

Preparation, Characterization Of Bentonite Carbon Composite And Design Application In Adsorption Of Bromothymol Blue Dye

Farida M. S. E. El-Dars¹, Hamed M Ibrahim², Heba A. B. Farag², M. Zakaria Abdelwahhab², M.E.H Shalabi^{3*}

¹ Chemistry Department, Faculty of Science, Helwan University, Helwan, 11795 Cairo, Egypt.

² Chemical Engineering Department, Faculty of Engineering, Minya University, Egypt

³ Central Research and Development Institute, CMRDI, Cairo. Egypt,

*Corresponding author: Central Research and Development Institute, CMRDI, Cairo. Egypt, E-mail : shalabimeh@hotmail.com .

Abstract—New bentonite carbon composite was prepared and characterized by Fourier transform infra red spectroscopy, Scanning electron microscope, X-ray fluorescence & X-ray diffraction. The X-ray diffraction profile of the composite showed different characteristics in relation to its precursor clay and coke breeze carbon, a displacement of the diffraction peaks occurs, suggesting carbon intercalation between the clay layers. The optimum adsorption efficiency for bromothymol blue dye on bentonite carbon composite, was obtained. Under these conditions the adsorbent dose was $\approx 20\text{g.l}^{-1}$, the equilibrium between the adsorbate in the solution and the adsorbent surface was practically achieved in 90min at pH 1.0. Adsorption kinetics was found to follow a pseudo-second-order rate expression and equilibrium adsorption data of bromothymol blue dye on bentonite carbon composite was best represented by the Langmuir isotherm.

Keywords—Bentonite clay; coke breeze carbon; composite; characterization; bromothymol blue

I. Introduction

Bentonites are defined as a sedimentary rock consisting of a large portion of expandable clay minerals with three-layer structures (smectites) such as montmorillonites (80%), beidellite, nontronite etc with minor amounts of non-clay minerals such as quartz, calcite, dolomite and feldspar [15]. Bentonites or smectite clays have properties such as high cation exchange capacity, are readily available and offer a low cost alternative for organic compounds removal, and are reusable [4]. Natural clays are hydrophilic and, therefore, inefficient for the adsorption of organic compounds in water. When subjected to chemical treatments, such as for example, with quaternary ammonium salts, surface properties of bentonite can be greatly changed presenting a hydrophobic and organophilic character, which exhibit a high affinity for organic compounds. These modified bentonites have been

widely used in wastewater treatment process [3, 4, 10].

Textile industries discharge large amounts of coloured wastewaters due to the unfixed dyes on fibers during the colouring and washing steps. The presence of these pollutants in water streams causes problems related to their carcinogenicity, toxicity to aquatic life and their probable undesirable aesthetic effect. Dyeing effluents are very difficult to treat, due to their resistance to biodegradability and stability to light, heat and oxidizing agents [20]. A wide range of wastewater treatment techniques have been tested [2, 11]. Biological processes are probably the most inexpensive ones, although dyes are inhibiting bacterial development [2, 11]. A pre-treatment is often necessary to increase the biodegradability. A large number of physico-chemical processes have been proposed: coagulation with alum, ferric chloride, magnesium chloride and lime or polymers, adsorption on activated carbon, polymer or mineral sorbents, chemical oxidation, photolysis, suspended or supported, photocatalysis, and electrophotocatalysis. Combination between these methods has been also utilized [2, 11].

Among the available physico-chemical treatments, adsorption is one of most promising methods for the removal of dyes from aqueous effluents; identification and development of new adsorbents has gained more importance during last decades [2].

Composite materials are engineered materials made from two or more constituent materials with significantly different physical or chemical properties and which remain separate and distinct on a macroscopic level within the finished structure. Composite materials have some advantages as: light weight, high specific stiffness and strength, ease of moldability 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, internal energy storage and release [7]. The use of bentonite carbon composite material (BCC) had been

previously evaluated for the removal of bromophenol blue, eriochrome black T, bromocresol purple and methylene blue [8, 9].

The aim of the present work is to characterize and explore the possibility of utilizing bentonite carbon composite material (BCC) for the adsorptive removal of bromothymol blue (BTB) dye from aqueous solutions. The effects of pH, contact time (t), composite dosage (m), and initial dyes concentrations (C_0) on the bentonite carbon composite material had been studied. Batch extraction mode has been employed. The kinetics of BTB adsorption onto the bentonite carbon composite material was analyzed by fitting various kinetic models. Experimental equilibrium data was fitted to the Freundlich, Langmuir, and Temkin isotherms equations to determine the best fit isotherm equation.

II. Materials and Methods

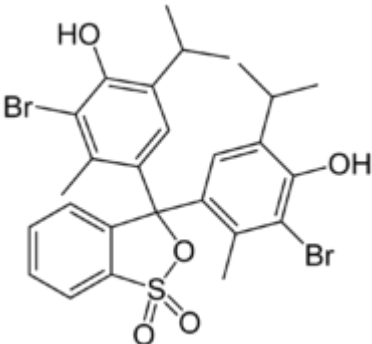
A. Materials

The bentonite used in this investigation was obtained locally from Egypt. The composition of the bentonite is illustrated in Table 1 (determined by x-ray fluorescence spectrometry XRF). The chemical composition of coke breeze used contains 84.75 % fixed carbon, 1.25% volatile matter, 14% ash.

Table 1: Chemical composition of bentonite (w/w %)

Element	w/w %
SiO ₂	61.16
TiO ₂	0.59
Al ₂ O ₃	19.44
Fe ₂ O ₃	4.6
MnO	0.06

Table 2: Chemical and physical properties of Bromothymol blue (BTB)

BTB Dye	Chemical Structure	Mol. Wt (g/mol)	λ_{max} (nm)	pK _a
Bromothymol blue (BTB)		624.38	432	7.0

MgO	2.2
CaO	1.38
Na ₂ O	1.22
K ₂ O	2.05
SO ₃	0.5
L.O.I, 1000 °C	6.8

B. Composite preparation

Bentonite carbon composite material (50% bentonite and 50% activated carbon) were heated together in a muffle furnace at 1000 °C for one hour at inert atmosphere as described previously [8,9].

The molecular weight of the adsorbate, (BTB dye) and the maximum wavelengths of absorbance (λ_{max}) are shown in Table 2. An accurately weighed quantity of the dye was dissolved in bidistilled water to prepare a stock solution (1000 mg.l⁻¹). Experimental solutions of the desired concentrations were obtained by dilutions.

C. Materials characterization

X-ray diffraction pattern were performed using a Bruker D8 Advance Phaser diffractometer operated under the following conditions: 40 kV, 40 mA, copper source ($\lambda = 1.45\text{\AA}$ step 0.02 (2 θ), with time of 0.4 s per step; scanning range 4°-70° (2 θ).

The infrared spectra were obtained using a Gasco FTIR-6300 spectrophotometer. The Fourier transform infrared (FTIR) spectra were collected in the range of 400-4000cm⁻¹.

The surface of the char obtained was viewed under a Scanning Electron Microscope SEM (FASEM – Quanta FEG 250).

D. Characteristics

The surface area of the adsorbent (BCC) was calculated to be $(174.3 \text{ m}^2 \cdot \text{g}^{-1})$ using methylene blue $(0.02 \text{ g} \cdot \text{l}^{-1})$ [13] as follows:

$$A_s = G N_{AV} \emptyset 10^{-20} / M M_W \quad (1)$$

Where G is the amount of methylene blue adsorbed (g), N_{AV} is Avogadro's number (6.023×10^{23}) , \emptyset is the methylene blue molecular cross-section (197.2 \AA^2) , where \AA is angstrom unit, M_W is the molecular weight of methylene blue $(319.3 \text{ g} \cdot \text{mol}^{-1})$, and M is the mass of the BCC adsorbent.

Pycnometer was used to determine the density of homogeneous solid object that does not dissolve in working liquid (water). The volume of added water V'_{H_2O} was obtained as

$$v'_{H_2O} = \frac{m'_{H_2O}}{\rho_{H_2O}} \quad (2)$$

The volume of measured solid object V_s is the difference between the volume of water that fills the empty pycnometer V and volume V'_{H_2O}

$$v_s = v - v'_{H_2O} = \frac{m_{H_2O} - m'_{H_2O}}{\rho_{H_2O}} \quad (3)$$

Density of measured object ρ_s can be then calculated as

$$\rho_s = \frac{m_s}{v_s} \quad (4)$$

According to the pycnometer method the density of the local bentonite, coke breeze, and bentonite carbon composite (50% - 50%) were 0.595, 1.295, and $0.95 \text{ g} \cdot \text{cm}^{-3}$ respectively.

The particle size distributions of bentonite, coke breeze, and bentonite carbon composite (50% - 50%) materials were presented in Figs. 1, 2, and 3 respectively. Based on the analysis of the given diagram the average particle diameter size D_{50} for bentonite, coke breeze, and bentonite carbon composite were 0.115mm, 0.08mm, and 0.33mm respectively.

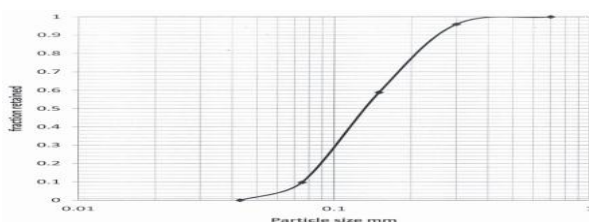


Fig. 1: Particle size distribution for bentonite

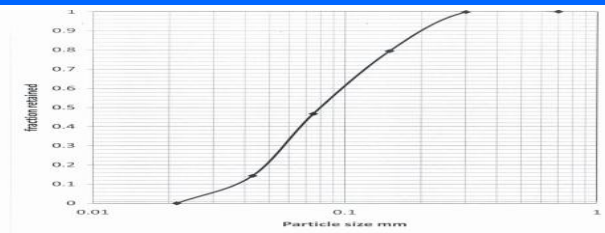


Fig. 2: Particle size distribution for coke breeze

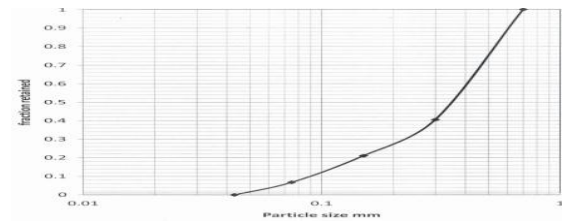


Fig. 3: Particle size distribution for BCC

E. Analytical measurements

Concentrations of dyes were determined by finding out the absorbance at the characteristic wave length using a double beam UV/VIS (Jasco v - 630 double beam spectrophotometer, Japan, using quartz cuvettes, its photometric accuracy is ± 0.005 Abs. at 1.0 Abs.). Filtration of dyes were obtained using centrifuge (Benchtop centrifuges C2006, Frequency :50 – 60 Hz, type:T6 – 3A). Temperature- controlled shaker (model RUMO 4050 with shaking rate 10-250 rpm) was used for agitation.

F. Batch experimental program

To study the effect of important parameters like pH, BCC dosage (m), and contact time (t) on the adsorptive removal of BTB dye, batch experiments were conducted at 298 K. For each experimental run, 20 ml of BTB solutions of known concentration, and pH and a known amount of the composite material (BCC) were taken in stoppered bottles. These mixtures were agitated in the temperature-controlled shaker at a constant speed of 250 rpm. The effect of pH on BTB dye removal was studied over a pH range from 1 to 10. pH was adjusted using NaOH or HCl solutions. For determination of optimum m, 20ml aliquots containing the tested dye was contacted with different amount of composite adsorbent till equilibrium was attained. The kinetics of adsorption was determined by analyzing the adsorptive uptake of the tested dye from the aqueous solution at different time intervals. For adsorption isotherms, BTB solutions of different concentrations $(10 - 50 \text{ mg} \cdot \text{l}^{-1})$ were agitated with the adsorbent at the optimum (m) till the equilibrium was achieved.

III. Results and Discussion

The XRD patterns of bentonite clay, coke breeze and bentonite carbon composite (50% - 50%) were presented at Figs. (4, 5, 6). In the scattering curve of the bentonite a prominent broad peak occur at

$2\theta=25^\circ$. Bentonite carbon composite sample (50% - 50%) were characterized by x-ray diffraction fig. (6), it can be observed that the composite material has a peak indicating that they are layered material of the montmorillonite clay type. A displacement in the diffraction peaks was observed for the composite is due to the process of intercalation of the carbon between the layers of clay. It was noted that local bentonite possessed a 2θ peak at approximately 14.02° , which was not present for the composite, suggesting the presence of carbon in the composite [5].

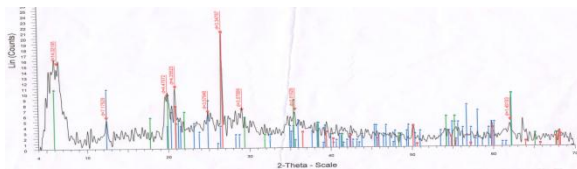


Fig. 4: X-ray diffraction patterns of local bentonite

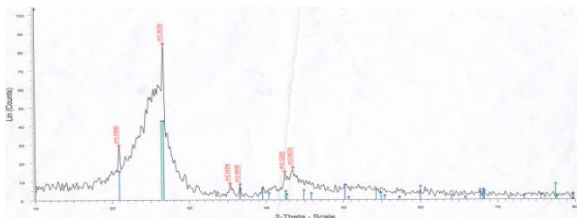


Fig. 5: X-ray diffraction patterns of coke breeze

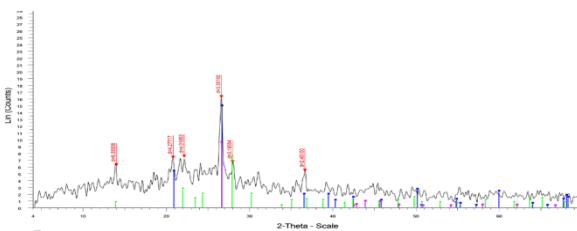


Fig. 6: X-ray diffraction patterns of bentonite carbon composite

Figs. 7, 8, and 9 illustrated FTIR spectra of the local bentonite, coke breeze, and bentonite carbon composite (50% - 50%) band at 3698.8 cm^{-1} , 3864.65 cm^{-1} , and 3918.64 cm^{-1} is corresponding to stretching (OH-) for the local bentonite, coke breeze, and bentonite carbon composite (50% - 50%) respectively, the band at 3621.66 cm^{-1} , 3710.037 cm^{-1} , and 3814.51 cm^{-1} is corresponding to stretching (OH-) also. The observed bands at 3444.24 , 3432.67 , and 3428.81 is corresponding to OH-vibrations (stretching). The band observed at 1643.05 cm^{-1} , 1527.35 cm^{-1} , and 1527.35 cm^{-1} for the local bentonite, coke breeze, and bentonite carbon composite (50% - 50%) respectively is due to adsorbed water. The band at 1033.66 cm^{-1} , 1056.8 cm^{-1} , and 1079.94 cm^{-1} for the local bentonite, coke breeze, and bentonite carbon composite (50% - 50%) respectively is related to the Si-O vibrations. Peaks characteristic of the octahedral sheets present in the clay can be observed between 532.257 cm^{-1} , and 462.832 cm^{-1} [5].

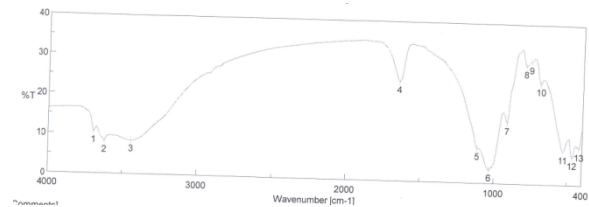


Fig. 7: FTIR spectrum of local bentonite

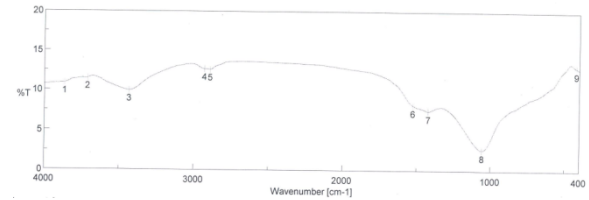


Fig. 8: FTIR spectrum of coke breeze

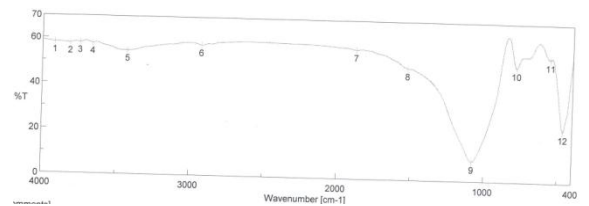


Fig. 9: FTIR spectrum of BCC

Table (3): Result of peak picking for local bentonite

No	1	2	3	4	5	6	7	8	9	10	11	12	13
Position	3698.8	3621.7	3444.2	1643.1	1114.6	1033.7	914.1	790.7	755.9	690.4	532.3	466.7	420.4
Intensity	10.433	8.064	8.386	24.804	8.7007	3.4150	15.170	29.479	30.537	25.11	8.286	6.966	9.066

Table (4): Result of peak picking for coke breeze

No	1	2	3	4	5	6	7	8	9
Position	3864.7	3710.4	3432.7	2931.3	2892.7	1527.4	1432.2	1056.8	420.4
Intensity	10.88	11.47	9.943	12.65	12.58	8.184	7.463	2.615	12.99

Table (5): Result of peak picking for BCC

No	1	2	3	4	5	6	7	8	9	10	11	12
Position	3918.6	3814.5	3748.9	3664.1	3428.8	2927.4	1878.3	1527.4	1079.9	786.8	555.4	462.8
Intensity	58.12	57.71	58.10	57.77	54.77	57.39	57.04	49.3	8.79	50.47	54.53	22.88

Figs. 10, 11, 12 show the SEM images of the local bentonite, coke breeze, and bentonite carbon composite (50% - 50%). The bentonite clay evidences aggregates of uniform size and shape and of a porous nature, in the form of large rounded pieces with no sharp points. The coke breeze evidences irregular shapes, such as those of broken glass, while the clay contains less irregular shapes of varying sizes. In the electronic scanning micrographs of the bentonite carbon composite (Fig. 12), it can be

seen various coke breeze fragments can be observed on the bentonite clay surface [5].

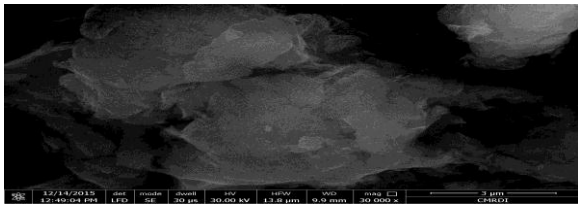


Fig. 10: SEM image for bentonite

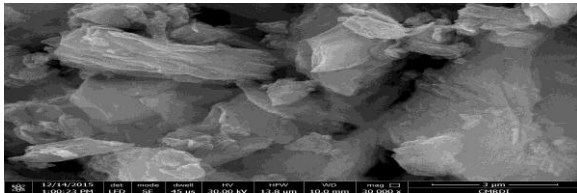


Fig. 11: SEM image for coke breeze

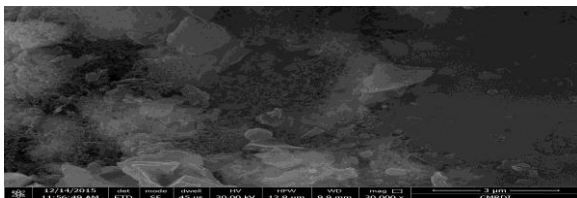


Fig. 12: SEM image for BCC

A. Effect of pH

The pH is one the most important factors controlling the adsorption of dye onto adsorbent. Fig. 13 shows the percent uptake with the composite material over a pH range from 1 to 10. It was found that the color was stable. The percent uptake decreased for BTB as pH increased. This is because at low pH, the adsorbent surface is positively charged and this will lead to a significantly strong electrostatic attraction between the positively charged bentonite carbon composite surface and the anionic dye molecules thus resulting in an increase in dye adsorption [18].

B. Effect of contact time

The effect of contact time on percent uptake of dyes by the BCC is shown on Fig. 14. The % uptake increased gradually as the contact time increase for BTB.

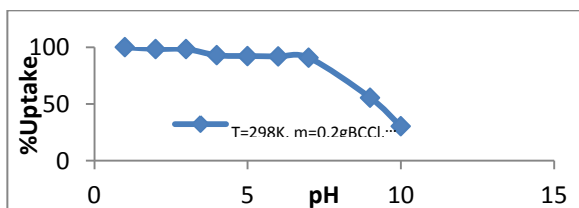


Fig. 13: Effect of pH on the uptake of the BTB dye

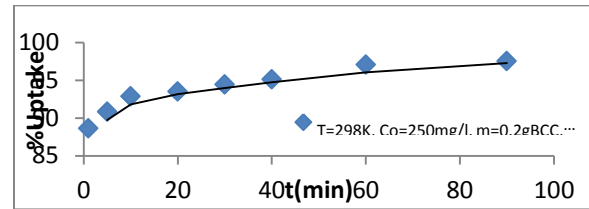


Fig. 14 Effect of contact time on the uptake of the BTB dye

C. Effect of the adsorbent dosage

The effect of BCC dosage (m) on the percent uptake of the BTB dye at $C_{0BTB} = 250 \text{ mg.l}^{-1}$ and $T=298\text{K}$ is carried out in Fig. 15. The adsorption in case of BTB is clear to be constant beginning from a dose of 20g.l^{-1} , which may suggest an equilibrium condition.

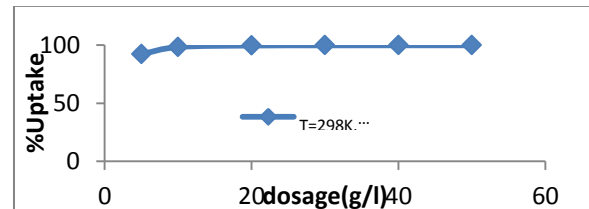


Fig. 15: Effect of BCC dosage on the uptake of the BTB dye

IV. Adsorption kinetic study

In order to investigate the adsorption kinetics of BTB dye onto BCC, pseudo-first order, pseudo-second-order, Bangham and intra-particle diffusion models were trialed.

A. Pseudo-first-order model

The pseudo-first-order equation is given by equation (1)

$$\log(Q_e - Q_t) = \log Q_e - (k_f / 2.303)t \quad (1)$$

The values of the adsorption rate constant (k_f) for BTB dye adsorption on BCC were determined from the plot of $\log(Q_e - Q_t)$ versus t [17] (shown in Table 6).

B. Pseudo-second-order model

The pseudo-second-order model [12] is represented by :-

$$Q_t = t / ((1/h) + (1/Q_e)t) \quad (2)$$

$$h = k_s \cdot Q_e^2 \quad (3)$$

Where k_s is the pseudo-second-order rate constant ($\text{g.mg}^{-1}.\text{min}^{-1}$), h is the initial sorption rate ($\text{mg.g}^{-1}.\text{min}^{-1}$). 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_s can be determined from the value of h . The best-fit values of h , Q_e and k_s along with correlation coefficients for the

pseudo-first-order and pseudo-second-order models are shown in Table 6. Therefore, the sorption can be more appropriately approximated by the pseudo-second-order kinetic model for the adsorption of BTB dye.

Table 6: Kinetic parameters for the removal of BTB dye by BCC (T =298K, Co = 200 and 250mg.l⁻¹, m = 0.2 g)

P1 st order				
C ₀ (mg.l ⁻¹)	Q _e (mg.g ⁻¹)	k _f (min ⁻¹)	R ² (linear)	
200	0.0748	0.02994	0.962	
250	0.0885	0.02764	0.942	
P2 nd order				
C ₀ (mg.l ⁻¹)	Q _e (mg.g ⁻¹)	h(mg.g ⁻¹ .min ⁻¹)	K _f (g.mg ⁻¹ .min ⁻¹)	R ² (linear)
200	0.800	1.0373	1.6208	0.999
250	0.985	1.3514	1.3928	0.999
Bangham				
C ₀ (mg.l ⁻¹)	K ₀ (g)	α	R ² (linear)	
200	0.0715	0.022	0.961	
250	0.0704	0.023	0.954	
I.P.-diffusion				
C ₀ (mg.l ⁻¹)	K _{id1} (mg.g ⁻¹ .min ^{-1/2})	I _f (mg.g ⁻¹)	R ² (linear)	
200	0.009	0.716	0.972	
250	0.011	0.885	0.957	

C. Bangham's equation

Bangham's equation [17] presented as

$$\log \log (C_0 / (C_0 - Q_t)) = \log (k_0 m / 2.303 V) + \alpha \log (t), \quad (4)$$

Where V is the volume of the solution (ml), α (<1) and k₀ are constants. As shown in Table 6 when the initial concentration (C₀) increased, the values of k₀ decreased for BTB dye. The calculated correlation coefficients, R² (linear) (shown in Table 6) are closer to unity for the adsorption of BTB dyes by BCC.

D. Intra-particle diffusion study

The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intra-particle diffusion model [17] presented as:-

$$Q_t = k_{id} t^{1/2} + I, \quad (5)$$

Where k_{id} 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 [14]. From Table 6, it may be seen that intraparticle diffusion is one of the rate determining step for BTB [1].

V. 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, those of Freundlich, Langmuir,

and Temkin have been used to describe the equilibrium characteristics of adsorption.

A. Freundlich isotherm

Freundlich isotherm [17] 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:-

$$\log Q_e = \log K_f + (1/n) \log C_e, \quad (6)$$

Where (K_f = K_R / a_R) is the Freundlich constant (l.mg⁻¹). A plot of logQ_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, R² are listed in Table 7 for the BTB dye.

B. Langmuir isotherm

Langmuir equation [6] is given as:-

$$C_e / Q_e = (C_e / Q_m) + (1 / K_L Q_m), \quad (7)$$

A plot of C_e/Q_e versus C_e enables the determination of the isotherm constants Q_m and K_L 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 [16] as:-

$$R_L = 1 / (1 + C_0 K_L) \quad (8)$$

Where C₀ is the higher value of initial dye concentration (mg.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) . From Table 7 it is found that the determination coefficient values for the Langmuir isotherm are higher than the values obtained for the Freundlich isotherm for BTB dye.

C. Temkin isotherm

The Temkin isotherm is given as [17]:

$$Q_e = RT/b \log(A C_e), \quad (9)$$

$$Q_e = B_1 \log A + B_1 \log C_e \quad (10)$$

It is evident from Table 7 that the correlation coefficient values for Temkin isotherms are relatively lower than the values obtained for Langmuir isotherm for BTB dye at almost all temperatures, so the Temkin isotherm cannot be used for adsorption of these dyes on BCC.

Table 7: Isotherm parameters for the removal of BTB dye by BCC (t=120min, and m = 0.2 g)

Freundlich				
T(K)	$K_d(\text{mg g}^{-1})(\text{mg l}^{-1})^{-1/n}$	1/n		$R^2(\text{linear})$
298	0.263	0.261		0.888
305	0.0796	0.460		0.952
313	0.136	0.279		0.925
Langmuir				
T(K)	$K_L(\text{l mg}^{-1})$	$Q_m(\text{mg g}^{-1})$	R_L	$R^2(\text{linear})$
298	0.1427	0.8097	0.0655	0.994
305	0.0217	0.9074	0.315	0.945
313	0.0182	0.6301	0.355	0.937
Temkin				
T(K)	$A(\text{l mg}^{-1})$	B_1		$R^2(\text{linear})$
298	1.1625	0.292		0.950
305	0.8007	0.431		0.915
313	1.0119	0.234		0.847

VI. Thermodynamic studies

Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_L \quad (11)$$

$$\Delta G^\circ/T = \Delta H^\circ/T - \Delta S^\circ \quad (12)$$

Where R is the universal gas constant ($8.314 \text{ kJ}\cdot\text{kmol}^{-1}\cdot\text{K}^{-1}$), T is temperature in Kelvin (K) and K_L is the Langmuir adsorption constant that can be obtained from the equilibrium studies. The enthalpy (ΔH°) and entropy (ΔS°) can be obtained from the slope and intercept of Van't Hoff from (12) [19].

From Table 8 the negative values of ΔG° indicate spontaneous adsorption of BTB on BCC.

Table 8: Thermodynamic parameters of adsorption of BTB dye on BCC

	$\Delta G (\text{KJ mol}^{-1})$			$\Delta H (\text{KJ mol}^{-1})$	$\Delta S (\text{J mol}^{-1} \cdot \text{K}^{-1})$
	298K	305K	313K		
BTB	-78.098×10^3	-79.93×10^3	-82.024×10^3	-105.84	261.72

VII. Conclusions

The characterization results showed the intercalation of activated carbon between the layers of the bentonite clay. The composite material (BCC) prepared at 1000°C showed better efficiency in removal of bromothymol blue (BTB) than carbon, suggesting enhancement of in their properties as adsorbent in general. The results indicate that the morphology, surface area and chemical composition of the composites play an important role in adsorption processes, especially for removal of dyes in wastewater.

A higher percentage of BTB dye removal was possible provided that the C_0 in the solution was low (10 mg. l^{-1}) at optimum $\text{pH}=1$. The optimum adsorbent dose was $\approx 20 \text{ g. l}^{-1}$ for BTB dye. The equilibrium between the adsorbate in the solution and the adsorbent surface was achieved in 90min for

BTB dye. Adsorption kinetics was found to follow a **pseudo-second-order** rate expression for BTB dye. Equilibrium adsorption data of BTB dye on BCC was best represented by the **Langmuir** isotherm. The negative values of ΔG° indicate spontaneous adsorption of BTB on BCC.

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