

# Adsorption Kinetics of Bromophenol Blue and Eriochrome Black T using Bentonite Carbon Composite Material

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**Abstract** - The present study deals with the adsorption of Bromophenol blue (BB) and Eriochrome black T (EBT) – two anionic dyes – onto bentonite carbon composite material (BCC). Batch studies were performed to evaluate the influence of various experimental parameters such as: pH, contact time, adsorbent dose and initial dye concentration. The optimal conditions for the dyes removal were found to be at pH = 1, applying a dose of 10 g.L<sup>-1</sup> and 20 g.L<sup>-1</sup> and for an equilibrium time of 40 mins for both dyes BB and EBT removal, respectively. The results also showed that process followed pseudo-second-order rate expression for dyes with a degree of intraparticle diffusion for BB and intraparticle and pore diffusion for EBT and it was found to be best represented by the Freundlich isotherm.

**Index Terms**— Adsorption, bentonite carbon composite material, Bromophenol blue, Eriochrome black T.

## 1 INTRODUCTION

Pigments and dyes are extensively used in the textile, paper and leather dyeing, printing, pharmaceutical and cosmetic industries [1]. With a global production of about 10,000 different dyes, 8×10<sup>5</sup> tons of the produced synthetic dyes were reported to be consumed within the textile industry alone worldwide [2]. Nonetheless, about 10-15% of these utilized dyes were reported to be discharged with its wastewaters [1,3].

Essentially, the effluent discharged from the textile industries is considered to be complex in nature and contains a high and variable mixture of polluting substances including dyes [2]. However, while these colored wastewaters are aesthetically unpleasant, once discharged into surface waters they could potentially degrade its quality by hindering the oxygenation ability of water, disturbing the whole of the aquatic ecosystem and food chain [2,4]. This in turn may have serious

impacts on human health as these dyes are known to be generally toxic and some may have carcinogenic as well as mutagenic properties [4]. Moreover, and from a technical perspective, these synthetic dyes have low removal rates when subjected to aerobic wastewater treatment because they are inert and non-biodegradable [2,4]. Therefore, treatment of wastewaters containing these soluble dyes requires its complete removal to ensure the safe disposal of the produced sludge.

In Egypt, the textile industry is considered one of the most polluting industrial activities. Generally, this industrial sector has the largest share of the annual 6.1 ×10<sup>9</sup> m<sup>3</sup> of the country's industrial water budget and, thus, its impact on the environment is considered significant [4]. More specifically, it was stated that 93% of the water intake in such an industry was released as effluent containing high concentrations of non-biodegradable synthetic organic dyes and heavy metals [2]. Hence, these wastewaters are very difficult to treat given the fact that the required is not only to decolorize the effluent but also to safely remove mixtures of spent dyes.

Generally, dyes are classified into cationic (all basic dyes), anionic (direct, acid, azo dyes and reactive dyes) and non-ionic dyes (dispersed dyes) [3,5,6]. Moreover, it was reported that both basic and reactive dyes were extensively used in the textile industry because of their favorable characteristics of being bright in color, easily

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soluble in water, cheaper to produce, and easier to apply onto fabric [5,6]. As well, it was indicated that 10%–50% and 0%–5% were lost during the dyeing process of the applied reactive and basic dyes, respectively, and were discharged with the effluents [6]. On the other hand, azo dyes are considered the largest class of reactive dyes used in the textile industry [3]. Overall, an estimated 130 of 3,200 azo dyes in use were reported to form carcinogenic aromatic amines during degradation under anaerobic conditions, which in turn may be toxic and carcinogenic [3]. Thus, the removal of anionic dyes is considered a challenging task as conventional wastewater treatment plants have a low removal efficiency for reactive and other anionic soluble dyes [3,6].

Various physical and chemical techniques have been used for the removal of organics as well as inorganics from wastewaters [5,7]. These include adsorption, coagulation/ flocculation, advanced oxidation processes, ozonation, membrane filtration, electroflotation, electrokinetic coagulation, electrochemical destruction, ion-exchange, irradiation, precipitation and biological treatment, membrane separation, and solvent extraction processes [5,7]. More specifically, conventional methods that have been applied for the treatment of colored effluents include photocatalytic degradation, microbiological decomposition, electrochemical oxidation, membrane filtration, and adsorption techniques [8]. However, while these methods may be effective in the decolorization of these industrial effluents, they are expensive and produce large amounts of sludge inciting obvious disposable problems [7]. Subsequently, sorption has become the most accepted treatment method as it gives better results and may be used to eliminate diverse types of coloring materials. This is because adsorption is a physiochemical wastewater treatment in which dissolved molecules are attached to the surface of an adsorbent by physical/chemical forces [4,5]. As well, this technique is simple in application due to the availability of a wide range of adsorbents that are able to remove non-biodegradable pollutants from wastewater.

Commercial activated carbon has been extensively used in the removal of dyes from wastewaters. However, due to its high cost of

production and inability for regeneration, researchers are developing cost effective and non-conventional potential adsorbents [3,9]. These include clay, minerals, industrial and solid wastes as well as agricultural solid wastes. Clays are considered to be a good adsorbent because of its large surface area; high cations exchange capacity, chemical and mechanical stability and layered structure [3,10,11]. As well, they are low cost and abundant around the world which makes them be a part of many industrial applications and in environmental control [10]. As well as in Egypt, bentonite, a naturally occurring clay, is considered a cheap adsorbent that has been used as an alternative material for the removal of dyes [11].

From another perspective, composites are natural or synthesized materials made from two or more materials with significantly different physical and chemical properties which remain separate and distinct at the microscopic or macroscopic scale within the material [12,13]. In general, these composites are synthesized to combine the desired properties of the materials in the composite. Composites' properties frequently represent a synergic or totally new combination in relation to the isolated components [13]. The matrix in any composite materials is a continuous phase which involves another phase namely denoted as a dispersive phase and this multi-phase material exhibits a significant proportion of properties of all its constituent phases [12]. Clay composite or nanocomposites are new adsorbent materials in which the major component is clay in combination with other materials like metals, polymer, and others [13]. Furthermore, composite materials have some advantages such as: light weight, high specific stiffness and strength, ease of mold ability to complex forms, ease of bondability, good dumping, low electrical conductivity and thermal expansion, good fatigue resistance, part consolidation due to lower overall system costs, and internal energy storage and release [14].

This study is concerned with the removal of two commonly used anionic dyes namely: Bromophenol blue (BB) and eriochrome black T (EBT) from aqueous solutions. Bromophenol blue is widely used as an industrial dye in food, drugs, cosmetics, textile, printing inks, as a laboratory indicator and a biological stain [15]. Eriochrome Black T (EBT), on the other hand, is an acidic dye

which is used for dyeing silk, wool, nylon multifibers after pretreatment with chromium salts [16]. Pure EBT is also used as an indicator in complexometric titrations for the determination of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  ions and for biological staining. EBT is hazardous as such and its degradation products are still more carcinogenic [16]. As well, as both in solution may be absorbed in harmful amounts through intact skin and causes skin irritation.

The objective of present study is to investigate the feasibility of the use of a prepared carbon-bentonite composite for of both BB and EBT aqueous solution. Batch adsorption experiments were utilized to study the dye removal efficiency using the selected sorbent material. The effect of various parameters such as contact time, initial metal concentration, pH, adsorbent mass, and temperature upon the removal of both dyes were studied and the kinetics of the process were elucidated. The kinetics of BB and EBT adsorption onto the bentonite carbon composite material were analyzed by fitting the experimental data to various kinetic models. The experimental data obtained were fitted to Langmuir, Freundlich and Temkin models to analyze the adsorption equilibrium and the thermodynamic parameters for free energy, enthalpy, and entropy change were calculated.

## 2 MATERIALS AND METHODS

### 2.1 Preparation of Bentonite-Carbon-Composite (BCC):

The bentonite used in this investigation was obtained locally from Egypt and its chemical composition is provided in Table (1). The formed bentonite-carbon composite material was composed of 50% bentonite and 50% activated carbon which were combined then heated at 1000 °C together in a muffle furnace for one hour at inert atmosphere.

Specific surface area is defined as the accessible area of solid surface per unit mass of material [17]. The method of adsorption of methylene blue in liquid phase for specific surface area determination has adopted widely for various natural solids: activated carbon, charcoal, graphite, and silica. This method can provide a common

reference method for adsorbent characterization in quality control, much like other mechanical properties. The specific surface area of the prepared BCC adsorbent was calculated using the methylene blue method according to the following equation [17]:

$$S_{\text{BCC}} = (q_m \times a_{\text{MB}} \times N_A \times 10^{-20}) / M_{\text{MB}} m_{\text{BCC}} \quad (1)$$

where  $q_m$  is the amount of methylene blue adsorbed (g),  $N_A$  is Avogadro's number ( $6.023 \times 10^{23}$ ),  $a_{\text{MB}}$  is the methylene blue molecular cross-section ( $197.2 \text{ \AA}^2$ ),  $M_{\text{MB}}$  is the molecular weight of methylene blue ( $319.3 \text{ g.mol}^{-1}$ ), and  $m_{\text{BCC}}$  is the mass of the BCC adsorbent.

TABLE 1  
 Chemical composition of Bentonite (w/w %)

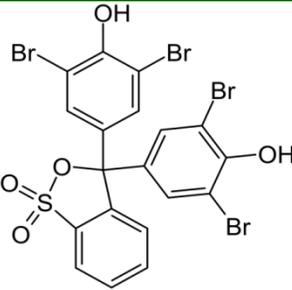
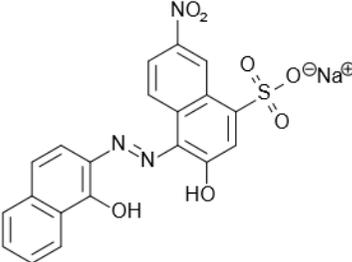
Element	w/w %
SiO <sub>2</sub>	61.16
TiO <sub>2</sub>	0.59
Al <sub>2</sub> O <sub>3</sub>	19.44
Fe <sub>2</sub> O <sub>3</sub>	4.6
MnO	0.06
MgO	2.2
CaO	1.38
Na <sub>2</sub> O	1.22
K <sub>2</sub> O	2.05
SO <sub>3</sub>	0.5
L.O.I, 1000 °C	6.8

### 2.2 Preparation of Dye Stock Solutions:

The chemical and physical properties of the tested dyes (BB and EBT), including chemical structure, molecular weights, dissociation constant ( $\text{p}K_a$ ) and maximum wavelengths of absorbance ( $\lambda_{\text{max}}$ ) are shown in Table (2).

To prepare a 1000  $\text{mg.L}^{-1}$  stock solution of each dye, an accurately weighed quantity of each dye was dissolved in bidistilled water. Experimental solutions of the desired concentrations were obtained by dilutions from these stock solutions thereafter. The initial concentration of each dye and its residual amount in solution was determined using calibration curves prepared at the individual dye ( $\lambda_{\text{max}}$ ) using a double beam US/VIS (JASCO V-630 double beam Spectrophotometer, Japan).

TABLE 2  
Chemical and physical properties of Bromophenol Blue (BB) and Eriochrome Black T (EBT)

Dye	Chemical Structure	Mol. Wt (g/mol)	$\lambda_{\max}$ (nm)	pKa
Bromophenol blue (BB)		669.96	497	4.0
Eriochrome Black T (EBT)		461.38	520	6.2, 11.55

### 2.3 Adsorption Experiments

Batch adsorption experiments were carried out in a thermostated water bath/shaker at a constant shaking rate (model RUMO 4050; shaking rate 10-250 rpm). The effect of contact time, concentration, solution pH, adsorbent dose and temperature were studied. 20 mL of dye solution of known concentration (10- 50 mg.L<sup>-1</sup>) were shaken in stoppered bottles with different weights of adsorbent material (5- 50 g.L<sup>-1</sup>) at different temperatures (25- 40°C), for various mixing time (1- 60 min) and throughout the pH range of (1-10) which was adjusted using NaOH or HCl solutions. Separation of the solid phase from liquid was achieved first by centrifuging for 5 min (6000 rpm) followed by filtration.

For adsorption isotherms, BB, and EBT solutions of different concentrations (10 and 50 mg.L<sup>-1</sup>) were agitated with the adsorbent at optimum (m) till the equilibrium was achieved.

The %of dye removal was calculated as follows [9]:

$$\% \text{ Dye removal} = [C_0 - C_f / C_0] \times 100 \quad (2)$$

where  $C_0$  and  $C_f$  are the initial and final concentration of dye in solution (mg.L<sup>-1</sup> or ppm), respectively. The amount of dye accumulated per unit mass of adsorbent was evaluated using the following equation [9]:

$$q_t = (C_0 - C_t) V/m \quad (3)$$

contact time  $t_e$ ,  $C_t$  becomes  $C_e$  and the amount of dye sorbed ( $q_t$ ) is equivalent to amount at equilibrium ( $q_e$ ).

### 2.4 Adsorption Kinetics:

To a series of 20 mL capacity bottles containing the desired amount of dye solution with known concentrations, a predetermined amount of adsorbent was added and the mixture was agitated in a thermostated water bath shaker. At set time intervals, the solutions were centrifuged, filtered and the metal ion concentration was determined.

Thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$ ) were calculated from the adsorption results. The optimum weight of each adsorbent material/L was added to a solution of each dye (10 mg.L<sup>-1</sup>) at pH 1 and was shaken for 40 mins at different temperatures.

## 3 RESULT AND DISCUSSION

### 3.1 Effect of Adsorbent Dose

The effect of BCC dose on the % uptake of BB and EBT at an initial concentration of both dyes of 50 mg.L<sup>-1</sup> and T=298K was studied and the results are shown in Figure 1. The increase in the adsorption with the increase of adsorbent weight may be attributed to the surface area of the

composite that was calculated to be  $174.3 \text{ m}^2\cdot\text{g}^{-1}$  which allows increases the adsorption sites. The optimal adsorbent dose for BB and EBT was found to be 10 and 20  $\text{g}\cdot\text{L}^{-1}$  respectively. After this dose the adsorbent surface becomes saturated and thus the residual dye concentration in aqueous solution more or less remains constant.

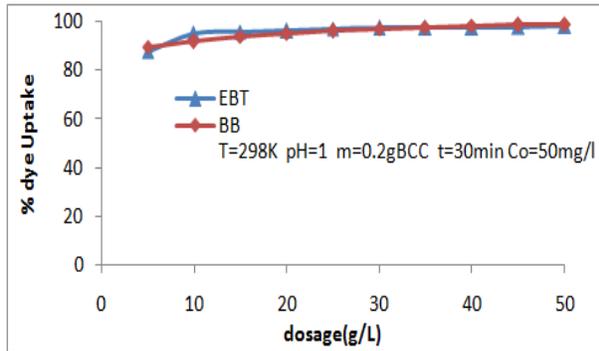


Fig 1 The effect of varying BCC dose upon the uptake of the two dyes ( $C_0 = 50 \text{ mg}\cdot\text{L}^{-1}$ ,  $t = 40 \text{ min}$ ,  $\text{pH} = 1$ )

### 3.2 Effect of pH

The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization of the materials present in the solution; pH therefore affects the structural stability of dyes and hence, their color intensity. Figure 2 shows the % uptake of dyes using the optimal weight of BCC of 10 and 20  $\text{g}\cdot\text{L}^{-1}$  for EBT and BB respectively, over the pH range of 1 - 10. It was found that the % uptake decreased for both BB and EBT as pH increased. The maximum percent uptake was at  $\text{pH} = 1$  for both BB, EBT dyes respectively Fig. 2.

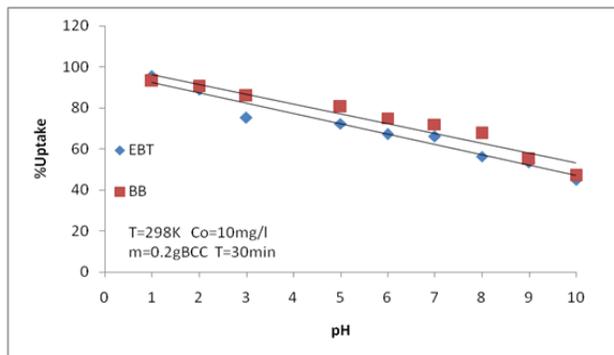


Fig.2 Effect of pH on the uptake of the two dyes

### 3.3 Effect of Contact Time

#### 3.3 Effect of contact Time

The effect of contact time on % uptake of dyes by the BCC is shown on Fig. 3 by adjusting the pH of the aqueous solution to  $\text{pH} = 1$ . A rapid adsorption of both dyes was observed in the first five minutes. The adsorption rates then decreased gradually and the adsorption reached equilibrium in about 40 min for both dyes. The adsorption curves were smooth, and continuous leading to saturation and indicating the possible mono-layer coverage on the surface of the adsorbent by the dyes molecules [18,19].

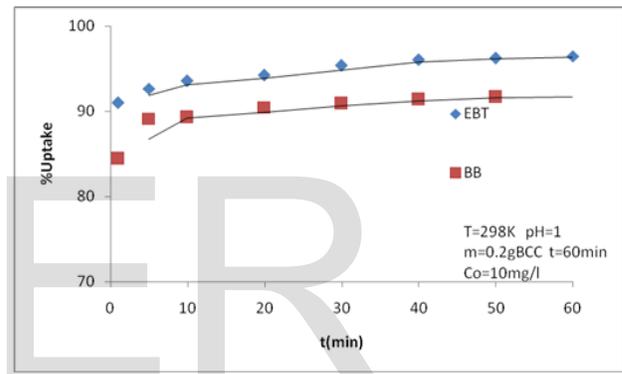


Fig.3 Effect of contact time on the uptake of the two dyes

#### 3.4 Effect of Initial Dye Concentration ( $C_0$ )

The effect of initial dye concentration ( $C_0$ ) on % uptake of the BB, and EBT dyes by BCC was investigated using dyes concentrations ranging between 10 – 50  $\text{mg}\cdot\text{L}^{-1}$ . Although the  $C_0$  increased from 10 and 50  $\text{mg}\cdot\text{L}^{-1}$ , the percent uptake was almost constant for both BB, and EBT dyes as shown on Fig. 4.

The initial concentrations provides the necessary driving force to overcome the resistances to the mass transfer between the solid and aqueous phase, moreover the number of collisions between dye molecules and adsorbent is increases, increasing the adsorption [20]. The increase in dye concentration, don't affect the adsorption yield. This will be attributed to the unsaturation of adsorption sites on the adsorbent surface [21].

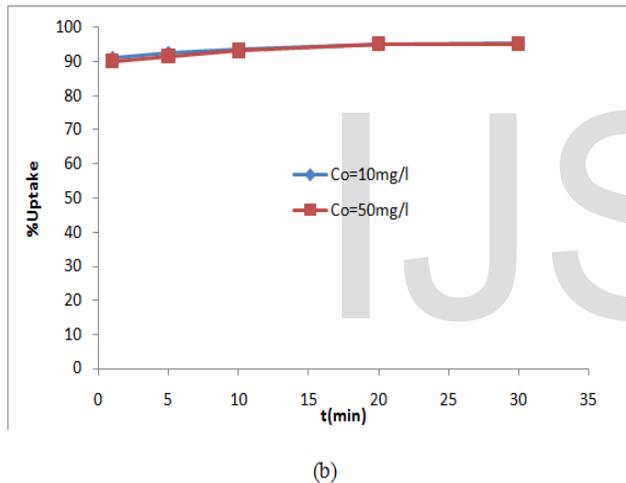
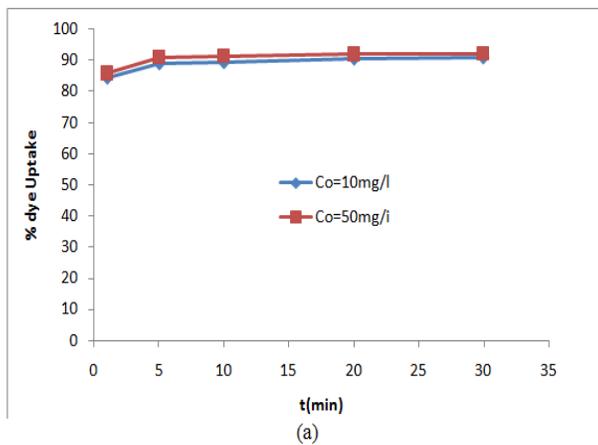


Fig.4 Effect of varying initial dye concentration on the uptake of the two dye  
 (a): BB (b): EBT  
 At pH=1, T=298K, m=0.2gBCC, t=30min

### 3.5 Adsorption Kinetic Study

In order to investigate the adsorption of BB, and EBT dyes onto BCC, pseudo-first-order, pseudo-second-order, Bangham and intra-particle diffusion models were used.

The pseudo-first-order equation is given by

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ ) are the adsorption capacities at equilibrium and at time  $t$ , respectively. The rate constant  $k_1$  ( $\text{min}^{-1}$ ) and the

process activation energy were obtained from the slope of the plot of  $\log(q_e - q_t)$  versus  $t$  for each adsorbent [22]. For BB dye these values ( $k_1=0.122$ , and  $0.193\text{min}^{-1}$  for  $C_0= 10$ , and  $50\text{mg.L}^{-1}$ , respectively) and for EBT dye, ( $k_1=0.064$ , and  $0.198\text{min}^{-1}$  for  $C_0= 10$ , and  $50\text{mg.L}^{-1}$ , respectively). The pseudo-second-order model [23] is represented by

$$q_e = \frac{t}{(1/h) + (1/q_e)t} \quad (5)$$

$$h = k_2 \cdot q_e^2 \quad (6)$$

Where  $k_2$  is the pseudo-second-order rate constant ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ). The initial sorption rate,  $h$  ( $\text{mg.g}^{-1}.\text{min}^{-1}$ ). the value of  $q_e$  and  $h$  can be calculated from a plot of  $t/q_t$  versus  $t$ . Since  $q_e$  is known from the slope, the value of  $k_2$  can be determined from the value of  $h$ . The  $q_e$  values for the pseudo-first-order model and pseudo-second-order models are also shown in Table (3), for BB, and EBT dyes. The calculated correlation coefficients,  $R^2$  (linear) are closer to unity for pseudo second-order kinetics than those for the pseudo first-order kinetics. Therefore, the sorption can be more appropriately approximated by the pseudo-second-order kinetic model for the adsorption of both BB, and EBT dyes.

Bangham's equation [22] is given as

$$\log \log \left( \frac{c_0}{c_0 - q_t.m} \right) = \log \left( \frac{k_0.m}{2.303.V} \right) + \alpha \log(t) \quad (7)$$

Where  $V$  is the volume of the solution (ml),  $\alpha$  ( $<1$ ) and  $k_0$  are constants. As shown in Table (3) when the initial concentration ( $C_0$ ) increased, the values of  $k_0$  decreased for BB, and EBT dyes. The calculated correlation coefficients,  $R^2$  (linear) (shown in Table (3)) are closer to unity for the adsorption of BB, and EBT dyes by BCC, which give a proof that the Bangham's equation can be considered also as an approximation for the kinetic behavior of the dyes considered.

Intra-particle diffusion study

The possibility of intra-particle diffusion resistance

TABLE 3

Kinetic parameters calculated for the removal of BB and EBT dyes using  $R^2$  is the correlation coefficient

affecting adsorption was explored by using the intra-particle diffusion model [22] as

Dye	Con c (mg/ L)	Pseudo-first-order			Pseudo-second-order		
		$K_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g)	$R^2$	$K_2$ (g $\text{mg}^{-1}$ $\text{min}^{-1}$ )	$q_e$ (mg/ g)	$R^2$
BB	10	0.122	0.368	0.895	1.203	6.494	0.9999
	50	0.193	2.173	0.844	0.278	27.03	0.9990
EBT	10	0.064	0.0009	0.941	327.42	0.019	0.9990
	50	0.198	1.0083	0.947	67.216	0.091	0.9999

$$q_t = k_s t^{1/2} + I \tag{8}$$

Where  $k_s$  is the intra-particle diffusion rate constant and values of  $I$  give an idea about the thickness of the boundary layer, i.e., the larger the intercept, the greater is the boundary layer effect [24]. A plot of  $q_t$  versus  $t^{1/2}$  is presented for adsorption of BB, and EBT dyes onto BCC. From Table (3), it may be seen that intraparticle diffusion is one of the rate determining step [25].

### 3.6 Adsorption Equilibrium Study

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like those of Freundlich, Langmuir, and Temkin have been used to describe the equilibrium characteristics of adsorption.

The Freundlich isotherm [22] is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface.

The Freundlich isotherm is given as

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \tag{9}$$

Where  $K_f$  is the Freundlich constant ( $1 \text{ mg}^{-1}$ ), and  $(1/n)$  is the heterogeneity factor. A plot of  $\log q_e$  versus  $\log c_e$  enables the determination of the isotherm constants  $1/n$  and  $K_f$  from the slope and the intercept, respectively.

The isotherm constants and the correlation coefficients,  $R^2$  are listed in Table (4) for the BB, and EBT dyes respectively. The correlation coefficients for the Freundlich isotherms are higher at low temperatures for BB dye, while for EBT dye the correlation coefficient values are almost near to each other. From Table (4) it is found that the determination coefficients values for the Freundlich isotherm are higher than the values obtained for the Langmuir isotherm for BB, and EBT dyes.

In the Langmuir theory [22], the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent.

The Langmuir equation [26] is given as

$$\frac{c_e}{q_e} = \frac{c_e}{q_0} + \frac{1}{b \cdot q_0} \tag{10}$$

Where  $b$  is the Langmuir adsorption constant ( $1 \text{ mg}^{-1}$ ) related to the energy of adsorption and  $q_0$  signifies adsorption capacity ( $\text{mg} \cdot \text{g}^{-1}$ ). A plot of  $\frac{c_e}{q_e}$  versus  $c_e$  enables the determination of the isotherm constants  $q_0$  and  $b$  from the slope and the intercept, respectively.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (separation factor) defined by [27] as:

$$R_L = \frac{1}{1 + c_0 \cdot b} \tag{11}$$

where  $c_0$  is the higher value of initial dye concentration ( $\text{mg} \cdot \text{L}^{-1}$ ).  $R_L$  values indicate the type of isotherm: to be irreversible ( $R_L = 0$ ), favorable

( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), or unfavourable ( $R_L > 1$ ).

As can be seen from Table (4) that the correlation coefficients for Langmuir isotherm are almost high at low temperature for BB, and EBT dyes and the value of  $R_L$  indicates favorable type of isotherm.

TABLE 4  
Isotherm parameters for the removal of BB and EBT dyes by BCC (t=120min, and m = 0.2 g) and values of  $R^2$ .

Dye	Tem p K	Freundlich isotherm			Langmuir isotherm				Temkin Isotherm		
		1/n (mg/L)	$K_f$ (K mg/g)	$R^2$	$q_0$ (mg/g)	b (L/mg)	$R_L$	$R^2$	$K_t$	$B_1$	$R^2$
BB	298	0.744	2.393	0.965	4.587	0.9732	0.146	0.902	414.7	3.16	0.777
	305	0.888	1.758	0.974	0.936	2.782	0.056	0.993	3.871	4.057	0.811
	313	0.523	2.864	0.874	6.536	0.8999	0.156	0.861	45.02	1.711	0.747
EBT	298	0.464	11.51	0.957	2.899	114.98	0.0800	0.959	1531	302.1	0.915
	305	0.382	6.24	0.970	1.626	307.5	0.0315	0.862	7639	3.570	0.824
	313	0.334	5.09	0.954	1.215	823.1	0.0120	0.946	18334	452.0	0.921

The Temkin isotherm contains a factor that explicitly takes into the account adsorbing species—adsorbent interactions. This isotherm assumes that: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to dyes (adsorbate) – BCC (adsorbent) interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [28]. A plot of  $q_e$  versus  $\ln c_e$  enables the determination of the isotherm constants  $B_1$  and  $k_t$  from the slope and the intercept, respectively.  $k_t$  is the equilibrium binding constant (l mol<sup>-1</sup>) corresponding to the maximum binding energy and constant  $B_1$  is related to the heat of adsorption. It is evident from Table (4) that the correlation coefficient values for Temkin isotherms are relatively lower than the values obtained for Freundlich isotherm (for BB, and EBT dyes at almost all temperatures), so the Temkin isotherm cannot be used for adsorption of BB, and EBT dyes on BCC.

### 3.7 Thermodynamic Studies

Thermodynamic parameters such as Gibbs free energy  $\Delta G^0$ , enthalpy  $\Delta H^0$  and entropy  $\Delta S^0$  are calculated using the following equations:

$$\Delta G^0 = RT \ln K_L \tag{13}$$

$$\frac{\Delta G^0}{T} = \frac{\Delta H^0}{T} - \Delta S^0 \tag{14}$$

where  $R$  is the universal gas constant (8.314 kJ.kmol<sup>-1</sup>.K<sup>-1</sup>),  $T$  is temperature in Kelvin (K) and  $K_L$  is the Langmuir adsorption constant that can be obtained from the equilibrium studies. The enthalpy  $\Delta H^0$  and entropy  $\Delta S^0$  can be obtained from the slope and intercept of Van't Hoff from [29] eq.(14). From Table (5) the negative values of  $\Delta H^0$  indicate spontaneous adsorption of BB, and EBT on BCC.

TABLE 5  
Thermodynamic parameters for BB and EBT removal using BCC.

Dye	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (kJ/mol. K)	$\Delta G^0$ (kJ/mol)		
			298 °K	305 °K	313 °K
BB	2.628	122.632	-36.54 x10 <sup>3</sup>	-37.4 x10 <sup>3</sup>	-38.38 x10 <sup>3</sup>
EBT	101.73	489.28	-145.7 x10 <sup>3</sup>	-149.1 x10 <sup>3</sup>	-153.04 x10 <sup>3</sup>

## 4. CONCLUSION

The present study shows that the bentonite composite material used is an effective adsorbent for the removal of Bromophenol Blue (BB), and Eriochrome Black T (EBT) dyes from aqueous solution.

1. A higher percentage of BB, and EBT dyes removal was possible provided that the  $C_0$  in the solution was low ( $10 \text{ mg.L}^{-1}$ ) at optimum  $\text{pH}=1$ .
2. The optimum adsorbent dose was  $\approx 10$  and  $20 \text{ g.L}^{-1}$  for BB and EBT respectively.
3. The equilibrium between the adsorbate in the solution and the adsorbent surface was practically achieved in 40min for both BB and EBT dyes.
4. Adsorption kinetics were found to follow a second-order rate expression for BB, and EBT dyes.
5. Equilibrium adsorption data of BB, and EBT dyes on BCC were best represented by the Freundlich isotherm.
6. The negative values of  $\Delta G^\circ$  indicate spontaneous adsorption of BB, and EBT on BCC.

As an overall conclusion, the used bentonite – carbon black composite material showed excellent adsorptive characteristics for removal of BB, and EBT from aqueous solutions polluted by them in the industrial effluents of the textiles manufacturing factories.

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