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THERMODYNAMIC AND KINETIC STUDY OF ADSORPTION OF THE AZO DYE FROM AQUEOUS SOLUTION ON THE SURFACE OF IRAQI FLINT

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ABSTRACT

This research focused on studying the ability of Iraqi Flint to remove methyl orange of aqueous solutions of different concentrations of adsorbent and it was studied by changing the contact time, pH, temperature, and amount of adsorbent. Using 0.1 g of Iraqi Flint, the maximum adsorptionof dye (>37%) was achieved in aqueous solutions. The experimental data have been examined using Langmuir, Freundlich and Temkin isotherms models, the adsorption pattern on Iraqi flint appears to follow the Freundlich and Temkin isotherms, according to the outcomes obtained at (303, 313, and 323) K. In this work, four kinetic models (the pseudo first-order, the second-order, Elovich, and Intraparticle Diffusion) were used, to fit the experimental data. The adsorption kinetic process was found to follow a pseudo-second-order model. The slope and intercept of the linear plots of Ln K_{eq} versus 1/T were used to compute thermodynamic parameters such as ΔG^o, ΔS^o, and ΔH^o it showed that adsorption of MO^- was spontaneous, exothermic and randomness at a different temperature.

KEY WORDS : Adsorption, Iraqi Flint, Methyl orang, Thermodynamic and kinetic parameters

INTRODUCTION

Water is the most important source for human life, where the human use it for drinking, washing, agriculture and other uses to support his life. Water can be contaminated when the quality or composition of water is different due to the activity of humans. Increasing industrial activities increase environmental pollution problems (Montazer Rahmati *et al.*, 2011). There are a lot of substances that can pollution water such as inorganic acids, salts, alkali, organic matter, and dyes. Wastewaters contaminated with dye represent the most amounts of the discharged industrial water. Water polluted happened due to the use of large quantities of water in manufacturing processes and the first clear sign of water-polluting is color because of dyes (Chong *et al.,* 2010). Dyes are widely used by a human from antiquity and it was extracted from plants such as indigo and animals such as carmine.

Until 1856, humans depended on natural sources of dyes.

Then William Henry Perkin attempted to synthesize artificial quinine to use allyl toluidine and treat malaria. William succeeded in producing a basic dye, aniline, and this was the first discovery of material synthetic dye (Belaid *et al*., 2013).

Methyl orange (MO^-) is used in printing manufactory, textile, and paper and it is a water-soluble anionic azo dye (Neethu and Choudhury, 2018). MO^- can cause intestinal cancer in humans as it is converted into aromatic amines during the metabolism process once it enters the human body (Almasian *et al*., 2016). Generally, industrial effluent contaminated with dyes are believed to be extremely toxic and a hazardous to the environment. Therefore, dyes must be removed from industrial discharges (Adak *et al*., 2005). Moreover, to remove dye from wastewater there are several treatment techniques such as adsorption (Crini *et al*., 2008; Janoš *et al*., 2003). Photodegradation (Mohamed, 2004), coagulation-flocculation (Sivalingam *et al*., 2003), chemical oxidation (Salem, 2001), electrochemical oxidation (Vlyssides *et al*., 1999), biological process (Ledakowiez *et al*., 2001).

Many methods are mentioned and among those mentioned is adsorption. Adsorption is defined as the process of transferring a pollutant from a fluid phase (gaseous or liquid) or its source environment to the surface of a solid (adsorbent). This treatment method remains so limited in eliminating various dyes. Only, the cationic dyes, mordant dyes, dispersed, reactive and vat are eliminated by this technique (Gautam *et al*., 2013).

In this work, the aim is toward studying the removal of MO^- on Iraqi Flint adsorbent. The effects of adsorbent mass, effect of contact time, effect of temperature, effect of Ionic strength, effect of pH were studied.

EXPERIMENTAL

Reagents and materials

The Iraqi Flint was obtained from Akashat area at-Anbar governorate / Iraq. The adsorbent powders were washed with de-ionized water more than one and dried at 80 °C. The Iraqi Flint in this work was sieved to ≤ 75µm. Table 1 illustrates the chemical structure of Iraqi flint with the percentage of each element.

Table 1. The chemical composition of Iraqi Flint

SiO_2	Al_2O_3	Fe_2O_3	L.O.I	Total
35.41%	45.6%	0.69%	13.79%	95.49%

The adsorbate methyl orang (MO^-) was obtained from BDH (purity of 99.9%) with molecular weight of 327.33 g/mol, where it has been used as an adsorbate. The chemical formula ofMethyl orang was $C_{14}H_{14}N_3NaO_3S$. The chemical structure of (MO^-) is shown in Figure 1. A stock solution (1000 ppm) was prepared by dissolving 1g of MO^- in 1L of de-ionized water.

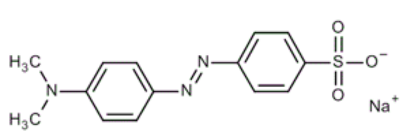

Fig. 1. The chemical structure of MO^-

Adsorption Isotherm studies

When adsorption experiments were conducted, it was used 0.1g adsorbent Flint with10 mL of MO^- at different initial concentrations (3, 5, 7, 9, 11, 13 and 15) ppm. The adsorption equilibrium, adsorbent weight, pH, Ionic strength, kinetics, temperature effect at (30, 40, and 50) °C and thermodynamics are described below. The concentration of MO- was determined by measuring the absorbance utilize a UV-VIS spectrophotometer (T 80) at ($\lambda_{max} =$ 464 nm). An equation (1) was used to compute the mass of the adsorbed amount of MO^- (q_e mg/g).

$$q_e = (C_0 - C_e)\ V / W \quad .. (1)$$

Where C_e mg/L is a residual concentration at equilibrium, V is volume (L), C_0 mg/L represents initial concentration, while W represents adsorbent mass dosage (g). The percentage of MO^- removal calculated according to the equation (2).

$$\%Removal \ \frac{(C_0 - C_e)}{C_0} \times 100\% \quad .. (2)$$

RESULTS AND DISCUSSION

The Impact of the quantity of Adsorbent

In this work, the impact of the Iraqi Flint dose on MO^- dye elimination was studied at30°C and initial concentration of (6ppm) as illustrated in Fig. 2. When the increase in sorbent dose of 0.05 to 0.1 g, the percentage of dye removal (R %) onto Iraqi Flint increased from 35% to 37.59%. After adsorbent dosage of 0.1g, surface showed no effect on the removal and adsorption are nearly constant 37.59%. The high concentration gradient among the solid adsorbent and solution and the abundance of free adsorbent sites can also be attributed to this increase (Xu *et al*., 2015).

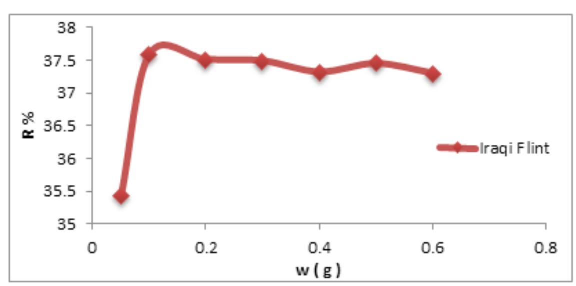

Fig. 2. Impact of Adsorbent dose on the adsorption of (MO^-) dye on Iraqiflint

Impact of the Contact Time

The impactof contact time on the adsorption of MO^- ontoIraqi flint at temperature (30, 40, 50) °C, initial concentration of (6 ppm, and 0.1 g) of adsorbent was the adsorption capacity a constant value at a certain time. The results showedthat 50 min is the equilibrium time required for the MO^- adsorption process on the Iraqi flint as shown in Figure 3.

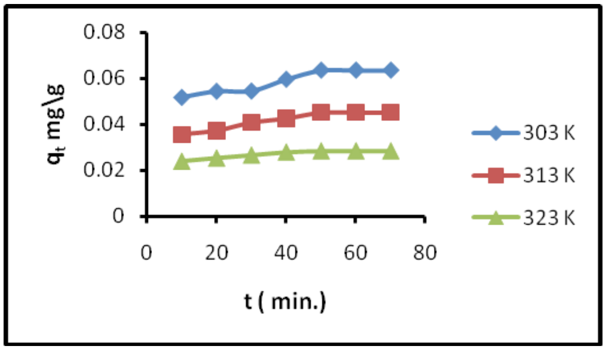

Fig. 3. Impact of Contact Time on the adsorption of (MO^-) dye on

Iraqi flint at different temperature

pH Effect

We found that the values of the adsorption capacity decrease as the acidic function increases with respect to the surface of the Iraqi flint as shown in the Fig. 4. And since the charge prevailing on the surface of the Iraqi flint is the negative charge, so when the medium is basic, a repulsion occurs between the OH^- base and the Iraqi Flint, and this leads to a decrease in the value of the adsorption capacity

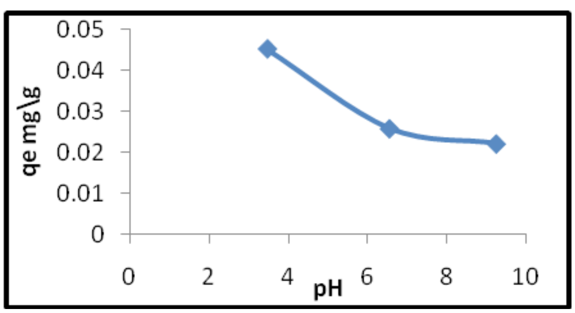

Fig. 4. The effect of the acidic function in adsorption of the MO^- dye on the surface of the Iraqi flint at 303K

when increasing the acidic pH (Al-Kazraqi *et al.*, 2017).

Effect of Ionic Strength

The increase in the amount of adsorbate on the surface of the Iraqi Flint is the reason that the solubility of the salt is more in the solvent than the solubility of the dye and this leads to the dye being pushed to the surface more, and thus the amount of adsorbate will increase (Güzel *et al.*, 2015). As in the Figure 5.

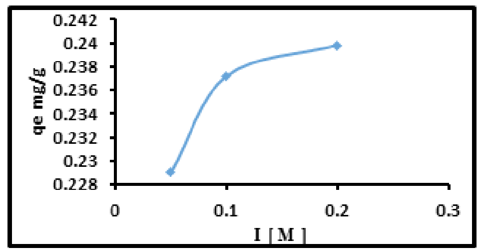

Fig. 5. The effect of ionic intensity on adsorption of MO^- dye on the Iraqi

Flint surface at 303 K.

Adsorption Isotherms Models

Usingthe initial concentration of the dyes, the adsorption capacity of the dye through Iraqi flint was studied. As for the experimental conditions, they are similar to those that were used previously. The results obtained were fitted through three experimental models, namely (Langmuir, Freundlich, and Temkin). The three experimental models are a vastly used instrument for quantification and adsorption mechanism of adsorbent. The Langmuir model is presented as follow (Jasem, 2015).

$$\frac{C_e}{q_e} = \frac{1}{q_{emax} K_L} + \frac{C_e}{q_{emax}} \quad .. (3)$$

where q_{emax} (mg/g) is the maximum amount of the MO per weight unit of Iraqi Flint to form a complete monolayer surface bound, K_L Langmuir

Table 2. Langmuir, Freundlich and Temkin isotherm constants for adsorption methyl orang dye on Iraqi Flint

Adsorben	Isotherm	303 K			313 K			323 K		
Iraqi Flint	"Langmuir	K_L L/mg	$q_{e\,max}$ mg/g	R^2	K_L L/mg	$q_{e\,max}$ mg\g	R^2	K_L L/mg	$q_{e\,max}$ mg/g	R^2
		0.0403	0.7642	0.2031	0.1018	0.3583	0.7881	0.1929	0.2330	0.9424
	FrenudlichF	$K_f$mg/g	N	R^2	$K_f$mg/g	n	R^2	$K_f$mg/g	n	R^2
		0.0460	1.5101	0.7842	0.0495	1.8158	0.9233	0.0541	2.2920	0.9382
	Temkin	K_TL/mg	B_T KJ/mol	R^2	K_TL/mg	B_T KJ/mol	R^2	K_TL/mg	B_T KJ/mol	R^2
		0.7664	0.1075	0.704	1.0757	0.0753	0.862	1.8115	0.0515	0.9167

constant in (L/mg) which can be calculated from plotting C_e/q_e against C_e, while Ce and qe are concentrations at equilibrium (mg/L) of dye and quantity adsorbed (mg/g) of dye on to Iraqi Flint.

The Freundlich isotherm which normally used to describe the adsorption of The heterogenous sysatems (Waheeb, 2016). The equation is shown

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

Where K_f (intercept, mg/g) and n (slope without unite) are the Freundlich constants related adsorption capacity and adsorption intensity respectively. The K_f and n calculated plotting Log q_eVs Log C_e.

Equation (5) is used to calculate Temkin (Ullah H *et al.*, 2017).

$$q_e = B_T \ln kT + B_T \ln C_e \quad ..(5)$$

drawing (q_eVsLnC_e) enables a limitation of Temkan constant (B and K_T).

Table 2 Summarizes the isotherm parameters and their correlation coefficients, R^2. From the results shown in the table, we observe the non-applicability of the Langmuir isotherm. In conformity the high correlation coefficient (R^2) in Temkin and Freundlich equations at all temperatures, it shows that the Temkin and Freundlich isotherms are more appropriate for experimental data than Langmuir. In Freundlich isotherm, when n values being between 1 to 10, the removing process will be useful adsorption (Lee *et al.*, 1999). The n values for Iraqi Flint is equal or more than 1 for all systems indicate favorable for corresponding adsorption.

Adsorption Kinetics

Four kinetic models are used in this research to explore the behavior of the adsorption process and to test the mechanism of the MO^- to examine the experimental data. The adsorption data were analyzed using the pseudo-first-order (PFO) and pseudo-second-order (PSO), Elovich and Intraparticle Diffusion models.

The linear form of (PFO) is given as follows (Maderova *et al.*, 2016; Fil *et al.*, 2013).

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad ..(6)$$

Where k_1 is rate constant (min^{-1}), q_e and q_t (mg/g) are the amounts of (MO^-) adsorbed at equilibrium and at time (t), respectively, K1 obtained from the slope of the linear plot of in (qe-qt) Vs (t) as illustrated in Figure (7).

Equation (7) represents the (PSO) kinematic model (Mahdavinia and Zhalebaghy, 2013).

$$t/qt = 1/k_2 q_e^2 + t/q_e \quad ..(7)$$

Where k_2 is rate constant of (PSO) adsorption computed from the intercept of plotting t/qt versus time (t) as illustrated in Figure (7).

Equation (8) represents the (Elovich) kinematic model (Wu *et al.*, 2009).

$$qt = \frac{1}{\beta}\ln(\beta\alpha) + \frac{1}{\beta}\ln(t) \quad (8)$$

Where β, α is constants of (Elovich) adsorption computed from the slop, intercept of plotting $q_t$versus time Ln t as illustrated in Figure 7.

Equation (9) represents the (Intraparticle Diffusion) kinematic model (Itodo *et al.*, 2010).

$$q_t = k_{diff}\, t^{1/2} + C \quad ..(9)$$

Where $\mathbf{k_{diff}}$ is constant of (Intraparticle Diffusion) adsorption computed from the slope of plotting q_t versus ($t^{1\backslash 2}$) as illustrated in Figure 7.

In the Table 3. There is an agreement between experimental q_e and calculated q_e values for the (PSO) model. Besides, the correlation coefficient (R^2) obtained several values. These values demonstrated the adsorption mechanism of (MO^-) on the Flint was fitted well to the PSO.

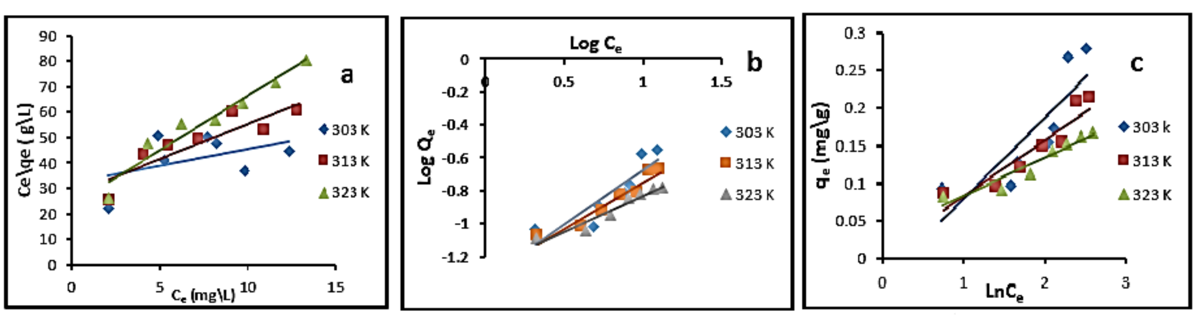

Fig. 6. The Langmuir (a), Freundlich (b), Temkin (C) isotherms for adsorption of the MO^- dye on the Iraqi Flint surfaceWith different temperatures

Table 3. Kinetic parameters for the adsorption of (MO^-) on to Iraqi Flint

Adsorbent Iraqi Flint	T (k)	Pseudo-first order K_1 (min^{-1})	Pseudo-first order q_e mg/g	Pseudo-first order R^2	Pseudo-second order K_2 $g.mg^{-1}.min^{-1}$	Pseudo-second order q_e mg/g	Pseudo-second order R^2
	303	0.0331	0.0178	0.7935	6.3411	0.0617	0.9926
	313	0.0452	0.0168	0.9610	5.8927	0.0460	0.9961
	323	0.0714	0.0112	0.9197	11.8764	0.0295	0.9981
		Elovich			**Intraparticle Diffusion**		
		β $g.mg^{-1}$	α $mg.g^{-1}. min^{-1}$	R^2	K_{diff} $mg.g^{-1}/min^{1\backslash 2}$	C mg/g	R^2
	303	208.33	20.8192	0.7717	0.0022	0.0444	0.8235
	313	196.07	0.4821	0.9206	0.0023	0.0278	0.9588
	323	357.1428	1.3029	0.9674	0.0013	0.0198	0.9934

Thermodynamic Parameters

Thermodynamic parameters such as ΔS° (entropy), $\Delta H^{\%}$ (enthalpy), and ΔG° (Gibbs free energy) were computed by the following equations: (Kaur *et al.*, 2020)

$$\Delta G = -R\ T\ Ln\ K_{eq} \quad .. (10)$$

$$K_{eq} = (q_e\ /\ C_e) \times (m/v) \quad .. (11)$$

$$\Delta G = \Delta H - T\Delta S^o \quad .. (12)$$

Where T is absolute temperature, R is gas constant. Keq is the equilibrium constant for the adsorption process, m is mass of Iraqi Flint (g), V is a volume of (MO^-) solution used (L), C_e is the equilibrium dye concentration in solution (mg/L), and q_e (mg/g) is the amount of (MO^-) adsorbed at equilibrium. ΔH° and ΔS° from adsorption were computed from vents Hoff equation (13) (Hussein *et al.*, 2020; Masson, Sylvain *et al.*, 2017).

$$In\ K_{eq} = \Delta S^o/R - \Delta H^o/RT \quad .. (13)$$

By plotting In K_{eq} versus 1/T (Figure 8) the ΔH° and ΔS° can be obtained from the slope and intercept, receptively. Table 4 shows the thermodynamic functions values at different temperatures. ΔG° showed negative values at all temperatures and becomes more negative as the temperature increased; this indicates that at a high temperature the process is more spontaneous. The

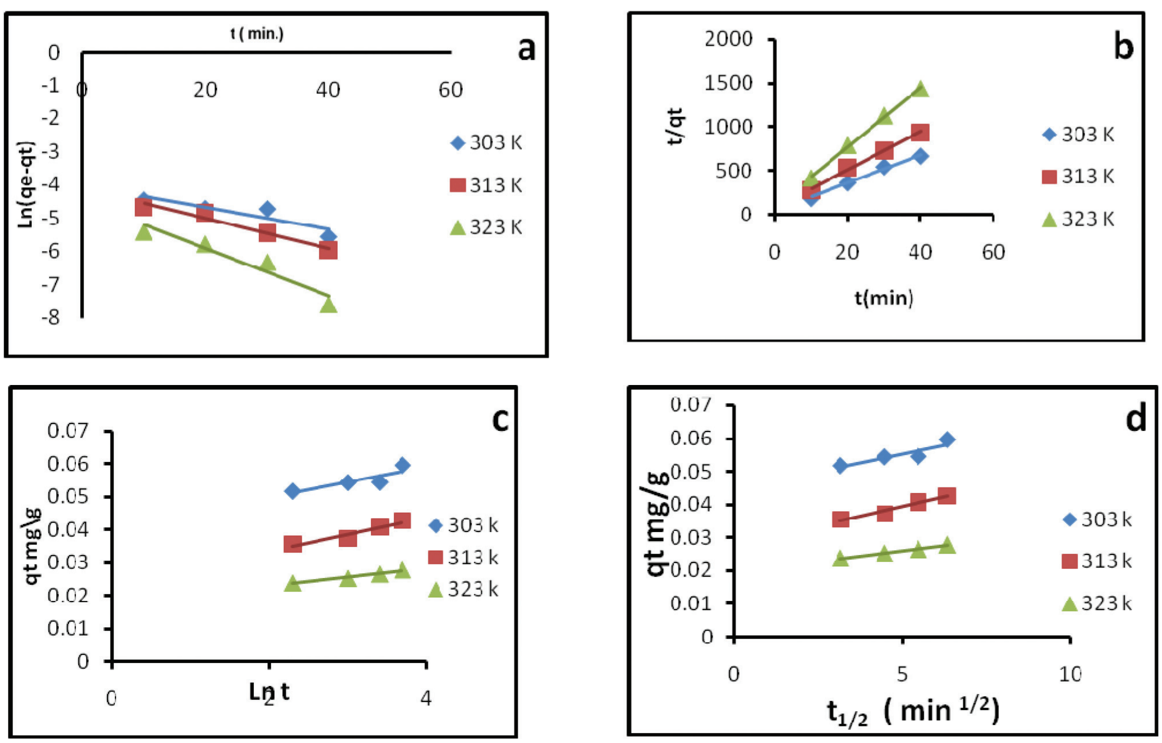

Fig. 7. The PFO (a), PSO (b), Elovich (c), Intraparticle Diffusion (d) kinetic models for adsorption of the MO dye on the surface of the Iraqi Flint at different temperatures

Table 4. The values of the thermodynamic functions for the adsorption of MO^- dye on the surface of the Iraqi Flint

Flint			
ΔS (J/mol.K)	ΔH (KJ/mole)	ΔG (KJ/mole)	T (k)
3.9865	-2.0529	-3.1154	303
	-3.2554	313	
	-3.2660	**323**	

negative enthalpy change (ΔH°) (Mohammed *et al*., 2019; Li, Yanfei *et al*., 2020), indicates the adsorption of MO^- on Iraqi Flint is an Exothermic process. the positive values entropy change (ΔS°) indicates theincrease in disorder and randomness of (solid-liquid) interface during the adsorption process (Al-Haidari *et al*., 2017).

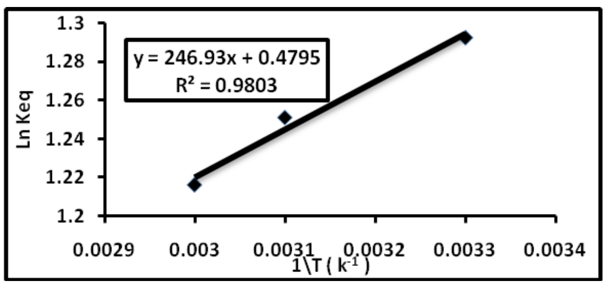

Fig. 8. Plotting Ln K_{eq} Vs. 1/T

CONCLUSION

In this study, the adsorption of methyl orang dye from aqueous solutions was investigated using Iraqi Flint. The outcomes indicated alow adsorption of MO^- using Adsorbent and the Freundlich and Temkin models showed more appropriateness than Langmuir for experimental data. The values of thermodynamic functions (ΔG°, ΔH° and ΔS°) obtained indicated that the MO^- adsorption was exothermic, spontaneous, randomness increasing for Iraqi Flint. The adsorption mechanism was studied and found the (pso) was the best kinetic model.

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