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Comparison of kinetic study of the adsorption of bromothymol blue on activated Attapulgite clay and commercial activated carbon

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Abstract

This work includes studying the removal efficiency method of bromothymole blue (BTB) from industrial waste water by using thermally activated Attapulgite clay (ATC) and by activated carbon (AC) as adsorbent when applying adsorption technology. The most efficient dose obtained for the removal of BTB by AC and ATC is then using 20 mL of dye solution with $3*10^{-4}$ M concentration are 0.03 and 0.1 g respectively. The use of AC required 0.03g of AC to give % ads 95.97 while the use of o.1 g of ATC gave % ads. 91.71, The results gave a preference of the clay ATC to be used as a cheap and efficient adsorbent. Comparison of the adsorption efficiency of the Attapulgite clay with commercial activated carbon where carried out. The optimal conditions of the adsorption systems under study such as effect of dose, initial concentration, and temperature were investigated. Two isotherm models, Langmuir and Freundlich were fitted to the experimental data of adsorption. The thermodynamic Functions of the studied systems (**Δ**H^o**, Δ**G°**, Δ**S°**)** were estimated. The results of the thermodynamic study showed that the forces controlling the adsorption process of the systems under consideration are physical in nature. The adsorption process is exothermic, occur spontaneously in the direction of connecting the dye to the clay surface, and forming less random system. The research also included achieving kinetic study by application of the pseudo first-order and pseudo second-order reaction models on the experimental data of the studied system, this indicted by the value of R^2 (0.999) and the agreement between the experimental and calculated (q_e) . The second order equation were better fitted to the experimental data of the system under consideration. In addition, the matching of the calculated q_e value (34.843 mg/g) with the practical (33.821 mg/g) one sustain this results. The application of the intra-particle diffusion method showed that, the diffusion process of the adsorbed molecules into the pores present on the adsorbent surface is not the only mechanism driving the adsorption process in the studied reaction $K_{diff.}(mg.g^{-1}.min^{-½}) = 0.893$, $R^2 = 0.943$.

Introduction

One of the major problem facing the environment now days is the presence of several types of toxic dyes in wastewater due to industrial activities in various fields such as rubber, textile, paper, leather and plastic industries representing one of the huge development and big challenges in the environment[1]. Harmful dyes and/or their bio decomposition products affecting the ecosystem, plants, and human as a result. They have wide applications such as coloring paper, dying cotton, and wool [1]. Bromothymol blue has various names such as bromothymol sulfone phthalate or BTB, it also works as a pH indicator in the applications those required measuring pH near 7 [2]. Its pka values were used in common for measuring and estimating the pH of the carbonic acid in a liquid (Figure 1). The carbonic acid is a weak acid in the solution with protonated and deprotonated forming color ranges from yellow to blue according to pH ranges (Figure 1). It is also used in many applications such as observing photosynthetic activities, respiratory indicator to carbon dioxide[3], in conjunction with phenol red or methyl red to monitor asparaginase enzyme[4]. Pollution is usually occurs by introducing a hazardous substances into the environment with industrial waste water without a proper treatment before sending it to the environment. Water pollution could be the biggest problem to universe with many types of pollutants such as chemical, biological, or naturally existing pollutants [5-7]. Water pollution has great effect on the environment, as well as human and animals [8, 9]. It is subjected to the effects of various causative factors and exhibits significant effects at various time [9]. Now day, there are many attempts to develop various technique to control all types of pollutions [10].

The bromothymol blue is considered one of the most effective pollutant in waste industrial water [11]. Recently, the need for safe and economical methods for the removal of dyes from waste water such as Bromothymol blue (BTB)[1], was become an essential task to get rid of this pollutant.

Attapulgite clay, is known as a palygorskite, its composition is a $Mg.Al_2Si_4O_{10}(OH).4H_2O$ Magnisum aluminum phyllosilicate , which is a type of fuller’s earth [12, 13].

Conventional methods such as photodegradation, biosorption, reverse osmosis, coagulation, ozonation, electrochemical oxidation, and adsorption are commonly used to remove the hazardous pollutants [14-16]. However, adsorption process found particular interest because of its high efficiency, ease of use and economic consideration [14, 17-19]. Many types of adsorbents such as carbon materials, clays, biomaterials, nanoparticles, nanocomposites, leaves fly ash and many other adsorbent have been extensively used for the removal of dye from aqueous solution [20-23].

Freundlich equation is an adsorption isotherm. It is an empirical relationship that is applicable on to gas- solid and liquid- solid systems [24]. However, Langmuir isotherm model is designed to explain the adsorption dependence on the assumed adsorbate behaving as an ideal gas at isotherm conditions. The relation between adsorption and desorption is a reversible relationship [25, 26]. According to this survey, this work is aimed to get efficient method to remove bromothymol blue from industrial waste water via using thermally activated Attapulgite clay with activated carbon from their aqueous solutions via using adsorption technology. Comparison between the adsorption efficiency of Attapulgite clay and activated carbon is carried out.

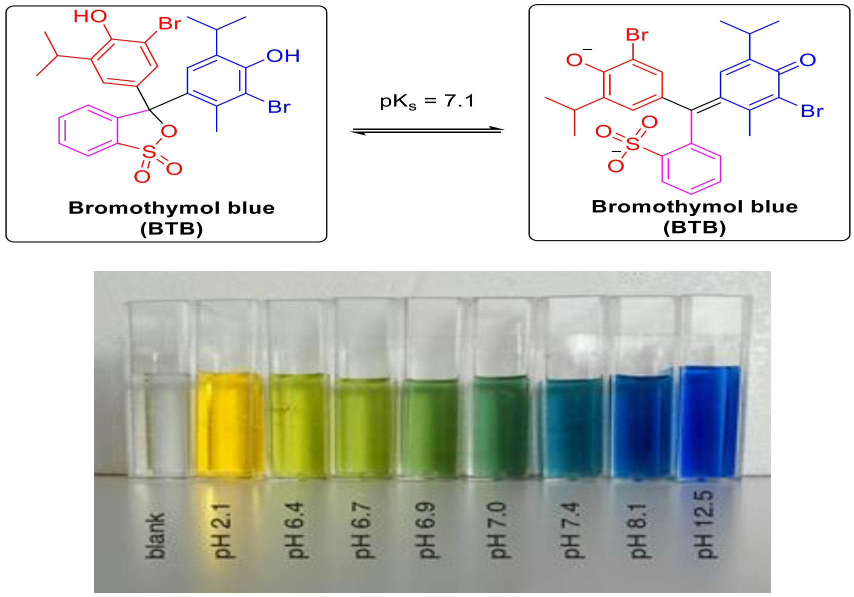

Figure 1: BTB Structure and different colors at various pH conditions [4].

Thermodynamic study

The advantages of this study can give indication to the spontaneity of the reaction could it occurs without the need for external conditions. It also determines the nature of the forces controlling adsorption in addition the order of studied system.

The thermodynamic study is usually carried by calculating the equilibrium (K) constant of adsorption system at certain concentration and at varies temperature. The values of standard Gibbs free energy (ΔG^o) at certain condition is estimated by equation (1)

$\Delta G^o = - nRTlnK$ ....(1)

Where n is the number of mole, T is the absolute temperature and R is the gas constant (8.314 J. mol $^{-1}$. K^{-1}). The value of standard enthalpy ΔH^o is determined from Vant' Holf equation (2)

$$\text{Ln K} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{..........(2)}$$

The plot of ln K versus 1/T give a straight line with a slope equal ($-\Delta H/R$ .... $\Delta H = -\text{slope} * R$) and intercept = ($\Delta S^o/R$)

In this study the thermodynamic function (ΔG^o, ΔH^o, ΔS^o) are calculated at various initial concentration in the range ((1-9)* 10 $^{-4}$ M. The obtained results are given in Table 1.

Table 1 indicate that at certain concentration the increase of temperature decreases the value of equilibrium constant. This means that the adsorption effecting decreases with increases temperature. In same time at various concentration and constant temperature, the adsorption decreases with increasing concentration. All these phenomenon are supporting the exothermic nature of adsorption. These resulted show that, the adsorption of the studied system is physical adsorption signalized by the values of $\Delta H < 40$ (KJ.mole^{-1}). The negative values of ΔG^o refer to that , the adsorption system under consideration could occur spontaneously and increase the order of the system .

Estimation of thermodynamic functions from isotherm constants, the application of isotherm equation on the experimental obtained data is usually carried out by applying a single temperature and various concentration. In order to calculate the thermodynamic functions from isotherm constants.

In order to calculate the thermodynamic constant, various temperature must be used each of them must be applied on various concentration (i.e., application of isotherm at different temperatures). Two isotherm namely Freundlich and Langmuir are used for this purpose (figure 2,3,4).

Table 1: values of equilibrium constants and thermodynamic functions at equilibrium for adsorption of BTB at different initial concentrations and in the absolute temperature range (283-318 K)

Bromothymol blue (BTB)	Temp. K	K	ΔHº ($kJ.mol^{-1}$)	ΔGº ($kJ.mol^{-1}$)	ΔSº ($J.mol^{-1}.K^{-1}$)
$1*10^{-4}$	288	15.952	-17.496	-37.7248	-6.632
	298	12.247		-37.8836	-6.207
	308	11.561		-36.4566	-6.268
	318	8.976		-36.7744	-5.802
	328	6.068		-38.3521	-4.917
$3*10^{-4}$	288	11.474	-14.737	-30.8680	-5.8427
	298	9.345		-30.8580	-5.5370
	308	8.057		-30.4862	-5.3430
	318	7.331		-29.7673	-5.2667
	328	5.045		-31.4614	-4.4134
$5*10^{-4}$	288	8.751	-11.278	-21.1264	-5.1940
	298	8.374		-20.1785	-5.2653
	308	6.755		-20.7363	-4.8917
	318	6.076		-20.4657	-4.7704
	328	4.992		-21.0186	-4.3843
$7*10^{-4}$	288	7.472	-10.9666	-21.3575	-4.8156
	298	6.368		-21.4084	-4.5868
	308	6.062		-20.6239	-4.6144
	318	4.746		-21.5378	-4.1176
	328	4.298		-21.3116	-3.9763
$9*10^{-4}$	288	6.009	-12.716	-29.2497	-4.2937
	298	5.986		-27.7990	-4.4335
	308	5.055		-27.8183	-4.1496
	318	3.945		-28.5817	-3.6286
	328	3.267		-28.9301	-3.2285

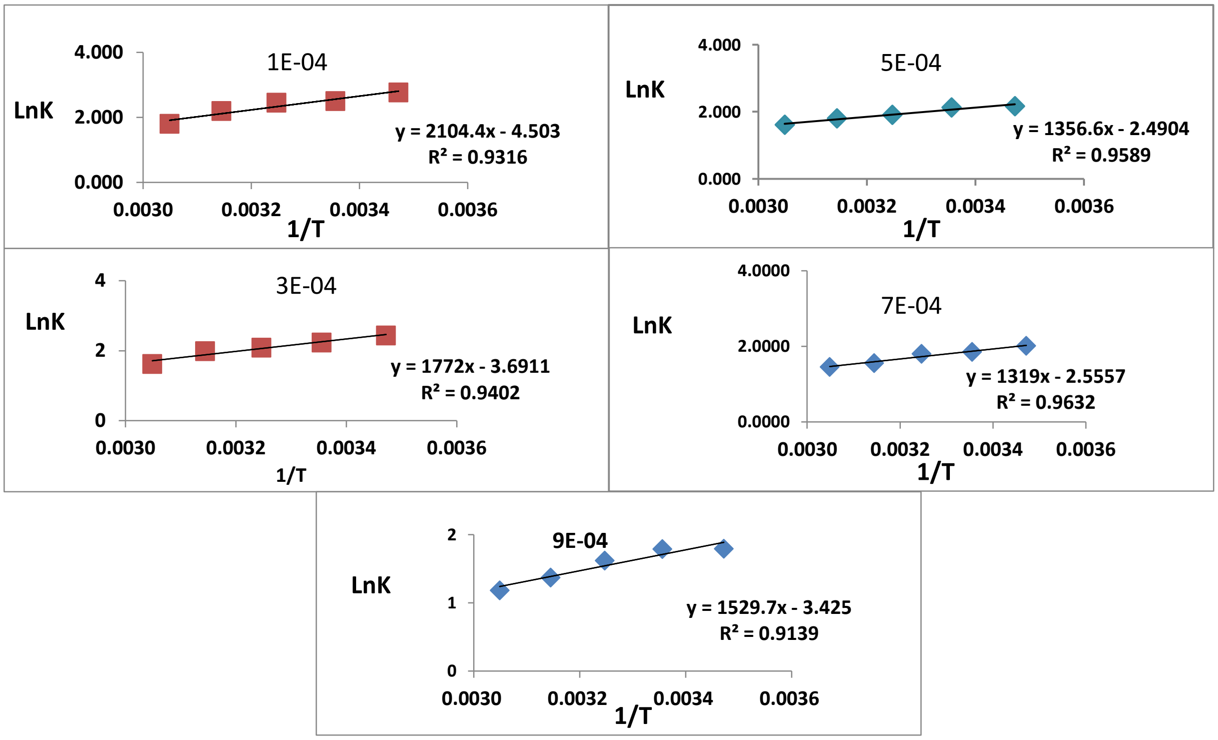

Figure 2: The relationship between lnK (equilibrium constant) versus 1/T to calculate the enthalpy of adsorption value for BTB dye.

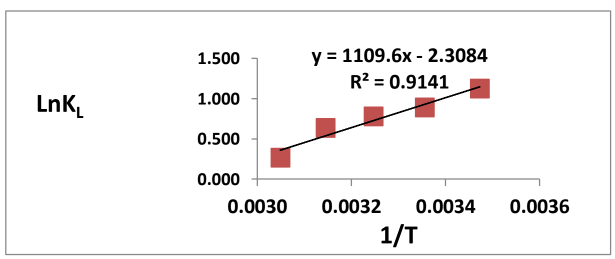

Figure 3: Relationship of LnK_L to Langmuir's constant vs. 1/T

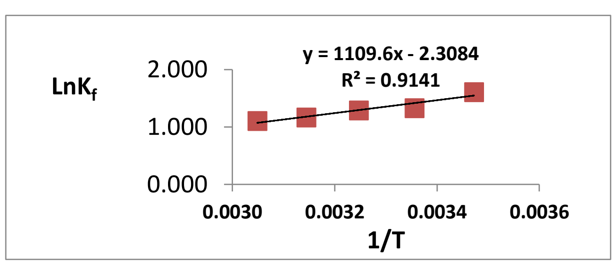

Figure 4: Relationship of LnK_f to Frendlich's constantvs.1/T

Experimental method

The BTB is supplied by the chemical company (Merck). It has the structure shown in Figure 1 and a molecular weight (624) g. $mole^{-1}$ distle water is used as a solvent to prepare all solutions in mixture with ethanol. UV-Vis spectrophotometer of type (Cecil CE-1021.) is employed to measure the absorption of the dye at its λ_{max} = 434nm.

Adsorbent

Two adsorbents were selected for performing this study

1- Activated carbon

Commercial activated carbon supplied by Merk were selected for achieving this study. It was used for comparing its efficiency to that of clay as adsorbent for the removal of the BTB dye from aqueous solution. The commercial carbon was placed in an electric oven at 150 C^o before using it for drying.

2- Thermal Activated Atabalguide Clay

The raw atabalguide clay, is first grinded finely and then placed in a large beaker containing distilled water. The colloidal part is representing the clay particles, while the stony parts are fallen into the bottom of the beaker.

The clay particles were then isolated by decantation and the stony part is neglected. The suspended part is then filtered, washed well in water, then ground again, and the clay particles were separated into certain sizes using molecular sieves. The thermal activation of clay is carried out by placing the clay in an electric oven at temperatures ranging between (100-400 C^0)

Batch Method

This Study is included the determination of effect of contact time, effect of initial concentration, effect of pH of solution and effect of temperatures. A single component batch method was carried out to achieve these studies. The amount of adsorption capacity (mg/g) estimated by the determination of residual dye using equation (3)

$$qe = \frac{C_i - C_e}{m}\, v \ldots\ldots\ldots\ldots (3)$$

$$\%\ \text{Adsorption} = \frac{Ci - Ce}{Ci} * 100 \ \ldots\ldots\ (4)$$

Where the (C_i) and (C_e) are the initial and equilibrium (mg/L) dye concentration respectively, (m) is the weight of the adsorbent (ATC) (g) and (V) is the volume (liter) of the solution used.

Preparation of stock solutions:

Preparation of standard solutions

A 100 mL solution was prepared with a concentration of ($3*10^{-4}$ M) of Bromothymol blue (BTB) by using a mixture of ethanol-water with a ratio 30:70% (V:V) as a solvent. All the solutions used in the study were measured at the (λ_{max}) of the dye using the solvent as a blank.

Results and Discussion

Calibration Curve and Wavelength

As a first step of this work, calibration curve is made up using a range of concentration ($1x10^{-5}$-$1x10^{-4}$ M) for the estimation of the amount of adsorbed dye the curve was within the detection limit of Beers law. A straight line is obtained with R^2 = 0.9996. This calibration curve is presented in figure 5.

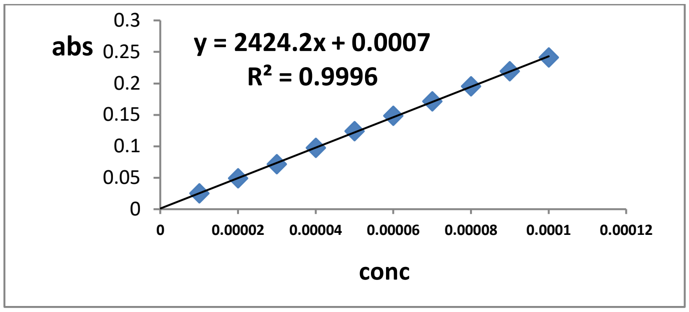

Figure 5: Calibration curve of the BTB according to Beers law

Effect of dose

The effect of dose is usually carried out by using a certain dye concentration and varying the amount of the adsorbent. This study is carried out often to estimate the amount of adsorbent required to reach equilibrium within a range of dye concentrations without total removal of the dye, so the effect of other parameter, kinetic and thermodynamic studies can be achieved.

The study is conducted as a measure of the efficiency of Attapulgite clay (ATC) as adsorbent compared to the commercial activated carbon (CAC). The clay was chosen as an alternative adsorbent since it was collected from a local area and can simply obtained. It is therefore, even if we use more amount of the clay to achieve the same result, it would be economically better compared to the CAC. In the rest of the study, the ATC used for further applications. The results obtained from using CAC and ATC as adsorbent for the removal of BTB from its aqueous solution.

The result of the Table 2, indicate that, the most efficient dose obtained for the removal of BTB by AC and ATC is then using 20 mL of dye solution with $3*10^{-4}$ M concentration are 0.03 and 0.1 g respectively. The use of AC required 0.03g of AC to give % ads 95.97 while the use of o.1 g of ATC gave % ads. 91.71, The results gave a preference of the clay ATC to be used as a cheap and efficient adsorbent.

Table 2: Effect of adsorption capacity and adsorption % at 298K by using Dye solution of 3*10^{-4} M

Compd.	Adsorbent	Dose g/l	qe (mg/g)	Ads. %
BTB	AC	0.01	349.020	93.22
		0.02	177.084	94.60
		0.03	119.772	95.97
		0.05	71.966	96.11
		0.07	52.066	97.35
BTB	ATC	0.07	42.506	79.47
		0.09	34.776	83.60
		0.1	34.336	91.71
		0.2	18.300	97.76
		0.3	12.235	98.03

Effect of initial concentration

The effect of initial concentration is very important for studying adsorption. The resulted data can be used for the application of the isotherm equation on the experimental data. It also can provide a strong driving forces to overcome all the resistances precluding the mass transfer between the solution and solute.

The mass transfer phenomenon occurs in three stages. First the dye molecule moves from its location in the solution into the boundary of the solid surface. The dye molecules move to attach to the solid surface and finally diffuse into the adsorbent pours structures.

The results of the effect of initial concentrations of BTB on the ATC listed in Table 3 in the range between 1*10^{-4} - 9*10^{-4} M show that the best adsorption percentage in at 3*10^{-4} M. This can be interpreted, as the dye concentration increased the number of dye molecules increased and since a certain amount of clay (ATC) contain a certain number of active sites available for adsorption, when increasing the concentration more dye molecules will be left in the solution. This will decrease the adsorption percentages calculated numerically.

Effect of contact time

20 mL of dye solution of concentration (1×10^{-4}) M are placed in a nine conical flasks. Same amount (0.1 g) of adsorbent was added to them. The conicals were shacked at constant temperature and after continuous shaking (100 cycles/min).

Nine solutions containing equal concentrations (1×10^{-4}M) of the dye were prepared and the same amount 0.1 g of adsorbent was added to 0.1 them . The cared were shouted at constant temperature and at continuous shaking (100 rpm). The nine solutions were filtered at different times (10,20, 30, 40, 50, 60, 70, 90, 80)mintes respectively. The adsorbed quantities were estimated using the

Spectrophotometer method. The adsorption capacity (qt mg/g) at any time of the adsorbed BTB dye by ATC is determined using equation (3). This effect of contact time is presented in figure 6.

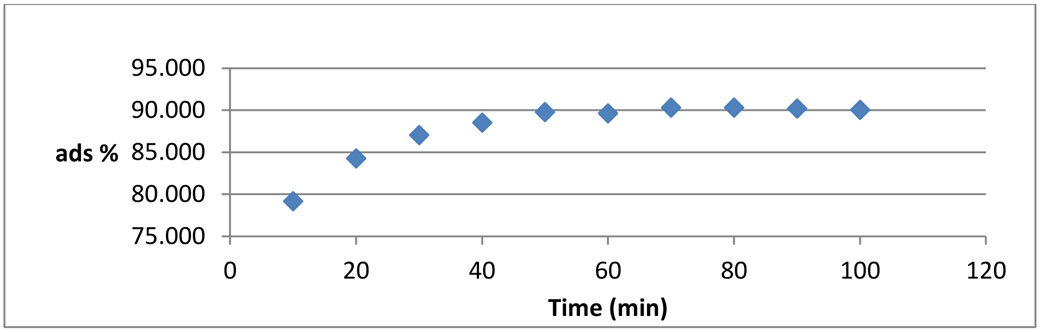

Figure 6: The variation of % ads of BTB with time.

Temperature effect

The effect of temperature is studied by varying temperature in range (283 - 323 K) while keeping all the other factors constant. 20 mL of dye solution ($3*10^{-4}$ M) shacked with 0.1 g of clay for 70 min at constant speed (100 rpm) with various temperatures in the range mentioned above.

Application of isotherm equations:

In this study two isotherm equations are applied on the experimental data of the studied system named, Freundlich and Langmuir isotherms equation (5, 6). In order to use these isotherms for the calculation of thermodynamic function the isotherm equation is fitted to the experimental results for range of concentrations ($(1-9)*10^{-4}$) at range of temperature (288-318K).The obtained results are listed in Table 3 and illustrated in Figures (7,8).

Looking at table 3 it was found that, the value of n is lying in the range (1-10) indicating favored adsorption. The values of n decreasing with increasing temperature. The same trend is seen in the variation of (K_F) values with temperature. The Langmuir constants are varied as follow; the maximum theoretical adsorption capacity (Q_{max})increased with increasing temperature. The values of b are related to the rate of adsorption process. Looking at the value of R^2 one can concludes that, the Freundlich (R^2=0.9942-0.9981) is better fitted to the studied systems than the Langmuir (R^2=0.9538-0.99958). This means the characteristic of the clay used as adsorbent is more consisting to the assumptions of Freundlich which is based with adsorption occurs on a heterogeneous surface.

$$\frac{C_e}{q_e} = \frac{1}{Q_{max\,b}} + \frac{1}{Q_{max}} C_e \ldots\ldots\ldots\ldots (\ 5\ )$$

$$\log q_e = \lg K_F + 1/n \ \log C_e \ldots.(6)$$

One of the most important factors used to describe the adsorption isotherm of Langmuir is the dimension less separation factor (R_L) which can be expressed by equation (7):

$$R_L = \frac{1}{bC_\circ} \ldots\ldots\ldots (7)$$

Where C_o is the initial concentration of the dye under consideration. When RL > 1 indicates to un-favored adsorption, (RL = 1) refers to linear adsorption, $0<R_L<1$ indicates to physical adsorption and when $R_L= 0$ means chemical or irreversible adsorption. The valves of R_L obtained from this investigation are listed in Table 3 referring to favored adsorption.

To estimate the thermodynamic functions from Freundlich and Langmuir constants, the equilibrium constant is assumed to be represented by the value of K_F since it is related to the adsorption capacity whereas the value of equilibrium constant according to Langmuir is presumed to be equal to $K_L=Q_{max}b$. The values of K_F and K_L are estimated for a range of concentrations $(1\text{-}9)*10^{-4}$ at various temperatures, starting from 288K and repeated at 298 ,308 ,318 and finally 328K.The calculated thermodynamic functions from K_F and K_L are listed in table (3,4,5).

Table 3: Constants of Freundlich and Langmuir adsorption isotherm applications via using clay as adsorbent.

Isotherm		Freundlich const.			Langmuir const.		
Comp.	Temp C^o	n	K_F	R^2	Q_{max} (mg/g)	b(L/mg)	R^2
BTB	283	1.499	1.0095	0.9943	28.740	0.0203	0.9701
	288	1.363	0.7761	0.9942	33.568	0.0147	0.9845
	298	1.341	0.7087	0.9958	35.549	0.0125	0.9958
	308	1.358	0.6168	0.9937	32.282	0.0115	0.9937
	318	1.107	0.2560	0.9981	75.029	0.0027	0.9538

Table 4: Constants of Langmuir equations (R_L and b) for adsorption of BTB on the considered clay at 298K

Comp.	b(L/mg)	C_i(mg/I)	R_L
BTB	0.0147	62	0.522
		187	0.267
		312	0.179
		437	0.135`
		562	0.108

Table 5: The thermodynamic functions obtained from Freundlich and Langmuir constants using clay as adsorbent for a range of concentrations $(1\text{-}9)10^{-4}$ M .

Dye	Temp K	K_F	ΔGº	ΔH	ΔSº	K_L	ΔGº	ΔH	ΔSº
BTB	288	5.005	-3.856	-9.2253	-18.6435	3.0784	-2.6923	-15.3745	-44.0355
	298	3.778	-3.293		-19.9056	2.4407	-2.2107		-44.1739
	308	3.639	-3.308		-19.2130	2.1795	-1.9951		-43.4398
	318	3.222	-3.093		-19.2831	1.8937	-1.6881		-43.0390
	328	3.029	-3.022		-18.9132	1.3059	-0.7278		-44.6545

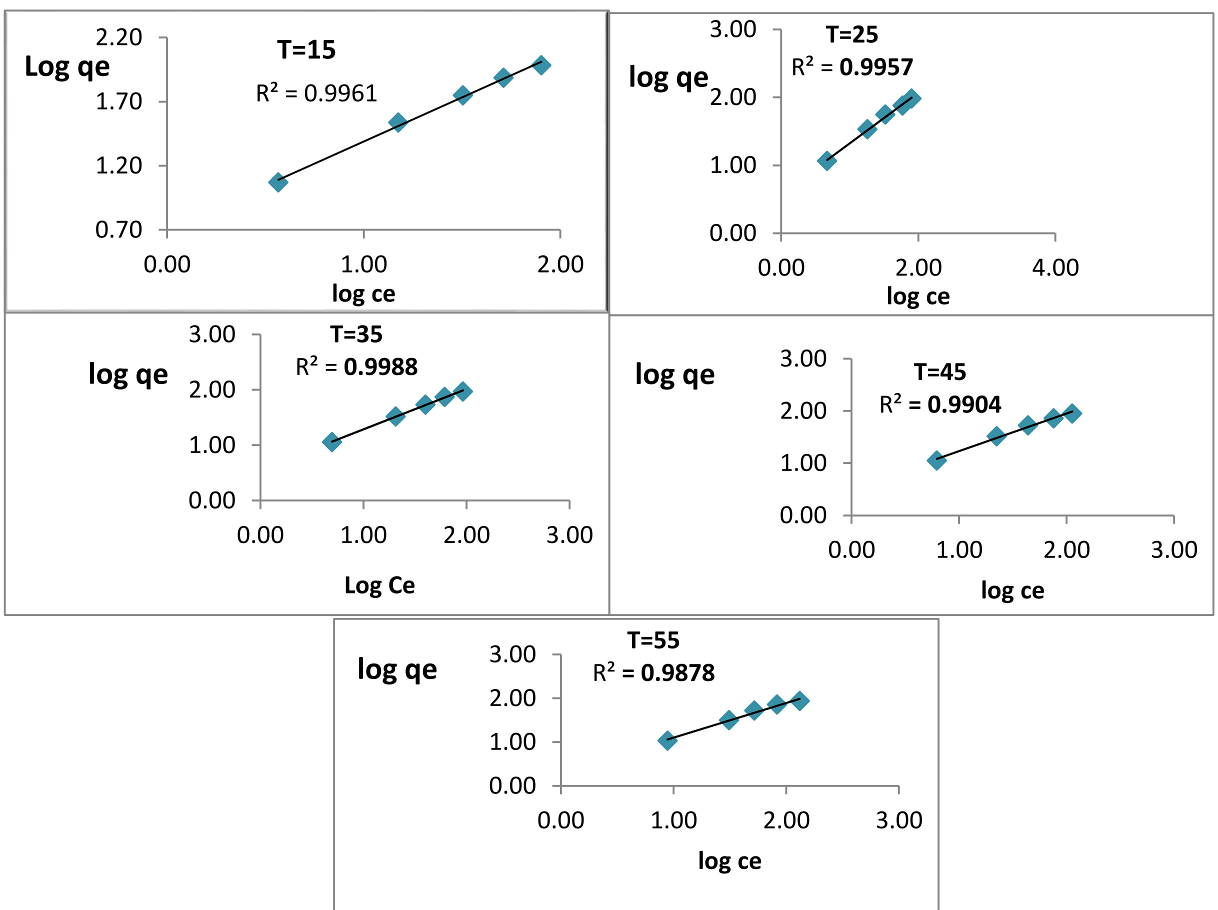

Figure 7: Adsorption Freundlich isotherm of BTB dye

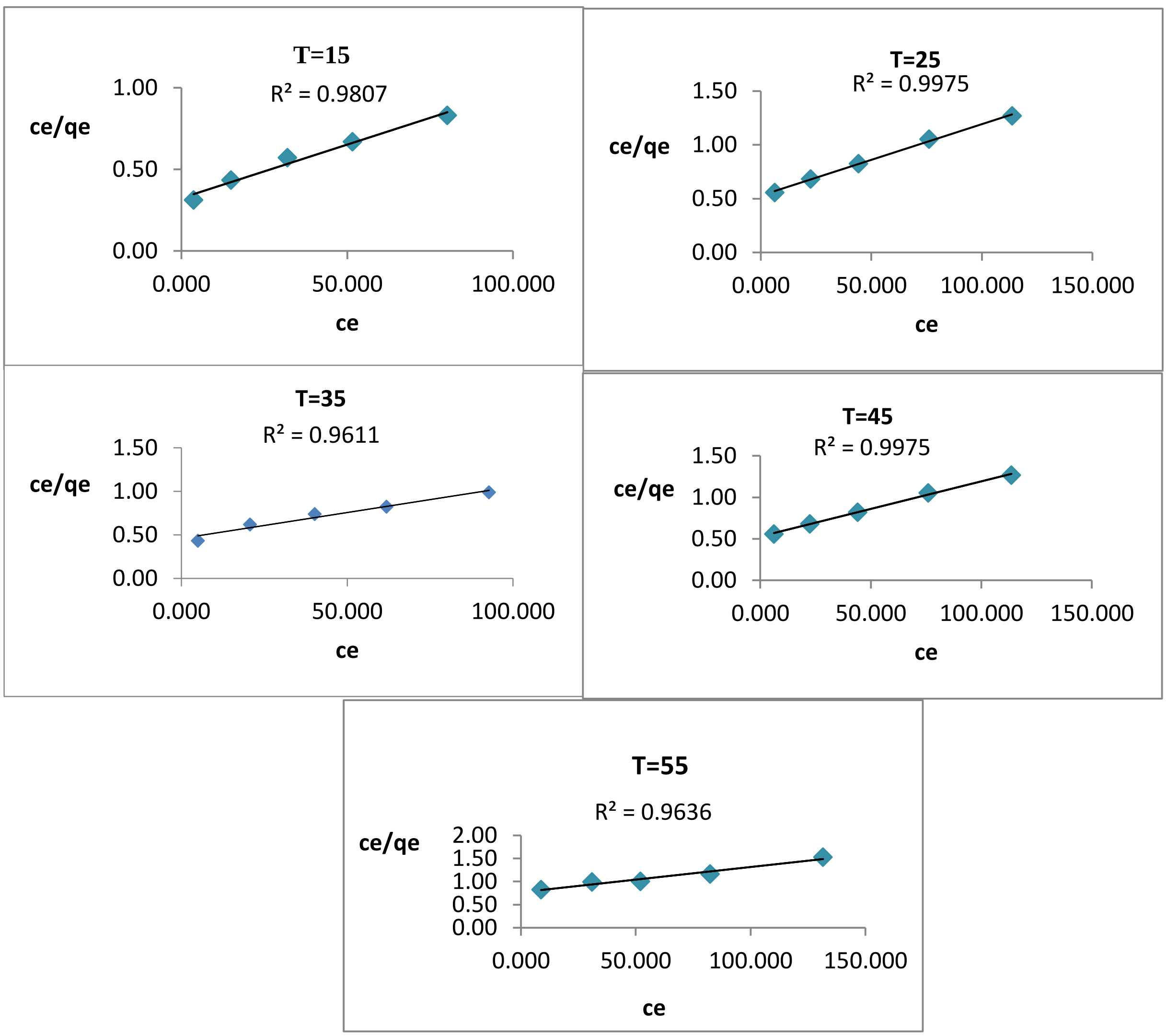

Figure 8: Adsorption Langmuir isotherm of BTB dye

Kinetic study

Two models, pseudo first order and pseudo second order were applied on experimental data of considered system. The first model is known as a lagergren. It can be presented as in eq(8) :

$Ln (q_e-q_t)= lnq_e - kt$ (8)

Where q_e and q_t are adsorption capacities at equilibrium and at any time (mg/g) respectively, t is the time (min), and k is the rate constant (min^{-1}).

The second model is the pseudo second order equation, Its known as Ho and McKay equation. It can be presented as in eq. (9)

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{1}{qe}t \ldots\ldots\ldots (\ 9\ )$$

where is the value of k is the second order rate constant (g/mg . min) and t is the time (min).

In order to apply those two models these equations were fitted to the experimental results of the studied system. The first order is fitted when the plot ln (q_e - q_t) versus t, should give a straight line with correlation coefficient (R^2) close to unity and standard error less than 5 % of the experimental error and the value of q_e calculated from the plot is consisted with the calculated experimentally. The experiment was performed at 293K and initial concentration equal to ($3*10^{-4}$ M) and using 0.1 g. of the clay.

The same conditions are applied when fitting the second order equation. Both equations are applied on the experimental data of the system under consideration. The results obtained for the pseudo first and second order are given in Table 6.

It is obvious that, the experimental results of the considered system is better fitted to the pseudo second order model. This indicted by the value of R^2 (0.999) and the agreement between the experimental and calculated (qe) as shown in Table (6) figure (9). Another parameter was calculated from the second order equation known as the initial rate (h $mg.g^{-1}.min^{-1}$), its value is high when compared to the value of (k_2) figure (10). This can be clarified by the availability of large number of the free active sites on the adsorbed surface and the presence of large number of the dye molecules. This speed will be decreased gradually with the time as the active sites are occupied and the repulsion among the dye molecules are increased.

The intra particle diffusion (IPD) equation

The adsorption kinetic is not just a simple kinetic system. It passes through three steps with three different rate i.e. of three different activation energies, so it could be considered as a complex reaction. The intra-particle diffusion model describes the mechanism of such process. The first step is a mass transfer of the dye from its location in the solution into the boundary of the adsorbent surface after passing all forces precluding the dye molecules movement in solution. In the second step the dye molecules attracted to the active sites present on the solid surface of the adsorbent and finally the dye molecules diffuse into the adsorbent pores. The intra particles diffusion law can be expressed as in eq. (10):

$q_t = k_{diff}\, t^{1/2} +C$ ……(10)

Where k $(mg/g.min)^{1/2}$ is the rate of diffusion, C is the boundary layer effect and representing the intercept, which indicate the effect of surface sorption in the rate determining step, when plotting q_t versus $t^{1/2}$ a straight line will be obtained. If the intra particle diffusion is the only mechanism controlling the rate determining step, the line must pass from the origin.

In this work, the intra - particle diffusion model is applied by the experimental data using initial concentration 62 mg/l and 0.1 g from ATG at 25 c°. The result obtained are given in Table (6) and portrayed in figure (11). The plot of q_t versus $t^{1/2}$ showed straight line passing through three steps, the first one is straight and sharp line indicating to high rate of adsorption. Then the second step showed gradual decrease in the rate of adoption referring to decrease in the adsorption rate due to the occupation of active site on the clay surface. Finally, the third step showed equilibrium region. None of these lines passes through the origin means that, there are more than one mechanism controlling the adsorption process.

Table 6: Kinetic model constant values for adsorption of BTB dye on clay at 298 k.

Dye	Kinetic model	$qe_{(Calc)}$ mg/g	K	$qe_{(exp)}$ mg/g	R^2
BTB	1st order	13.027	0.085	33.821	0.9614
	2nd order	34.843	0.0147	33.821	0.999
	Ipd	C_i (mg/L)	$K_{diff.}$ $(mg.g^{-1}.min^{-½})$	C(mg/g)	R^2
		62	0.893	27.289	0.943

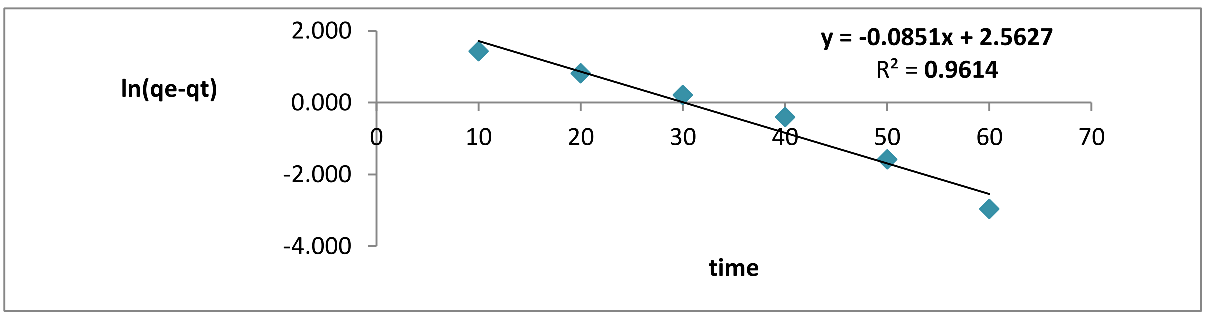

Figure 9: Linear plots of Pseudo-first-order at 298 k.

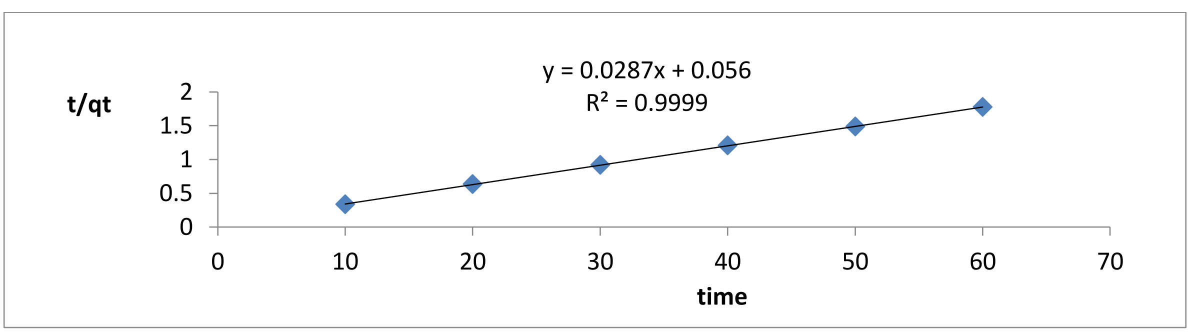

Figure 10: Linear Pseudo-second-order at 298 k

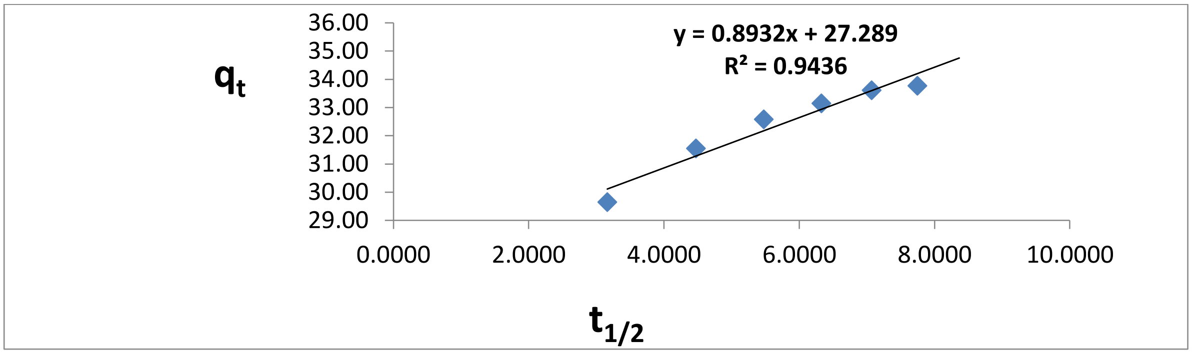

Figure 11: Linear plots of Intra particle diffusion model (IPD) kinetic for BTB dye on clay at 298 K.

Conclusions

The research work prove that activated Attapulgite clay (ATC) can be used as a good adsorbent for the removal of the bromothymole blue (BTB) dye and represent a cheap and available adsorbent material taken from western desert in Iraq. The application of Langmuir and Freundlic isotherm on the experimental result of the study system proved that the Langmuir isotherm is better fitted to our system. Thermodynamic studied provide that the adsorption system under concentration could occur spontaneously in the direction of adsorption, and forces controlling the adsorption process are physical nature leading to less random system.

Using the isotherm parameter of langmuir (k_l) and freundlich(k_f) which are calculated at varies concentration and different temperature gave thermodynamic functions ehith the same tendency similar to those calculated in the thermodynamic study. The kinetic study of the study system indicated that the adsorption process obey the pseudo second order reaction and the inter particle diffusion process is not the only mechanism controlling the adsorption process of the study system.

References

1. Agarwal, S. Sadegh,H. Monajjemi,M. Hamdy,A.S. Ali,G.A. Memar,A.O. Shahryari-ghoshekandi,R. Tyagi,I. Gupta,V.K. (2016) .Efficient removal of toxic bromothymol blue and methylene blue from wastewater by polyvinyl alcohol, Journal of Molecular Liquids 218 191-197.

2. Ran, R. Wang, L . Su, Y. He, S. He,B. Li,C. Wang,C. Liu,Y. Chen,S. (2021) . Preparation of pH-indicator films based on soy protein isolate/bromothymol blue and methyl red for monitoring fresh-cut apple freshness, Journal of Food Science.

3. Sabnis,R.W. (2007) Handbook of acid-base indicators, CRC Press .

4. Dhale,M.A. Mohan-Kumari,H.P. (2014) A comparative rapid and sensitive method to screen L-asparaginase producing fungi, Journal of microbiological methods 102 66-68.

5. Dufour,P. Kouassi,A. Lanusse,A. (1994) Les pollutions, Environnement et ressources aquatiques de Côte d'Ivoire 2 320-331.

6. MacLeod,M. Arp, H.P.H. Tekman, M.B. Jahnke, A. (2021) The global threat from plastic pollution, Science 373(6550) 61-65.

7. Douglas,M. Pollution, (1968) International encyclopedia of the social sciences 12 336-342.

8. Goel,P. 2006 Water pollution: causes, effects and control, New Age International.

9. Sheng,J. Tang,W. (2021) Spatiotemporal variation patterns of water pollution drivers: The case of China's south-north water transfer project, Science of the Total Environment 761 143190.

10. Gonzalez-Martin,J. Kraakman, N.J.R. Perez, C. Lebrero, R. Munoz, R. (2021) A state–of–the-art review on indoor air pollution and strategies for indoor air pollution control, Chemosphere 262 128376.

11. Motamedi, E. Kavousi, K. Motahar, S.F.S. Ghaffari, M.R. Mamaghani, A.S.A. Salekdeh, G.H. Ariaeenejad, S. (2021) Efficient removal of various textile dyes from wastewater by novel thermo-halotolerant laccase, Bioresource Technology 337 125468.

12. Ferraz, E. Alves, L. Sanguino, P. Santarén, J. Rasteiro, M.G. Gamelas, J.A. (2021) Stabilization of palygorskite aqueous suspensions using bio-based and synthetic polyelectrolytes, Polymers 13(1) 129.

13. Almeida, R. Ferraz, E. Santarén, J. Gamelas, J.A. (2021) Comparison of Surface Properties of Sepiolite and Palygorskite: Surface Energy and Nanoroughness, Nanomaterials 11(6) 1579.

14. Abdel Ghafar, H.H. Ali, G.A. Fouad, O.A. Makhlouf, S.A. (2015) Enhancement of adsorption efficiency of methylene blue on Co3O4/SiO2 nanocomposite, Desalination and water treatment 53(11) 2980-2989.

15. Zare, K. Najafi, F. Sadegh, H. (2013) Studies of ab initio and Monte Carlo simulation on interaction of fluorouracil anticancer drug with carbon nanotube, Journal of Nanostructure in Chemistry 3(1) 1-8.

16. Rajabi, M. Mirza, B. Mahanpoor, K. Mirjalili, M. Najafi, F. Moradi, O. Sadegh, H. Shahryari-Ghoshekandi, R. Asif, M. Tyagi, I. (2016) Adsorption of malachite green from aqueous solution by carboxylate group functionalized multi-walled carbon nanotubes: determination of equilibrium and kinetics parameters, Journal of Industrial and Engineering Chemistry 34 130-138.

17. Annadurai, G. Juang, R.-S. Lee, D.-J. (2002) Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, Journal of hazardous materials 92(3) 263-274.

18. Khodaie, M. Ghasemi, N. Moradi, B. Rahimi, M. (2013) Removal of methylene blue from wastewater by adsorption onto ZnCl2 activated corn husk carbon equilibrium studies, Journal of Chemistry 2013.

19. Roosta, M. Ghaedi, M. Daneshfar, A. Sahraei, R. (2014) Experimental design based response surface methodology optimization of ultrasonic assisted adsorption of safaranin O by tin sulfide nanoparticle loaded on activated carbon, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 122 223-231.

20. Gupta, V. Moradi, O. Tyagi I., Agarwal, S. Sadegh, H. Shahryari-Ghoshekandi, R. Makhlouf, A. Goodarzi, M. Garshasbi, A. (2016) Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification: a review, Critical Reviews in Environmental Science and Technology 46(2) 93-118.

21. Ghaedi, M. Khajehsharifi, H. Yadkuri, A.H. Roosta, M. Asghari, A. (2012) Oxidized multiwalled carbon nanotubes as efficient adsorbent for bromothymol blue, Toxicological & Environmental Chemistry 94(5) 873-883.

22. Kong ,L . Gong ,L . Wang ,J . (2015) Removal of methylene blue from wastewater using fallen leaves as an adsorbent, Desalination and Water Treatment 53(9) 2489-2500.

23. Hawraa, K. Ruba, F.A. Emad, M. E.l. Neda, I.M. (2021) Applications of aluminum oxide and nano aluminum oxide as adsorbents, Samarra Journal of Pure and Applied Science 2(2) 19-32.

24. Freundlich, H. Kapillarchemie, 1922 eine Darstellung der Chemie der Kolloide und verwandter Gebiete, akademische Verlagsgesellschaft.

25. Hanaor, D.A.M. Ghadiri,M. Chrzanowski, W. Gan, Y. (2014) Scalable surface area characterization by electrokinetic analysis of complex anion adsorption, Langmuir 30(50) 15143-15152.

26. Raed,T. Neam, H.S. Emad, A.S. (2021) Kinetic and Equilibrium Studies of the Adsorption of Dichalcones on Activated Carbon, Samarra Journal of Pure and Applied Science 3 (4) 41-55.

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دراسة مقارنة امتزاز صبغة البرمو ثايمول الزرقاء على طين الالتباكايد المنشط حراريا والكاربون المنشط التجاري

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معلومات المؤلف

الخلاصة:

تضمن هذا البحث دراسة طرق فعالية ازالة صبغة البرموثايمول الازرق من مخلفات المياه الصناعية باستخدام طين الاتبالكايد المحفز حراريا بالاضافة الى نوع من الكاربون المنشط التجاري كمواد مازة عند تطبيق تقنية الامتزاز. وقد تم مقارنة الطين المستخدم مع الكاربون المنشط التجاري كمواد مازة بديلة حيث تم استخدام 0.03 g من الفحم و0.1g من طين اتبالكايد المنشط حراريا واعتمد 0.03 g من الطين كمادة مازة بديلة ارخص من الفحم. وقد تم دراسة الظروف المثلى لانظمة الامتزاز قيد الدراسة وتضمنت دراسة تاثير كمية المادة المازة وتم اعتماد (g0.1) من الطين والتركيز الابتدائي واختير مولاري$1*10^{-3}$ ودرجة الحرارة 25 م على كفاءة الامتزاز. فضلا عن ذلك تم تطبيق البيانات العملية للامتزاز التي حصلنا عليها على نوعين من الايزوثيرملت المتمثلة بمعادلة ايزوثيرم فرندلخ ولانكماير وكانت نتائج ايزوثيرم لانكماير هي الافضل ثم تم تقدير وحساب الدوال الثرموداينميكية للنظام المختار (ΔH^o, ΔG^o, ΔS^o) اظهرت الدراسة الثرموداينميكية ومن خلال القيم المحسوبة ان نظام الامتزاز قيد الدراسة يتم من خلال قوى فيزيائية وانه نظام باعث للحرارة وانه يؤدي الى تكوين نظام ناتج اكثر انتظاما .وتضمن البحث ايضا تطبيق معادلة تفاعل من المرتبة الاولى الكاذبة والمرتبة الثانية الكاذبة في دراسة حركية على النظام المدروس من البيانات المحصلة عليها عمليا وقد اظهرت النتائج ان النظام المدروس يخظع لتفاعل من المرتبة الثانية الكاذبة واستدل على ذلك من العلاقات الخطية المحصل عليها ($R^2 = 0.9614$) للرتبة الاولى الكاذبة و ($R^2 = 0.999$) للرتبة الثانية الكاذبة فضلا عن ذلك فان تطابق قيم qe النظرية (mg/g 34.843) اكثر توافقا مع قيمتها العملية(33.821 mg/g). واظهر تطبيق طريقة الانتشار الجزيئي الضمني ان عملية انتشار الجزيئات الممتزة داخل المسامات الموجودة على السطح الماز ليست الميكانيكية الوحيدة المسيرة لعملية الامتزاز في التفاعل المدروس $K_{diff.}(mg.g^{-1}.min^{-1/2}) = 0.893$, $R^2 = 0.943$.