

## Adsorption of Bromothymol Blue Dye onto Bauxite Clay

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### Abstract

The goal of the current work is to use an inexpensive, non-toxic material with a high water absorption capacity, bauxite clay, to adsorb the bromothymol blue dye from an aqueous solution. In the production of textiles, leather, paint, food, cosmetics, and pharmaceuticals, synthetic organic compounds are used as dyes almost exclusively in modern industrial processes. Because to their harmful side effects, which include their inherent carcinogenicity, toxicity, and mutagenicity as well as the results of their biological transformation, these dyes pose a serious hazard to the environment when they are released. Clay minerals are valuable as depolluting agents due to their swelling potential, colloidal behavior, and adsorption capacity. The adsorption behavior of bromothymol blue dye from an aqueous solution was studied using bauxite clay. Different variables such as contact time, dosage, ionic strength, and temperature were studied to show the effect on bromothymol blue adsorption onto bauxite clay from an aqueous solution using the batch adsorption method. This study showed that the adsorption decreased by increasing the temperature (15–40 C) and increased by increasing the clay weight from 0.2 to 1.6 g. It also showed as the amount of time rose, the adsorption grew until it reached an equilibrium time of 155 minutes. Thermodynamic metrics including change in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) all were assessed. A positive correlation was found between the absorbance and the range of concentrations of bromothymol blue (4–32 g/mL) with a correlation coefficient of 0.9911. The maximum wavelength was found and set to 432 nm for all measurements.

**Keywords:** Adsorption, Bauxite, Bromothymol, Clay, Dye.

### Introduction

Community water sources are negatively impacted by wastewater contamination, which can have negative health implications <sup>1</sup>. Large amounts of dyes are used in numerous businesses, causing the water in rivers and lakes to become contaminated. Dye products are used in a wide range of industries, including those related to paper, textiles, cosmetics, rubber, food, and medicine. Many dyes, especially

synthetic dyes, have a hazardous impact on human health and may even be carcinogenic due to their complex chemical structures that resist biodegradation and enable them to persist for a long time in aqueous media <sup>2</sup>. For the removal, recovery, and recycling of harmful materials from wastewater, adsorption has emerged as the method of choice. Due to their affordability and simplicity,

spectrophotometric approaches can be more beneficial for determining biological materials<sup>3,4</sup>.

The dyes are organic substances that can dissolve in water, especially the reactive, direct, basic, and acidic ones. It is challenging to get rid of them with traditional procedures because they are highly soluble in water. Due to the presence of chromophoric groups in its molecular structures, one of its characteristics is the capacity to color a certain substrate. However, the auxotrophic groups, which are polar and may interact with polar groups of textile fibers, are what give color to a material its ability to adhere to it<sup>5</sup>. Modern industrial processes nearly exclusively use synthetic organic chemicals as dyes in the manufacture of textiles, leather, paint, food, cosmetics, and pharmaceuticals<sup>6,7</sup>. It is estimated that more than 700,000 tons of synthetic organic dye are generated each year globally. A few examples of the several dye classes that can be separated based on their structure and application include reactive, acid, dispersion, vat, and azo dyes. These dyes constitute a major threat to the environment when they are released because of their negative side effects, including their inherent carcinogenicity, toxicity, and mutagenicity as well as the byproducts of their biological transformation<sup>6</sup>. More details about the degradation structure are required in order to improve the stability of health products and determine whether the degradation and contaminants are harmful. These abrupt changes have a significant impact on how chemical compounds affect the environment and human health<sup>8</sup>.

Clays are naturally occurring substances with a high capacity to absorb water. They are also often non-toxic. As a result, in addition to their usage for pollutant control, they are also beneficial as water adsorbents in contemporary, typically urban, applications such as pet litter, air conditioners, and tunnel sealing (to stop water leakage)<sup>9</sup>. These bauxites chemical, mineralogical, and physico-mechanical characteristics are greatly influenced by the parent rocks composition the generation process of the locations geomorphology the amount of time that has passed since formation and the age of the bauxite<sup>10,11</sup>.

A multitude of operational parameters affect how the adsorption process turns out. The process must have enough time to run until the equilibrium state is reached because contact time is a vital component. Longer contact times between the adsorbent and the adsorbate are also believed to

increase adsorption efficacy differently depending on the material's accessible sites<sup>12</sup>. The two main models used in adsorption research are Freundlich and Langmuir. The Langmuir model, which assumes that the surface has a specific number of binding sites with equal energy or heat and no lateral interactions, is one of the most basic equations of isotherm. One of the most crucial tests performed during the optimization process, the influence of contact duration, which requires significant care to produce the best results. When the thermodynamic analysis is finished, the other variables are kept constant while the adsorbent and adsorbate are subjected to interactions with one another at various temperatures. The outcomes might show a lot about the relationships between the various species. Calculations of the thermodynamic quantities free energy change ( $\Delta G^\circ$ ), entropy ( $\Delta S^\circ$ ), and enthalpy ( $\Delta H^\circ$ ) are based on how temperature affects the adsorption process. While the strength of the adsorption is indicated by enthalpy, entropy refers to a change in the system's overall order<sup>13</sup>.

There are several analytical methods for removing dyes, but adsorption is the most effective method since it is simple, generates a high yield, is easy to recover from, and allows the adsorbent to be reused. The adsorption of the dye bromothymol blue (BTB) onto four zeolitic materials was investigated by Tabti and colleagues. The outcomes demonstrated that an adsorbent had an efficiency of 83.44 % in removing dye<sup>14</sup>. It has been proven that Latvian sphagnum peat moss is an effective sorbent for removing BTB from aqueous solutions. The dye removal effectiveness of the solution showed significant fluctuation, with greatest removal at pH values of 7.5 and 2.5<sup>15</sup>. An aqueous media was treated with a mixture of Fe<sub>2</sub>O<sub>3</sub>, chitosan, and bamboo sawdust to remove the acid dye BTB (FeCBSD). With an adsorption efficiency (qm) of 217.39 mg/g over a contact period of 30 min and an adsorbent dosage of 0.5 g/L, the results most closely resembled the Langmuir adsorption isotherm. With an adsorption process of 225.13 mg/g at a flow rate of 20 mL/min and a bed level of 5 cm in column trials, the data closely matched the Thomas model. Abu Al Roos and colleagues looked into the possibility of removing the dye BTB from aqueous solutions using sphagnum sorbents that had undergone thermal treatment. Under ideal adsorption conditions, which included the proper shaking rate, equilibrium contact durations, and

solution pH, these sorbents were tested for dye removal. The untreated sphagnum material was used to conduct the experiment. These sorbents were also studied using infrared spectroscopy and thermogravimetric measurements. As a result, it was demonstrated that sphagnum sorbents could effectively remove both cationic and anionic dyes with little to no thermal treatment<sup>16</sup>. The adsorption of the Rhodamin dye on Iraqi bentonite was

assessed using various concentrations of nano compounds, such as ZnO, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>. To improve the bentonite's capacity for adsorption, rhodamin dye was taken out of aqueous solutions at a concentration of 0.01-0.1 g<sup>17</sup>.

The current study aims to use the adsorption method to remove the BTB dye from an aqueous solution using bauxite clay which is cheap, none-toxic, and has a high capacity to absorb water.

## Materials and Methods

Riedel-De Haen AG has supplied the bromothymol blue, while the bauxite clay samples were obtained from the General Company for Geological Survey and Mining. The chemical structure of BTB is shown in Fig. 1.

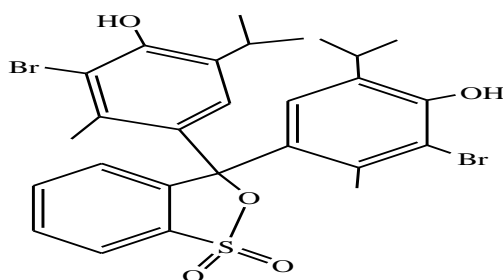


Figure 1. BTB's chemical structure.

## Apparatus

The UV-visible spectrophotometer was a double beam Shimadzu 1800 in a quartz cell with a 1 cm width from Japan. The LabTech LSB-045S thermostatic water bath shaker is produced in Korea. Germany produced the Radwag AS 220/C/1, ± 0.0001g, electronic balance, and centrifuge (6000 rpm).

## Preparation of Standard Solutions

The buffer solution was prepared by mixing 10 ml of potassium phosphate 0.1 M and 11.2 ml of sodium hydroxide 0.1 M. Because the color of the

dye changes to yellow when the pH changes, it was adsorbed at pH 6. A standard stock solution containing 100 mg/L of dye was created by dissolving 0.01 g of BTB dye in 100 ml of water. The dye was diluted to a concentration of 4-32 mg/L to produce solutions of various concentrations.

## Adsorption Experiments

All tests were carried out to investigate the impacts of contact time, adsorbent weight, and ionic strength. The absorption spectra and calibration curve of BTB dye are shown in Fig. 2 and Fig.3. The optimal wavelength is 432 nm, as seen in Fig.2. Therefore, the experimental values of solutions with concentrations ranging from 4 to 32 mg/L were measured and plotted against the BTB dye concentration. Eq. 1 and Eq. 2 were used to determine the amount of BTB dye that was adsorbed at contact times and the percentage of BTB dye that was removed by the BTB (R%) (Q<sub>e</sub>).

$$R\% = (C_0 - C_e) / C_0 \times 100 \quad 1$$

$$Q_e = V(C_0 - C_e) / W \quad 2$$

Where C<sub>0</sub> the initial concentration and C<sub>e</sub> the equilibrium concentration in mg/L, V is the solution volume (25 ml), and W is the weight of the clay sample that was used in grams.

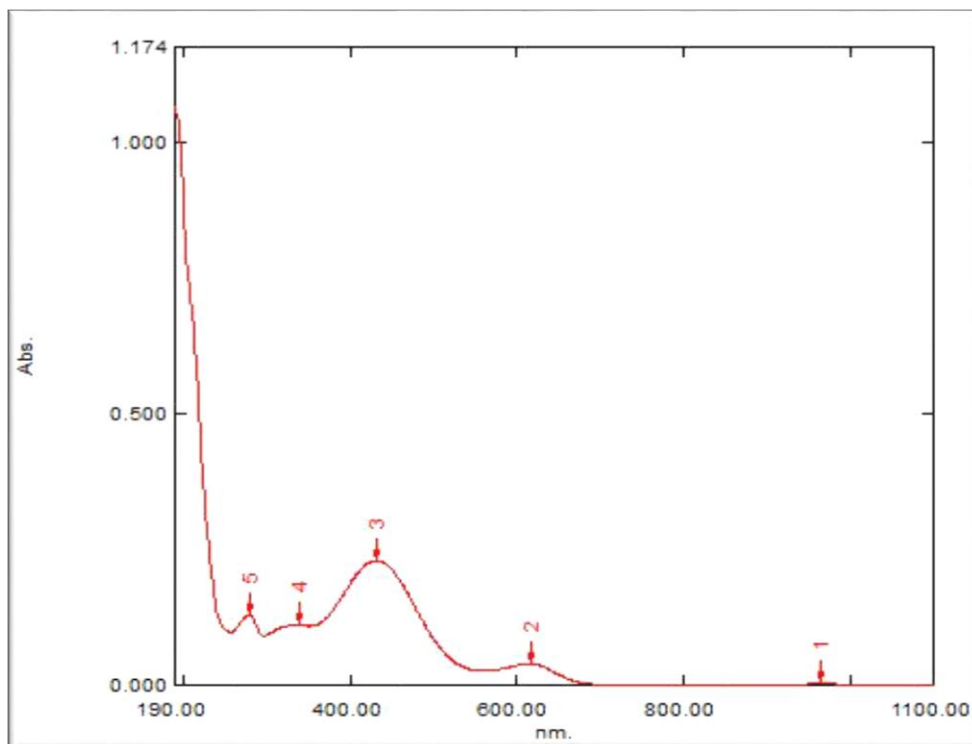


Figure 2. Absorption Spectrum of BTB dye at 10 mg/L.

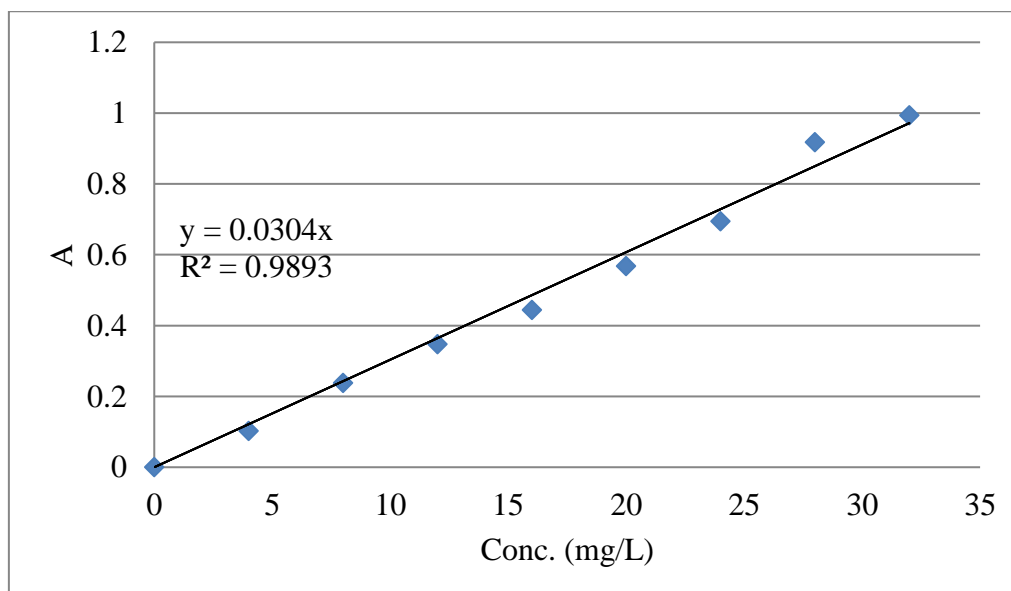


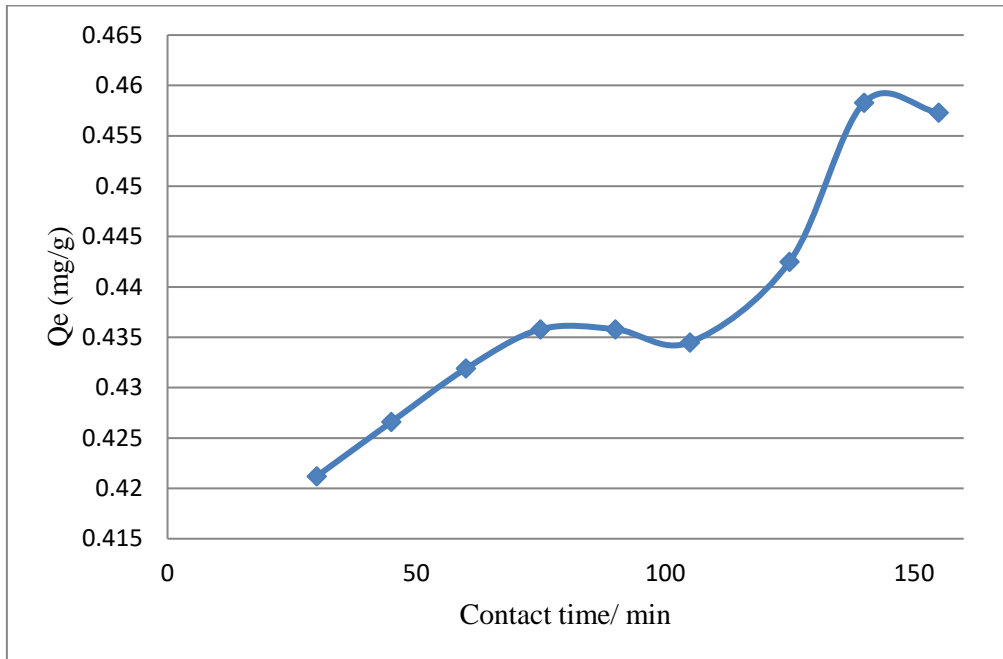
Figure 3. Calibration curve of BTB dye.

## Results and discussion

### Effect of Contact Time

At a constant beginning concentration of 20 mg/L of BTB dye and 0.6 g of bauxite at 25 °C, the effect of contact time on the adsorption of BTB dye on

bauxite clay was examined. The adsorption, as shown in Fig. 4, increased as the time increased to reach an equilibrium time of 155 minutes.

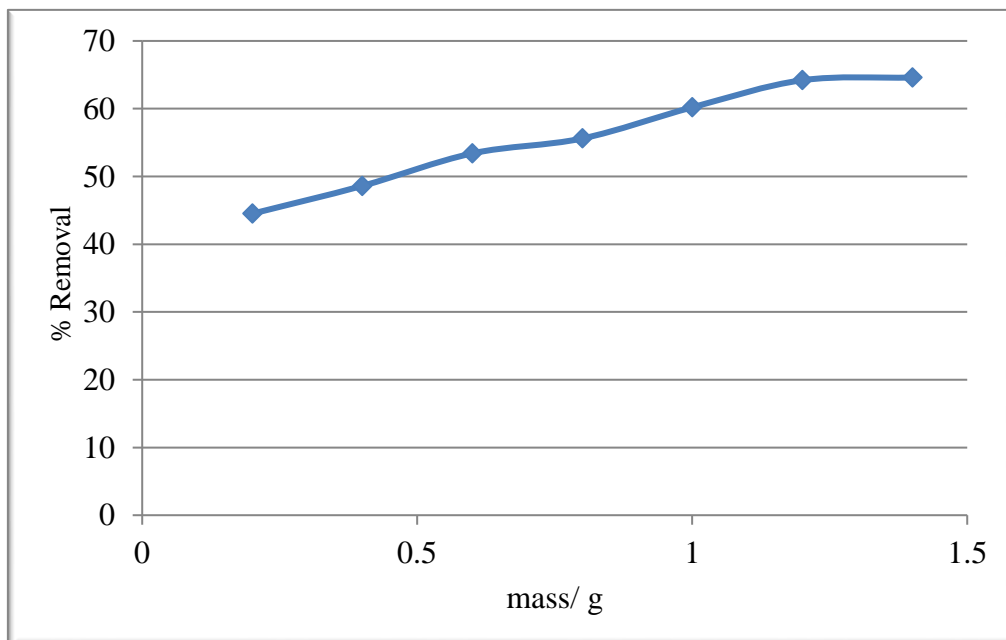


**Figure 4. Effect of contact time on BTB adsorption to bauxite surface.**

#### Effect of Weight on the Surface

The effect of adsorbent weight on the removal percentage of BTB dye adsorbed was examined using 25 ml of a 20 mg/L initial amount of BTB dye

at 25 °C. According to the data analysis Fig. 5, the sorption amount rises as the weight of the bauxite in the solution does.



**Figure 5. Effect of mass on removal of BTB on bauxite.**

#### Effect of ionic Strength

The ionic strength factor was investigated by varying the amount of sodium chloride (0.2, 0.4, 0.6, and 0.8 M) added to four solutions of BTB with

a constant concentration of 20 mg/L and 0.6 g of clay at 25 °C. According to Fig. 6, adsorption reduces as NaCl concentration rises. As the concentration of NaCl solution rises, the adsorption

of BTB on the surface of bauxite reduces as a result of an increase in ionic strength. The Na<sup>+</sup> and Cl<sup>-</sup> ions will compete with the dye molecules for the active sites of the surface because their attraction to the surface is stronger compared to that of the

molecules of dye, which explains why the electrolyte has an inhibitory impact on adsorption. Consequently, the surface causes a decline in adsorption.

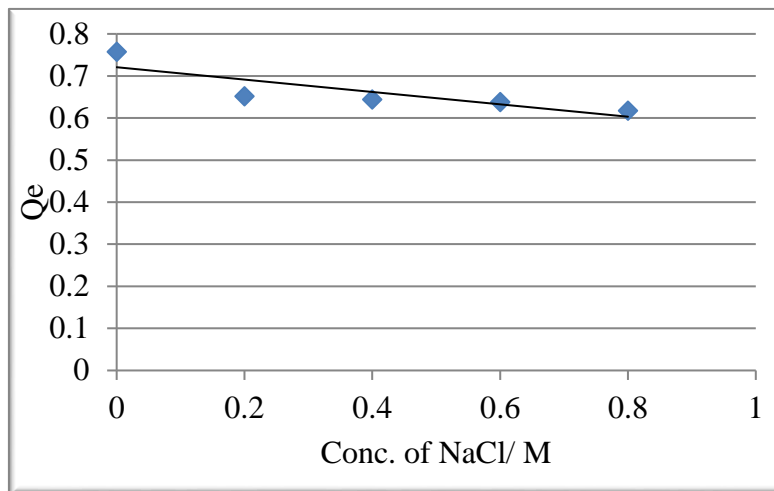


Figure 6. Effect of ionic strength on BTB adsorption to bauxite.

#### Effect of Temperature

The effects of the temperature on the adsorption of BTB on bauxite were investigated at three different Temperatures, 15, 25, and 40 °C. The results are

summarized in Table 1 and Fig. 7. Between 25 °C and 45 °C, there is a little decrease in the adsorption equilibrium capacities.

Table 1. Effect of temperature on the BTB adsorption on bauxite.

C <sub>0</sub>	15°C		25 °C		40 °C	
	C <sub>e</sub> (mg/L)	Q <sub>e</sub> (mg/g)	C <sub>e</sub> (mg/L)	Q <sub>e</sub> (mg/g)	C <sub>e</sub> (mg/L)	Q <sub>e</sub> (mg/g)
4	1.793	0.091	2.015	0.082	2.555	0.060
8	2.587	0.225	3.349	0.193	4.142	0.160
12	3.857	0.339	5.349	0.277	5.666	0.263
16	5.349	0.443	7.063	0.372	7.793	0.341
20	7.380	0.525	8.492	0.479	9.793	0.425
24	8.650	0.639	10.587	0.558	11.317	0.528
28	8.714	0.803	12.047	0.664	12.619	0.640

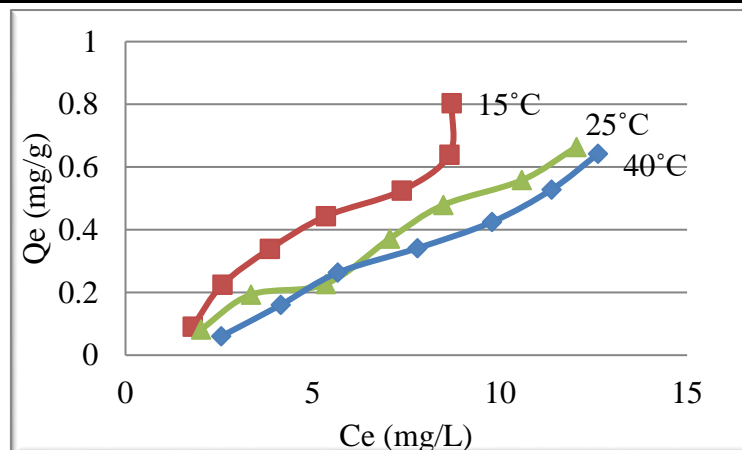


Figure 7. Effect of temperature on adsorption of BTB onto bauxite surface.

**Adsorption Thermodynamics**

Enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and free energy ( $\Delta G$ ) changes were calculated using Eq. 3, Eq. 4, and Eq. 5.  $\Delta H$  was calculated by the Eq. 4, and the slope is  $-\Delta H/2.303 RT$ , Fig. 8. The  $K_{eq}$  is calculated by the value of  $Q_e/C_e$  according to Fig.7 when  $C_e$  is constant, the  $Q_e$  is measured at each temperature. The results are summarized in Table 2. The characterization of bauxite samples was studied by Ghati and co-authors using atomic force microscopy (AFM) technique and shown in Table 3 18.

$$\Delta G = -RT \ln Q_e / C_e \quad 3$$

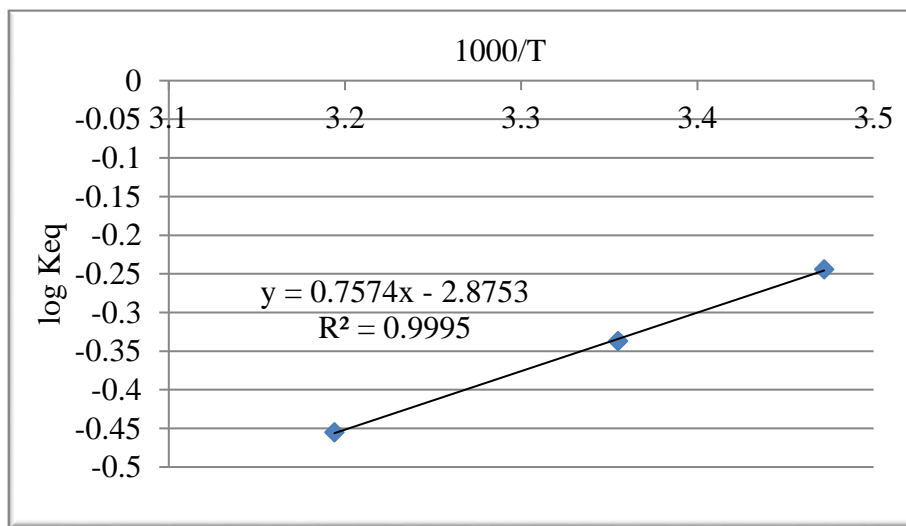
$$\text{Log } K_{eq} = (-\Delta H)/(2.303 RT) + \text{Con.} \quad 4$$

$$\Delta S = (\Delta H - \Delta G)/T \quad 5$$

Where T is the absolute temperature and R is the universal gas constant (8.314 J.mol<sup>-1</sup>K<sup>-1</sup>).

**Table 2. Thermodynamic function values for dye adsorption on bauxite at 15°C, 25 °C, and 40°C.**

Temperature (°C)	$\Delta H^\circ$ (KJ/mol)	$\Delta G^\circ$ (KJ/mol)	$\Delta S^\circ$ (KJ/mol)
15		+ 2.5137	- 0.0087
25	- 0.0145	+ 1.9239	- 0.0065
40		+ 1.4627	- 0.0047



**Figure 8. Relation between  $\log K_{eq}$  and  $1/T$  for adsorption dye.**

The adsorption reaction is exothermic, as indicated by the negative value of  $\Delta H^\circ$ . The  $\Delta G^\circ$  is positive value supports both the practicality of the procedure and the assertion that adsorption is not a

spontaneous process. The value of  $\Delta S^\circ$  is negative because adsorption necessitates a more complex arrangement of order, Fig. 8.

**Table 3. Granularity cumulating distribution and average diameter of natural bauxite using AFM technique. (Ref. 21)**

Diameter (nm) <	Volume (%)	Cumulation (%)	Diameter (nm) <	Volume (%)	Cumulation (%)	Diameter (nm) <	Volume (%)	Cumulation (%)
65.00	1.23	1.23	100.00	11.11	59.88	135.00	1.85	94.44
70.00	8.02	9.26	105.00	9.26	69.14	140.00	2.47	96.91
75.00	7.41	16.67	110.00	9.88	79.01	145.00	1.23	98.15
80.00	6.17	22.84	115.00	3.70	82.72	150.00	1.23	99.38
85.00	8.64	31.48	120.00	3.09	85.80	160.00	0.62	100.00
90.00	9.88	41.36	125.00	3.70	89.51			
95.00	7.41	48.77	130.00	3.09	92.59			

### Adsorption Model

Optimizing the design of an adsorption system for the adsorption of adsorbents requires finding the most appropriate correlation for the equilibrium curves. The equilibrium properties of adsorption have been described using a variety of isotherm equations, including those of Langmuir, Freundlich and Temkin.

Eq. 6 and Eq. 7, respectively, show the linear forms of the Freundlich isotherm and the Langmuir eq.

$$C_e/Q_e = 1/(K_L q_m) + C_e/q_m \quad 6$$

$$\log Q_e = \log K_f + 1/n \log C_e \quad 7$$

The equilibrium dye concentration is  $C_e$  (mg/L), the amount adsorbed is  $Q_e$  (mg/g), and the monolayer adsorption capacity of the adsorbent is  $q_m$  (mg/g),  $K_L$  is the Langmuir constant, and  $K_f$  and  $n$  are Freundlich constants. The Temkin isotherm and

Temkin linear have been applied in the manners described below, respectively:

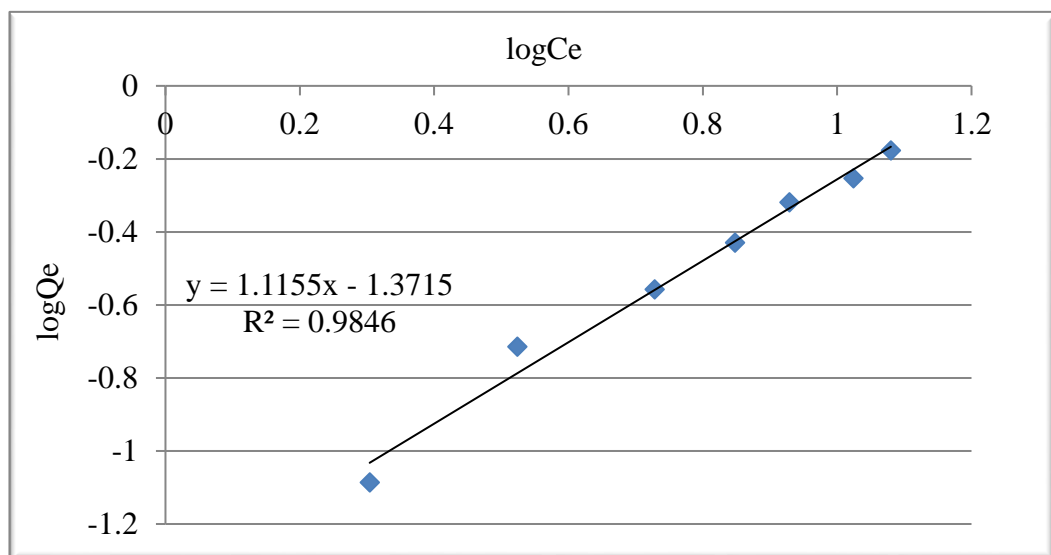
$$Q_e = RT/b \ln (AC_e) \quad 8$$

$$Q_e = RT/b \ln A + RT/b \ln C_e \quad 9$$

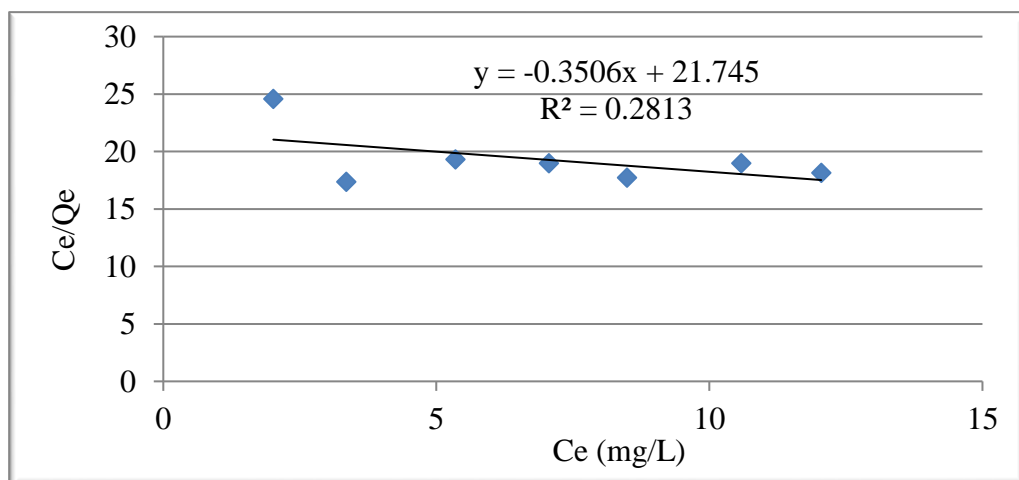
The results are displayed in Table 4, Fig. 9 and Fig. 10, which correspond to the Freundlich and Langmuir equations, which explain that when you plot  $\log Q_e$  versus  $\log C_e$ , the slope will be  $1/n$  and  $\log K_f$  is the cross, Fig. 9 According to the Freundlich isotherm, BTB was absorbed.

**Table 4. Freundlich constant for the BTB dye adsorption by bauxite clay at 25°C.**

$K_f$	$n$	$R^2$
23.523	0.8964	0.9846



**Figure 9. Freundlich linear adsorption isotherm of BTB dye.**



**Figure 10. Langmuir linear adsorption isotherm of BTB dye.**



## Conclusion

The textile industries produce effluents that have dangerous impacts on both the environment and people because they contain large concentrations of hazardous and resistant substances, such as dyes. The study aimed to investigate the adsorption of bromothymol blue dye using bauxite clay as an adsorbent. The current study demonstrates that initial concentrations, contact time, clay weight, ionic strength, and temperature all have a significant impact on the batch adsorption process for

removing dye from bauxite. The maximum adsorption capacity of BTB dye on the surface of bauxite decreases with increasing temperature, and the adsorption of dye onto bauxite follows the Freundlich isotherm. By increasing the temperature and using natural processes, it was possible to attain a higher adsorption capacity. According to isotherm models, the Freundlich equation may more accurately depict the adsorption process than the Langmuir model.

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## Author's Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Besides, the Figures and Images, which are not ours, have

been given the permission for re-publication attached with the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.

## Author's Contributions

A. N. Z. conceived of the presented idea. K. A. S. developed the theory and performed the computations. S. K. G. verified the analytical methods. A. N. Z. and S. J. M. carried out the

experiment. J. M. S. wrote the manuscript. The final text was developed with input from all authors after discussions about the findings.

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## امتزاز صبغة البروموثيمول الزرقاء بواسطة طين البوكسائيت

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قسم الكيمياء، كلية التربية للعلوم الصرفة ابن الهيثم، جامعة بغداد، بغداد، العراق.

### الخلاصة

الهدف من العمل الحالي هو استخدام مادة غير سامة وغير مكلفة ذات قدرة عالية على امتصاص الماء، وهي طين البوكسائيت، لامتصاص صبغة البروموثيمول الزرقاء من محلول مائي. تُستخدم المركبات العضوية الاصطناعية كصبغات بشكل شبه حصري في العمليات الصناعية الحديثة مثلًا في إنتاج المنسوجات والجلود والطلاء والأغذية ومستحضرات التجميل والمستحضرات الصيدلانية. تشكل هذه الأصباغ خطرًا على البيئة عند إطلاقها نظرًا لآثارها الجانبية الضارة مثل قدرتها على الإصابة بالسرطان والسمية والطفرات. يعتبر معدن الطين ذات قيمة كعوامل مزيل للتلوث بسبب سلوكها الغرواني وقدرتها على الامتصاص. في هذه الدراسة تمت دراسة سلوك الامتزاز لصبغة البروموثيمول الزرقاء من محلول مائي باستخدام طين البوكسائيت. كما تمت دراسة المتغيرات المختلفة مثل وقت التلامس، الجرعة، القوة الأيونية ودرجة الحرارة لإظهار التأثير على امتزاز البروموثيمول الأزرق على طين البوكسائيت من محلول مائي باستخدام طريقة الامتزاز. أظهرت هذه الدراسة أن الامتصاص قد انخفض بزيادة درجة الحرارة من 15 إلى 40 درجة مئوية، وزاد بزيادة وزن الطين من 0.2 إلى 1.6 غم. تم تقييم جميع المقاييس الديناميكية الحرارية بما في ذلك التغيير في الطاقة الحرة ( $\Delta G$ )، المحتوى الحراري ( $\Delta H$ ) والانتروبي ( $\Delta S$ ). تم الحصول على علاقة ايجابية بين الامتصاصية ومدى التراكيز للبروموثيمول الأزرق (4-32 غم/مل) مع معامل ارتباط 0.9911. بالإضافة إلى الحصول على الطول الموجي الأقصى 432 نانومتر وضبطه على جميع القياسات.

الكلمات المفتاحية: الامتزاز، البوكسائيت، البروموثيمول، الطين، الصبغة.