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توازن ودراسة ثيرموداينمكية لامتزاز صبغتين آزويتين بواسطة طين عراقي

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المستخلص

تضمنت هذه الدراسة تحضير صبغتين آزويتين من مفاعلة مركب ٤–أمينو– أنتي بايرين كجزء رئيس مع مركب التولوين للحصول على الصبغة الأولى (A1) وفي الصبغة الثانية (A2) تم استعمال مركب الانلين وحُضِرت الصبغتان عن طريق املاح الديازونيوم .وتم التحقق من إزالة هاتين الصبغتين من محاليلهما المائية بواسطة تقنية الامتزاز على سطح طين محلي (عراقي) (تم جمعه من منطقة القاضية في مدينة الموصل في الجزء الشمالي من العراق) باستعمال طريقة الوجبة الواحدة. كما اشتمل البحث على تحديد الظروف المثلى لنظام الامتزاز قيد الدراسة مثل تأثير كمية الطين المستعملة وتأثير ال pH وتأثير درجة الحرارة. وتم وضع البيانات العملية للامتزاز في ثلاثة نماذج من معادلات الايزوثيرمات وهي فرندلخ ولانكماير وتيمكن, وأظهرت النتائج أن معادلات الايزوثيرمات قابلة للتطبيق بشكل جيد على النتائج العملية للدراسة كما يتضح من قيمة معاملات الارتباط (R) القريبة من الواحد, وتم توضيح طبيعة الأنظمة المدروسة وفقًا لافتراض المعادلة وتم تقدير ثوابت المعادلة. أشارت الدوال الثيرموداينمكية المحسوبة (ΔG^{o}، ΔH^{o}، ΔS^{o}) إلى أن الامتزاز صبغات الآزو على الطين العراقي هي عملية باعثة للحرارة وتلقائية لتكوين نظام اقل عشوائية.

الكلمات المفتاحية: الامتزاز، ثرموداينميك الامتزاز، ٤–أمينو– أنتي بايرين، الطين.

Equilibrium and Thermodynamic study of the adsorption of two Azo Dyes by an Iraqi clay

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Abstract:
This study included the preparation of two azo dyes from 4-amino-antipyrene, and as a main part, the first dye (A1) was linked to toluene and the second (A2) to aniline, and the two dyes were prepared by diazonium ion, and the removal of these dyes from their aqueous solutions was verified by the adsorption technique on local (Iraqi) clay (collected from the Al-Kadiya area in Mosul city in the northern part of Iraq) using the batch method. The dose of clay used was determined, pH and temperature were studied, and experimental data for the adsorption process were placed in equilibrium in three adsorption equations, which are Freundlich, Langmuir, and Tampkin. The results showed that the equations of the equations are well applicable to the practical history of the study, as shown by the value of the correlation coefficients (R) close to one, and the nature of the studied systems was clarified according to the equation assumption, and the equation constants were estimated. The calculated thermodynamic parameters (ΔG^o, ΔH^o, ΔS^o) indicated that the adsorption of azo dyes on Iraqi clay is an exothermic and spontaneous process, resulting in a more ordered system.

Key words: Adsorption, Thermodynamic of adsorption, 4-amino-antipyrene,Caly

Introduction

The environment is the home of life, so the first thing that must be done is to protect this environment from pollution, which is considered one of the biggest and most widespread problems facing the world due to advances in technology, industry, and agriculture. (Asamudo et al., 2005) (Zhang B, et al., 2016; 50(21): 11837-43) (Javaid R, et al., 2021; 290:112605). Water pollution is also one of the most important environmental issues because water is essential in our daily lives. Water is the secret of life for everything that crawls on the earth and comes out of plants.(Ab Kadir NN, et al., 2017; 137:168-75) (Mattson JA, et al., 1969; 31(1):116-30).

Recently, water sources have witnessed a significant deterioration as a result of the discharge of thousands of chemical compounds daily, either directly or indirectly, without any significant treatment. (Ibrahim HK, et al., 2019; 12(10):4921-5) (Owa, F.W., 2014). There are also several types of water

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pollution, including organic pollution, chemical pollution, thermal pollution, and radioactive pollution. (Dąbrowski A, 2001; 93(1-3):135-224) [Abd, A. A., Naji, et al., 2020: 8(5), 104142]. Studies have also shown in the current era that humans face major problems that need to be reduced and treated, which is environmental pollution, in which individuals play a major and primary role in increasing these risks through the various activities they carry out, which have become a threat to human life.[R. K., K., Selvan M., et al., 2020: 55(1), 26-34] (Choi, H. Y., et al., 2020: 234, 115881) The global problem of pollution, recognized as a significant threat to both human populations and the environment, has been exacerbated by technological development.(ABDULHADY, Y. A. 2022). This pollution is characterized by the presence of deleterious organic and inorganic substances, as well as by imbalances in the natural concentrations of fundamental environmental constituents. (Eldamarawy et al., 2019: 293-300).

Dyes constitute a major class of water pollutants. Production figures for 1996 indicate an output of approximately 4.5 million tons. Most of these quantities are used in complementary industries, such as textile dyeing. (Nas et al., 2019: 296, 112100) (Luo, Y., et al., 2019: 375, 122019). Many of these dyes are either inert or non-toxic. There are also some dyes that have severe toxic effects on humans and some widespread dyes that have several noticeable effects on the living environment. (Ibrahim, A., et al., 2019: 62(3), 541-554). There are several methods used to get rid of dyes, the most important of which are adsorption processes, chemical oxidation, and ozone treatment, biological methods, reverse osmosis pressure, and many other processes. (Malash, G. F., et al., 2010: 163(3), 256-263) Clay is also considered one of the materials used to get rid of these dyes. (Zhou, C., et al., 2014: 251, 17-24). Adsorption is considered one of the most important methods used to get rid of pollutants; adsorption technology has become the most widespread and easiest to use to remove various pollutants from water due to its high efficiency and low economic cost compared to other methods. (Elsayed, A. E. 2021: 64(11), 5-6).

Experimental part

Materials and methods

Adsorbent

The raw material was first crushed and washed to remove all impurities and then dried in an oven at 110 °C. Iraqi Clay ground again and a colloidal was made. The heavy particles were eliminated by casting, then the colloidal was filtered and the resulting fine particles of slurry dried in sunlight and then in a furnace at 110°C, finally milled and sieved into multiple size fractions in the 75-600 nm range.(Cavallaro,G.,et al,2020 Clay nanoparticles) using the AMERICA Standard Test Sieve Series (ASTM). Fine nanoparticles (75nm) were used as the absorbent for this investigation, and backings were used to test the effect of particle size on adsorption.(Aldbouni, S. A., et al,2019: 28(2), 50-70).

Adsorbate

In this study two azo dyes were prepared both dyes were adopted by allocating the 4-amino-antipyrene using Toluene (A1) and in the second one (A2) by Aniline the two dyes were synthesized through of the preparation of dizomium ion. the name and structures of the synthesized dye are shown in Table (1).

Synthesis of dyes (Aldbouni, S. A., et al,2019: 28(2), 50-70)

Preparation of azo dyes

Step 1:

Preparation of diazonium salts

A- (3.048) g of 4-aminoantipyrine (4-AAP) is dissolved 15 ml HCl Baker of suitable size using magnetic stirrer while maintaining the solution temperature in the range of (0-5 C°). The temperature was adjusted using a thermometer.

B-(1g) of NaNO2 is placed in Baker (75 ml) containing (10 ml) distilled water in a temperature between 0-5C °. This solution is added in batches to solution(A) with stirring and keeping the mixture temperature less than (0-5C°) using ice bath .

Step 2:

Preparation Toluene Solution

A - Prepare (10 ml) of a solution of sodium hydroxide at a concentration of (10%) and put it on ice.

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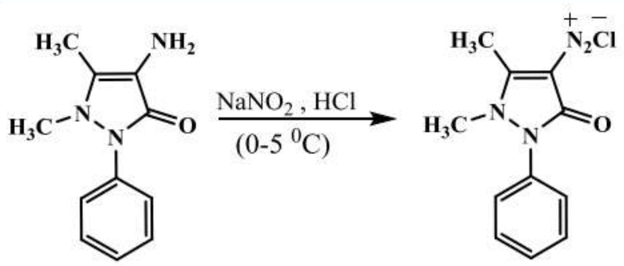
B . (2.09 ml) of Toluene was added to the prepared sodium hydroxide solution while maintaining the solution temperature between (0-5°C).

C- The solution prepared in the first step was added to the solution of the second step slowly with continuous stirring until the required dye crystals were formed, then the mixture was placed for half an hour in an ice bath, then filtered, washed with distilled water and dried.

The second dye was prepared in the same way .



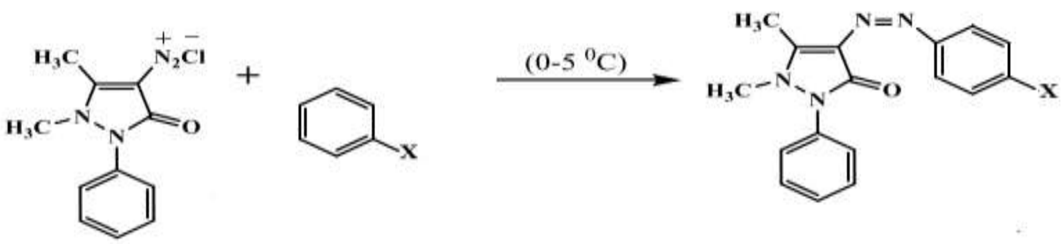


Table 1. Chemical composition , physical properties and molar absorptivity of the synthesized dyes

Dye	Structure	Color	M.P (°C)	λ Max(nm)	M.Wt g\mol	Solubility

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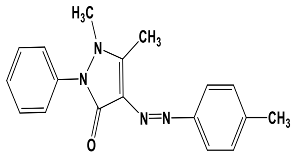
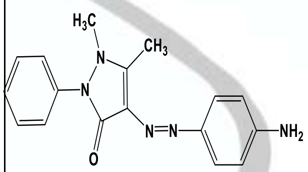
١,٥-dimethyl-2-phenyl-4-(p-tolyldiazenyl)-1,2-dihydro-3H-pyrazol-3-one	 A1	Yellow	137-140	465	306.38	Water, ethanol-soluble
٤-((٤-aminophenyl)diazenyl)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one	 A2	orange	140-142	496	307.37	Water, ethanol-soluble

Analytical method

One of the most important requirements of this study is to find an analytical method to estimate the amount of adsorbed material before and after the adsorption process. The spectroscopic method is one of the best methods that can be used for this purpose, as it is characterized by its accuracy and sensitivity to low concentrations and does not include any interference with other materials present in the studied system. Since the dye under study is a colored material, the spectroscopic method is the best choice for this study, through which the change in the absorption values of the remaining dye after the adsorption process and at its highest absorption value (λmax) and in the visible region of the spectrum is tracked. As a preliminary step.

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In this intriguing study, dove into the creation of a calibration curve for our dye, meticulously pinpointing its λmax value. To achieve this, we prepared a series of solutions, each with varying concentrations that aligned harmoniously with both the dye's sensitivity and the principles outlined by the Beer-Lambert law. What we discovered was quite remarkable: the linear relationship derived from our implementation of the Beer-Lambert equation—alongside impressively high correlation values (R^2) ranging from 0.9979 to 0.9960—suggests a robust applicability of this equation within the concentration ranges we've chosen for our dye's standard curves.

$$A = \varepsilon CL \qquad (1)$$

Where A represents the dye absorbance, the molar absorption coefficient in units of (Liter. $mol^{-1}.cm^{-1}$), L is the optical path length of visible light (L=1 cm), and C is the molar concentration (mol. $Liter^{-1}$).

The terms adsorption capacity and adsorption efficiency (percentage of adsorption) were used to express the amount of adsorbed material by estimating the amount of remaining material from the dye solution and then calculating the amount of adsorbed material from the difference between the initial concentration of the dye and the amount of remaining material. The calibration curve for each dye was adopted to calculate this concentration. The adsorption capacity of the adsorbent for the dye can be expressed by the following equation:

$$qeq\left(mg/g\right)=\frac{Ci-Ceq}{M}V \qquad (2)$$

Where Ci represents the initial concentration of the dye in the liquid phase (mg/l) and C_{eq} is the final concentration of the dye in the solution at equilibrium (mg/liter) and M is the weight of the adsorbent (Clay) (g/L). V is the volume of the dye solution used experimentally when studying adsorption (Liter). The percentage of the removed (adsorbed) dye or what is called the adsorption efficiency can also be calculated using the following equation:

$$\%REMOVAL = \frac{C_i - C_{eq}}{C_i} \times 100 \qquad (3)$$

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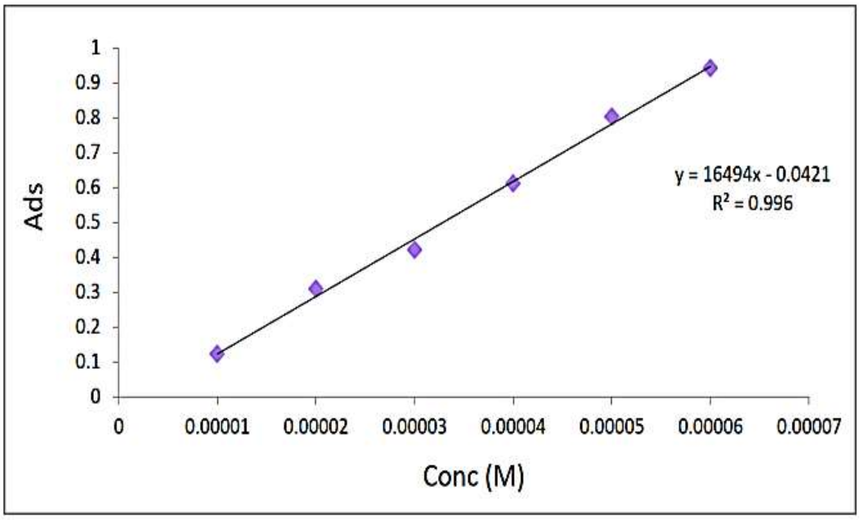

Figure 1. shows a calibration curve for the dye. A1

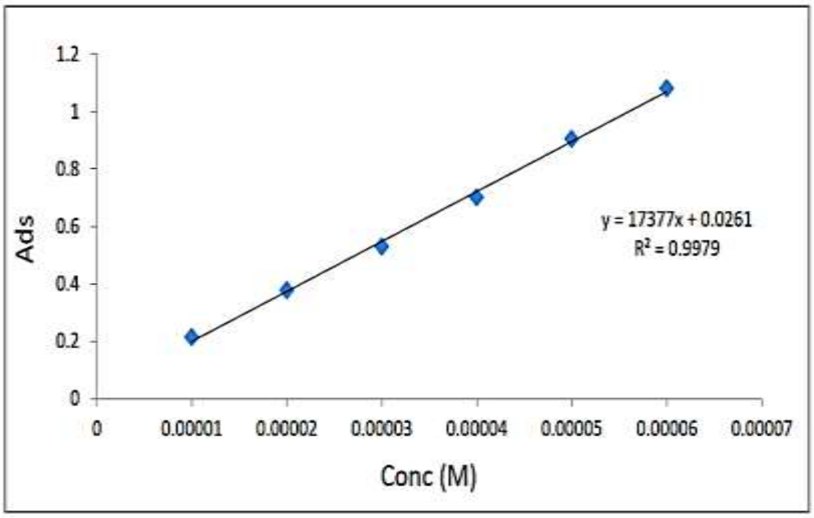

Figure 1. shows a calibration curve for the dye. A2

Effect of Adsorbent Dose

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To follow up the effect of the amount of clay on the adsorption of the dyes under study, the following conditions were determined: the initial concentration at
($3X10^{-4}$mol\L) with the amount of the adsorbent changing in a dose range of (0.005 – 0.05 g\L). The selection of these quantities was made in light of previous tests by researchers in this field [21]. These practical experiments were conducted in the laboratory at a temperature of (298 °K) and the natural acidity function of the two dyes. The results obtained for the dyes are listed in Table (2) .

Table 2. shows the effect of clay quantity on adsorption capacity and adsorption percentage.

Dye	C_i mgl\L)	C_{eq} (mg\L)	Dose (gm\L)	q_{eq} (mg/gm)	% Removal
A1	91.91	16.82	0.2	375.45	81.69
		15.79	0.4	190.30	82.80
		14.23	0.8	97.10	84.51
		13.76	1.0	78.15	85.02
		12.58	2.0	39.66	86.31
A2	٩٢.٢١	12.72	0.2	397.30	86.20
		11.96	0.4	200.62	87.22
		10.34	0.8	102.33	88.78
		9.83	1.0	82.38	89.33
		8.91	2.0	41.65	90.33
		Ceq (mg\L)	Dose (gm\L)	qeq (mg/gm)	% Removal
		16.82	0.2	375.45	81.69
		15.79	0.4	190.30	82.80
		14.23	0.8	97.10	84.51

		13.76	1.0	78.15	85.02
		12.58	2.0	39.66	86.31
		12.72	0.2	397.30	86.20
		11.96	0.4	200.62	87.22
		10.34	0.8	102.33	88.78
		9.83	1.0	82.38	89.33
		8.91	2.0	41.65	90.33

The experimental results indicated that a clay dosage of 2.0 g per liter of solution is effective. This concentration provided sufficient adsorption capacity for the experiments and will be used in further studies exploring different factors influencing the adsorption process.

Effect of pH on Adsorption Efficiency

The adsorption efficiency of different dyes containing various groups is greatly affected by the acidity of the adsorption medium due to the variation in the nature of these groups with the change in the acidity of the dye solutions, and in order to determine the optimum conditions for adsorption of the dyes under study, the adsorption of these dyes was tested in different acidic media. The research included testing the adsorption efficiency of the prepared dyes in solutions of their natural acidity, which ranged between (pH =4.95-5.40), in addition to studying them in neutral medium at (pH = 7) and basic medium at (pH = 9), and the results obtained from this study are listed in Table (3).

Table 3. Shows the effect of pH on the adsorption capacity and the percentage of adsorption.

Dye	pH	Ce(mg\L)	q_{eq} (mg\g)	% Removal
A1	4.95*	١١.٩٦	200.62	87.22

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	7.00	19.47	181.10	78.81
	9.00	29.72	155.47	67.66
A2	5.40*	13.41	197.00	85.45
	7.00	27.75	161.15	69.90
	9.00	31.55	151.65	65.78

***pHNatural**

The data included in Table (3) show that the adsorption efficiency increases in the acidic medium and then gradually decreases in the neutral medium until reaching the basic medium, at rates that vary according to the nature and location of the active group present on the aromatic rings in each dye.

Effect of temperature

In the study, the effect of temperature on the adsorotion of capacity the prepared dyes is conducted initial concentration of($3X10^{-4}$M) and the temperature range between (15-55^{O}C). All the study is carried and at the normal acidity of the dyes solution using(2.0g) of clay as an adsorbent .(25ml) of the solution mixture was shaked for (90).

Table 4. Effect of temperature on adsorption capacity and percentage of adsorption

Dyes	C_i (mg/L)	Temp(°C)	C_{eq} (mg/L)	q_{eq} (mg/g)	% Removal
A1	91.91	15	3.87	220.10	95.78
		25	9.03	207.20	90.17
		35	12.85	197.65	86.01
		45	13.22	196.72	85.61
		55	15.16	191.87	83.50
A2	92.21	15	6.96	213.21	92.45
		25	8.89	208.30	90.35
		35	9.94	205.67	89.22
		45	11.40	202.02	87.63
		55	12.45	199.40	86.49

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The results of Table (4) showed that, increasing the temperature of adsorption medium is accompanied by decreasing adsorption efficiency in all studied dyes regardless of the nature of the substitutes on the aromatic ring. This is a clear indication that, the adsorption of these dyes onto clay is a physical process . The higher the temperature, the greater the weakening of the bonding forces among the adsorbed particles and the clay surface. This results in the returning of the adsorbed molecules from the surface into the adsorption solution. In this case, the process is called desorption(Al-abady, F. M., et al,2019: 14(2))(Derylo-Marczewska, A., et al,2019: 214, 349-360)(Elmouwahidi, A., et al,2020: 9(1), 541-551)

In general, it is noticed that, the efficiency of adsorption and its capacity are decreased gradually with the elevation of temperature within the range used in the current research. As the adsorption is an exothermic process and the energy content of the system is high, increasing the temperature will lead to the departure of the adsorbate molecules from the clay surface.(Thommes, M. (2010) 82(7),1059-1073)(Mohammed, S. S., et al,2021: 64(12), 2-3)

Adsorption isotherms

Adsorption Isotherm are mathematical relationships thet used to represent the relationship between the mass unit of the adsorbent material and the concentration of the dye in the liquid phase at equilibrium. At a certain temperature it describes how dye is distributed between the liquid and solid phases at different equilibrium concentrations.

This study included testing of three types of known isotherml equations such as Freundlich, Langmuir, and Tempkin in order to describe the equilibrium properties of the adsorption system under study.

Langmuir isotherm

This isotherm assumes that the adsorption is distributed on solid surface with active sites of homogeneous energies as well as adsorption of one layer of solute attracted to the solid surface at a constant temperature. According of this model the adsorption process occurs with a fast start and then slow dawn to reach equilibrium when the rate of the association between the day molecules. With the clay surface equal the rate of their returning to the solution. According to this model, the amount of the adsorbed material is

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proportional to the exposed part of the adsorbent surface of the adsorption process, while the amount of particles returning to the solution is proportional to the covered surface of the adsorbent

The equation of Langmuir can be given As follows:

$$\frac{C_{eq}}{q_{ea}} = \frac{1}{bQ} + \frac{C_{eq}}{Q} \_\_\_\_\_\_\_\_\_\_ (4)$$

This passage describes the analysis of adsorption data, likely using the Langmuir isotherm model. Here's a breakdown:

q_{eq} (mg/g): This represents the equilibrium adsorption capacity. It's the amount of dye (in milligrams) adsorbed per gram of adsorbent when the adsorption process has reached a stable state (equilibrium).

Q: This is the maximum adsorption capacity. It's a theoretical value representing the maximum amount of dye that could be adsorbed per gram of adsorbent, assuming a complete monolayer coverage of the adsorbent surface. It's often determined by fitting experimental data to a model like the Langmuir isotherm.

C_{eq} (mg/L): This is the equilibrium concentration of the dye. It's the concentration of the dye remaining in the solution after the adsorption process has reached equilibrium.

C_{eq}/q_{eq} vs. C_{eq} Plot: This specific plot is used to linearize the Langmuir isotherm equation. The Langmuir isotherm describes the relationship between q_{eq} and C_{eq}. Plotting the data this way should yield a straight line if the Langmuir model is a good fit.

Good Coefficients: This likely refers to a high R^2 value (close to 1) from the linear regression of the plotted data. A high R^2 indicates a strong linear relationship, suggesting the Langmuir model adequately describes the adsorption behavior. Figure 3 likely shows this plot and the associated R^2 value.

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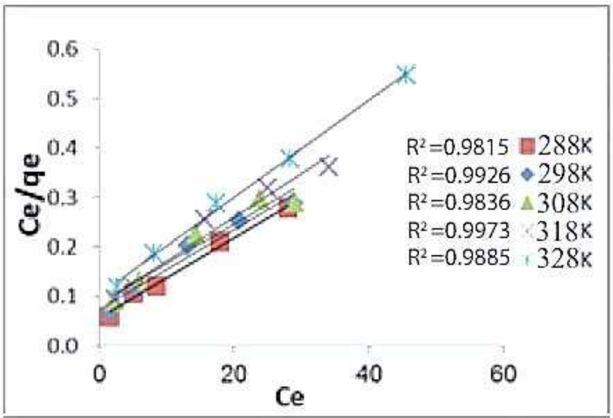

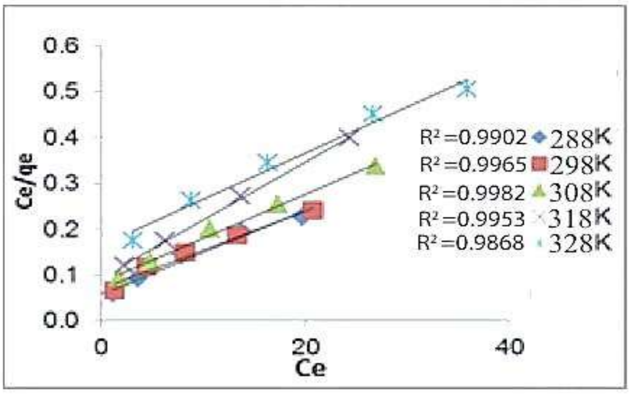

Figure 3. Application of Langmuir isotherm on the experimental data of dye A1,A2

The values of the Langmuir constants,(Q,b) and correlation coefficient R of the studied systems are listed Table (5) .

Table 5. Langmuir Isotherm Constants and Correlation Coefficients from the Application of Experimental Data to the Isotherm Equation

Dye	Temp.(°C)	b(L/mg)	Q (mg/g)	R
	15	0.107	119.04	0.9917

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A1	**25**	**0.086**	**125.00**	**0.9963**
	35	**0.095**	**138.88**	**0.9918**
	45	**0.058**	**138.88**	**0.9986**
	55	**0.049**	**147.05**	**0.9942**
A2	**15**	**0.026**	**153.84**	**0.9951**
	25	**0.023**	**163.93**	**0.9982**
	35	**0.020**	**172.41**	**0.9991**
	45	**0.017**	**192.30**	**0.9976**
	55	**0.015**	**204.08**	**0.9934**

Looking at the results of Table (5), the following points can be summarized :

1.The Langmuir equation model can be used to describe the clay-dye adsorption system under study when the practical data of adsorption obtained is fitted to the isotherm equation, giving indications that, these results are compatible with all the assumptions adopted by langmuir. This is evidenced by the straight lines resulting from the plot of C_{eq} / q_{eq} vs. C_{eq} indicated by correlation coefficients (R) close to one.

2.The maximum absorption capacity of Q (mg / g) is increased with increasing temperature. This pattern of changes can be clarified in the view that the temperature raise can stimulate new sites on the surface of the clay, enabling them to bind to the dye molecules increasing the adsorption capacity.

he values of the constant *b*, which reflects the strength of the bond between dye molecules and the clay surface, were found to decrease with rising temperature. This observation supports the conclusion that the adsorption process in the studied system is primarily physical in nature.(da Silva, P. M. M., et al,2020: 18, 100318)

Freundlich isotherm

Freundlich equation is one of the most important isotherms used successfully in the case of adsorption of solution. This model assumes that the distribution of active sites is not homogeneous on the surface of the clay material is This irregularity of energy changes giving adsorption sites have varying levels of energy. Accordingly the adsorption does not reach the state of saturation (ie, does not reach the maximum level). linear relationship. Of Freundlich can be expressed as follow:

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$$\log q_{eq} = \log K + 1/n \log C_{eq} \quad (5)$$

When K and n are Freundlich constants related to capacity and intensity of adsorption respectively their values depend on the nature of the absorption system, adsorbent surface, and the temperature The plot of log q_{eq} versus log C_{eq} gives a straight line with a slope of 1 / n, and intercept equal to log K_f, The values obtained are given in Table(6) .

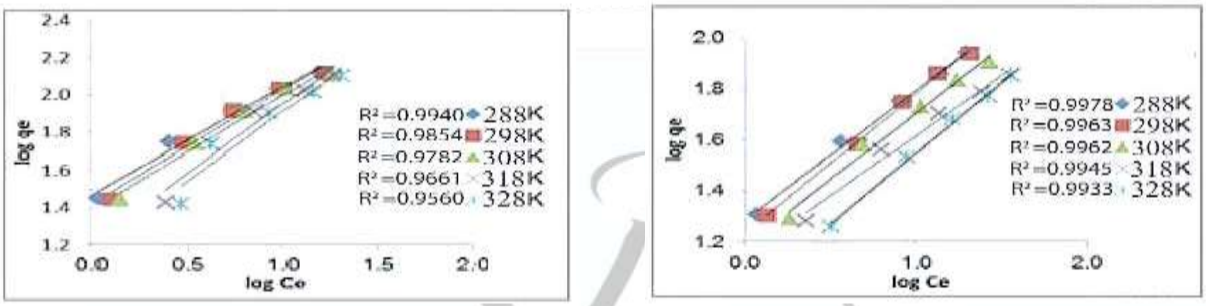

Figure 4. Application of Freundlich isotherm on of the experimental data of dye A1,A2

Table 6. Freundlich Isotherm Constants from Experimental Adsorption Data Analysis

dye	Temp.(°C)	n	K_f	R
A1	15	2.0572	17.282	0.9970
	25	1.8587	14.521	0.9927
	35	1.7343	12.673	0.9890
	45	1.6106	10.879	0.9829
	55	1.5291	9.544	0.9997
A2	15	1.3643	5.591	0.9989
	25	1.3245	5.160	0.9981
	35	1.2952	4.835	0.9981
	45	1.2497	4.372	0.9972
	55	1.2247	4.102	0.9966

results in Table (6) refer to the following

1.Applying the Isotherm-Frendelch model on the practical data of adsorption of the studied dye, it gave good linear relation shape at all temperatures in the considered range. This is indicated by the correlation coefficients (R). values obtained this isotherm can be give good fit to the practical data of adsorption of the studied system

2. The values of n, a parameter related to the adsorption intensity, are all greater than one. This indicates favorable adsorption in the studied system. Furthermore, the observed decrease in n with increasing temperature supports the conclusion that the adsorption process is primarily physical in nature.

3. The values of Kf, which reflect the adsorption capacity, decrease with increasing temperature. This trend is consistent with the changes observed in the experimental adsorption capacity (q_{eq}) presented in Table 6.(27. Tran, T. H., Le, et al,2020: 725, 138325)

Timpkin Isotherm

The isotherm assumes a linear decrease in adsorption temperature with increasing surface coverage due to interactions between dye molecules and the clay surface.

The Tempkin equation is usually formulated as follows:

$$q_e q = B_T \ln K_T + B_l \ln C_e q \qquad \text{———} \qquad (6)$$

This passage describes how to determine constants related to the adsorption process, likely using the Temkin isotherm model. Here's a breakdown:

BT = RT / b: This equation defines the relationship between BT, the gas constant (R), absolute temperature (T), and a constant 'b' related to the heat of adsorption.

R (Gas Constant): A constant value (8.314 J/mol/K) .

T (Absolute Temperature): Measured in Kelvin (K).

b: A constant related to the heat of adsorption (J/mol)

KT: The equilibrium bonding constant (mg/L), which is related to the maximum bonding energy.

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BT: A constant related to the differential surface capacity of the adsorption of the dye for each successive energy unit.

q_{eq} vs. ln(Ceq) Plot: By plotting the adsorption capacity (q_{eq}) against the natural logarithm of the equilibrium concentration ($\ln(C_{eq})$), you can obtain a straight line.

Slope and Intercept: The slope of this line is related to BT, and the intercept is related to KT. Specifically, the slope allows you to calculate 'b' (and thus the heat of adsorption), and the intercept allows you to calculate KT.

Table 7: This table contains the calculated values of BT and KT, likely obtained from the slope and intercept of the plot mentioned above.

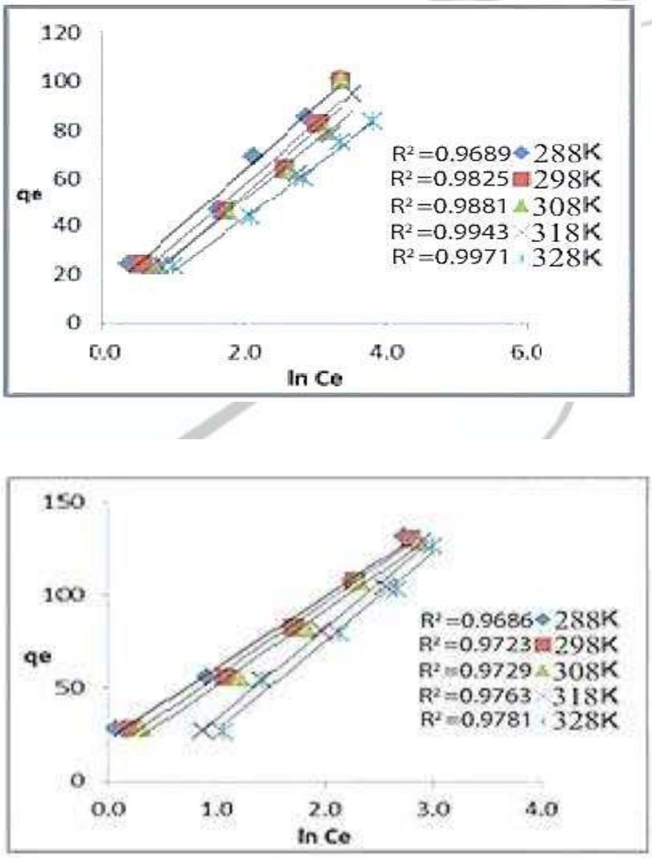

Figure 5. Application of Tempkin isotherm of the experimental data of dye A1,A2

Table 7. Temkin Isotherm Parameters Derived from Experimental Adsorption Data

dye	Temp.(°C)	B_T	K_T(Liter/mg)	R

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A1	15	22.553	1.574	0.9843
	25	25.090	1.079	0.9912
	35	26.936	0.846	0.9940
	45	29.073	0.668	0.9971
	55	30.681	0.565	0.9985
A2	15	27.388	0.379	0.9842
	25	28.141	0.352	0.9860
	35	28.688	0.332	0.9863
	45	29.653	0.306	0.9881
	55	30.183	0.292	0.9890

The observation of the results listed in Table (7), can be summarized as follows:

1.The values of correlation coefficients (R) indicate good linear relationships obtained from the application of the Tempkin isotherm on the practical data to adsorp the selected dyes in this study on clay within the selected temperature range, thus facilitating the application of this isotherm on such systems at different temperatures.

2.The values of the B_T constant are increased with the increasing of temperature. While the values of the K_T constant are decreased with the temperature rise. This is agree with the assumption of Tempkin in which the overlaps between the dye and the carbon surface decrease the heat of adsorption which in turn decreases linearly with increased surface coverage. This is also consistent with the fact that adsorption is of a physical nature.(Ezzati, R. 2020: 392, 123705)

Thermodynamic study

In order to evaluate the removal effectiveness of the clay to adsorp the dyes under consideration and to determine the nature of the adsorption system, thermodynamic study is carried out to estimate functions such as the variation is the Standard free energy of Gibs ΔG °ads (kJ.mol-1), Standard enthalpy ΔH ° ads (kJ.mol-1) and Standard entropy ΔS ° ads ($J.mol^{-1}$) $.K^{-1}$) were calculated by applying the following equation

$$\text{In}K_{ads} = \frac{-\Delta H^{\circ} ads}{RT} + \frac{\Delta Sads^{\circ}}{R} \quad \_\_\_\_\_\_ \quad (٧)$$

$$K_{ads} = Cads \;/\; C_{eq} \quad \_\_\_\_\_\_\_\_\_\_ \quad (8)$$

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$\Delta G^{o}{}_{ads} = -RT \ln K_{ads}$ ____________(9)

This passage explains how thermodynamic parameters for dye adsorption are calculated. Here's a breakdown:

K_{ads} (Adsorption Distribution Coefficient): K_{ads} represents the ratio of the amount of dye adsorbed onto the adsorbent to the amount of dye remaining in the solution at equilibrium. It essentially tells you how strongly the dye prefers to be on the adsorbent compared to being in the solution. A higher K_{ads} value indicates stronger adsorption .

R (Gas Constant): This is a constant value used in thermodynamic calculations (8.314 J mol^{-1} K^{-1}) .

T (Absolute Temperature): The temperature is measured in Kelvin (K). In this study, the temperature was varied between 288°K and 328°K (which would need to be converted to Kelvin for the calculations.

$\Delta G°_{ads}$ (Gibbs Free Energy Change): This value indicates the spontaneity of the adsorption process. A negative ΔG° value signifies a spontaneous (favorable) adsorption process .

$\Delta H°_{ads}$ (Enthalpy Change) and $\Delta S°_{ads}$ (Entropy Change): These values are determined from the slope and intercept of a plot of $\ln(K_{ads})$ versus 1/T. This plot is based on the van't Hoff equation.

ΔH° ads: Represents the heat absorbed or released during adsorption. A negative $\Delta H°_{ads}$ indicates an exothermic process (heat is released), while a positive $\Delta H°_{ads}$ indicates an endothermic process (heat is absorbed .

ΔS° ads: Represents the change in disorder of the system during adsorption.

Table 8. This table contains the calculated thermodynamic parameters ($\Delta G°_{ads}$, $\Delta H°_{ads}$, and $\Delta S°_{ads}$) obtained from the analysis.

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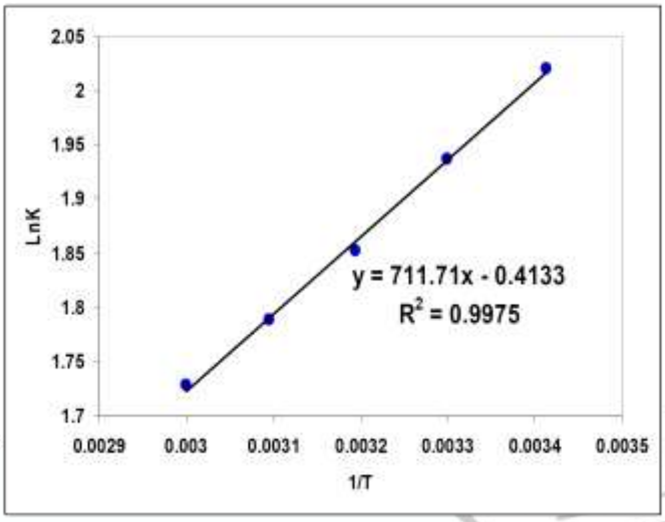

A1

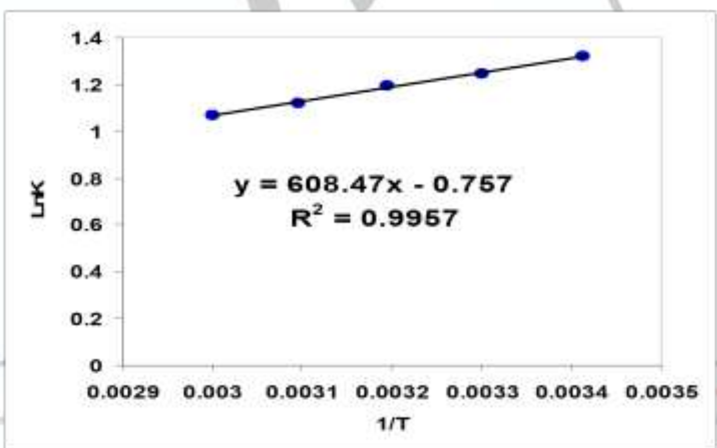

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Figure 6. The relationship between ln K and 1 / T to calculate the thermodynamic function values of the adsorption of A1 and A2 dyes

Table 8. Thermodynamic parameters of the studied dye A1 on Clay

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Ci (mg/l)	Temp ° K	K	ΔH (KJ.mol⁻¹)	ΔS (J.mol ⁻¹.K⁻¹)	ΔG° (KJ.mol⁻¹)	ΔS° (J.mol ⁻¹.K⁻¹)
91.91	288	22.74	-5.917	-20.54	-7.48	5.42
	298	9.17		-19.85	-5.49	-1.43
	308	6.15		-19.21	-4.65	-4.11
	318	5.95		-18.60	-4.71	-3.79
	328	5.06		-18.03	-4.42	-4.56

Table 9. Thermodynamic parameters of the studied dye A2 on Clay

Ci (mg/l)	Temp ° K	K	ΔH (KJ.mol⁻¹)	ΔS (J.mol ⁻¹.K⁻¹)	ΔG° (KJ.mol⁻¹)	ΔS° (J.mol ⁻¹.K⁻¹)
92.21	288	12.24	-5.058	-17.56	-6.00	3.27
	298	9.37		-16.97	-5.54	1.61
	308	8.27		-16.42	-5.41	1.14
	318	7.08		-15.90	-5.17	0.35
	328	6.40		-15.42	-5.06	0.006

The results of tables (8,9) indicate to the following The negative values of ΔH_{ads} refer that adsorption process is exothermic and the values of ΔH_{ads} less than 40 $KJ.mol^{-1}$ support the physical nature of the force controlling the adsorption process under study. and The negative values (ΔG^{o}_{ads}) calculated under certain conditions indicate that adsorption is a spontaneous process. The ΔG° ads decreases as the temperature increases (becoming less spontaneous), corresponds to the heat of reaction.

ΔS_{ads} was calculated at the equilibrium state and it is different from ΔS^oads that calculated at any stage of equilibrium. The Negative values of ΔS_{ads} indicate an increase in the order of the system resulting from the association of adsorbed dye molecules with the clay surface .

and The value of ΔS^oads do not change within the measured range of the temperatures of a single compound but varies depending on the nature and location of the groups offset on the different compounds.

and The values of ΔS^o_{ads} at a certain concentration increases with increasing temperature suggest that the increase in temperature increases the system randomization due to the desorption of the dye molecules and return from the surface of clay and to the solution. This support the physical nature of the forces controlling the adsorption process under study which is already proved these results are consisted with other results observed in similar studies in literature .(29. Talha,K.,et al,2020:8(1), 103642)

Conclusion

In this study, two azo dyes were adsorbed by Iraqi clay. The isotherm results showed that they are consistent with the Langmuir equation. The negative $\Delta H°$ value shows that the adsorption process is exothermic, the value less than (40 kJ/mol), $\Delta H°$ values indicate that the adsorption process is physical, the negative value of $\Delta S°$ indicates low randomness, in addition to the positive $\Delta G°$ values, which indicates that the adsorption process is non-spontaneous For the first dye, as for the second, we notice that $\Delta S°$ the value is positive.

References

1.Abd, A. A., Naji, S. Z., Hashim, A. S., & Othman, M. R. (2020). Carbon dioxide removal through physical adsorption using carbonaceous and non-carbonaceous adsorbents: a review. Journal of Environmental Chemical Engineering, 8(5), 104142..

2.ABDULHADY, Y. A. (2022). Magnetic Nano-Organo-Philic Clay and Zeolite to Remove Municipal Carbonaceous Wastes in Matrouh Station. *Egyptian Journal of Chemistry*.

3.Ab Kadir NN, Shahadat M, Ismail S. Formulation study for softening of hard water using surfactant modified bentonite adsorbent coating. Applied Clay Science. 2017;137:168-75.

4.Al-abady, F. M., Tapabashi, N. O., & Bahjat, A. N. (2019). Study of Thermodynamic and Kinetic Adsorption of Azo Dyes on Different Adsorbent Surfaces. Kirkuk Journal of Science, 14(2).
5.Aldbouni, S. A., Alhyali, E. A., & Alkazraji, A. A. (2019). Equilibrium and thermodynamic studys of adsorption of azo dyes on the local bentonite clay. Journal of Education and Science, 28(2), 50-70.
6.Asamudo, N. U., Daba, A. S., & Ezeronye, O. U. (2005). Bioremediation of textile effluent using Phanerochaete chrysosporium. African Journal of Biotechnology, 4(13).
7.Cavallaro, G., Fakhrullin, R. F., & Pasbakhsh, P. (Eds.). (2020). Clay nanoparticles: properties and applications. Elsevier.
8.Choi, H. Y., Bae, J. H., Hasegawa, Y., An, S., Kim, I. S., Lee, H., & Kim, M. (2020). Thiol-functionalized cellulose nanofiber membranes for the effective adsorption of heavy metal ions in water. Carbohydrate polymers, 234, 115881.
9.Dąbrowski A. Adsorption—from theory to practice. Adv Colloid Interface Sci. 2001;93(1-3):135-224.
10. Da Silva, P. M. M., Camparotto, N. G., Lira, K. T. G., Picone, C. S. F., & Prediger, P. (2020). Adsorptive removal of basic dye onto sustainable chitosan beads: Equilibrium, kinetics, stability, continuous-mode adsorption and mechanism. Sustainable Chemistry and Pharmacy, 18, 100318.
11. Derylo-Marczewska, A., Blachnio, M., Marczewski, A. W., Seczkowska, M., & Tarasiuk, B. (2019). Phenoxyacid pesticide adsorption on activated carbon–Equilibrium and kinetics. Chemosphere, 214, 349-360.
12. Eldamarawy, Y. A. E., Assaad, F. F., Youssef, R. A. E., & Mubarak, D. M. (2019). Adsorption Thermodynamics of Cu-Ca Ion Exchange on Nano-montmorillonite Clay System. *Egyptian Journal of Chemistry*, *62*(Special Issue (Part 1) Innovation in Chemistry), 293-300.
13. Elmouwahidi, A., Bailón-García, E., Pérez-Cadenas, A. F., Celzard, A., Fierro, V., & Carrasco-Marín, F. (2020). Carbon microspheres with tailored texture and surface chemistry as electrode materials for supercapacitors. ACS Sustainable Chemistry & Engineering, 9(1), 541-551.
14. Elsayed, A. E. (2021). Optimization of acidic activated conditions for natural clay and its application in waste oil bleaching. Egyptian Journal of Chemistry, 64(11), 5-6.
15. Ezzati, R. (2020). Derivation of pseudo-first-order, pseudo-second-order and modified pseudo-first-order rate equations from Langmuir and Freundlich isotherms for adsorption. Chemical Engineering Journal, 392, 123705.
16. Ibrahim, A., El Fawal, G. F., & Akl, M. A. (2019). Methylene blue and crystal violet dyes removal (as a binary system) from aqueous solution using local soil clay: kinetics study and equilibrium isotherms. *Egyptian Journal of Chemistry*, *62*(3), 541-554.

17. Ibrahim HK, Amy MA, Kreem ET. Decolorization of Coomassie brilliant blue G-250 dye using snail shell powder by action of adsorption processes. Res J Pharm Technol. 2019;12(10):4921-5.
18. Javaid R, Qazi UY, Ikhlaq A, Zahid M, Alazmi A. Subcritical and supercritical water oxidation for dye decomposition. J Environ Manage. 2021;290:112605.
19. Luo, Y., Wei, X., Gao, B., Zou, W., Zheng, Y., Yang, Y., ... & Dong, L. (2019). Synergistic adsorption-photocatalysis processes of graphitic carbon nitrate (g-C3N4) for contaminant removal: Kinetics, models, and mechanisms. Chemical Engineering Journal, 375, 122019.
20. Malash, G. F., & El-Khaiary, M. I. (2010). Piecewise linear regression: A statistical method for the analysis of experimental adsorption data by the intraparticle-diffusion models. Chemical Engineering Journal, 163(3), 256-263
21. Mattson JA, Mark Jr HB, Malbin MD, Weber Jr WJ, Crittenden JC. Surface chemistry of active carbon: specific adsorption of phenols. J Colloid Interface Sci. 1969;31(1):116-30.
22. Mohammed, S. S., Aziz, N. M., & Abdul Karem, L. K. (2021). Preparation and Diagnostics of Schiff Base Complexes and Thermodynamic Study for Adsorption of Cobalt Complex on Iraqi Attapulgite Clay Surface. *Egyptian Journal of Chemistry*, *64*(12), 2-3.
23. Nas, M. S., Calimli, M. H., Burhan, H., Yılmaz, M., Mustafov, S. D., & Sen, F. (2019). Synthesis, characterization, kinetics and adsorption properties of Pt-Co@ GO nano-adsorbent for methylene blue removal in the aquatic mediums using ultrasonic process systems. Journal of Molecular Liquids, 296, 112100.
24. Owa, F. W. (2014). Water pollution: sources, effects, control and management. International Letters of Natural Sciences, 3.
25. R. K, K., Selvan M, S., Rai, M. K., Priyadharshini, M., V. C, P., & Singh, R. S. (2020). Removal of Reactive Orange 16 by adsorption onto activated carbon prepared from rice husk ash: statistical modelling and adsorption kinetics. Separation Science and Technology, 55(1), 26-34.
26. Talha, K., Wang, B., Liu, J. H., Ullah, R., Feng, F., Yu, J., ... & Li, J. R. (2020). Effective adsorption of metronidazole antibiotic from water with a stable Zr (IV)-MOFs: Insights from DFT, kinetics and thermodynamics studies. Journal of Environmental Chemical Engineering, 8(1), 103642.
27. Thommes, M. (2010). Physical adsorption characterization of nanoporous materials. Chemie Ingenieur Technik, 82(7), 1059-1073.
28. Tran, T. H., Le, A. H., Pham, T. H., Nguyen, D. T., Chang, S. W., Chung, W. J., & Nguyen, D. D. (2020). Adsorption isotherms and kinetic modeling of methylene blue dye onto a carbonaceous hydrochar adsorbent derived from coffee husk waste. Science of the Total Environment, 725, 138325.

29. Zhang B, Zeng X, Xu P, Chen J, Xu Y, Luo G, et al. Using the novel method of nonthermal plasma to add Cl active sites on activated carbon for removal of mercury from flue gas. Environ Sci Technol. 2016;50(21):11837-43.
30. Zhou, C., Wu, Q., Lei, T., & Negulescu, I. I. (2014). Adsorption kinetic and equilibrium studies for methylene blue dye by partially hydrolyzed polyacrylamide/cellulose nanocrystal nanocomposite hydrogels. Chemical Engineering Journal, 251, 17-24.