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Adsorption of Bromothymol Blue dye from Aqueous Solutions using Sawdust treated by polyaniline

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ABSTRACT

The ability of sawdust (SD) and sawdust / polyaniline composite (SD/PANI), that considered as cheap and eco-friendly adsorbents have been tested for removal of Bromothymol Blue *(*BTB) dye from aqueous solutions using batch adsorption technique. Fourier Transform Infrared Spectrophotometer (FTIR), Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) techniques were adopted to characterize the adsorbent surface. The effect of amount of adsorbent, contact time, pH and temperature on adsorption process was studied also. Results obtained indicates that the maximum percentage removal of BTB dye was 99% by using sawdust / polyaniline composite as adsorbent at initial dye pH (3–4) , contact time 4 min, temperature 30 ^oC and BTB dye initial concentration of 100 mg/ L. The adsorption of BTB dye on natural and modified sawdust were analyzed using Langmuir and Freundlich isotherms models. Lagergren pseudo-first order; pseudo-second order and intraparticle diffusion kinetic models were also applied in order to investigate the kinetic of adsorption process. Thermodynamic parameters such as ΔG^o, ΔH^o and ΔS^o were evaluated.

Key words: Sawdust, Sawdust / Polyaniline composite, Bromothymol blue dye, Langmuir and Freundlich isotherms models.

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INTRODUCTION

Most industries use dyes to color their products, these colors effect on the nature of water and prevents the sunlight penetration into the stream and reduces photosynthetic activity. Also some of dyes are carcinogenic and mutagenic. Traditional technologies to treat wastewater include biological, physical and chemical methods that used efficiently but it require high capital and costs so it has become necessary to find new technique friendly ways and low-cost methods to clean up contaminants [1]. The adsorption technique is the most efficient and cost effective procedure for maximal removal of dyes in short time via small amount of adsorbent from wastewater is adsorption [2]. Bromothymol blue (figure1) is a pH indicator, it is vastly applied in biomedical, biological and chemical engineering applications and it is mostly used for the evaluation and estimation of the pH of pools and fish tanks and the determination of the presence of carbonic acid in liquid. Because of these application and hazards associated with dyes, the removal of this dye is very important [3].

<table>
<tr><td rowspan="3">pH indicator</td><td>pH = bluish green</td></tr>
<tr><td>pH > 7 yellow</td></tr>
<tr><td>pH < 7 Blue</td></tr>
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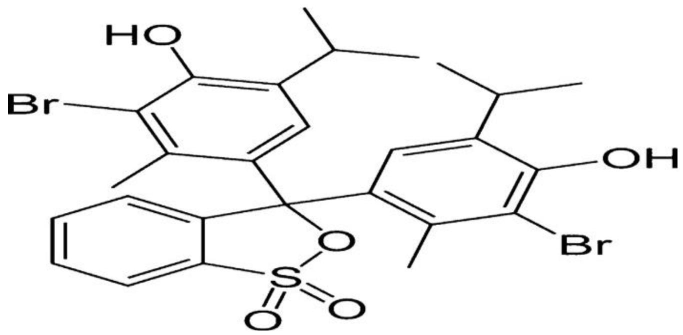


Figure (1): The structure of *BTB* dye.

Sawdust is one of the most popular and extensively used materials because of their effectiveness in removing dyes and being a low-cost material. In recent times, polymers has been used with the adsorbent material for the development of low-cost adsorbent and improve the adsorption process because of their good electrical conductivity, electro negativity , lack of composition of sludge and possible use in both systems column and batch [4]. Polyaniline (PANI) is widely used polymer because of the good electrical conductivity and it could be chemically or electrochemical synthesized from acidic aqueous solutions. Polyaniline can be found in different oxidation states depending on the ratio of imine to amine nitrogen [5]. Adsorption of dyes by sawdust / polymer composite is associated with the chemical and physical nature of the adsorbate where this process is done by the formation of complexes between the adsorbate and the functional groups in the adsorbent surface [6]. The structure of polyaniline as shown in figure (2):

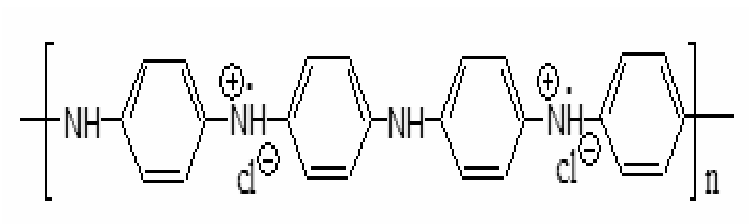


Figure (2): The structure of *polyaniline*.

METHODS

In order to determine a various parameters such as the pH, contact time, initial dye concentration, adsorbent dose and temperature on the percentage removal of bromothymol blue BTB, batch experiments were conducted. A 30 mL BTB solution at specified suitable concentration and pH were mixed completely with adsorbent over a fixed time. the pH was measured by addition of 0.1M HCL and/or NaOH. The concentrations of BTB were measured at 591nm by using UV vis. Spectrophotometer and the following formula was used for calculation of dye removal (%).

$$\% \text{ BTB removal} = ((C_o-C_t)/C_o) \times 100$$

Where C_o and C_t (mg.L^{-1}) are the initial dye concentration and concentration at time t, respectively. The equilibrium adsorption capacity of BTB was calculated from this equation:

$$Q_e = (C_o-C_e)\ V/W$$

Where Q_e (mg/g) is the equilibrium adsorption capacity, C_e is the dye concentration at equilibrium, V (L) is the volume of solution and W (gm) is the weight of adsorbent.

PREPARATION OF ADSORBENT

Preparation of Sawdust:

Sawdust (SD) was washed with tap water and then with distilled water to remove adhered dust particles. Then, the cleaned SD was kept in an oven for 24 hour at 110°C. After drying, the SD was ground into fine powder by grinding machine then sieved to a particle size of 75 μm as shown in figure (3). The dried powder of SD was kept in a glass bottle ready for further characterization [7].

Figure (3): The treated *SD*.

Preparation of *sawdust coated polyaniline*:

Sawdust coated polyaniline (SD/ PANI) was prepared by taking 5.0 g of sawdust (size 75µ or less) and immersed in 100 mL of 0.20 M freshly distilled aniline solution for 12 hrs before polymerization. The excess of the monomer solution was removed by simple decantation and then about 50 mL of 5 g ammonium persulphate ($(NH_4)_2S_2O_8$) as oxidant solution was added into the mixture of SD and aniline, and leave the reaction to continue for 5 hrs at room temperature. Sawdust coated polymer (SD /PANI) was filtered, washed with distilled water, then dried at temperature about 60 ^oC and sieved before use it [4]. The result powder is shown in figure (4).

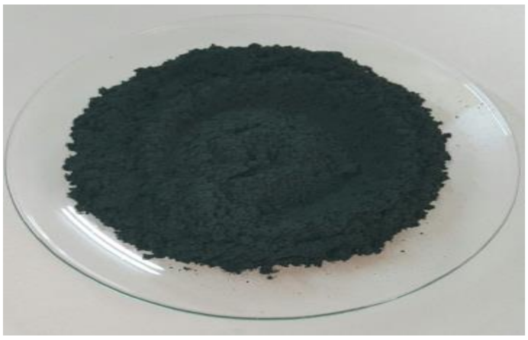


Figure (4): The *SD coated polyaniline*.

EXPERIMENTAL

Instruments and reagents:

Various concentrations of bromothymol blue (BTB) dye solution of 10, 15, 20, 25 and 30 mg.L^{-1} were daily prepared from stock dye solution (50 mgL^{-1}), that was simply prepared by dissolving 0.05 gm of BTB dye in 1000 mL distilled water. All other chemicals used in this research are of analytical grad. The pH meter model BP3001JiTrans was used for adjusted the pH of dye solutions by addition of dilute HCl and or NaOH solutions. Following the optimization of variables, the dependency of spectra to variables, especially pH was examined, and the calibration curve was obtained for studied range of concentrations at maximum wavelength. The concentration of the BTB dye was evaluated at 591 nm using Shimadzu. PC1650 Double beam UV–Visible spectrophotometer. Scanning Electron Microscope (SEM), Fourior transform Infrared Spectroscopy (FTIR) type (SHIMADZU IR PRESTIGE 21) and Atomic Force Microscope (AFM) instruments were used respectively to determine the morphology, organic functional groups present and to measure nano average particle size of the Sawdust and sawdust / polyaniline composite.

RESULT AND DISCUSSION

Characterization of Adsorbents

The maximum adsorption wavelength of BTB dye solution was measured by using UV-Visible spectrophotometer as shown in Figure (5). Data obtained show that the maximum adsorption of BTB dye solution was at 591 nm . Figure (6) show the scanning electron microscopy (SEM) image of SD and SD/PANI surfaces before the adsorption. The results indicate that both adsorbents have heterogeneous porous structure surfaces. FT-IR spectra of SD and SD/PANI adsorbents are shown in Figures (7& 8) and the data obtained are tabulated in tables (1) & (2). The data of adsorption bands indicating the complex nature of the adsorbents. The morphology for both sawdust (SD) and sawdust/polyaniline composite (SD/PANI) were determined by using AFM instrument at scan size of 20 µm. Figures (9 & 10) show the topographic structure in three-dimension image for adsorbents. The results indicate lower average diameter for SD/PANI composite as compared with SD adsorbent.

Table (1): The prominent IR bands for SD before adsorption.

Bond position (cm^{-1})	Assignment
3406.29	O-H stretch
2931.80	C-H stretch
1654.92	C=C stretch
1597.06	C=O stretch
1508.33	Aromatic region
1037.70	Si-O stretch
478.35	Si-O bend

Table (2): The prominent IR bands for SD/PANI before adsorption.

Bond position (cm^{-1})	Assignment
3448.72 & 3387.00	N-H stretch
1577.77	N-H bending
794.67	N-H out of plane

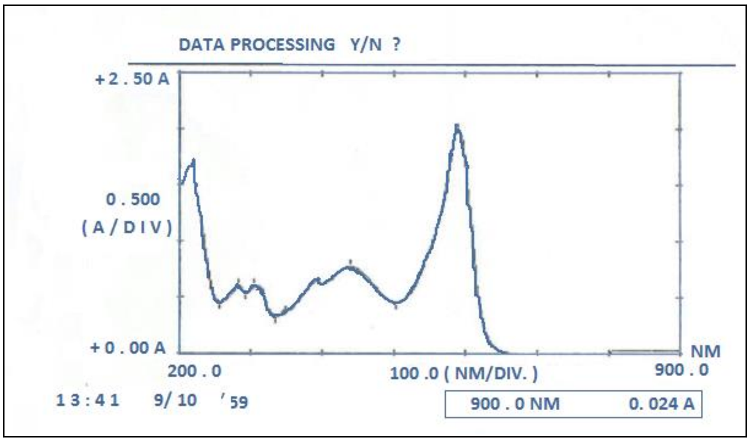
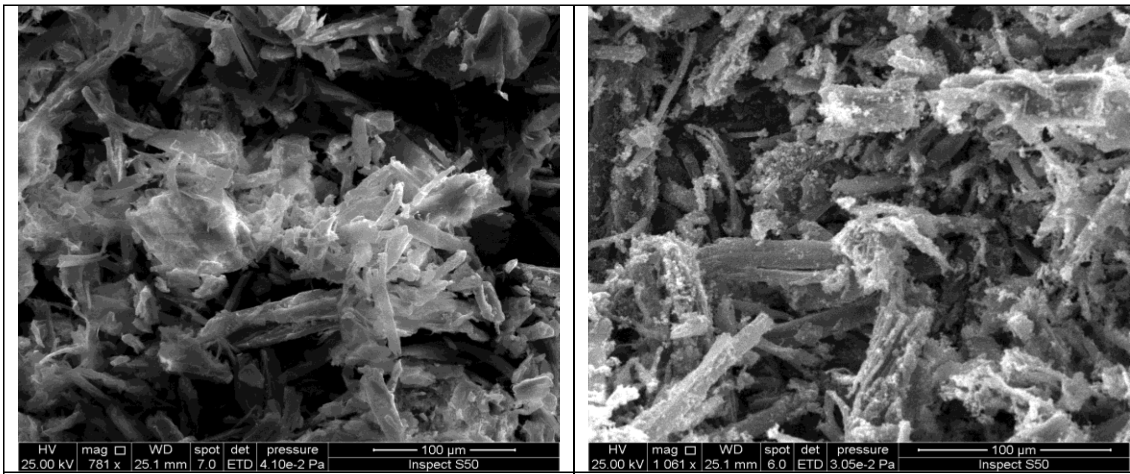


Figure (5): The λ_{max} of *BTB* dye.



SD	*SD/PAN*

Figure (6): SEM image of the adsorbents before and after the modification.

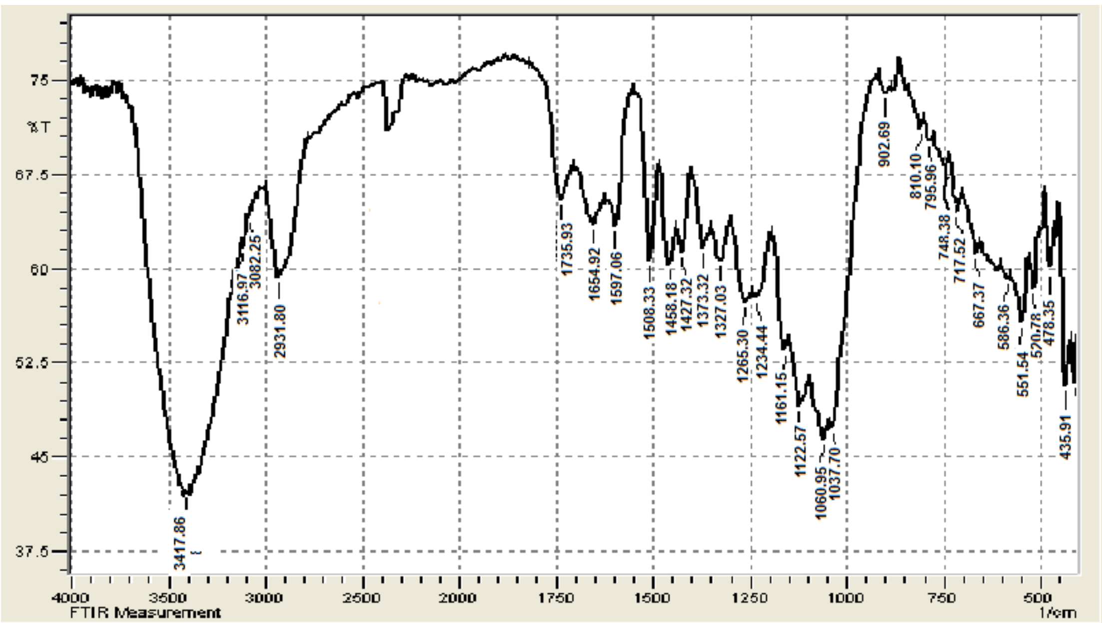


Figure (7): FT-IR of *SD*.

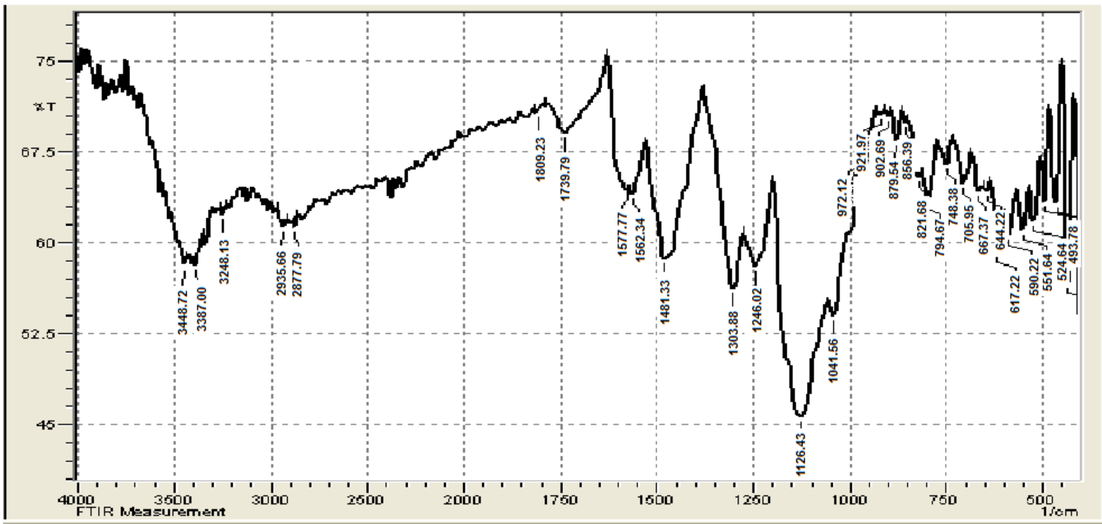


Figure (8): FT-IR of *SD/PANI composite*.

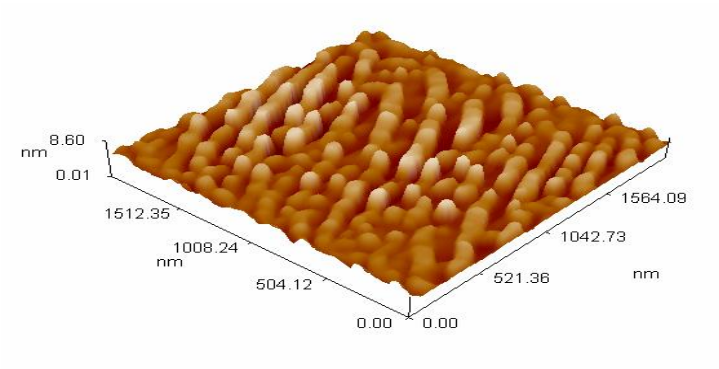


Figure (9): AFM of *SD*.

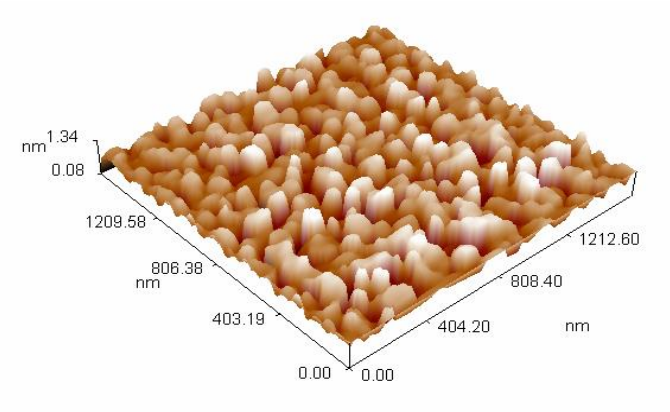


Figure (10): AFM of *SD/PANI composite*.

Adsorption Parameters Effects

The effect of several factors on the adsorption of bromothymol blue on the surface of sawdust and Sawdust coated polyaniline process include: study the effect of contact time between the dye and the surface which is the time required for the completion of the adsorption process on the surface of SD and SD/PANI and also studied the effect of adsorbent dosage on the adsorption process, as well as the impact of changing the function of the acidic solutions and temperature change on the adsorption process for both surfaces under study. The factors as shown below:

Contact time:

The effect of contact time on the adsorption of BTB dye was studied at constant dye concentration of (30 ppm), temperature of 25 °C and the weight of each adsorbents, SD and SD/PANI composite are 0.03 g. Absorbance of solutions were measured at different time periods of 5, 10, 15, 20, 25 and 30 minutes. Results obtained indicates that the percentage removal increased until time reached 15 min with percentage removal of 49% for SD and 98% for SD/PANI composite. After this time, the percentage removal was kept almost constant, as shown in figure (11). One of the reasons for high percentage removal for SD/PANI composite is due to its large surface area as compared with SD adsorbent.

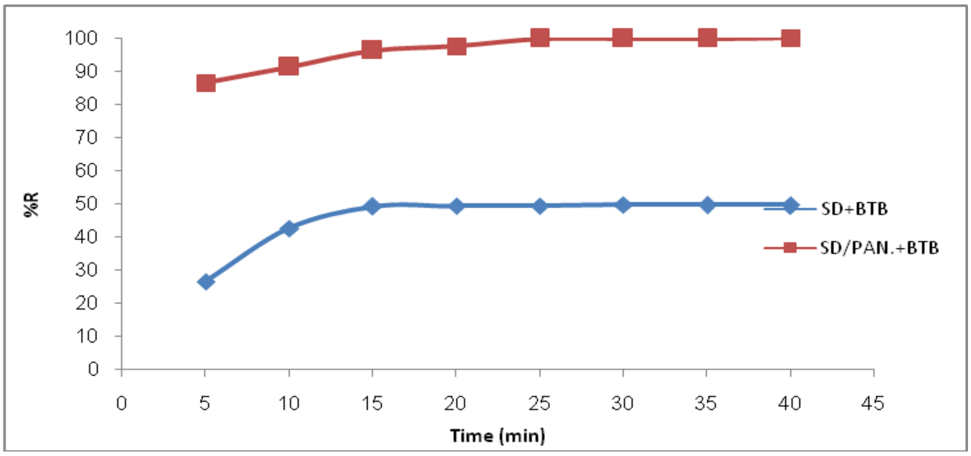


Figure (11): The effect of contact time in percentage removal of *BTB* in both adsorbents.

Effect of adsorbent dose:

The percentage removal of BTB dye on SD and SD/PANI adsorbents were studied at various adsorbents weights (0.005, 0.007, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04 and 0.05) g sequentially at constant BTB dye concentration (30ppm), temperature 25°C and contact time 15 min. It is clear (fig.12) that the percentage removal of BTB dye increases with increasing adsorbent dose . Increase in adsorbent dosage for SD and SD/ PANI composite from 0.005 to 0.015 g led to increase in percentage removal from 45% to 69% for SD, and from 65% to 97% for SD/PANI composite. Further increase in adsorbents dose does not effect the percentage removal of BTB dye, as shown in figure 12. The increase in percentage removal of BTB dye by raising adsorbents weight suggested due to existence of high number of the reactive site with high tendency for interaction with various pathways is polar-polar interaction and hydrogen bonding that significantly improved by electrostatic interaction. Therefore, increasing in the adsorbents weight led to an increase in available surface area and adsorption sites and simultaneously increased in the amount of mass transfer.

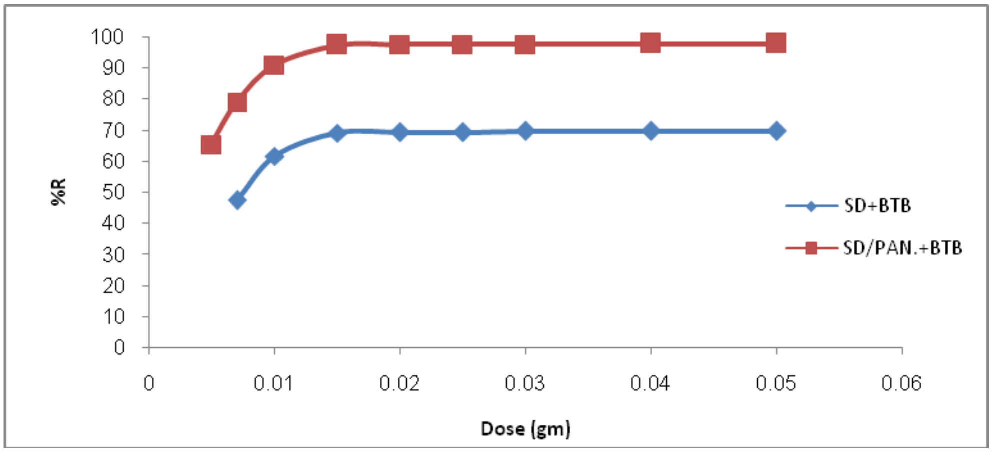


Figure (12): The effect of adsorbent dosage on the adsorption process.

Effect of pH:

Different concentrations of BTB dye were prepared (10, 15, 20, 25 and 30) ppm at different pH (3, 5, 7, 9 and 11) in addition to the original dye pH (from 3.5 to 4). Percentage removal for solutions at each concentration and pH and at temperature 25 °C , contact time 15 minutes and adsorbents weight 0.015 g for both SD and SD/PANI composite. The results obtained indicates that the highest percentage removal of the BTB dye on the SD adsorbent were achieved at acidic medium (pH = 3) and on the SD/PANI composite at the original BTB dye pH (3.5-4), as shown in Figure (13). From the measurements of FT-IR it was found that the SD surface was negatively charge so it gives high adsorption capacity of BTB in the acidic medium due to the presence of hydrogen ions. This occurred by protonation of the adsorbent surface lead to increase the attraction forces between the adsorbate and adsorbent surface and thus gives a higher percentage removal of BTB dye. On the other hand, the increase in pH values from 3 to 11 lead to decrease the percentage removal of BTB in SD surface from 81% to 36% due to the presence excess negative charges on the SD surfaces so electrostatic repulsion occurred between the BTB dye and SD surface [7]. On the other hand, SD/PANI surface has been getting high percentage removal of BTB dye as compared with SD surface at original dye pH (3.5-4) that give 99% percentage removal of dye due to the increase in the concentration of hydrogen ions which leads to gain amine group a proton and converting it to a positive charge and BTB dye carry a negative charge so it is possible to form a hydrogen bonding between the positive charge on the surface of SD/PANI composite and the functional groups on BTB dye [8]. When the pH increase to 9, the percentage removal of dye decrease to 74% due to the existence of different functional groups on BTB dye and adsorbent surface (SD/ PANI composite).

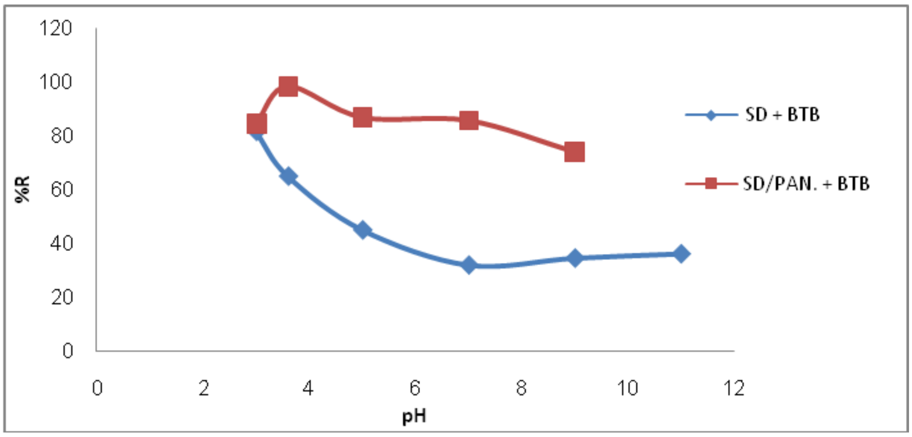


Figure (13): The effect of pH on the adsorption process.

Effect of temperature:

The effect of temperature on BTB dye adsorption on SD and SD/PANI composite has been discussed at three different temperatures (298, 308 and 318) K. Results obtained show that the amount of BTB dye adsorbed are increases with increasing temperature on both adsorbent surfaces(SD and SD/PANI). Since adsorption is endothermic process. Thus the removal of BTB dye caused an increase in the surface energy of the adsorbents through increase the forces on the surfaces of SD and SD/PANI composite.

Langmuir and Freundlich adsorption isotherms were used to determine the adsorption equilibrium data of BTB dye on SD and SD/PAN adsorbents. Freundlich adsorption isotherm model was more applicable for heterogeneous nature of surface. The equilibrium isotherm data were explained by using the linear form of Freundlich model as indicated in the following relation:

$$\text{Log } q_e. = \log K_F + 1/n \text{ Log } C_e.$$

Where qe is the amount of adsorbate in the adsorbent at equilibrium (mg/g), Ce is the equilibrium concentration (mg/L). K_F and n are the Freundlich constants indicating the adsorption capacity and adsorption intensity of the system [9]. The Langmuir adsorption isotherm model proposes that when the adsorbate occupies a site further adsorption cannot take place at those sites which is energetically equivalent and there is no interaction between molecules adsorbed on neighboring sites. The formula as shown:

$$Ce./qe. = 1/q_{max} K_L + 1/q_{max}Ce.$$

Where q_{max} (mg/g) and K_L are the Langmuir isotherm constants related to free energy [10]. The Langmuir isotherm depending on the values of R_L that indicate the type of isotherm [11].

irreversible	RL = 0
favorable	0 < RL < 1
linear	RL = 1
unfavorable	RL > 1

Since Freundlich isotherm depending on the values of n that indicate the strength of adsorption [12]. The date of adsorption isotherm shown in figure (14 & 15) and table (3) showed the data of adsorption of BTB on the both adsorbent surface.

n = 1	Linear
n < 1	physical interactions
n > 1	Chemical interaction

From the results that shown in table (3), the adsorption of BTB on SD and SD/PANI surfaces was fitting to the Freundlich isotherm model.

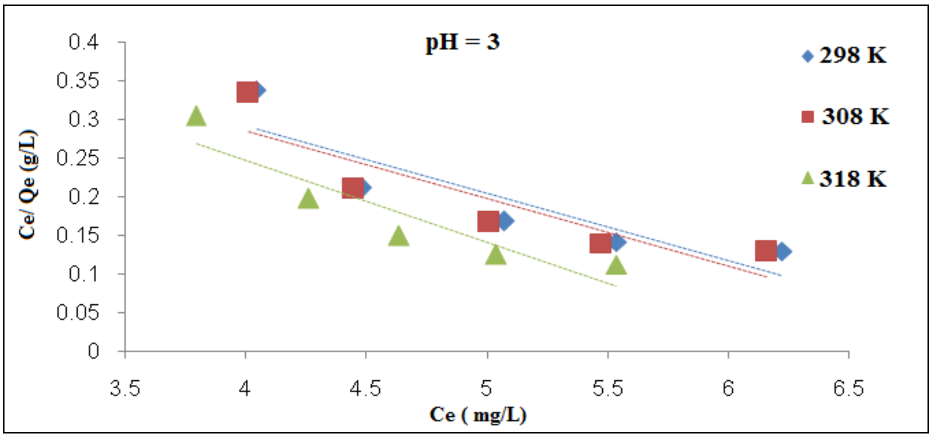


Figure (14.a): Langmuir isotherm model of adsorption *BTB* on *SD* surface.

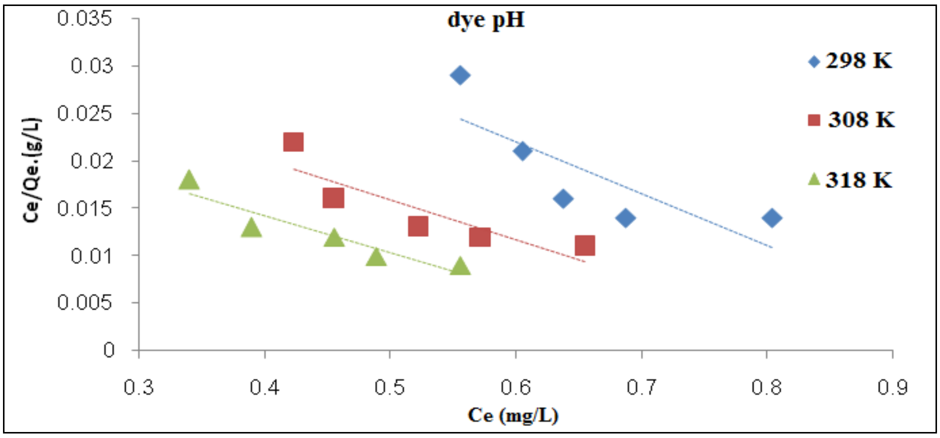


Figure (14.b): Langmuir isotherm model of adsorption *BTB* on *SD/PAN* surface.

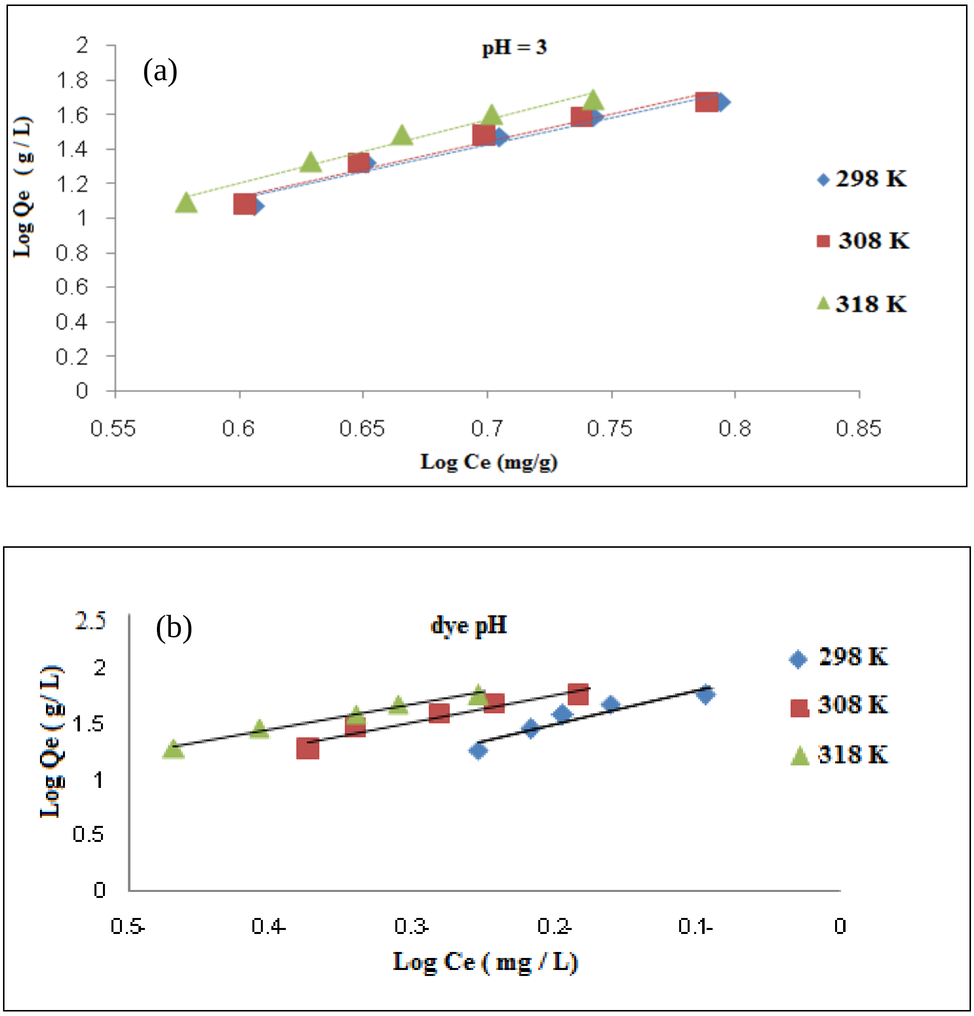


Figure (15): Freundlich isotherm model of adsorption *BTB* on (a) *SD* (b) *SD/PANI* surfaces.

Table (3): Adsorption Isotherm Constant of BTB dye on the SD & SD/PANI at different pH and Temperatures.

pH	T (K)	Langmuir constants				Freundlich constants		
		q max	K_L	R_L	R^2	n	K_F	R^2
SD								
3	298	-11.467	-0.136	-0.324	0.784	0.318	0.171	0.958
	308	-11.428	-0.136	-0.324	0.781	0.315	0.167	0.956
	318	-9.398	-0.158	-0.267	0.851	0.272	0.101	0.976
SD/PAN								
dye 's pH (3.5-4)	298	-65.789	-0.032	25.000	0.900	0.765	1.528	0.987
	308	-77.519	-0.030	10.000	0.848	0.794	1.781	0.986
	318	-93.458	-0.025	4.000	0.928	0.825	2.145	0.992

Thermodynamic studies:

Standard Gibbs free energy change ΔG^o, standard enthalpy change ΔH^o(kJ/mol), and standard entropy change ΔS^o(kJ/mol) are very useful thermodynamic functions that providing information about the feasibility and spontaneous nature of adsorption process[13].

The thermodynamic constant was calculated from the following relation:

$$\Delta G^o = - RT \ln K_o$$

Where ΔG^o is the free energy change (kJ moL^{-1}), R is the gas constant (8.315 J mol^{-1} K^{-1}), K_o is thermodynamic equilibrium constant and T refers to temperature (K). On the other hand, K_o value was obtained from the relation Qe / Ce. The results are tabulated in table (4). The negative values of ΔG^o refers that the adsorption process of BTB dye on SD and SD/ PANI adsorbents were spontaneous. On other hand, ΔG^o values were decrease with increasing temperature indicating better adsorption of dye was achieved at higher temperature.

Table (4): Thermodynamics Parameters for Adsorption BTB dye on the SD & SD/PANI at Different pH.

pH	T(K)	ΔH^o KJ/mol	ΔS^o J/mol	R^2	ΔG^o KJ/mol
SD					
3	298	5.660	35.733	0.952	-5.988
	308				-6.346
	318				-6.703
SD/PAN					
Natural Dye pH (3.5-4)	298	14.909	85.703	0.998	-10.630
	308				-11.488
	318				-12.345

In order to determine the standard enthalpy change ΔH^o(kJ/mol), and standard entropy change ΔS^o (kJ/mol) for the adsorption process, Van't Hoff equation was used [10]:

$$\text{Ln } K_o = -\Delta H^o/RT + \Delta S^o/R$$

Where ΔH^o and ΔS^o are respectively the slope and intercept of linear relation between Ln K_o and 1/ T as shown in figure (16). If the values of the ΔH between 2.1 kJ/ moL to 20.9 kJ/ moL, the type of adsorption is physisorption but if the values from 20.9 kJ/moL to 418.4 kJ/moL, the adsorption type is chemisorption. From the results of the table (4), the adsorption of BTB dye on SD and SD/PANI adsorbents are physisorption. On the other hand, the positive values of ΔS^o indicate an increase in randomness of the adsorption process [14].

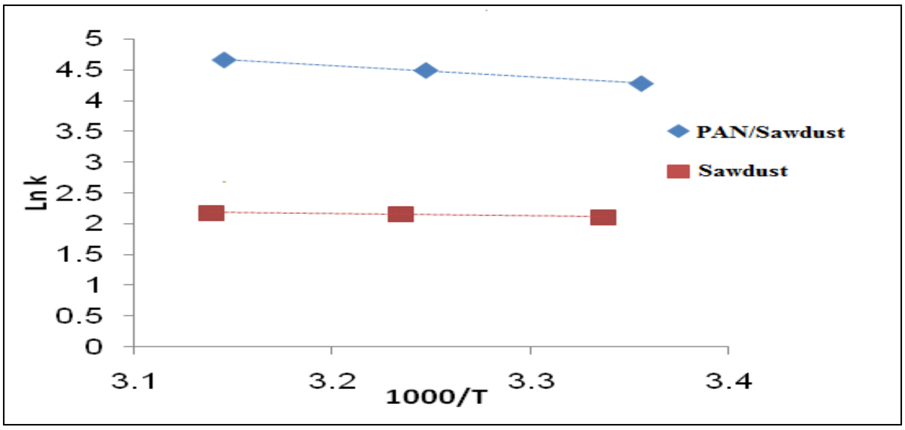


Figure (16): The Van't Hoff equation of the *BTB* adsorption at different temperatures on *SD* and *SD/PANI* surfaces.

Adsorption Kinetics:

The kinetic of adsorption of BTB dye on SD and SD/PANI composite were studied depending on the three kinetic equations, including pseudo-first order, pseudo-second order and intra-particle diffusion.

Pseudo-first order kinetic equation was represented by the following linear relation:

$$\log (q_e - q_t) = \log q_e - k_1 t$$

Where k_1 (min^{-1}) is the pseudo-first order rate constant, q_t (mg/g) and q_e (mg/g) are adsorption capacities at a given time t (min) and the equilibrium condition, respectively. Values of k_1 and q_e were determined from the slope and intercept of linear relation between log (q_e− q_t) versus t, as shown in figure (17). The data obtained are tabulated in table (5).

Table (5): Kinetic parameters for the adsorption of BTB dyes onto SD & SD/PANI surfaces.

	Pseudo-first order			Pseudo-second order			Intrapartical diffusion		
	K_1 (L/min)	qe. (mg/g)	R^2	K_2 (mg/g.min)	qe. (mg/g)	R^2	k_D (mg/g.min $^{1/2}$)	C	R^2
SD+BTB	-0.252	17.026	0.867	0.010	18.622	0.979	2.438	3.902	0.803
SD/PANI+ BTB	-0.244	52.699	0.794	0.013	62.500	0.999	2.925	45.575	0.980

Pseudo-second-order constant can be calculated by using the linear form as:

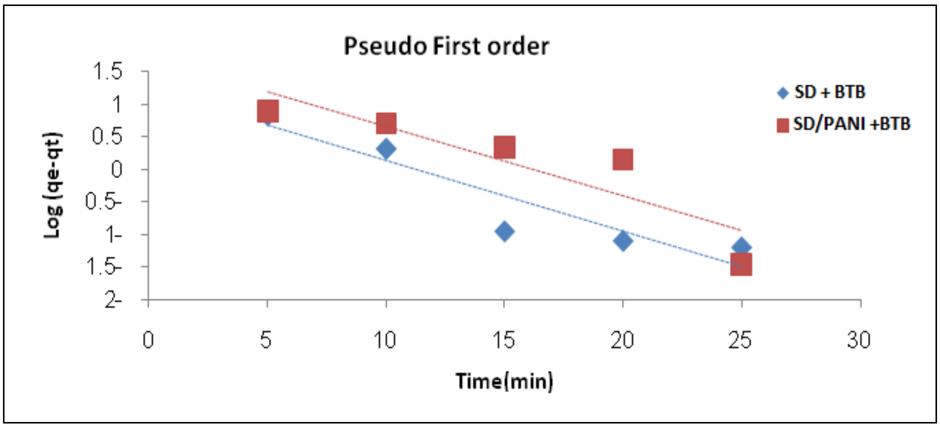
$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

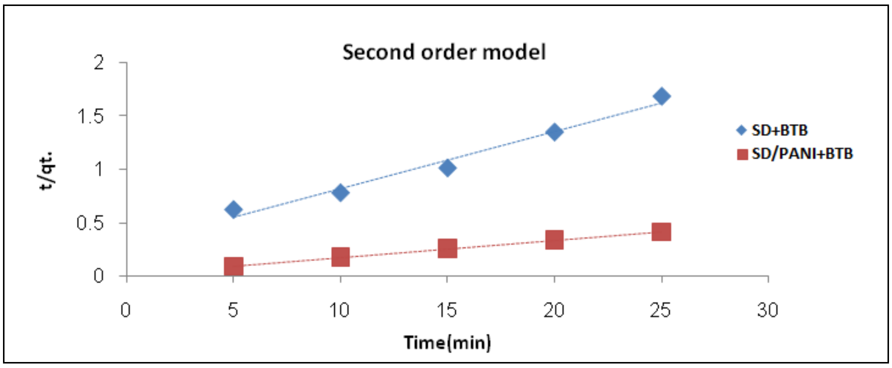
Where k_2 (g/mg min) is the pseudo-second-order rate constant. Values of k_2 and q_e can be obtained from the slope and intercept of linear relation between t/q_t versus t as shown in figure (18). Results are presented in table (5). The data show that the correlation coefficient, R^2 of pseudo-second-order equation are higher than those of pseudo-first-order equation indicating that the adsorption of BTB dye on SD and SD/PAN composite follows second order kinetic.

The equation of intra-particle diffusion was represented by the linear form as:

$$q_t = k_D t^{1/2} + C$$

Where C and k_D are constant parameters refers to the thickness of the boundary layer (mg/g) and intra-particle diffusion rate constant (mg/g.min$^{1/2}$), respectively [15]. Figure (17) shows the variation of q_t values for the adsorption of BTB dye on both adsorbents with the variation of $t^{1/2}$, and the values obtained of k_D and C are presented in table(5). it was found that the k_D values are greater than k_2 values , so this confirmed that the intra-particle diffusion was not rate-determining step for the adsorption process of BTB dye[16].





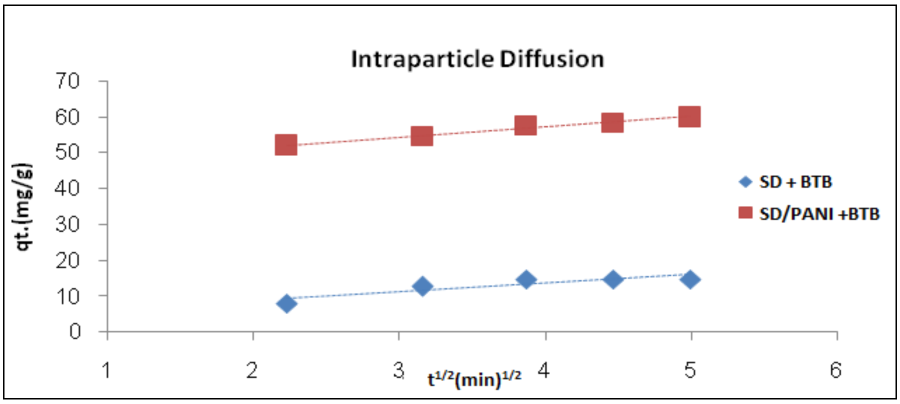


Figure (17): Kinetic studies of BTB adsorption on the SD and SD/PANI surfaces.

Mechanism of Adsorption

A proposed mechanism for the adsorption of BTB dye on SD/ PANI composite was presented in figure (18). In the figure (18) , Cl^- anion is doped in SD/PANI composite during the chemical oxidation process of aniline. It is generally accepted that HN^+ cations can act as adsorption sites of BTB dye molecules occurred by physisorption or chemisorptions on the surface of SD/PANI composite. The observed adsorption types (physi- or chemi- sorption) of BTB dye may be attributed to the large size and stereochemistry of adsorbed dye molecules. The overall adsorption efficiency of BTB dye on SD/PANI composite is larger than that of SD adsorbent, due to the possibility of more binding sites on the composite. This is also obvious from the values of thermodynamic function (ΔG°) which were more negative for BTB dye adsorption on SD/PANI composite surface than on SD surface.

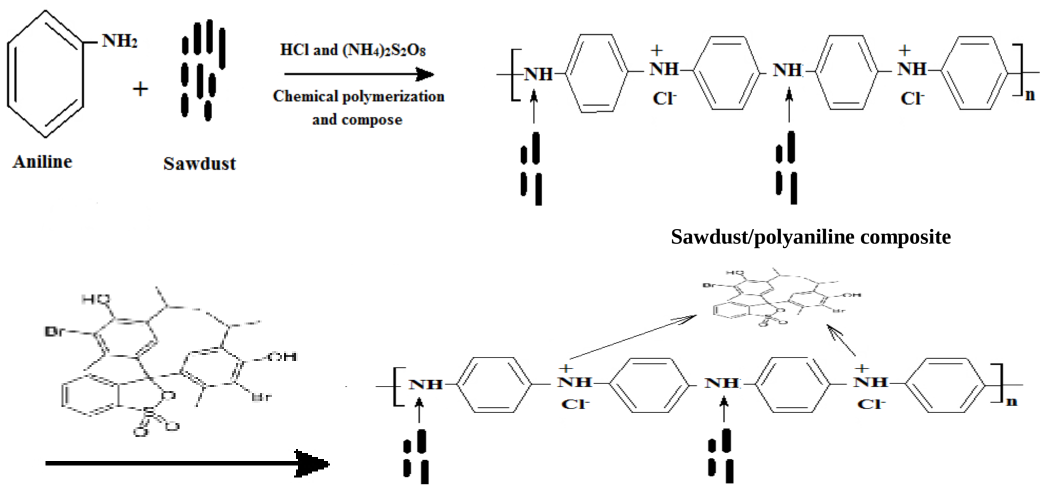


Figure (18): A proposed mechanism of *BTB* adsorption on the *SD* surface after modification with *polyaniline*.

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CONCLUSION

The results obtained from this study reveal that the sawdust coated polyaniline (SD/PANI) adsorbent have high efficiency to remove bromothymol blue (BTB) dye from the aqueous solution using batch adsorption, and the percentage removal reaches to 99% as compared with sawdust (SD) surface due to the presence of polyaniline that provides more active sites which leads to increase the surface area of sawdust and continuously increase its the adsorption ability towards BTB dye . From the thermodynamic parameters (ΔH^o, ΔS^o, ΔG^o), the adsorption process was considered to be spontaneous, endothermic and increased randomness. The adsorption isotherm showed that the Freundlich isotherm fit much better than the Langmuir isotherm because heterogeneous nature of the surface of adsorbents, so Vander walls force and hydrogen bonding may be formed between the functional groups of the adsorbate and adsorbent. The kinetic studies show that the adsorption of BTB on the adsorbent obey the pseudo second order model.

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