RSM) is a suitable technique to find optimal conditions, parameters interaction and estimate an optimum condition of the process by the lowest experiment number. The number and design of the experiments were performed using the RSM method and CCD technique. In a CCD design, the total number of experiments was obtained from the sum of the number of factorial experiments, the number of axial experiments, and the number of central experiments that follow Equation 1.

# $B=2^{k}+2k+n \tag{1}$

where B signifies the total number of experiments, k symbolizes the number of independence factors, and n is the number of central points. So, considering that the number of central points was 8 and the number of factors was 5, the sum of the total experiment obtained was 50. Design expert software was utilized to analyze the results of the experiments.

To perform the designed experiments, in 250 ml Erlenmeyer, the temperature was 25°C, and the mixing intensity was 180 rpm using an incubator shaker. Methyl orange solutions with specific concentrations of dilute methyl orange stock solution  $(1000 \ \mu g.ml^{-1})$  were prepared. 300 min after adsorption, the adsorbent was separated from the solution by a magnet. Using the spectrophotometer, the final adsorption rate of the solution at a wavelength of 464 nm (maximum wavelength of methyl orange) was studied. Then the percentage of dye removal was computed. The percentage of methyl orange removal by the synthesized adsorbent was obtained using Equation (2).

$$R\% = \left(\frac{C_{-\circ} - C_{-}e}{C_{-\circ}}\right) \times 100$$
(2)

Also, adsorption capacity  $q_t$  was calculated using Equation (3).

$$q_t = \frac{(C_0 - C_t)}{m} V \tag{3}$$

in which  $C_0$  denotes the initial concentration of the dye,  $C_t$  shows the equilibrium concentration of the solution (mg.l<sup>-1</sup>), m signifies the mass of the synthesized adsorbent (g), and V symbolizes the volume of the solution (L). The data obtained from each CCD-designed experiment can be calculated to examine the effects of the interaction of the parameters and their statistical analysis.

#### **2.5. Adsorption Experiments**

We have used Response surface methodology (RSM) to model the relationship between the quantitative factors and the response and to detect optimal factors that display the "best" response. These designs are able to fit a second-order prediction equation for the response as follows:

$$R = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} X_i X_j + e_0$$
(4)

Here, R is the predicted response (% Removal);  $X_i$  and  $X_j$  stand for variables;  $\beta_0$  denotes the constant coefficient; Also,  $\beta_i$  is a factor that defines the effect of factor i in the final response.  $\beta_{ij}$  denotes the cross-product coefficient, and  $\beta_{ii}$  is the quadratic coefficient, returning to the impacts of the interaction among independent variables. To obtain the coefficient, the multiple regression analysis could be used, and the Equation could be employed to forecast the response. The coded

values in connection with the parameters are possible to be determined with reference to Equation (5).

$$x_i = \frac{x_i - x_0}{\delta x} \tag{5}$$

whereby,  $X_0$  represents the real value of the independent variable at the center point, xi denotes the real value of the independent variable, and  $\delta X$  denotes the step change values between low (-2) and high (+2) levels. To compute the percentage of the elimination of color, Equation 6 was employed as follows:

Percentage Removal (%) = 
$$\frac{(C_0 - C_f)}{C_0} \times$$
  
100 (6)

In which,  $C_0$  denotes the initial concentration of dye and  $C_f$  signifies the final concentration of dye after adsorption.

To determine Kinetics of adsorption, we analyzed adsorbent sorption of the dye from an aqueous solution at different time intervals. Adsorption isotherms were identified by shaking dye solution at different temperatures (25–55  $^{\circ}$ C) with certain ratios of adsorbents until the equilibrium happened. We relied on Batch tests to make a comparison between the adsorptive capacity and intensity of different adsorbents. To compute the equilibrium adsorption capacity, we applied Equation (7) as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{7}$$

In which  $q_e (mg.g^{-1})$  signifies the equilibrium adsorption capacity,  $C_e$  denotes the dye concentration at equilibrium, V (L) symbolizes the volume of solution, and W (g) represents the weight of adsorbent.

#### 3. Results and Discussion

#### **3.1 Characterization**

We determined the morphologies of the whole synthesized samples via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. An X-ray diffract meter (XRD) with radiation ( $\lambda = 0.15418$  nm) was utilized to analyze the crystal phases of the samples. Recording the powder XRD patterns for 2 $\theta$  in the range of 10–70° was relized through a scan rate of 0.11 s<sup>-1</sup>. A 100 mg KBr pellet with 1 mg of the sample was employed to take the Fourier transform infrared (FT-IR) spectra of the as-synthesized at room temperature. We took the

absorbance measurement through UV–Visible spectrophotometer (Cintra 101 GBC Scientific Equipment Ltd.). To compute the specific surface area from the adsorption isotherms, we used Brunauer–Emmett–Teller method.

XRD diffraction pattern of Fe<sub>3</sub>O<sub>4</sub>@HA (50%) and Fe<sub>3</sub>O<sub>4</sub>@HA(50%)/MMT-Na(12.5%) samples were shown in Figure 1.



Figure 1. XRD patterns for the nanocomposites.

The peaks at  $2\theta = 57.8$ , 43.2, 35.6, and 30.2 are related to iron oxide. The peaks appeared at  $2\theta = 27.8$ , 35.1, 62.5, 68.1, and 74.2 are attributed to sodium montmorillonite structure. The presence of peaks in both iron oxide and sodium montmorillonite structures in the XRD pattern of nanocomposites indicate that successful crystalline structure and dispersion of sodium montmorillonite with Fe<sub>3</sub>O<sub>4</sub>@HA core-shell structure [11, 12].

The surface morphology of the nanocomposites was evaluated using SEM method. Figure 2-a reveals the SEM images of the nanocomposites. A core-shell structure was found that was related to  $Fe_3O_4$  surrounded by HA. Also, in Fig. 2b surface structure of  $Fe_3O_4$ @HA core-shell composites with sodium montmorillonite was detected.



Figure 2. SEM micrographs of the (A) Fe<sub>3</sub>O<sub>4</sub>@HA, (B) Fe<sub>3</sub>O<sub>4</sub>@HA/MMT

TEM images of synthesized adsorbent are demonstrated in Fig. 3. That indicated the core-shell structure of Fe<sub>3</sub>O<sub>4</sub>@HA. Also, dispersion of montmorillonite structure was observed alongside core-shell structure.



Figure 3. TEM images of the Fe<sub>3</sub>O<sub>4</sub>/HA/MMT nanocomposite

The spectra obtained from the Fourier transform infrared analysis are shown in Figure 4. It could be seen a peak at 3445 cm<sup>-1</sup> in the sodium montmorillonite FTIR spectra which was related to vibration attraction OH silicate layer. The peaks around 674 and 449 cm<sup>-1</sup> were ascribed respectively to vibration attraction of O-Al and vibration bending of O-Si. The absorption at 1030

 $cm^{-1}$  was linked to vibration attraction of the O-Si silicate layer. Also, it could be seen the presence of absorption around 890 and 1052  $cm^{-1}$  that were assigned to vibration of MMT hydroxylans consisting of Al<sub>2</sub>OH and MgAlOH. The OH group at 3450 and 1600  $cm^{-1}$  in humic acid spectra were detected clearly. Also, carboccylate C=O vibration bond at 1680  $cm^{-1}$  was observed. In the Fe<sub>3</sub>O<sub>4</sub>@HA spectra, the peak at 560  $cm^{-1}$  indicates that Fe-O vibration bond. As observed from synthesized Fe<sub>3</sub>O<sub>4</sub>@HA/MMT composite spectra, two peaks were found at 584 and 440  $cm^{-1}$  that are most likely to be ascribed to Fe-O vibration attraction bond, Al-O vibration attraction, and O-Si vibration bending, which means the formation of synthesized adsorbent. COO-Fe bond was also observed at 1591 and 1395  $cm^{-1}$  [11, 12].



Figure 4. FT-IR spectra for the nanocomposites.

The BET method is one of the most popular ways to determine the porous space properties of solids, besides other methods like BJH, t and  $S_{\alpha}$  that used to specify the quality of pores distribution. These methods provided general information about the surface, volume, behavior, and curve of their surface absorption and the average size of the pores [12, 13]. Figure 5 shows the

absorption-desorption curve of nitrogen gas at a constant temperature on the surface of  $Fe_3O_4@HA$  and  $Fe_3O_4@HA/MMT$ .



Figure 5. the absorption-desorption curve of Fe<sub>3</sub>O<sub>4</sub>@HA and Fe<sub>3</sub>O<sub>4</sub>@HA/MMT.

According to IUPAK classification, the samples follow IV type isotherm, which illustrates the presence of material with meso pore's structure. Using BET analysis data, special surface area for Fe<sub>3</sub>O<sub>4</sub>@HA and Fe<sub>3</sub>O<sub>4</sub>@HA/MMT were obtained 11.19 and 30.23 m<sup>2</sup>g<sup>-1</sup>, respectively. In the Fe<sub>3</sub>O<sub>4</sub>@HA, several iron oxide particles created a core and were surrounded by humic acid as a shell. The spherical core-shell structure of Fe<sub>3</sub>O<sub>4</sub>@HA with MMT has a higher specific surface than the Fe<sub>3</sub>O<sub>4</sub>@HA structure. This increase of specific surface area in Fe<sub>3</sub>O<sub>4</sub>@HA/MMT is due to the location of Fe<sub>3</sub>O<sub>4</sub>@HA between MMT layers. The general volume of pores for Fe<sub>3</sub>O<sub>4</sub>@HA/MMT and Fe<sub>3</sub>O<sub>4</sub>@HA were obtained at 0.098 and 0.04908 cm<sup>3</sup>g<sup>-1</sup>, respectively. Comparing the results of BET analysis and the surface area of the synthesized photocatalyst are in agreement with the results of previous reports in this field. The distribution of the size of the pores that was calculated using the BJH method, and the surface desorption curve are shown in Figure 6. It could be observed that the size of pores diameter for Fe<sub>3</sub>O<sub>4</sub>@ HA/MMT and Fe<sub>3</sub>O<sub>4</sub>@HA is in the range of 1-10 nm, which confirms the theory of mesopress [12].



Figure 6. The distribution of the size of the pores.

The pH of dye solutions has a vital function in surface adsorption processes, especially adsorption capacity. Its importance is due to the surface charge of the adsorbent, the degree of ionization of the substances in the solution, and the separation of the functional groups in the adsorbent sites. According to Figure 7,  $pH_{pzc}$  was calculated at 4.55. At pH values less than  $pH_{pzc}$ , the adsorbent surface bears a positive charge, and at pH values more than  $pH_{pzc}$ , the adsorbent surface carries a negative charge. The adsorption rate was changed depending on whether the substance was cationic or anionic, and its interaction with the positive or negative adsorbent surface.



Figure 7. pH<sub>pzc</sub> the Fe<sub>3</sub>O<sub>4</sub>@HA/MMT

In this study, methyl orange dye is absorbed, which is an anionic compound. Hence at higher pHs than  $pH_{pzc}$ , adsorption is not desirable due to the presence of electrostatic repulsive forces between

anionic dye molecules and negatively charged sites at the adsorbent surface [14, 15]. In alkaline pHs, hydroxyl groups in the environment increase, which makes the surface charge of the adsorbent negative. Therefore, a weak interaction or even repulsive force between the absorbed and the adsorbent surface will be created, reducing the adsorption rate.

#### 4. Results of the Analyses

In this research, we applied design expert software to investigate the effect of five parameters on methyl orange dye removal using Fe<sub>3</sub>O<sub>4</sub>@HA/MMT adsorbents. The design of the experiment was performed using the response surface method using the CCD model. Each independent parameter was examined at five levels in the central compound model. In this study, the value of  $\alpha = 1$  was considered. The methyl orange dye removal percentage in the determined experiments was calculated using Equation 1.

## 4.1. Analysis of Variance (ANOVA)

We employed the ANOVA method to statistically determine the major impacts and essential interactions. We computed the parameters including mean squared, a sum of squares, parameter p-value, and ratio F. Table 1 reveals the analysis of variance of the quadratic model. According to Table 1, the following can be considered:

ANOVA for Response Surface Quadratic model							
Analysis of variance table [Partial sum of squares - Type III]							
	Sum of		Mean	F	p-value		
Source	Sulli Ol	df	Caucan	Value	Prob >		
	Squares Square Valu		value	F			
Modal	4560.00	20	228 40	16.00	<	significant	
WIGGET	4309.90	20	228.49	10.90	0.0001	significant	
лнл	683.11	1	683 11	50.52	<		
A-11A	003.11	1	005.11	50.52	0.0001		
B-MMT	149.94	1	149.94	11.09	0.0024		

C-pH	2148.88	1	2148.88	158.91	< 0.0001	
D-amount of adsorbent	255.48	1	255.48	18.89	0.0002	
E-intitial of concentration	29.74	1	29.74	2.20	0.1488	
AB	22.61	1	22.61	1.67	0.2062	
AC	71.10	1	71.10	5.26	0.0293	
AD	66.99	1	66.99	4.95	0.0340	
AE	73.51	1	73.51	5.44	0.0269	
BC	8.51	1	8.51	0.63	0.4341	
BD	15.54	1	15.54	1.15	0.2925	
BE	60.23	1	60.23	4.45	0.0436	
CD	1.16	1	1.16	0.086	0.7714	
CE	503.24	1	503.24	37.22	< 0.0001	
DE	7.813E-003	1	7.813E- 003	5.777E- 004	0.9810	
A <sup>2</sup>	4.669E-003	1	4.669E- 003	3.453E- 004	0.9853	
<b>B</b> <sup>2</sup>	81.96	1	81.96	6.06	0.0200	
C <sup>2</sup>	355.77	1	355.77	26.31	< 0.0001	
$D^2$	126.68	1	126.68	9.37	0.0047	
$E^2$	11.36	1	11.36	0.84	0.3669	
Residual	392.15	29	13.52			
Lack of Fit	326.87	22	14.86	1.59	0.2721	not significant
Pure Error	65.28	7	9.33			
Cor Total	4962.05	49				

The p-value of <0.0001 indicates that the model is significant, with 99.99% assurance that can be used to forecast the ideal feedback of the removal over the Fe<sub>3</sub>O<sub>4</sub>@HA/MMT nanocomposite. The Model F-value of 15.36 implies the model as noticeable. Due to the noise, only a 0.01% chance exists that an F-value of this size can take place. The "Prob > F" values less than 0.05 demonstrate that model terms are considerable. In this case A, B, C, D, AC, AD, AE, CE, C<sup>2</sup>, D<sup>2</sup> are significant model terms.

 $R \% = +63.39 + 4.48*A + 2.1*B - 7.95*C + 2.74*D - 0.7*E + 0.84*AB 1.49*AC + 1.45*AD + 1.52*AE + 0.52*BC - 0.7*BD + 1.37*BE - 0.19*CD + 3.97*CE + 0.016*DE + 0.93*A^2 - 4.87*B^2 + 12.88*C^2 - 0.97*E^2$ (8)

Table 2 presents the effective value of every parameter, standard errors, regression coefficients, and standard effect values. By writing the values of the parameters with reference to actual values, Equation 9 is obtained:

R% = +108.80673 - 0.057990 \* MMT - 21.24692 \* pH + 104.55757 \*amount of adsorbent - 1.02932 \* intitial of concentration + 5.60417E - 003 \* HA \* MMT - 0.024844 \* HA \* pH + 0.36172 \* HA \* amount of adsorbent + 7.57813E - 003 \* HA \* intitial of concentration + 0.022917 \* MMT \* pH - 0.46458 \* MMT \*amount of adsorbent + 0.018292 \* MMT \* intital of concentration - 0.31771 \* pH \* amount of adsorbent + 0.13219 \* pH \* intital of concentration + 7.81250E - 003 \* amount of adsorbent \* intital of concentration + 2.31552E - 003 \* HA<sup>2</sup> - 0.086645 \*  $MMT^{2} + 1.43069 * pH^{2} - 156.84483 * amount of adsorbent^{2} - 9.73793E - 003 *$ intital of concentration<sup>2</sup> (9)

Concerning the values given in Table 2 and the values of the P ratios, it can be concluded that the proposed model can be considered statistically significant.

Source	Std.	<b>R-Squared</b>	Adjusted	Predicted	PRESS
	Dev.		<b>R-Squared</b>	<b>R-Squared</b>	
Linear	6.21	0.6584	0.6196	0.5461	2252.43
2FI	5.06	0.8243	0.7467	0.6420	1776.56

Table 2. Statistical fetures of the Model.

Quadratic	<u>3.68</u>	<u>0.9210</u>	0.8665	0.7345	<u>1317.55</u>	<u>Suggested</u>
Cubic	3.57	0.9640	0.8740	-0.0425	5175.86	Aliased

#### 4.2. Design of Response Surface Experiment

One of the most powerful designs is the complete factorial RSM technique. The CCD technique was used to provide surface data because the optimization experiments based on the response surface approachare the EEquation for this technique. We applied the response surface of the suggested linear model, and studied five different factors. Every single factor was set at five levels. The five major and significant factors are pH (3-9), amount of adsorbent (1-5 g/l), w/w% HA (10-50%), w/w% MMT (5-20%), and the concentration of dye (5-25 ppm). The 3D and 2D contour plots show graphical representations of the interaction between variables factors within specific ranges. Figure 8 illustrates the response surface plot as a function of %HA vs. pH.

The impact of %HA and pH are the same and very significant. The dye degradation rose by raising the %HA and decreasing the pH. Maximum %HA (50%) and pH 3. Maximum helped to obtain dye degradation percentage. Figure 9 indicates the response surface plot as a function of % HA vs. adsorbent amount. The effect of % HA is more significant compared with the amount of adsorbent. The rise of the %HA led to dye degradation. Figure 10 describes the response surface plot as a function of % HA vs. dye concentration. The effect of % HA on the decolorization is more substantial than the effect of concentration. Degradation of dye molecules increased by grew up the HA%. The highest dye degradation percentage belonged to a maximum amount of %HA (50%). Figure 11 exhibits the 3D and 2D response surface produced to dispaly the impact of pH and dye concentration on the COD decrease. By surging the pH of the solution, COD reduction decreased, and the maximum response occurred at pH 3 and 15 ppm concentration of dye solution. By raising pH from 3 to 4, a dramatically increase in COD reduction was observed, while, under the same condition, maximum decolorization could be seen at pH 3 [16].



Figure 8. Interaction effect of %HA and pH on removal of MO.



Figure 9. Interaction impact of %HA and adsorbent on the removal of MO.



Figure 10. Interaction effect of %HA and concentration of MO.



Figure 11. Interaction impact of concentration of MO and pH on removal of MO.

#### 5. Optimum Conditions

When it was proved that the model was fit, the optimization process of the Design-Expert software was used so that define the best values of the independent variables would be defined to yield the most removal of dye. Regarding every parameter, we applied the upper and lower limits of the operating ranges as a restriction to achieve the optimum values. By means of the optimization function of the Design-Expert software, it was possible to predict the maximum removal (96.011%) under treatment conditions, pH 3, %MMT 13.1563, %HA 49.9998, initial of concentration of 5.00002 ppm with using the amount of adsorbent 3.58468 g/L. We use this condition for kinetic and thermodynamic study.

#### 6. Kinetic Models

The adsorption of the solid/solution interface is a phenomenon having mostly intricate kinetics. To study the adsorption processes of MO on the adsorbents, pseudo-first-order (PFO), pseudo-second-order (PSO), modified pseudo-first-order (MPFO), modified pseudo-second-order (MPSO), modified pseudo-first-order-2 (MPFO-2), modified pseudo-second-order-2 (MPSO-2), Elovich and intra-particle diffusion kinetic models were studied (Table 3).

Table 3. The kinetic models.

Model	Equation	Liner	Initial time
pseudo first order (PFO)	$\frac{dq}{dt} = k(q_e - q)$	$\ln\left(1-\frac{q}{q_e}\right) = -kt$	q = kt
modified pseudo-first-order (MPFO)	$\frac{dq}{dt} = k(\frac{q_e}{q})(q_e - q)$	$\frac{q}{q_e} + \ln(q_e - q) = \ln q_e - kt$	$q = k't^{1/2}$
modified pseudo-first- order-2 (MPFO-2)	$\frac{dq}{dt} = k(\frac{q_e^2}{q^2})(q_e - q)$	$\ln(1-\frac{q}{q_e}) + \left(\frac{q^2}{2q_e^2}\right) + \frac{q}{q_e} = -kt$	$q = k't^{1/3}$
pseudo-second-order (PSO)	$\frac{dq}{dt} = k(q_e - q)^2$	$\frac{\mathrm{t}}{q} = \frac{1}{kq_e^2} + \frac{t}{q_e}$	q = kt
modified pseudo-second-order (MPSO)	$\frac{dq}{dt} = k(\frac{q_e}{q})(q_e - q)^2$	$\frac{q}{(q_e - q)} + \ln(1 - \frac{q}{q_e}) = ktq_e$	$q = k' t^{1/2}$
modified pseudo-second-order-2 (MPSO-2)	$\frac{dq}{dt} = k(\frac{q_e^2}{q^2})(q_e - q)^2$	$\frac{q}{q_e} + 2\ln(1 - \frac{q}{q_e}) + \frac{q_e}{(q_e - q)}$ $-1 = ktq_e$	$q = k't^{1/3}$
Elovich	$\frac{dq_t}{dt} = \alpha e^{-\beta q_e}$	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	α

In the PFO modelm, as the oldest and simplest Equation, the rate of absorption is obtained in terms of absorption capacity [17]. A new correction equation, the first first-order Equation for surface adsorption kinetics, has been reported, named the modified pseudoirst-order equation (MPFO) [18]. To improve the kinetic models, Azizian [19] added a new term to the kinetic Equation of the first order and created a new model named modified pseudo-first-order Equation 2 (MPFO-2). In 1999 [20], the pseudo-second-order (PSO) kinetic equation was introduced. The formulation of the PSO model equation is expressed in table 4. Azizian, by adding a new term to the kinetic Equation of the second-order produces a new model named modified pseudo-second-order Equation (MPSO). To modify the kinetic models, a new term was added to the kinetic Equation of the -order by Azizian and creates a novel model titled modified pseudosecond-order equation-2 (MPSO-2).

Another kinetic equation for chemical adsorption was proposed by Elovich recently [21], having been applied to account for the process of absorbing pollutants present in aqueous solutions. Intraparticle diffusion is one of the diffusions-based kinetic models used to describe multistage and competitive absorptions. This model is used to explain the adsorption process, in which the amount of adsorption depends on the velocity diffused on the adsorbent. The diffusion process of particles into the adsorbent is not limited to one step. The diffusion rate is high at first, and the particles diffuse into the large pores, then it slows down, and then particles diffuse inside the smaller pores. The first step is the diffusion of methyl orange dye molecules from the solution mass to the adsorbent surface through the mass diffusion. The second stage is a transmission of colored pollutant molecules from the surface to the adsorbent internal pores, occurring via intra-particle diffusion. The third step is to absorb the species on the material's surface with a chemical reaction by changing the ionization, complexing, and Chelating [22]. Finally, the second-order kinetic model showed the most correlation coefficient. It can be said that the kinetic reaction is of the second-order kinetic type. Also, by drawing a diagram of models, the parameters of the models are computed, as can be seen in Table 4.

Kinetic model	k	$(\text{mg. g}^{-1})q_e$	<b>R</b> <sup>2</sup>	$R_{Adj}^2$	Pearson's r
pseudo-first-order (PFO)	0.01171	1.0544	0.987	0.984	-0.994
pseudo-second-order (PSO)	0.01144	1.566	0.997	0.996	0.998
modified pseudo first order (MPFO)	0.00859	1.5617	0.990	0.987	-0.995
modified pseudo second order (MPSO)	0.02821	-	0.932	0.919	0.966
2-modified pseudo first order (2- MPFO)	0.0048	-	0.966	0.960	-0.983
2-modified pseudo second order (2- MPSO	0.03146	-	0.974	0/969	0.987
Elovich equation	$(mg.g^{-1}.min^{-1})\alpha$	(g.mg <sup>-1</sup> )β	<b>R</b> <sup>2</sup>	$R_{Adj}^2$	Pearson's r
1	0.0241	1.862	0.991	0.990	0.996
Intra-particle diffusion	k <sub>id</sub>	Ci	$R^2$	$R_{Adj}^2$	Pearson's r
1	0.10172	1.57	0.999	0.997	0.999
2	0.04111	0.63827	0.932	0.866	0.966
3	0.03865	0.67863	0.989	0.977	0.994

Table 4. Parameters of the kinetic models.

#### 7. Study of Absorption Isotherms

The study of surface absorption isotherms is of particular importance in designing an absorption system. The shape of an isotherm contains information about the tendency of absorbed molecules to adsorb on the adsorbent surface. Optimization of the design of a surface adsorption system depends on the high correlation coefficient of the studied isotherms is essential. To obtain the absorption capacity of Fe<sub>3</sub>O<sub>4</sub>@HA (50%)/MMT-Na (16.13%), MO dye equilibrium adsorption isotherms on the adsorbent were investigated using five isotherm model: Longmoir, Frondelich, Tamkin, Dubbin-Radeshkovich (D-R), and Harkins-Jora (H-J). The experiments for isotherm testing were performed by adding 0.3585 g of Fe<sub>3</sub>O<sub>4</sub>/HA (50%)/MMT-Na (16.13%) adsorbent to 100 mL of MO dye solution with a specified concentration (3, 5, 8, 10, 15 and 20 mg/L). Using an incubator, the sample was stirred at a constant temperature of 25 °C at 180 rpm. Samples were picked up after 300 minutes to achieve equilibrium concentration. After separating the adsorbent using a spectrophotometric device, the absorption rate of the solution was checked at a wavelength of 464 nm (maximum wavelength of MO). The equilibrium adsorption capacity was calculated.

#### 7.1. Langmuir Isotherm

The following assumptions explaine the Langmuir isotherm: Absorption is a single layer, the adsorbent surface is perfectly homogeneous and has a limited number of identical sites, and there is very little interaction between neighboring absorbed molecules. Equation 10 is the mathematical presentation of the Langmuir equation in solution:

$$\frac{C_e}{q_e} = \frac{1}{k_L Q_m} + \frac{C_e}{Q_m} \tag{10}$$

In which  $k_L$  denotes Langmuir adsorption constant in L.mg<sup>-1</sup>,  $Q_m$  signifies the maximum capacity of absorption or single-layer capacity of absorption in mg. g<sup>-1</sup>. Figure 12 demons the curve of Langmuir isotherm. The parameter of Langmuir isotherm is shown in Table 5.



Figure 12. The curve of Langmuir isotherm.

Table 5. The parameter of Langmuir isotherm.

$(L.mg^{-1})k_L$	(mg. $g^{-}Q_m$ <sup>1</sup> )	R <sup>2</sup>	$R^2_{Adj}$	Pearson's r
0.5044	11.906	0.95446	0.94308	0.97697

In the Langmuir isotherm,  $R^2=0.954$ , and the predicted  $R^2$  was obtained 0.943. These data are closely related. The Pearson correlation value was obtained 0.977. The maximum adsorption capacity attained was 11.906 mg. g<sup>-1</sup>. The value of k<sub>L</sub>, was equal to 0.504. Q<sub>m</sub> value was largely due to the abundance of adsorption sites in the unit of mass and caused a large number of ions to be absorbed on its surface, while the connection of these ions to the surface can be weak and cause a reduction in k<sub>L</sub>. The separation factor indicates the type of adsorption performed at the adsorbent surface. If R<sub>L</sub>=0 the type of adsorption is irreversible, and if R<sub>L</sub>=1, the adsorption type is reversible. If  $0 < R_L < 1$  the absorption is desirable, and it is unpleasant if R<sub>L</sub>>1. R<sub>L</sub> was obtained using Equation 11. The results are shown in Table 6.

$$R_L = \frac{1}{1 + k_L C_0}$$
(11)

Table 6. The values of  $R_L$  in different concentrations.

C <sub>0</sub> (mg. L <sup>-1</sup> )	3	5	8	10	15	20
$R_L$	0.398	0.284	0.199	0.165	0.117	0.090

The value of separation factor was obtained between 0, and 1 suggesting the process of absorption is satisfactory by synthesized adsorbent [23]

# 7.2. Freundlich Isotherm

In the Freundlich isotherm process, the absorption is assumed to be heterogeneous. This heterogeneous adsorption can be due to differences in absorbed or adsorbent surfaces [24]. Equations 12 and 13 express the mathematical and linear form of the Freundlich equation for absorbing liquid on a solid surface, respectively.

$$q_e = k_F C_e^{1/n} \tag{12}$$

$$Logq_e = Logk_F + \left(\frac{1}{n}\right)LogC_e \tag{13}$$

In which  $k_F$  signifies Freundlich constant as the value of the multilayer absorption capacity of the adsorbent. 1/n is a constant related to absorption intensity or heterogeneous surface that named heterogeneous factor. Figure 13 shows the curve of the Freundlich isotherm. Table 7 represents the parameters of the Freundlich isotherm.



Figure 13. The curve of the Freundlich isotherm.

$(mg. g^{-1})k_F$	1/ <sub>n</sub>	<b>R</b> <sup>2</sup>	$R_{Adj}^2$	Pearson's r
3.924	0.781	0.998	0.998	0.999

In the Freundlich isotherm,  $R^2$ =0.998 and equal to predicted  $R^2$  were obtained. The Pearson correlation value was obtained 0.999. The value of 1/n give information about surface heterogeneity. So, the surface is more heterogeneous if 1/n be closer to zero. Here the value of 1/n lies in the range of 0.2 to 0.8. Therefore, the synthesized adsorbent is a promising adsorbent for removing MO dye.

#### 7.3. Temkin Isotherm

The Temkin isotherm is defined as equation 14 [25]:

$$q_e = \frac{RT}{b} \ln(k_T C_e) \tag{14}$$

If,  $B = \frac{RT}{b}$ , then the linear form of the Equation is defined as Equation 15:

$$q_e = BLnk_T + BLnC_e \tag{15}$$

Where  $k_T$  denotes the Temkin constant depending on the maximum bonding energy. R signifies the global constant of gas (8.314), T shows the absolute temperature in terms of Kelvin and b symbolizes the free energy of the network, which depends on the sidelong interactions between the absorbed particles. Because of the interaction of the absorbed molecule with each other, the adsorbent is covered in a linear layer. This coverage has reduced the heat absorption of the molecules.

The curve for the Temkin isotherm is demonstrated in Figure 14. The Temkin isothermal parameters of obedience are shown in Table 8.



Figure 14. The curve for the Temkin isotherm.

In the Temkin isotherm,  $R^2$ =0.939 and predicted  $R^2$  were obtained 0.924, which are close to each other. The Pearson correlation value was obtained 0.969.

Table 8. The Temkin isothermal parameters of

$(\text{L.mg}^{-1})k_T$	$b(kJ.mol^{-1})$	<b>R</b> <sup>2</sup>	$R_{Adj}^2$	Pearson's r
9.075	1.379	0.939	0.9249	0.969

#### 7.4. Dubinin-Radushkevish Isotherm

In the Dubinin-Radushkevish (D-R) isotherm, the hypothesis that the surface is homogeneous is not considered. The D-R model is explained by Equation 16 [26].

$$q_e = q_m e^{-\beta \varepsilon^2} \tag{16}$$

In which  $q_e$  denotes the concentration of absorbed ions on adsorbent in equilibrium condition in terms of mg. g<sup>-1</sup>,  $q_m$  is theoretical saturation capacity,  $\beta$  is D-R constant showing the average free energy of adsorption in terms of mol<sup>2</sup>.kJ<sup>-2</sup>, and  $\varepsilon$  denotes the polani absorption potential, which defines as follow: the amount of energy needed to separate an absorbed molecule from the surface of its absorbing position. The linear type of the D-R isothermal is expressed in Equation 17.

$$\ln q_e = \ln q_m - \beta \epsilon^2 \tag{17}$$

That  $\varepsilon$  was obtained using Equation 18.

$$\varepsilon = \operatorname{RT}\ln\left(1 + \frac{1}{C_{e}}\right) \tag{18}$$

in which R denotes the global constant of gas, T denotes the temperature in Kelvin, and Ce denotes the equilibrium absorbed concentrate. The average of free energy absorption was obtained using Equation 19.

$$E = \frac{1}{\sqrt{2\beta}} \tag{19}$$

From the average energy absorption value, physical and chemical absorption were obtained. Figure 15 reveals the curve for the D-R isotherm, and Table 9 illustrates the parameters of D-R.



Figure 15. The curve for the D-R isotherm.

Table 9. The isothermal parameters of D-R.

$\beta$ (mol <sup>2</sup> .kJ <sup>-2</sup> )	$q_m(mg.g^{-1})$	$E(kJ. mol^{-1})$	R <sup>2</sup>	R <sup>2</sup> <sub>Adj</sub>	Pearson's r
0.0668	4.49	2.736	0.932	0.914	-0.965

In the D-R isotherm,  $R^2$  equals 0.932, and the predicted  $R^2$  is 0.914. The Pearson correlation value is -0.965. In the D-R isotherm, if the amount of absorption energy is less than 8 kJ.mol<sup>-1</sup>, the absorption comes as physical owing to the weak forces of the Vanderwal. If it was in the range of 8-16 kJ.mol<sup>-1</sup>, the absorption has been done by ion exchange mechanism, and when the energy was between 20-40 kJ.mol<sup>-1</sup>, the absorption is of chemical type [27]. Table 9 reveals that the energy absorption is 2.736 kJ.mol<sup>-1</sup>, which indicates the physical absorption of methyl orange on the adsorbent surface of Fe<sub>3</sub>O<sub>4</sub>@HA/MMT.

#### 7.5. Harkins-Jura Isotherm

Harkins-Jura isotherm (H-J) describes the amount of multilayer absorption and the presence of heterogeneous pores at the surface of adsorbents, which are introduced in Equation 20.

$$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) LogC_e \tag{20}$$

Where, A and B are constant. Figure 16 shows the isotherm diagram of the H-J isotherm.



Figure 16. The curve for the H-J isotherm

In the H-J isotherm,  $R^2$  equals 0.782, and the predicted  $R^2$  is 0.727. Pearson's correlation value was -0.884.

In the present study, five widely used isotherms were used to investigate the appropriate isotherm model. Longmore, Frondelich, Tamkin, D-R and H-J models were examined. As can be seen from the diagrams, R<sup>2</sup> of Langmuir, Freundlich, Temkin, D-R, and H-J isotherms are equal to 0.954, 0.998, 0.939, 0.932, and 0.782, respectively. Due to the coefficient R<sup>2</sup>, the absorption of methyl orange on the adsorbent followed the Freundlich isotherm.

## 8. Thermodynamic Study

Thermodynamic parameters are one of the principles which have particular importance in describing the adsorption process. Evaluating the desirability of the process of adsorption process can be carried out by determining thermodynamic parameters in all adsorption mechanisms. By examining changes in the rate of absorption (in terms of temperature), it could be possible to find the reaction's nature whether it was exothermic or endothermic. The optimal temperature was obtained by examining the effects of temperature to achieve maximum absorption. Also, it could

be found that adsorption occurs as a chemical or physical bond. To scrutinize the impact of temperature on MO dye absorption on synthesized Fe<sub>3</sub>O<sub>4</sub>@HA (50%)/MMT-Na (13.16%), thermodynamic parameters were examined to acknowledge the nature of adsorption of this research. The calculation of the thermodynamic constants, variation in free energy, enthalpy, and entropy was done to evaluate the process's thermodynamic possibility and the spontaneous nature. The experiments related to the calculation of thermodynamic parameters were performed as follows: Adding 0.3585 g of Fe<sub>3</sub>O<sub>4</sub>@HA (50%)/MMT-Na (13.16%) to 100 mL of 5 mg/L solution of MO dye solution and stirred for 300 min at 25, 35, 45 and 55°C temperature in a shaker incubator at 180 rpm. The thermodynamic parameters required for adsorption, including Gibbs free energy, enthalpy, and entropy changes pertaining to equilibrium adsorption constant, are calculated according to Equation 21.

$$K_0 = \frac{C_0 - C_e}{C_e} \tag{21}$$

Where  $C_0$  and  $C_e$  are initial and equilibrium concentrations. Gibbs free energy was obtained in different temperatures using Equation 22 [28].

$$\Delta G_{ads}^{\circ} = -RT \ln K_0 \tag{22}$$

Enthalpy absorption was obtained of Van 't Hoff Equation from the slope of  $\ln K_0$  curve in term of 1/T, using the following EEquation

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$
(23)

Where  $\Delta S^0$  is the variation of entropy in terms of J.mol.K<sup>-1</sup> and T,  $\Delta H^0$  and R are in kelvin, J.mol<sup>-1</sup>, and J.mol<sup>-1</sup>k<sup>-1</sup>, respectively. The absorption thermodynamics constant is shown in Table 10.

Tem. (K)	$\Delta G^0, \frac{kJ}{mol}$	$\Delta S^0, \frac{J}{mol. K}$	$\Delta H^0, \frac{kJ}{mol}$	$E_0, \frac{kJ}{mol}$	S <sup>o</sup>
288	-6.259				
298	-7.279	88.843	+19.314	+18.470	3.04×10 <sup>-5</sup>
308	-7.873				

Table 10. Thermodynamic parameters for the adsorption of MO dye onto Fe<sub>3</sub>O<sub>4</sub>@HA/MMT.

To investigate the dominant absorption-type in this study, we estimated activation energy  $(E_a)$  and adhesion probability  $(S^*)$  from experimental data. Activation energy is computed from equation 24, applying the modified Arrhenius equation pertaining to surface coverage.

$$S^* = (1 - \theta)e^{-(^{Ea}/_{RT})}$$
(24)

Where  $\theta$  is surface coverage and S<sup>\*</sup> is adhesion probability which Its value is in the range of 0-1, and this value depends on the temperature of the system. S<sup>\*</sup> indicates the amount of absorbed ability to stay in the adsorbent. Equation 25 could be applied to compute surface coverage [29].

$$\theta = \left[1 - \frac{C_e}{C_0}\right] \tag{25}$$

From the graph of  $\ln [1 - \theta]$  in terms of 1/T, the amount of activation energy was obtained. In Table 11,  $\Delta G^{\circ}$  values were obtained at all negative temperatures. Notably, the amount of  $\Delta G^{\circ}$  to -20 kJ.mol<sup>-1</sup> is harmonious with the electrostatic interaction between adsorption sites and adsorbed molecules (physical adsorption) whereas  $\Delta G^{\circ}$  has a more negative value compared with -40 kJ.mol<sup>-1</sup> indicating the formation of a chemical bond between the adsorbent and the adsorbent molecules (chemical adsorption) [30]. The values of  $\Delta G^{\circ}$  obtained at all studied temperatures are less than -10 kJ.mol<sup>-1</sup>, indicating the process's physical absorption. The positive value of  $\Delta H^{\circ}$ suggests the process of dye adsorption is endothermic on the adsorbent surface, which is due to increasing the temperature on the amount of opening of the adsorbent layers, causes more dye trapping on the adsorbent surface. The results of increasing absorption are quite consistent with increasing temperature. The positive  $\Delta S^{\circ}$  indicates an increase in irregularity and probability of collisions between methyl orange molecules and the adsorbent surface in the process of dye absorption. From the slope of the diagram, the activation energy value of 187.47 kJ.mol<sup>-1</sup> was obtained. The values of positive activation energy exhibit the endothermic make-up of the adsorption process. The value of S\* is minimal and close to zero, indicating the high probability of adhesion methyl orange molecules to the adsorbent surface because  $S \ll 1$  (Table 10) confirms that the process is of physical adsorption.

#### 9. Conclusions

In this study, the natural ingredients of montmorillonite and humic acid, along with iron oxide, were used to synthesize strong and natural adsorbents with magnetic properties. With the software design software, the effect of five parameters were studied: adsorption value, pH, the weight percentage of humic acid, the weight percentage of montmorillonite, and initial concentration of methyl orange dye on dye adsorption rate. The results showed that adsorbent with 50% humic acid in the forming shell for iron oxides and 13.1566% of montmorillonite was obtained the highest dye removal efficiency when the adsorbent value was 3.5846 g/l and at pH=3 and with an initial concentration of 5.00002 ppm of methyl orange solution. The second quasi-kinetic model showed the highest correlation coefficient among the studied kinetic models. It can be said that the kinetic reaction is of the second quasi-type. Examination of the isotherm used the Langmuir, Freundlich, Tamkin, D-R, and H-J models. It has been observed that the absorption of methyl orange on the adsorbent adheres to the Frondelich isothermal formulation. The  $\Delta G^{\circ}$  values obtained indicate physical absorption in this adsorption process. A value of  $\Delta H^{\circ}$  shows the process of dye adsorption appears as endothermic. A positive  $\Delta S^{\circ}$  indicates an increase in irregularity and the probability of collision between methyl orange molecules and the adsorbent surface in the dye adsorption process. Positive E<sub>a</sub> values suggest the nature of the endothermic absorption process. The value of S\* is minimal and close to zero, which confirms the process of physical absorption.

#### Declarations

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

#### Authors' contributions

All authors contributed to the study's conception and design.

Zahra Abbasi: analysis and interpretation of data, Drafting the manuscript and revising the manuscript.

Elisa Isabel Garcia Lopez: Conception and design of the study. Abdolhadi Farrokhnia, Zahra Zohrabzadeh: Drafting the manuscript, analysis and interpretation of data and revising the manuscript. Yashar Behnamian, Ermia Aghaie: Drafting the manuscript, analysis and interpretation of data.

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