

## Investigation and optimization of reactive orange-3R dye surface absorption by nano-MMT/NZVI composite absorbent in a process of textile industry wastewater treatment

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Removal of the dye pollutants of factories effluents always has been a challenge. In this study zero-valent iron montmorillonite nanocomposite as an absorbent for removing azo-dye from industrial wastewater and in different test situations in a batch process was used. Synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles and nanocomposite absorbent were verified by conventional XRD and SEM methods. Then by provision of water-based solution from well-known reactive orange-3R, surface absorption ability of the absorbent was investigated. In this method, NZVI was applied as reducer for dye removing, and the factors such as absorbent quantity, contact time, solution initial pH, dye concentration and temperature influence were studied. For exploring of removed dye quantity, UV spectroscopy and Beer-Lambert law were used. According to the achieved results of MMT/NZVI absorbent efficiency, by increasing the absorbent content, the removed dye quantity was increased, but by application of 0.5 g absorbent in pH=6 for removing 50 ppm dye concentration in 10 ml solution, orange-3R was removed effectively. In investigation of temperature parameter, the test results in different temperatures showed that dye removing of solution increases in higher temperatures up to 40 °C. At last, Langmuir and Freundlich isotherm absorption models for orange-3R dye removing by application of MMT/NZVI nanocomposite were predicted and also isotherm model parameters and correlation coefficient of ion removal were achieved. According to achieved results Langmuir isotherm model in comparison of Freundlich isotherm model showed more correlation with practical values. The most dye absorption capacity of solution in pH=6 at 40 °C, for Langmuir model was determined. Dye absorption process on absorbent was exothermic and the kinetic data was in accordance to pseudo-second order model. Also dye desorption from absorbent was done using 0.1 M NaCl solution.

**Keywords:** Absorption isotherm and kinetics; treatment; azo dye; nanocomposite; zero valent iron; montmorillonite

### INTRODUCTION

One of the most important environmental pollutants is wastewater containing textile industry chemical materials that makes pollution for humans and environment. Textile dyes through diffusion to surface and ground water lead to dye pollution of water resources [1]. Furthermore, not degradation of these dyes and absorption of them into the plants can lead to genetic mutations in next generations. Therefore, it seems really necessary to treatment of colored wastewater and removal of these pollutants before discharging them into environment. Discharged wastewater of dyeing factories contains colored wastewater including different kinds of dyes such as complex and fully aromatic structures [2]. Azo dyes are from the most applicable industrial dyes and always we had needed to use this kind of dyes regarding to the varieties of their chemical structures. Most of this kind of dyes is stable in exposure of UV-visible and heat, so making them resistant to whitener, sun light and oxidation doesn't lead to elimination of them by conventional water waste treatment systems. Totally, the

treatment methodologies are divided to 3 methodologies of physical methodology [3 & 4] (surface absorption, ionic exchange), chemical methodology [5-7] (oxidation, coagulation and sedimentation) and biologic methodology [8] (aerobic and unicellular). Nowadays, among existed methodologies, utilization of absorbents for removing pollutants in surface absorption method has attracted almost of researchers attention [9 & 10]. In general, absorbents can be divided to 2 types of conventional absorbents (that the most famous of them is activated carbon) and low cost absorbents (unconventional) those rather entrap the pollutants based on reaction with absorbed particles. However the activated carbon is one of the most proper absorbent for removing several types of pigments, but its use is limited in some cases because of its high prices. Also after using, the activated carbon (for cleaning waste water) will be saturated and cannot absorb more pigments. When activated carbon is saturated, its recycling needs different methods such as thermal, chemical, oxidation, electrochemical methods that all of them are expensive. In addition, in the recycling process some activated carbon is destroyed and also its absorption capacity will be less than initial state. Therefore, the use of low cost and effective

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alternative absorbents to the activated carbon seems to be essential [11]. The absorbers that are used for absorption of pollutants should be having sufficient porosity and surface area for trapping pollutants constituents. Moreover, the low prices, availability, mechanical and thermal stability, recycling and reusing capability are also characteristic of a suitable absorbent. Among these absorbers, using inorganic nanoparticles such as titanium dioxide (TiO<sub>2</sub>) [12], zinc (ZnO) [13] and iron (Fe<sub>3</sub>O<sub>4</sub>) [14] oxides as an absorbent for polluted wastewater is a developing process and has been reported as very effective process. In recent Years, the use of nano ZVI particles to remove toxic chemicals from contaminated water has attracted widespread attention. The ZVI is a strong reducing agent and also cheap. The results have shown that this method is doing well to remove contaminations such as heavy metals cations [15], chlorinated organic substances [16], aromatic nitro compounds [17], insecticides [18] and the nitrates [19]. Recently has reported an optimal performance of ZVI complex with multi-walled carbon nanotubes in a quasi-Fenton catalytic process to eliminate herbicide atrazine too [20]. In many methods and recent researches, nano ZVI particles have been used simply [21-23], with surface modification [24 & 25] or as a composite with a suitable substrate [26-28]. However, using these nano particles has been reported very effective, rapid and cheap in all cases. Here is evaluated how to produce ZVI nanoparticles on montmorillonite substrate and its application for removing orange-3R dye from water. Montmorillonite is nanoclay based on layered silicates that because of its special properties has significant importance, but so far it hasn't been used in this way. This combination can produce a suitable composite with ZVI nanoparticles for removing reactive orange-3R dye.

## EXPERIMENTAL

### Materials

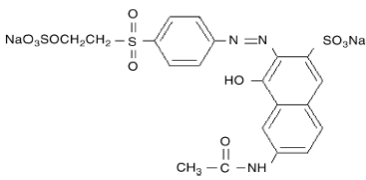
Used materials in this project included iron (III) chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O), sodium borohydride (NaBH<sub>4</sub>), sodium hydroxide (NaOH), and hydrogen chloride (HCl) and montmorillonite salts those were prepared from Merck (German) Co. In order to prepare the industrial reactive orange-3R dye, the product of Hamedan Alvan Sabet Co. was used. This dye is one of the reactive dyes and is one of the most widely used dyes in Iranian textile industry. Table (1) shows some characteristics of the investigated dye.

The Investigated parameters in this study included pH (in the range of 4-12), contact time (0.5, 1, 1.5, 2, 2.5, and 3 hours), initial dye concentration (50,100,150, and 200 ppm), the initial absorbent value (0.01, 0.1, 0.2, 0.3, 0.4 and 0.5 g), temperature range (10, 20, 30, and 40 °C) and in order to adjust the pH, NaOH (0.1 M) and HCl (0.1 M) solutions were used.

### Apparatus

A double beam UV-visible Shimadzu spectrophotometer (spectrophotometer model 6320 D) equipped with a cm<sup>-1</sup> quartz cell was used for recording the visible spectra and absorbance measurements. Infrared measurements were performed on a Bruker-IFS48 FTIR spectrometer (Ettlingen, Germany). The spectra of solids were carried out using KBr pellet. Vibrational transition frequencies are reported in wave numbers (cm<sup>-1</sup>). X-ray diffraction patterns (XRD) were performed at room temperature on an X-ray diffractometer (Siemens model D 5000, Germany) using Ni-filtered CuK α radiation (40 kV, 25 mA) with scanning rate of 3°/min. Field emission scanning electron microscope (FE-SEM), model Hitachi S-4160, 30 KV, on gold-coated powders. A Metrohm 692 pH meter was used for monitoring the pH values. A water ultrasonicator (Sonic VCX750, USA) was used to disperse the nanoparticles in solution and a super magnet Nd-Fe-B (1.4 T, 10×5×2 cm) was used.

**Table1.** Some characteristics of the investigated dye.

Characteristic	Molecular formula	Molecular Weight (g/mol)	Class	λ <sub>max</sub> (nm)	Chemical structure
Reactive Orange-3R	C <sub>20</sub> H <sub>17</sub> N <sub>3</sub> Na <sub>2</sub> O <sub>11</sub> S <sub>3</sub>	617.54	azo (-N=N-bond)	388, 494 (2nd)	

### Preparation methods

#### Synthesis of iron nanoparticles

At first, a 250 ml balloon of NaBH<sub>4</sub> (0.8 M) was prepared. NaBH<sub>4</sub> due to its instability in the water reduction property loss was prepared just as much as needed amount in each stage. In other balloon, 250 ml FeCl<sub>3</sub> (0.2 M) was prepared and were placed on the electromagnetic shakers with magnet for 1 hour. The prepared NaBH<sub>4</sub> solution in the presence of nitrogen gas was added to FeCl<sub>3</sub> solution slowly, by burette. Experiment lasted 10 minutes in the shakers with 500 rpm. After a while the nanoparticles were gathered at its end. Brown iron (III) chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O) solution was in a distillation balloon and nitrogen gas was passed over it. Sodium borohydride solution was added to the solution containing iron chloride (FeCl<sub>3</sub>) by burette to form nanoparticles for appearing black sediment. In the next phase, the iron nanoparticles deposition was filtered by filter paper for two times and was washed with deionized water and acetone. At last, the dark obtained deposition was collected, dried in an oven and powdered, respectively.

#### Preparation of NZVI/MMT nanocomposite

For preparing the absorbent, 3 grams of montmorillonite was mixed in 30 ml of distilled water and 1 gram of prepared nanoparticles was added to the solution and was placed for 1 hour in oven at 300 °C to be dried and then was collected in form of solid powder. Dark brown powders were obtained.

#### Measuring the absorption of orange-3R by spectrometry method

The wavelength of maximum absorption was scanned using a uv spectrometer in the wavelength range of 100-700 nm and the maximum absorption was obtained at wavelength of 494 nm. The calibration curves for the solutions with different concentrations were drawn around maximum adsorption wavelength(λ max). According to the results, increasing dye concentration in solution leads to growing absorption intensity. Finally, knowing absorption quantity and regarding to linearity of the calibration curve and using Beer-Lambert equation, dye concentration was determined in each stage. To calculate the percentage of removal and absorption capacity, the equations 1 and 2 were used, respectively.

$$R (\%) = \frac{C_o - C_e}{C_o \times 100}, \quad (1)$$

$$q_e = \frac{(C_o - C_e) \times v}{w}, \quad (2)$$

That R is removal percentages, C<sub>o</sub> and C<sub>e</sub> are initial and equilibrium concentration after adsorption respectively, v is solution volume, and w is absorbent mass. The calibration curve of orange-3R at wavelength number of 494 nm in a straight line for 0,5, 10, 15, and 20 mg.l<sup>-1</sup> was drawn. It is illustrated in figure (1).

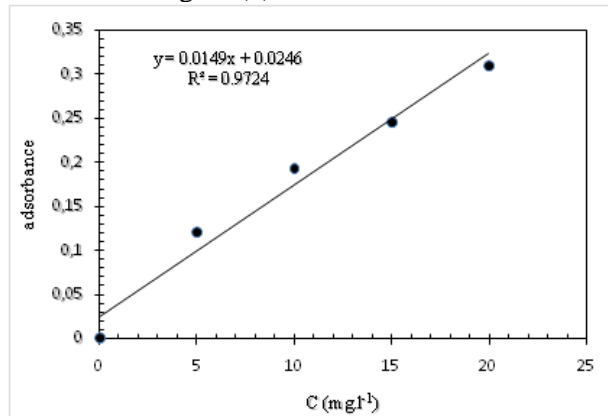


Fig.1. Calibration curve of orange-3R at wavelength number of 494 nm.

## RESULTS AND DISCUSSION

### Characterization

#### X-ray diffraction pattern (XRD)

The X-Ray diffraction method, because of being a direct method for determining phase types and material crystalline structures has significant importance. According to performed studies on the X-Ray diffraction of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in 2θ, 18, 21, 30, 35.5, 43.5, 54, 57.5, 64, the peaks with different intensities appear. In this experiment, the obtained results of XRD analysis was shown in Figure 2.

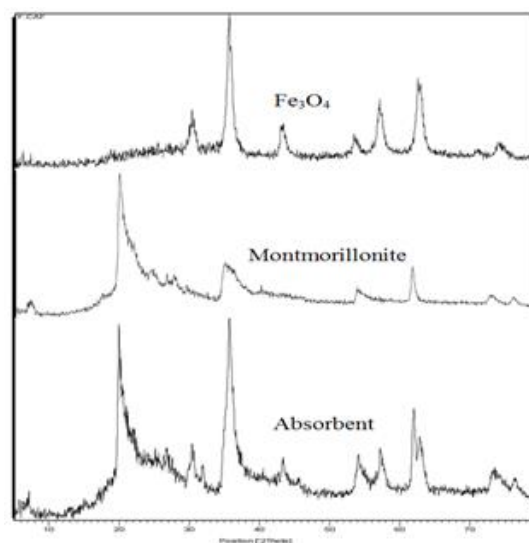
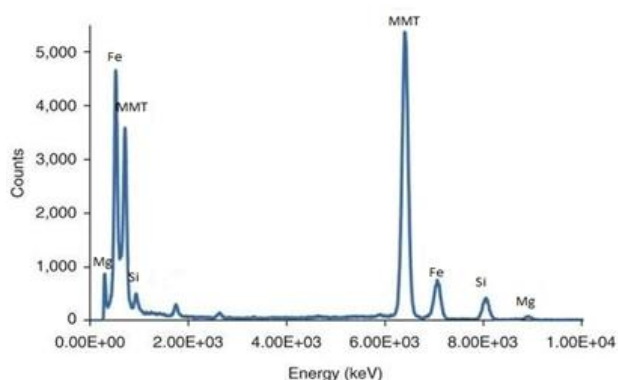


Fig. 2. XRD patterns of Fe<sub>3</sub>O<sub>4</sub>, nanoparticles, MMT and MMT/ZVI composite.

The maximum peak (35.5) is related to cubic crystals of iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles that actually this analysis confirms the presence of  $\text{Fe}_3\text{O}_4$  particles. As shown in Figure 2, in X-Ray diffraction pattern of the prepared nanocomposite, the presence of both magnetic iron oxide and montmorillonite nanoparticles is quite evident.

*Surface study of used absorbents using scanning electron microscopy (SEM)*

Obtained results of SEM\_EDX analysis of synthesized absorbent sample showed that in magnetic composite there are Fe, Silica, Mg, and MMT parts, produced peaks of Fe in this study confirms that MMT as a substrate includes iron nanoparticles.

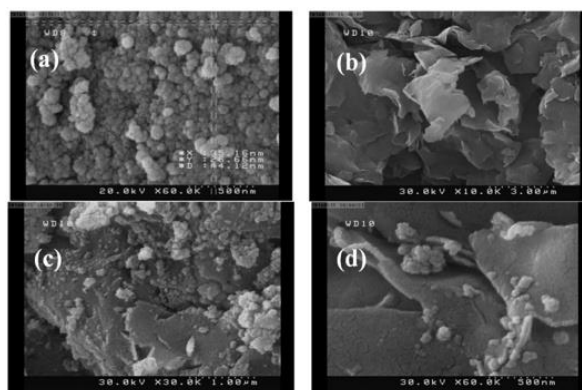


**Fig.3.** EDX analysis of prepared absorbent sample.

As it shown in electronic microscope images, magnetic nanoparticles were synthesized in nano scale and well dispersed in the entire montmorillonite matrix. They located into cavities of MMT in absorbent without agglomeration.

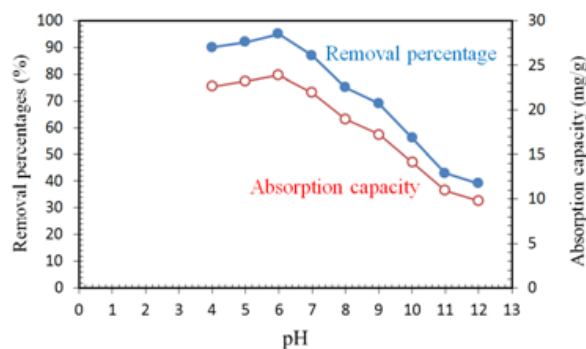
*Study of effective factors to optimize absorption process of reactive orange-3R using MMT/ZVI nanocomposite. Study of pH influence on dye removal efficiency*

In different bottles, 50 ml of the dye syrup in pH (4, 5, 6, 7, 8, 9, 10, 11 and 12) were prepared. To adjust pH of dye syrup, NaOH (0.1 M) and HCl (0.1 M) solutions were used and measured by pH meter. 0.1 gr absorbent was added to each one of solutions. For proper mixing of absorbable and absorbent, the samples were placed in a shaker machine with 320 rpm. The test was performed at 25 °C and was lasted 3 hours. After 180 minutes, the absorbent was separated from the solutions using a magnet during less than 1 minute. For each solution, the absorption quantity was measured using a spectrophotometer. In order to more accuracy, the test was repeated in two stages.



**Fig.4.** SEM images of  $\text{Fe}_3\text{O}_4$  (a), montmorillonite (b), synthesized absorbent (c), and (d)

The figure (5) shows the effect of pH on absorption capacity and absorption efficiency. In this figure, it can be seen that the absorption process at pH=6 has better efficiency in comparison of other pH. So by increasing the pH from 6 to 10, both of percentage of absorption and absorption capacity are reduced. At pH=6 due to electrostatic attraction between the negatively charged molecules of dye and positively charged of absorbent surface, the absorption efficiency is high. But at higher pH, the absorbent surface is negatively charged and therefore, the electrostatic repulsive force between negatively charged ions of anionic dye and absorbent, lead to decrease the amount of dye absorption. So pH=6 was selected as the optimal value for the next tests of absorption process.

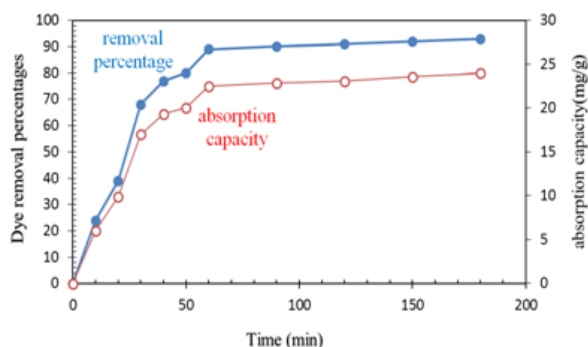


**Fig.5.** Diagram of pH effect on removal amount of dye (Absorbent doze: 0.1 g, temperature= 25 °C and initial dye concentration= 50 mg/l)

*Study of contact time and absorption kinetics*

In order to obtain the suitable for maximum removal efficiency in an Erlenmeyer flask, the dye (pH=6) was prepared and 0.02 gr of absorbent was added to the solution and it was placed on the shaker machine (T= 25 °C and 320 rpm) in time periods of 10, 20, 30, 40, 50, 60, 90, 120, 150, 180 minutes. It was observed that in the first hour the curve has sharp slope and absorption capacity

increases rapidly. This may be due to many active and unsaturated sites in outer surface of absorbent. In continue, the slope decreased during the time gradually and finally after 1 hour, the absorption amount has stabilized approximately at the room temperature and has balanced, so one hour, was evaluated as a suitable balance time at the room temperature.



**Fig. 6.**Diagram of contact time effect on removal efficiency (absorbent doze: 0.1 g, pH=6, Temperature= 25 °C and dye concentration = 50 mg/l)

Kinetic equations were applied to describe the transfer of azo dye molecules per time unit or to evaluate the variables affecting the reaction rate. In this study, the pseudo-first and pseudo-second kinetic models those are mostly used to examine factors influencing the reaction rate of reactive dye absorption process on the NZVI / MMT absorbent were used. Linear kinetic equations are as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (3)$$

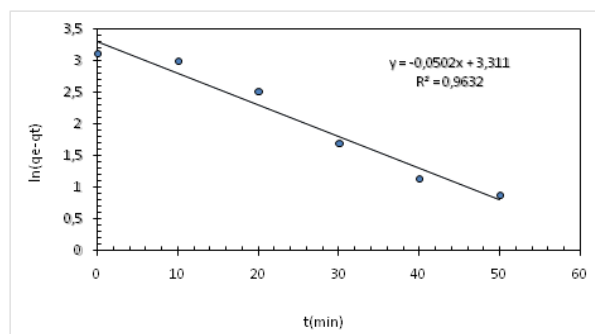
$$\frac{t}{q_t} = \frac{1}{q_e^2 \cdot k_2} + \frac{1}{q_e} t, \quad (4)$$

Which, ( $k_1$ ), rate coefficient constant ( $\text{min}^{-1}$ ) and ( $k_2$ ), pseudo-second reaction rate constant in terms of  $\text{mg} \cdot (\text{g} \cdot \text{min})^{-1}$ ,  $q_e$ , is balanced absorption capacity in terms of  $(\text{mg} \cdot \text{g}^{-1})$ , ( $q_t$ ) is absorption capacity at time of ( $t$ ) in terms of  $(\text{mg} \cdot \text{g}^{-1})$ , ( $q_e$ ) and ( $k_1$ ) values are determined as linear intercept and the slope of  $\ln(q_e - q_t)$  versus ( $t$ ) and also ( $q_e$ ) values and ( $k_2$ ) through the slope and intercept of linear graph  $[(t) \cdot (q_t)^{-1}]$  in terms of ( $t^{-1}$ ) are determined.

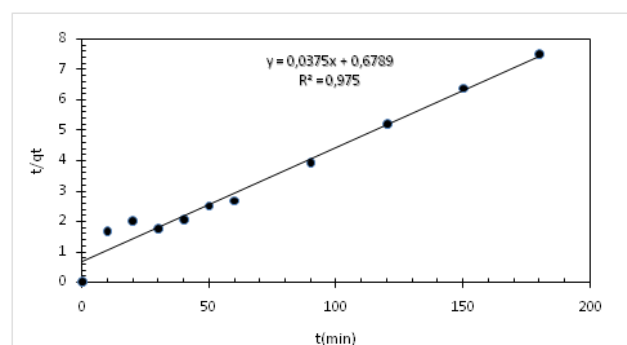
#### Study of temperature effect on removal efficiency and gaining thermodynamical coefficients

To evaluate the effect of temperature, solutions were prepared at pH = 6. The amount of 0.1 g of absorbent was added to the solutions. The solutions for 30 minutes on a shaker with 320 rpm were placed. Temperature ranges were selected as 10, 20, 30, and 40°C. It is visible that increasing the temperature increases the absorption capacity in all the initial absorbents concentration. This increasing can be due to raise of dye solubility and

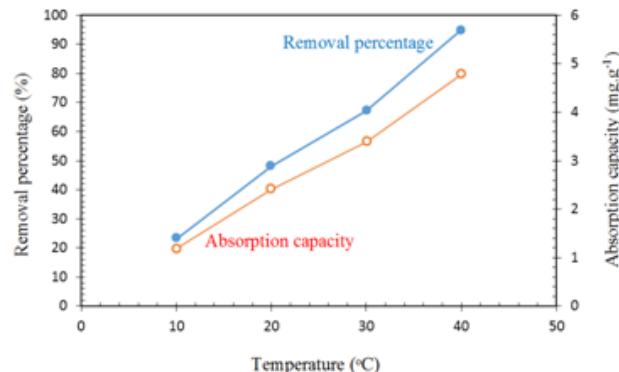
consequently increasing of effective contacts of absorbable and absorbent materials and growth of pores size on absorbent surface that it leads to pollutant absorption.



**Fig. 7.** The pseudo-first kinetic model.



**Fig.8.** The pseudo-second kinetic model



**Fig. 9.** Graph of temperature effect on removal efficiency [absorbent dose of 0.1 g, pH =6, time of 30 minutes and 50 ( $\text{mg} \cdot \text{l}^{-1}$ ) of dye concentration]

In order to study the thermodynamic absorption process, determination of three factors of standard enthalpy  $\Delta H$ , standard free energy  $\Delta G$  and standard entropy  $\Delta S$  is essential.

The obtained  $\Delta H$  and  $\Delta S$  values were obtained using Van'tHoff equations: [17]

$$\text{Ln}k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \quad (5)$$

$$K_d = \frac{q_e}{c_e}, \quad (6)$$



That (R) is constant equals to 0.0082 and ( $K_d$ ) is the ratio of absorbed dye on adsorbent to its remaining in the solution.  $\Delta H$  and  $\Delta S$  values are obtained from drawing linear graph of ( $\ln K_d$ ) versus ( $1/T$ ) those are the slope and intercept of the linear graph.  $\Delta G$  values are calculated by following equation:

$$\Delta G = -RT \ln K_d \quad (7)$$

The calculated values of thermodynamic variables are shown in the table (3). According to the positive values of ( $\Delta H$ ), can be said that adsorption process has endothermic nature and with previous results based on increasing the amount of absorption by increasing of the solution temperature is compatible, this positive values also represents forming a strong chemical bond between azo dye molecules and the adsorbent surface. The obtained values of Gibbs free energy ( $\Delta G$ ) represents the absorption reaction is a spontaneous reaction and the increased values by increasing the temperature, shows high intention of adsorbent to absorb dye in higher temperatures.

*Study of the adsorbent dosage effect on the removal amount*

At this stage, 6 bottles of dye solution were prepared with pH = 6 and 0.08, 0.1, 0.2, 0.3, 0.4 and 0.5 gr of adsorbent were added to each solution. The temperature of 25 ° C and 1 hour of

contact time were selected. The solution was placed on a shaker with 320 rpm. It was observed that by increasing the amount of adsorbent, the dye removal percentages are increased and as well as the absorption capacity is reduced. Increasing of the removal percentage is due to increase of adsorbent surface and consequently augmentation of the absorbable molecules access to absorption sites on NZVI-MMT versus of fixed values of orange-3R molecules. Reduction of absorption capacity can be due to unsaturation of active site on adsorbent surface during the absorption process and the particle reactions, such as compaction or aggregation due to high absorption concentrations [29]. Finally, 0.5 gram of NZVI-MMT composite was selected as an optimal amount of adsorbent to remove orange-3R.

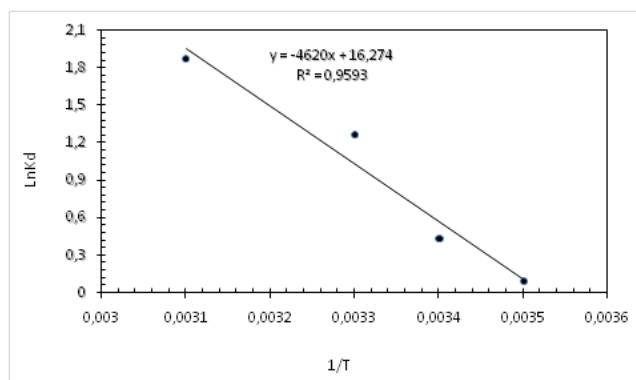


Fig.10. Van't Hoff diagram of absorption.

Table2. Calculated values to thermodynamic study

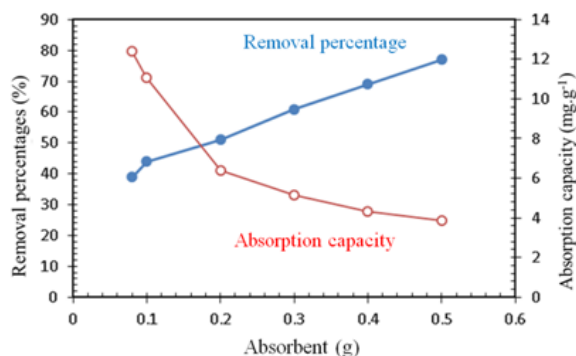
Solution Temperature (K)	C <sub>e</sub>	q <sub>e</sub>	K <sub>d</sub>	lnK <sub>d</sub>
283	15.5	17.25	1.10	0.09
293	12.14	18.93	1.55	0.43
303	6.17	21.89	3.54	1.26
313	3.54	23.23	6.54	1.87

Table3. Thermodynamic variables

Solution Temperature (K)	ln K <sub>d</sub>	ΔG (kj.mol <sup>-1</sup> )	ΔH (kj.mol <sup>-1</sup> )	ΔS kj.(mol.K) <sup>-1</sup>
283	0.09	- 0.2	37.88	0.133
293	0.43	- 1.03		
303	1.26	- 3.13		
313	1.87	- 4.79		

Table4. Comparison of the obtained results of experimental data and Langmuir and Freundlich isotherm models.

Freundlich model			Langmuir model		
R <sup>2</sup>	K <sub>F</sub> (mg/g)(l/mg) <sup>1/n</sup>	1/n	R <sup>2</sup>	K <sub>L</sub> (l/mg)	q <sub>m</sub> (mg/g)
0.833	4.46	0.0842	0.987	0.123	7.34

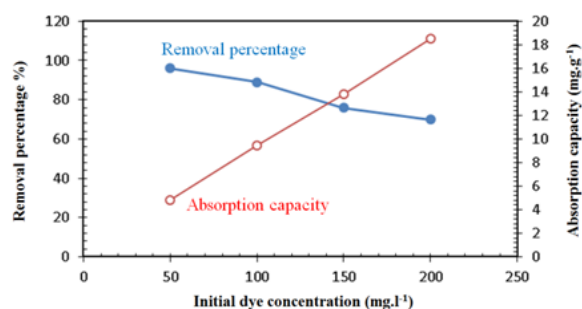


**Fig. 11.** The effect of adsorbent dosage on removal efficiency diagram (pH= 6, 1 hour, adsorbent dose of 0.08, 0.1, 0.2, 0.3, 0.4 and 0.5 g, temperature of 25°C and dye concentration of 50 ppm).

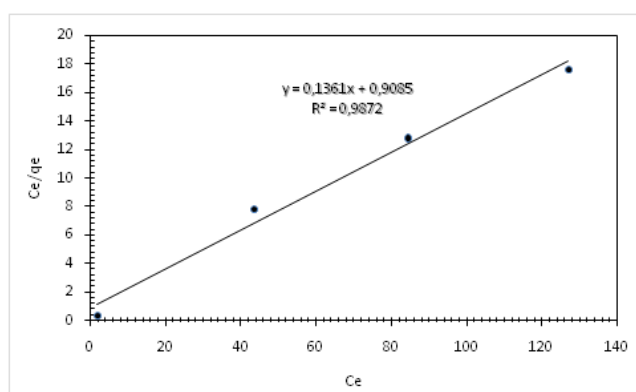
*Study of the initial dye concentration effect and its impact on the isotherm adsorption models*

At the last stage, the effect of orange-3R initial dye concentration on the removal efficiency of it by the adsorbent in different primary concentration ranges of dye was examined. Then the obtained results were used to draw the Langmuir and Freundlich isotherms. The isotherm is often used to determine the equilibrium adsorption potential and to evaluate the effectiveness of different environmental masses that in this model was used to describe the performance of montmorillonite in dye removal. In the Langmuir isotherm, surface bonds caused by physical forces are observed so the absorption is done only in form of single layer and it is assumed that the absorbing affinity of all sites is the same [30]. This model corresponded well with the vast values of experimental data and its linear form, is as the equation (3). Freundlich model in 1907 was presented as an experimental relationship by Freundlich. But then was used to multi-layer modeling on the heterogeneous surfaces or surfaces with different active sites in action and binding affinity to absorbing material. In this model it was assumed that at first, the stronger sites are filled and the bonding force is decreased by increasing the amount of the filled sites, where (Kf) and (nf) are Freundlich isotherm constants. In Freundlich isotherm, (Kf) and (nf) show the absorption amount and the absorption intensity, respectively [31]. The solutions with pH = 6 and 50, 100, 150, 200 mg.l<sup>-1</sup> of dye were prepared. 0.5 g of adsorbent was added to the solution and the solutions were placed on the shaker with 320 rpm at temperature of 40°C, for 60 minutes. It was observed that with increasing the initial dye concentration from 50 mg to 200 mg, the dye removal percentage was reduced. Probably, this decreasing trend was due to the fixed quantity of active sites on the adsorbent versus the increased quantity of dye molecules or in other words,

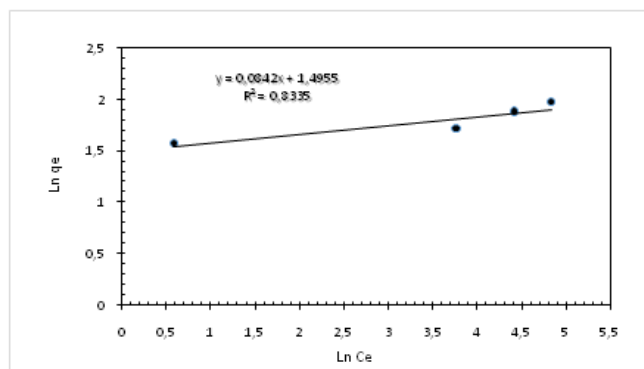
saturation of the absorbent surface in high dye concentrations



**Fig.12.** Effect of initial concentration (adsorbent dosage of 0.5 g, pH= 6, 1 hour, temperature of 40°C and dye concentration of 50, 100, 150 and 200 mg.l<sup>-1</sup>)



**Fig. 13.** The Langmuir isotherm model



**Fig. 14.** The Freundlich isotherm model.

**CONCLUSION**

In the process of removal dye contaminants from water by adsorbent of NZVI/MMT nanocomposite, produced in optimized conditions, desired results were achieved. The results of the study showed that at pH = 6, azo dyes removal efficiency by the adsorbent was better and adsorption reaction time by increasing the temperature from 25 to 40 °C, (15 °C), was reduced from an hour to half an hour and the obtained results for the thermodynamic parameters showed that dye removal increased with increasing the

temperature and it has endothermic and spontaneous nature and has formed a strong chemical bond between the molecules of dye and absorbent surface. According to the investigations can be concluded that adsorbed Fe<sub>3</sub>O<sub>4</sub> nanoparticles onto a suitable substrate of montmorillonite, has very good effectiveness and efficiency in removing dye contaminants of orange-3R. In this regard, the removal percentage, with increasing of initial concentration of dye and the amount of absorption was decreased and increased, respectively. Due to the widespread use of zero-valent iron (ZVI) nanoparticles as an appropriate adsorbent for the removal of contaminants and to remove toxic chemicals from contaminated water is expected that this method is an effective way to solve problems and remove pollutants. According to the obtained results from the performance of nanocomposite zero-valent iron montmorillonite adsorbent, however, that by increasing the amount of absorbent, dye removal amount increases but by increasing it to the amount of half a gram, at ambient temperature at, to remove 10 ml dye solution with concentration of 50 ppm can completely remove orange-3R According to the Langmuir isotherm model results in comparison of Freundlich isotherm model, there is the most correlation with experimental results. There is the most dye adsorption capacity of the solution at 40°C in pH = 6 that shows it is correlated with Langmuir adsorption process model. In this study, the positive variations of absorption heat has proved the exothermic nature of absorption process and the negative variations of free energy has proved spontaneous of absorption process and reduction of free energy associated with increasing of temperature means more effective absorption of metallic ions in higher temperatures.

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