Study - Thermodynamic Adsorption of Bismarck Brown Y on Different Adsorbent Surfaces

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Abstract

Koura clay and pottery clay as a pecuniary besides conservational-approachable adsorbent, was consumed to eradicate of Bismarck Brown Y (BBY). Koura clay and pottery clay subdivision and other factors on the surface of Koura clay is (2h), while its adsorption on the surface of pottery clay was (0.5h), (Frendelich, Elovich, Temkin, Harkin – Jura and Dupin). The results showed (Bismarck Brown Y) for Koura clay follows Langmier model, while its adsorption on the surface of the pottery clay follows the (Elovich) model. The adsorption isotherm was also applied to obtain thermodynamic functions within the experimental temperature range (290-320k). The standards depend on the equilibrium constant (Keq).

Key Words: Adsorption, Water Pollution, Bismarck Brown Y Dye, Pottery Clay, Koura Clay.

DOI Number: 10.14704/nq.2022.20.5.NQ22223 **NeuroQuantology 2022; 20(5):672-683**

Introduction

Pollution has converted additional severe as a consequence of social fiscal progress around the ecosphere. Different industries, such as textiles, plastics, coatings, and paper, use "dyes" at various stages of the manufacturing process (Naushad, M et al 2019). Textile wastewater disposal is currently a big challenge on a global scale (Bharagava, R.N et al 2018). Textile mills generate a large amount of wastewater, which contains a variety of contaminants such as acidic or caustic dissolved solids, hazardous chemicals, and dyes (Chowdhury, S. and Saha, P 2011). Dyes are chemical compounds that may absorb and reflect light at specific wavelengths in the visible spectrum. To transfer to the colored material, the dyes mostly require a liquid medium (Lorenc-Grabowska, E 2007). Clay has been successfully utilized to remove several heavy metals from aqueous solution in both natural and modified forms (Anirudhan, T.S et al 2012) Earth is mostly made up of fine-grained minerals that occur naturally (Ahmed, D.N. et al 2020). which, given the right water concentration, may be plastic and harden when it has been dried or burnt. Clay minerals have a lot of negatively charged ions on their surface, which makes them extremely effective at removing positive ions from wastewater because of its higher specific surface area, cation exchangeability, and pore volume locality. Clay materials have a number of advantages over other materials (Abegunde, S.M., et al 2020). Bismarck Brown is a diazo dye that is cationic and basic. It is used in colouring paper, pulp, wool, and leather, among other materials, for both short and long periods of time and dye contact with the eye for an extended period of time and skin irritates, resulting in redness. In the same vein, Bismarck Brown Y (BBY) is a cationic or basic dye that is toxic to aquatic species (Mizhira, A.A et al 2020). Dyes breakdown into poisonous, carcinogenic, or mutagenic chemicals when they enter the aquatic environment benzidine, naphthalene, and other carcinogens are present as well as other aromatic compounds.

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Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Received: 25 March 2022 **Accepted:** 29 April 2022

The various water treatment procedures are used to cure organic dyes Adsorption has proven to be one of the most effective methods Due to its high efficiency (A.D. Atasoy, et al 2013), this procedure is used to remove dyes Service simplicity, cheap cost, and easy absorption. The adherence or aggregation of a liquid or gaseous adsorbate on the surface of a solid material is known as adsorption. The degree of adsorption of molecules or atoms densely concentrated on a solid's surface is determined by the relationship between the nature and volume of the adsorbent and the adsorbent's surface area, and adsorption is also defined as the transfer of dissolved pollutants (adsorbent material) from aqueous solutions to the surface of a solid material (adsorbent surface). Adsorption can be either physical or chemical (Jaroniec M, Deryło A, 1983). They are required mechanically, chemically, and thermally stable high porocapacity (Ghodbane I. et al 2008).

Actual attention was paid to studying the environmental behavior of these dyes after receiving notice regarding the danger and toxicity of these materials. Originally, dyes are one of the factors that cause cancerous diseases because of the decomposition of these dyes, and their presence in wastewater is an undesirable thing, so it is better to erase these dyes before they are put into the environment (Harrache Z, Abbas et al 2019).

Methodology

1. Prepare the Adsorbent Surface

Each of (Pottery Clay and Koura Clay) was ground ,then they were filtered, dried, and the clay was collected and ground again and sieved through a porous sieve (200 µm) as shown in (Figure (1) Koura Clay) and Figure (2) (Pottery Clay).The chemical analysis of Pottery Clay and Koura Clay is listed in Table 1.

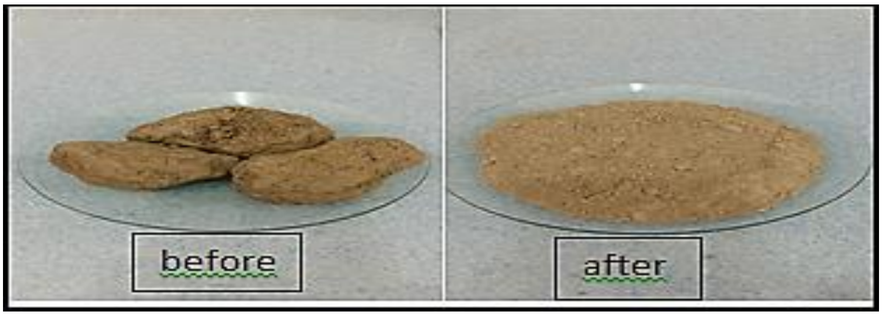

Figure 1. (Koura Clay) Before and after washing drying and grinding

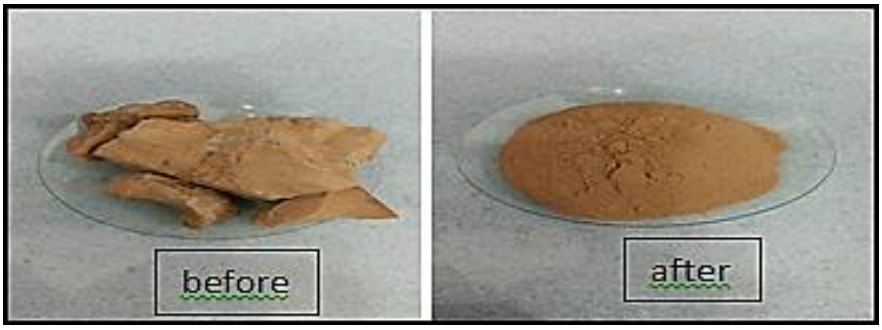

Figure 2. (Pottery Clay) Before and after washing, drying and grinding

Table 1. The Chemical analysis of Pottery Clay and Koura Clay.

Constituent	Pottery Clay (Wt%)	Koura Clay (Wt%)
SiO_2	40.85	39.71
CaO	15.05	18.32
Al_2O_3	10.11	9.624
Fe_2O_3	8.44	6.905
MgO	6.775	5.063
K_2O	2.206	1.343
TiO_2	0.779	0.929
Na_2O	0.509	1.357

2. Preparation of Standard Solutions and Calibration Curve

The standard stock solution of the Bismarck Brown Y (BBY) dye was prepared at a concentration of (50 ppm), by dissolving a weight of (0.05 gm) in (1000 ml) of condensed water. After ranging from (2 to 20 ppm) as shown in Figure (3). The wavelength length λmax has measured to get the greatest absorption of the dye using distilled water

(Reference) (Blank). Then, the absorbance was measured for each of the ten samples by UV-visible spectrophotometer (as shown in Figure (4) to determine the calibration curve of the dye. The calibration curve was drawn for the dilute solutions, and the straightness of the calibration curve is a good indication that the calibration curve is subject to Beer's law. (Beer-Lambert) as shown in Figure (6).

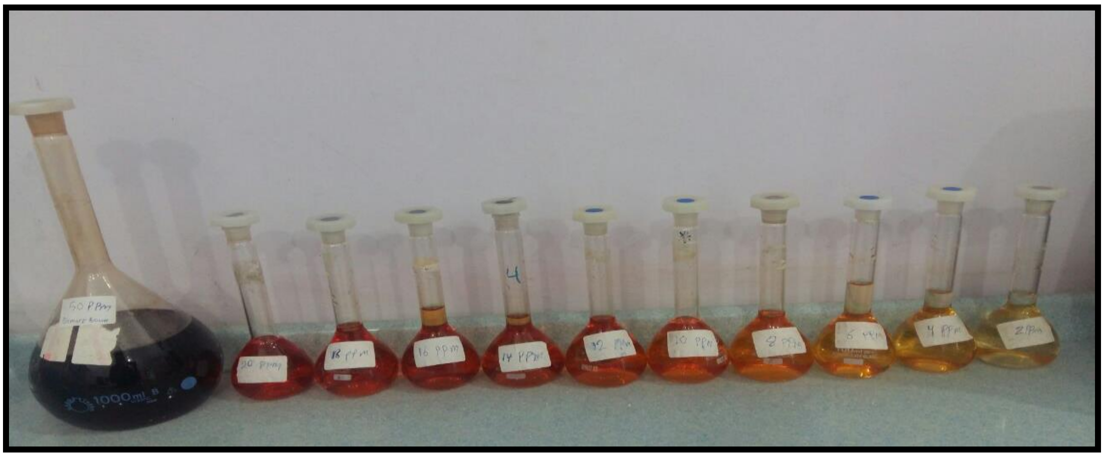

Figure 3. Preparing of Bismarck Brown Y (BBY) dye in different concentrations

Figure 4. UV-visible spectrophotometer and UV-visible spectroscopy devices

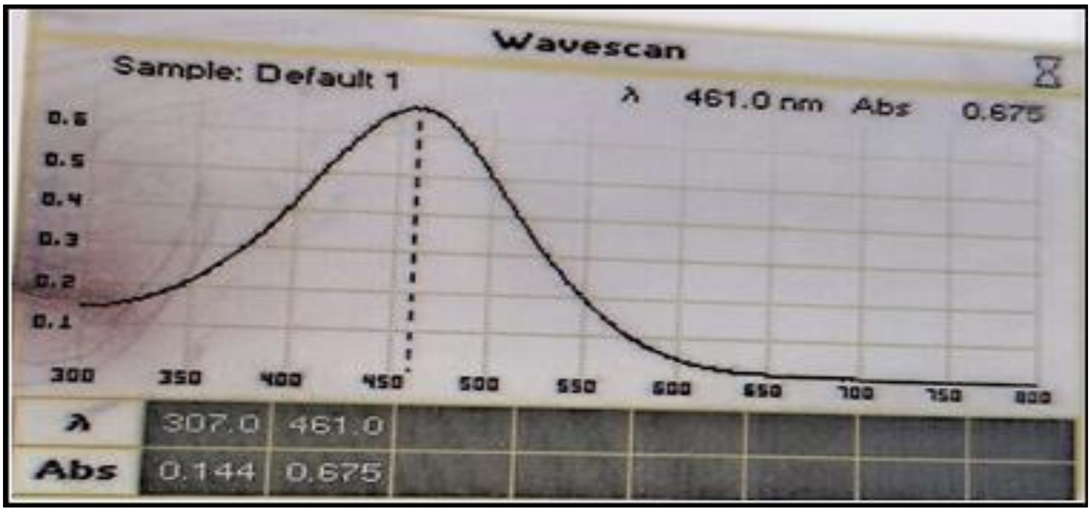

Figure 5. The maximum wavelength of Bismarck Brown y dye

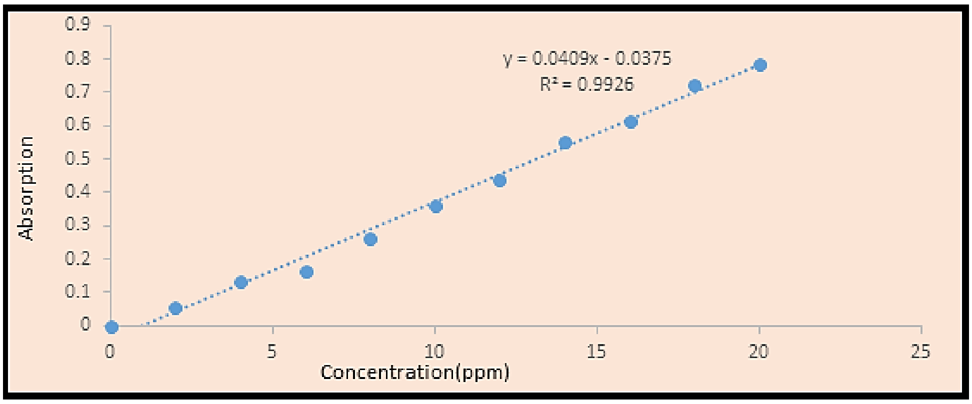

Figure 6. Calibration curve for Bismarck Brown y at 2902K and pH=7

3. Determination of Contact Time (Equilibrium)

This experiment was conducted at a temperature (290k) and (pH = 7) to find out the equilibrium time between the adsorbent surface and the adsorbent material. The volume of all samples was (15 ml) at a concentration (20 ppm) and the surface weight from (koura clay and pottery clay) is (0.2 gm), and at different times (1/2 h, 1 h, 1.5h, 2h, 2.5h, 3h) after placed. The samples were in the vibrating water bath, of the filtrate was measured by UV-visible spectroscopy as shown in Figure 4.

4. Determination the weight of the Adsorbent Surface

Under constant conditions and temperature (290 K) and (pH = 7) the experiment was carried out with different weights (0.05, 0.1, 0.15, 0.2, 0.25, 0.3 g) of both surfaces (Kora clay and pottery clay) and volume (15 ml) at a concentration of (20 parts per million) and a time of (2) hours for Koura clay and (½) hour for pottery clay. The samples were placed in a vibrating water bath and then filtered with filter paper several times.

5. Acidic Function

Acidity tested by preparing five samples of the solution with a volume of (15 ml) from the concentration (20 ppm), where the pH of the five samples was adjusted (2, 4, 6, 8, 10) by using an acidic solution of HCl and NaOH at a concentration of (0.1 M) respectively. Then, the adsorption surface with a weight of (0.05 g) from both surfaces (Koura clay and pottery clay) was placed in the five samples and placed in a vibrating water bath for 2 hours for Koura clay, and (1/2) hour for pottery clay at 290k.

6. Effect of Zero Point Charge

Absorbent material, for five trials of (BBY) dye (15 ml) were prepared for each volumetric flask (20 ppm), and then (10 ml) of NaNO3 salt solution (0.1 M) was added as Adjusting the pH in the five samples (2, 4, 6, 8, 10) respectively, using an acidic solution of HNO3 and basic NaOH at a concentration of (0.1 Molar), then placing the adsorption surface by weight (0.05 g) for both surfaces (Koura clay and pottery clay). At a temperature of (290 K) and left for (24 hours) after which the filter absorption is measured after the filtration process of the models. The pH for each ΔpH is extracted by the following equation (1):

$$\Delta pH = pHf - pHi \qquad (1)$$

pHi: Before adsorption with the (BBY) dye.

pHf: After adsorption with the (BBY) dye.

7. Effect of salt

This factor studied for the surface of Koura clay and pottery clay, different weights of salt (0.05, 0.1, 0.15, 0.2, 0.25, 0.3 g) were added. For a dye mixture of concentration (20 ppm) with surface (0.05 g) for both surfaces (in six volumetric flasks, the flasks were placed in a water-bath shaker containing a shaker and temperature controller (at 290 K), the solution was filtered and the absorbance measured after filtration (Harrache Z, Abbas et al 2019).

Adsorption Isotherms

The determine the adsorption isotherms, ((0.05g) from the surface of Kora clay and (0.05g) from the surface of pottery clay were placed into ten volumetric flasks with different concentrations of Bismarck Brown Y dye, then (15ml) was added to each flask at a concentration of (2, 4, 6, 8, 10, 12, 14, 16, 18, 20ppm), then these flasks were placed in a shaker water bath containing a vibrator and a temperature controller) at different temperatures (290, 300, 310, 320 K) and for a period of time

(1/2 hour) For the surface of the pottery clay, (2 hours) for the surface of the Koura clay, and after the end of the equilibrium time, the sediment was separated from the sediment by filtering by filter paper several times, then after separation the absorbance of the clear solution was measured by a spectrophotometer device. VIS at (λmax) for the dye (BBY), then the concentration at equilibrium Ce was measured in units (ppm) through the calibration curve, from which the adsorption amount of the dye was calculated. At equilibrium qe is in unit ((mg/g)) and according to the following relationship: -

$$qe = (c° - ce)\, Vsol \qquad (2)$$

Results and Discussion

1. Contact Time Effect

This experiment was conducted at a temperature (290 k) and (PH = 7) to discover the equilibrium Time between different surfaces (koura clay and pottery clay) and BBY dye. The size of all samples was (15ml) with concentration (20ppm) and weight (0.2 g) for both surfaces (pottery clay and koura clay) at different times. The results showed that the equilibrium time on the surface of the Koura clay was (2 hours), while the equilibrium time for the same dye, BBY, on the surface of the pottery clay was (1/2 hour). Contact time is the amount of time it takes for the adsorption process to reach equilibrium [18]. And plotted the ratio of the expressed adsorption quantity (Qe) versus contact time between the adsorbent and solution surface (t).

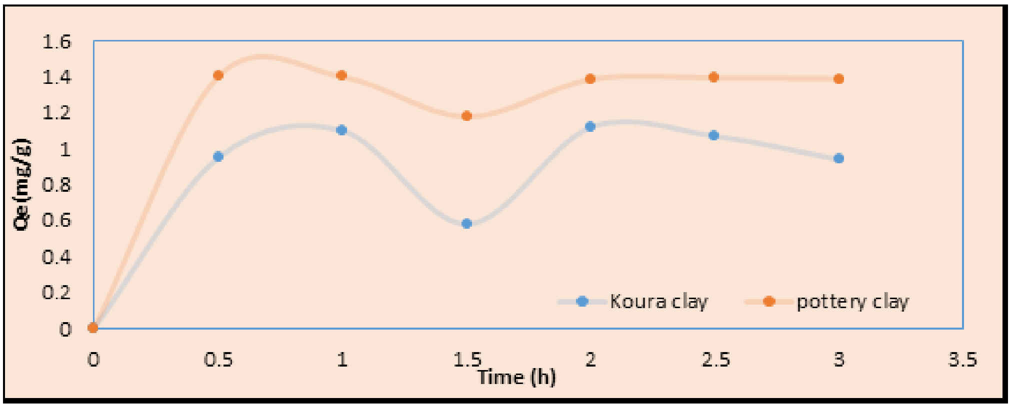

Figure 7. Effect of Contact Time for Adsorption at 2902K and pH=7

2. The Effect of Surface Weight on Adsorption

This Consequence examined by taking different weights from the surfaces of Koura clay and pottery clay ranging from (0.05-3 g). It showed the finest weight of the surfaces used was (0.05 g) for both surfaces. The reason for this is that at these weights all the effective sites of the adsorption surface are saturated (the saturation limit) after which the increase in the amount of adsorbing surfaces is not affected by the adsorption of dyes [19]. As shown in Figure (8). By raising the adsorbent weight increases, but as time passes, active sites get saturated, decreasing dye removal [20].

The Figure shows that the amount of adsorption decreases as the surface weight increases and for both surfaces (koura clay and pottery clay).

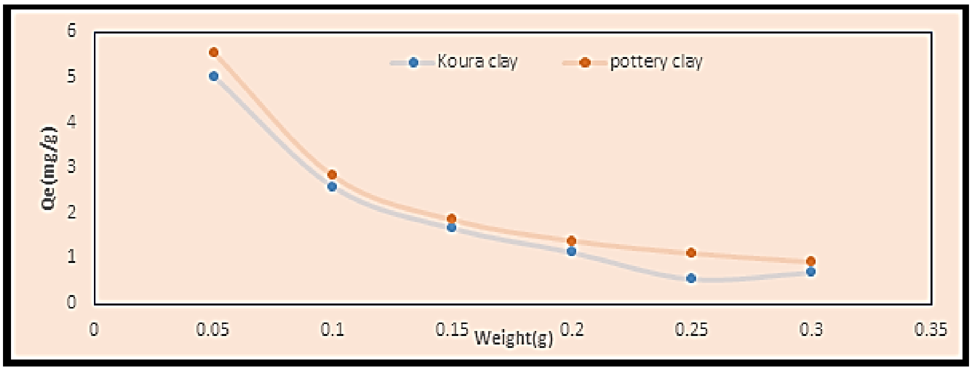

Figure 8. The effect of surface weight for adsorption of 15mg / L of Bismarck Brown with different weights at a temperature of 290k at pH = 7

3. Effect of Temperature

The following figures show the effect of temperature for absorbing 15mg/L of Bismarck Brown Y dye with a surface weight of (0.05 g) for both Koura and Pottery clays. When acidic function pH = 7 At different temperatures (290, 300, 310, 320) K. Line graphs are fluctuating with all. The results showed that BBY dye on the surface of pottery clay, in which a gradual decrease in the adsorption efficiency was observed with increasing temperature, regardless of the compensated chemical groups on the aromatic rings. The bonding forces break down and this type of adsorption is exothermic [21, 22] and this shows that the reaction is endothermic.

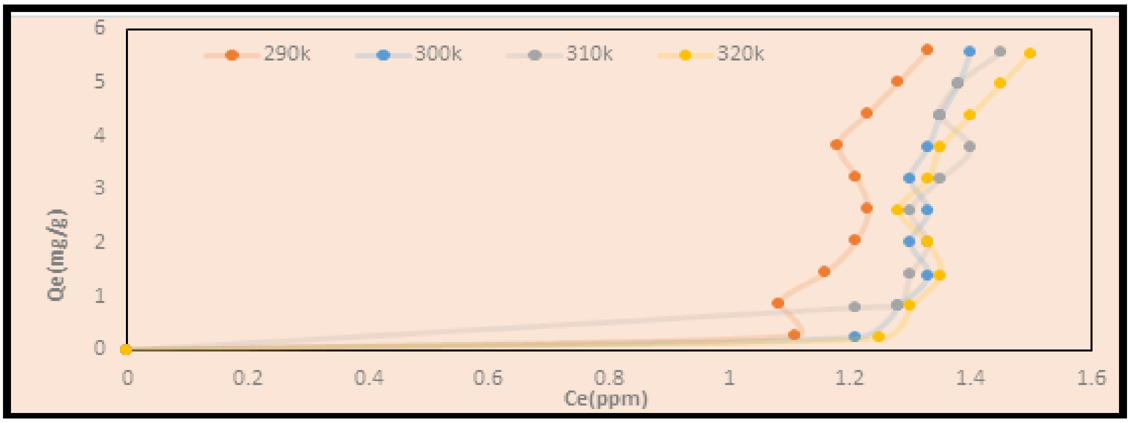

Figure 9. Effect of temperature for adsorption of 15 mg/L of Bismarck Brown on pottery clay at temperature 290-320 k

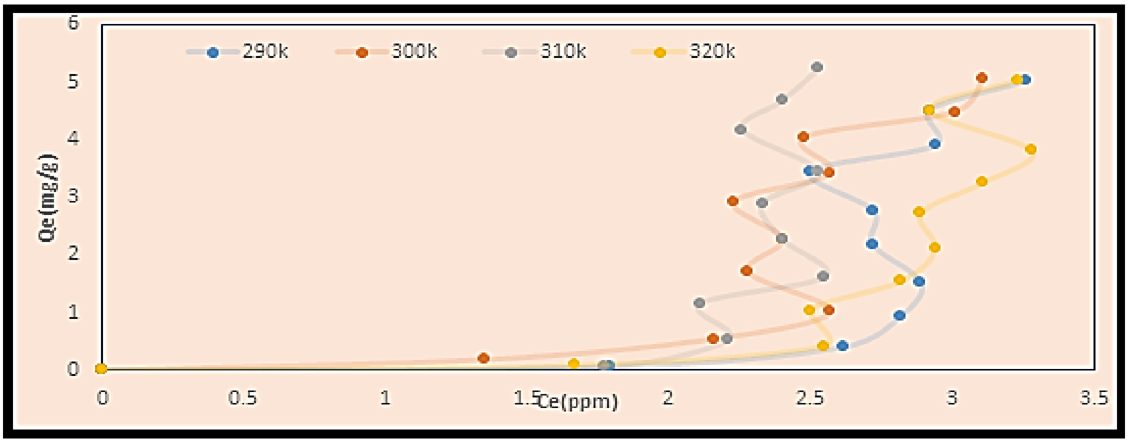

Figure 10. Effect of temperature for adsorption of 15 mg/L of Bismarck Brown on Koura clay at temperature 290-320 k

4. Thermodynamics of Absorption

The figure below shows the thermodynamic study, which is the relationship between temperature inversion and the equilibrium constant for the absorption of (15 mg/L) of BBY dye with (0.05 g) of Koura clay and pottery clay at (290 K). The acidic function pH = 7. The relationship between them two variables (1/T and Ln Kqe).

$$\Delta G^0 = -RT\ln Kc \qquad (3)$$

Both used to describe the amount of energy in a system. Van't Hoff's equation was used to derive [23].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (4)$$

$$\ln Kc = \Delta S^0/R - \Delta H^0/RT \qquad (5)$$

As ΔH^0 is change in enthalpy, ΔS^0 is degree to which a response is disordered.

Where the results showed that the reaction (endothermic) koura clay.

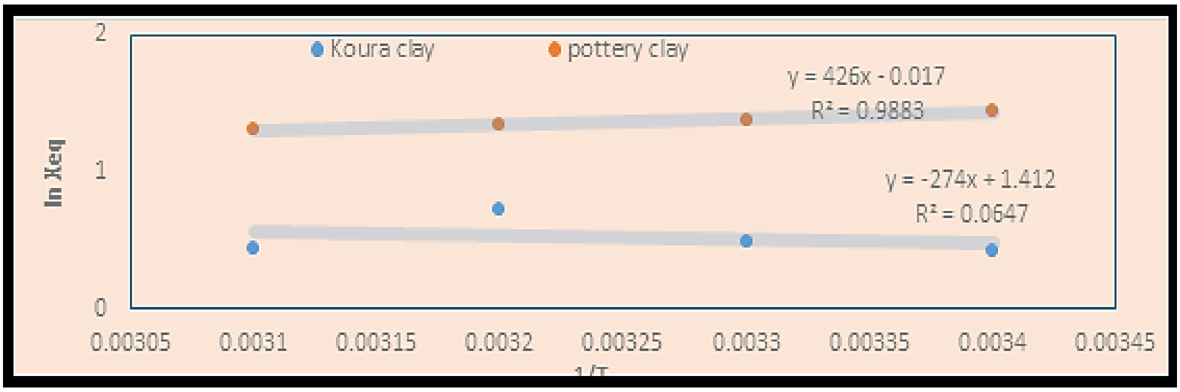

Fig. 11. Relationship between the temperature inversion and the equilibrium constant for adsorption of 15mg / L of Bismarck Brown with different weights at a temperature of 290k at pH = 7

Table 2. Principles of functions for Bismarck Brown Y dye

Koura clay			Pottery clay		
ΔH. (KJ/mol .K)	ΔS. (J/mol .K)	ΔG. (KJ/mol .K)	ΔH. (KJ/mol .K)	ΔS. (J/mol .K)	ΔG(KJ/mol.K)
0.23	11.739	0.199	-0.354	-0.141	0.3582

5. Adsorption Equilibrium and Adsorption Isotherms Models

The Langmuir parameters calculated via Ce/qe plot respectively,against Ce, qe values that are close to those that have been tested. In addition, the KL values gained in value as time went on temperature rises, indicating a Adsorption is becoming more powerful [23].The determine ln Qe vs. lnCe connection using the following equation (6, 7): [24]. are presented in Table 3 and Figure 12,13.

$$ce/qe = ce/q\max + 1/KLq\max \quad (6)$$

$$\ln Qe = \ln kf + 1/n \ln Ce \quad (7)$$

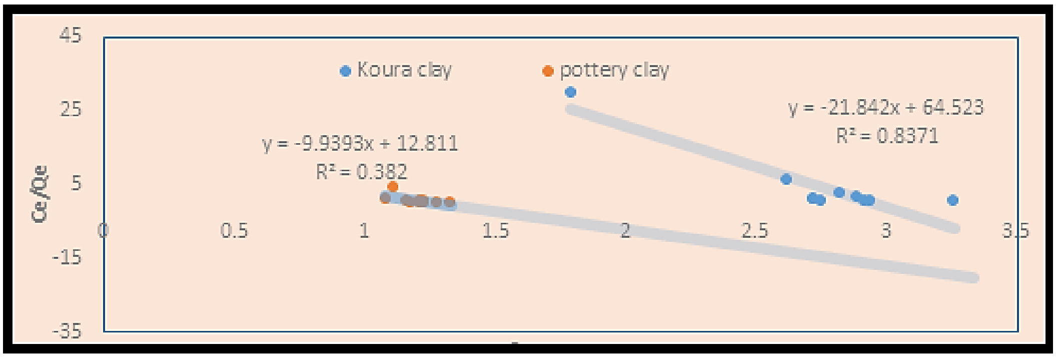

Figure 12. The langmuir isotherm for adsorption 15mg/L of Bismarck Brown with 0.05 gm of different surfaces at 290k and pH= 7

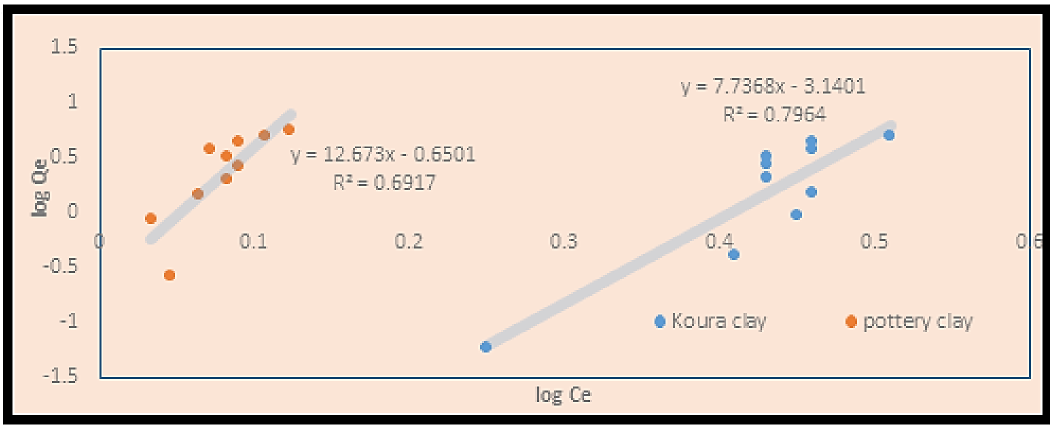

Figure 13. The freundlich isotherm for adsorption 15mg/L of Bismarck Brown with 0.05 gm of different surfaces at 290k and pH= 7

Figure (14) shows: Temkin's Isotherm This isotherm includes a component that specifically considers adsorbent-adsorbate interactions. Instead of being logarithmic,. By ignoring the extreme low and high concentration values, coverage can be achieved [25]. It is characterized by a standardized slope and intercept are both constants connection using the following equation (8): are presented in Table 3.

$$qe\& = B\ln KT + B\ln Ce \qquad (8)$$

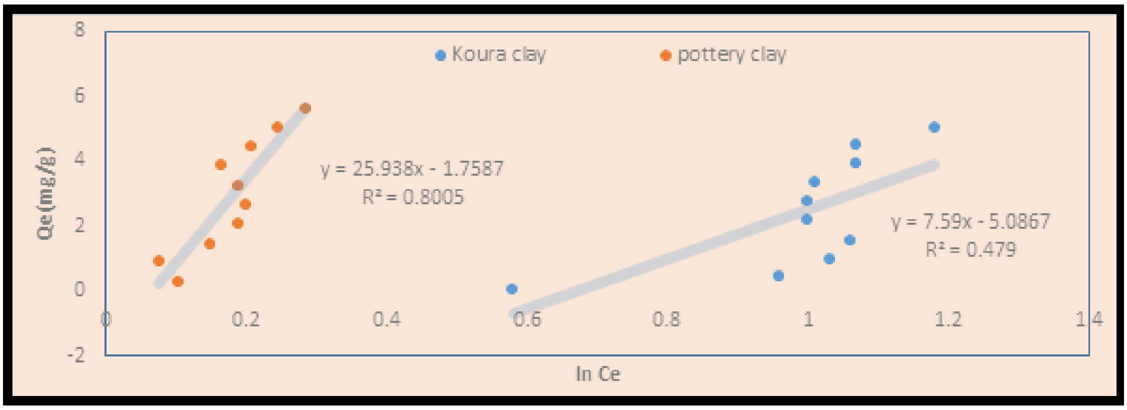

Figure 14. The Temkin isotherm for adsorption 15mg/L of Bismarck Brown with 0.05 gm of different surfaces at 290k and pH= 7

Figures (15) and (16) Elovich and Harkin-Jura isotherm adsorption of 15 mg/L of BBY dye with 0.05 g of different surfaces (Kora clay and pottery clay) at 290 K and pH of acid function = 7. are presented in Table 3 and Figure 15, 16.

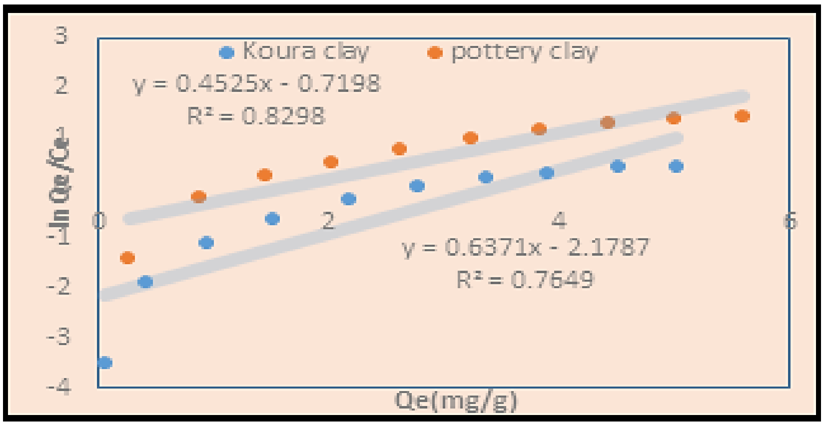

Figure 15. The Elovitch isotherm for adsorption 15mg/L of Bismarck Brown with 0.05 gm of different surfaces at 290k and pH= 7

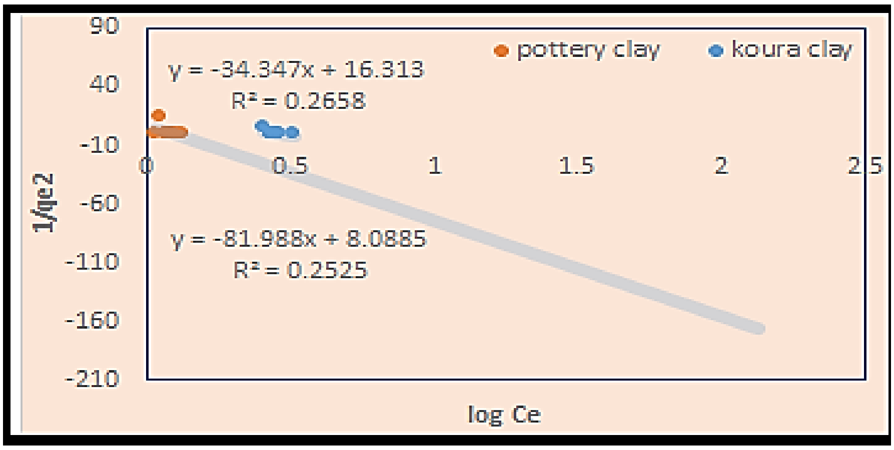

Figure 16. The Harkin-Jura isotherm for adsorption 15mg/L of Bismarck Brown with 0.05 gm of different surfaces at 290k and pH= 7

Dubinin proposed the Radushkevich (DKR) model, which does not imply a homogeneous sorbent surface. It's used to figure out how things stick together (physical or chemical). (DKR) has the following [26], equation (9): [27]. In Table 3 and Figure 17.

$$E = (-2\,\beta)^{-0.5} \qquad (9)$$

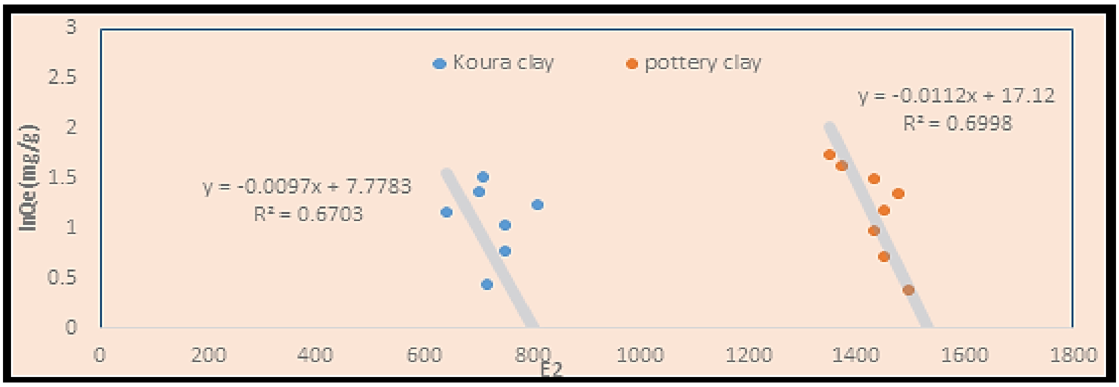

Figure 17. The Dupin isotherm for adsorption 15mg/L of Bismarck Brown with 0.05 gm of different surfaces at 290k and pH= 7

Table 3. Parameters of the isothermal models of adsorption of Bismarck Brown Y dye on the surface of Koura clay and pottery clay at 290 K and acidity function pH = 7

adsorption isotherm	Koura clay			pottery clay		
	Constants			Constants		
langmuir	KL	Qm	R2	KL	Qm	R2
	0.339	-0.045	0.837	0.776	-0.1006	0.382
Freundlich	Kf	N	R2	Kf	N	R2
	7.242	0.129	0.796	0.2238	0.078	0.691
Temkin	KT	B	R2	KT	B	R2
	0.214	7.59	0.479	0.855	25.938	0.801
Elovich	Qm	K	R2	Qm	K	R2
	-1.569	24.408	0.764	-2.2	2.113	0.829
Harkins-Jura	A	B	R2	A	B	R2
	0.029	0.473	0.2658	0.0122	0.098	0.2525
Dupin	LnQm	B	R2	lnQm	B	R2
	7.778	0.0097	0.6703	17.12	0.0112	0.6998

6. Consequence of Salt

Adsorption of BB dye for surface - Koura clay and pottery clay, where we notice that the amount of adsorption decreases with the increase in the amount of salt. The effect of ionic strength is an important factor affecting the water balance between the adsorbed dye and the adsorbent. The adsorption of BBY dye (decreases in the presence of electrolytes, as the ions on the adsorbent surface are greatly affected by the presence of different weights of sodium chloride. Because of Competition between the ions of electrolyte for the active sites; Because it is related to the adsorbent surface and this is the main reason for noticing the effect of ionic strength (adsorption decreases due to the shrinkage in the electrostatic state of material, where the sodium ions are characterized by their small size) i.e. its selective solutions are faster. [28-29].

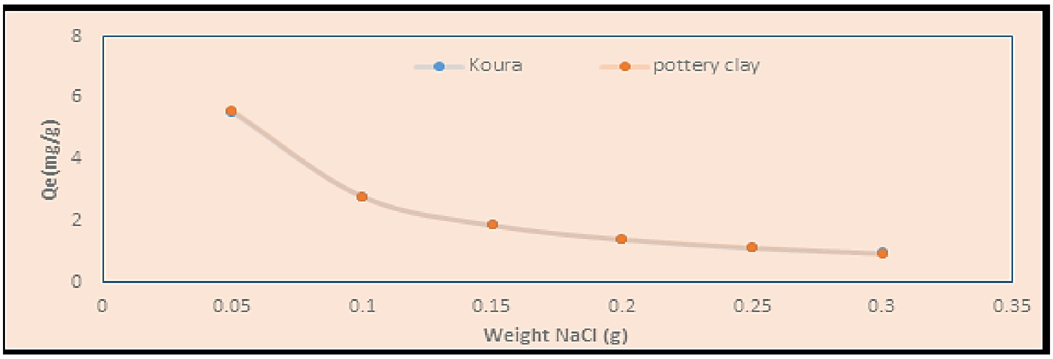

Figure 18. 15mg / L of Bismarck Brown with different weights at a temperature of 290k at pH = 7

7. Effect of pH

The dye solution's acidity directly with particularly on the adsorption capacity. As shown in Figure (19) depicts acidity capabilities at various acidity levels ranging from (2 to 10) the highest amount of adsorption for both surfaces (Al Koura clay and pottery clay) was at the pH 2 and the higher the basicity of the solution, the less the adsorption amount of the dye of the koura clay and pottery clay are calculated [30].

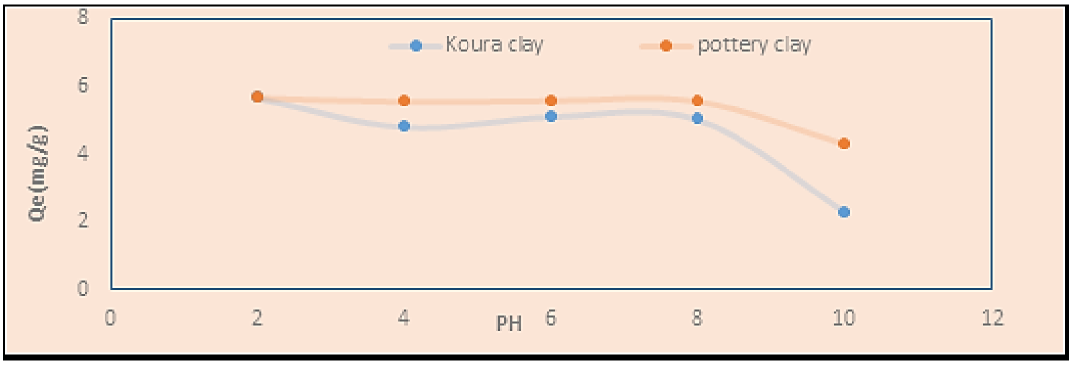

Figure 19. The effect of the acidic function for adsorption of 15mg / L of Bismarck Brown with different weights at a temperature of 290k at pH = 7

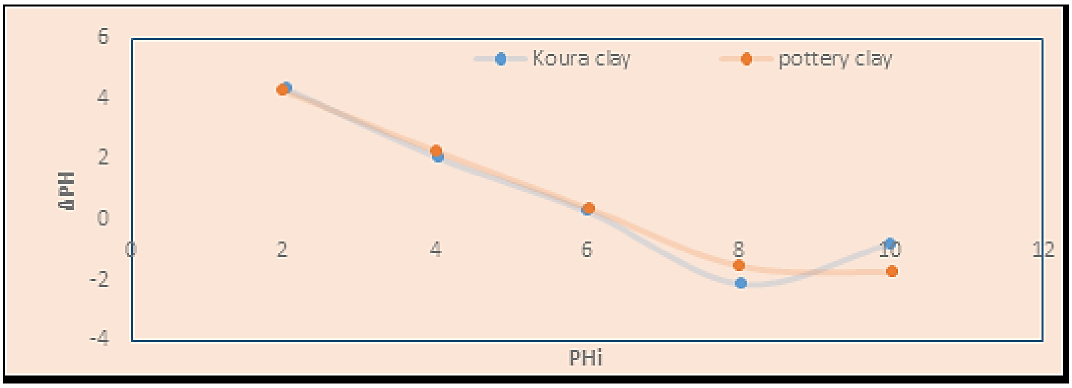

Figure 20. Zero charge point for adsorption of 15mg / L of Bismarck Brown with different weights at a temperature of 290k at pH = 7

Conclusions

1. The study showed Koura clay were following the Langmuir model, while on the surface of the pottery clay it was following the Elovitch model.
2. The study showed that the surface of pottery clay was more efficient in adsorption of BBY with a removal rate of 93.35%, while the removal rate of the same dye on the surface of Koura clay was 83.7% at a temperature of 290K and a weight of 0.05 g for both surfaces.
3. The study showed the acid function BBY dye on the two surfaces of Koura clay and pottery clay was at PH =2. While the zero point charge for both surfaces = 7.

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4. The study showed the study showed the effect of temperature of BBY dye on the surface of Koura clay, where the adsorption was (endothermic) and the value of ΔG is positive indicating that the adsorption is not spontaneous, and ΔS was positive and indicates randomness during adsorption, while the clay stayed Pottery clay (exothermic) and ΔG are positive, and the value of ΔS is negative.

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