

Using bentonite carbon composite material for adsorption of bromocresol purple and methylene blue

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Abstract - This study deals with the adsorption of bromocresol purple (BCP), and methylene blue (MB) dyes onto bentonite carbon composite material (BCC). Batch studies were performed to evaluate the influence of various experimental parameters: pH, contact time (t), adsorbent dose (m) and initial dye concentration (C_0). Optimum conditions for removal of BCP, and MB dyes were found to be: $m = 30$ and 40 gram per liter respectively, and the equilibrium between the adsorbate in the solution and the adsorbent surface was practically achieved in 60min for both BCP and MB dyes. The results showed that adsorption kinetics were found to follow a pseudo-second-order rate expression for the two dyes with a degree of inert particle diffusion and it was found to be best represented by the Langmuir isotherm.

Index Terms - Bentonite carbon composite material, bromocresol purple, methylene blue.,

1 INTRODUCTION

The pollution of water resources with industrial effluents containing organic compounds and toxic substances is a matter of great concern. Environmental contamination has been pointed as one of the greatest problems of modern society, mainly due to the population explosion and the increased industrial activity [1,2]. Generally, effluents from textile industries, paper printing and photography contain residues of dyes and chemicals. However, the textile industry stands out because it produces large amounts of effluents which can cause serious environmental problems since they contain colored compounds resulting from dyes unfixed to fibers during the dyeing process [2]. Synthetic dyes have increasingly been used in the textile and dyeing industries due to low-cost in synthesis, high stability to light and temperature, compared with natural dyes [3].

Dye molecules have two major components: the chromophore groups, responsible for making the colour such as $-C=C-$ and $-N=N-$, and the auxochrome groups, as for example: $-NH_2$, $-OH$, $-COOH$ and $-SO_3H$, which render the solubility of the molecules and give affinity for the fibers [2,3]. Synthetic dyes in the water bodies, even at very low concentrations, can be highly toxic to living organisms, reducing the growth of bacteria and preventing the photosynthesis in aqueous flora [4 - 6]. Due to the dyes are recalcitrant molecules having complex aromatic structures, they are usually biologically non-degradable and present high stability and toxicity. Most of the dyes decompose to give out hazardous products, such as carbon monoxide (CO), carbon dioxide (CO₂) and hydrogen chlorides and can reduce light penetration photosynthesis [7] and it is therefore necessary to eliminate organic pollutants by proper treatment techniques. Removal methods of dye molecules from water can be classified in many categories such as physical, chemical, biological, radiation and electrochemical processes.

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Among these methods, adsorption can be thought to be efficient process for the treatment of wastewater due to its low-cost and ease of operation as well as greater efficiency. Although activated carbon seems to be an efficient adsorbent, it has high operation costs. For this reason, many studies revealed that other alternative adsorbents such as clays, including bentonite [3,8], montmorillonite [9], sepiolite [10], raw red mud [11] and zeolite [12], are used as adsorbents which could effectively treat wastewaters. 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 [13]. 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 [3,13,14].

The aim of the present work is to explore the possibility of utilizing bentonite carbon composite material for the adsorptive removal of dyes from aqueous solutions. The use of bentonite carbon composite materials (BCC) have been evaluated for the removal of bromocresol purple (BCP) and methylene blue (MB). 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 BCP, and MB adsorption onto the bentonite carbon composite material were 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.

2 EXPERIMENTAL

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 [15]. 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 [15]:

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

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

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
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

2.2 Preparation of Dye Stock Solutions:

The chemical and physical properties of the tested dyes (BCP and MB), including chemical structure, molecular weights, dissociation constant (pK_a) and maximum wavelengths of absorbance (λ_{max}) are shown in Table (2). To prepare a 1000 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 (λ_{max}) using a double beam UV/VIS (JASCO V-630 double beam Spectrophotometer, Japan).

2.3 Adsorption Experiments

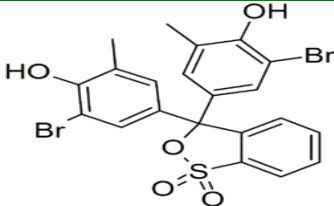
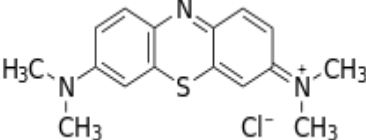
Batch adsorption experiments were carried out in a thermostated water bath/shaker at a constant shaking rate (model RUMO 4050; shaking rate 10-250 rpm). The effect of contact time, concentration, solution pH, adsorbent dose and temperature were studied. 20 mL of dye solution of known concentration (10- 50 mg.L⁻¹) were shaken in stoppered bottles with different weights of adsorbent material (5- 50 g.L⁻¹) 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, BCP, and MB solutions of different concentrations (10 and 50 mg.L⁻¹) were agitated with the adsorbent at optimum (m) till the equilibrium was achieved.

The %of dye removal was calculated as follows [16]:

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

TABLE 2: Chemical and physical properties of Bromocresol purple (BCP) and Methylene blue (MB)

(MB Dye	Chemical Structure	Mol. Wt (g/mol)	λ_{max} (nm)	pK_a
Bromocresol purple (BCP)		540.22	432	6.3
Methylene blue (MB)		319.85	665	3.8

where C_0 and C_f are the initial and final concentration of dye in solution (mg.L^{-1} or ppm), respectively. The amount of dye accumulated per unit mass of adsorbent was evaluated using the following equation [16]:

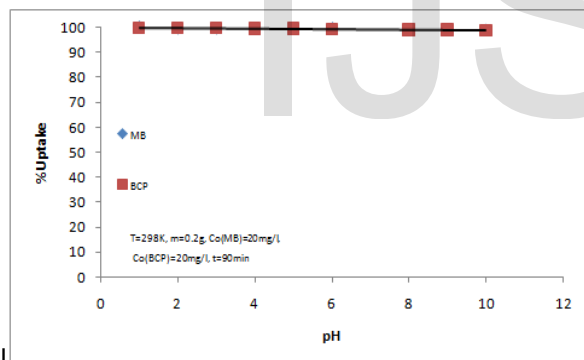
$$q_t = (C_0 - C_t) V/m \quad (3)$$

where m is the weight of sorbent used (g) and V is the volume of dye solution (L). At equilibrium 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).

3 RESULT AND DISCUSSION

3.1 Effect of pH

The pH is one the most important factors controlling the adsorption of dye on to adsorbent. As the pH increases, it is usually expected that adsorption also increases. Fig.(1) shows the percent uptake with composite materials over a pH range from 1 to 10. It was found that the colour was stable. The percent uptake for both BCP, and MB was nearly 100% at all pH values.

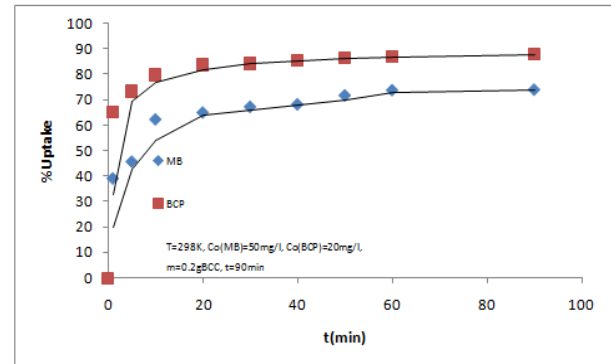


Fig(1): Effect of pH on the uptake of the two dyes

3.2 Effect of contact time

The effect of contact time on percent uptake of dyes by the BCC is shown on Fig.(2). A rapid adsorption of both dyes was observed in the first fifteen minutes. The adsorption rates then decreased gradually and the adsorption reached equilibrium in about 60 min for both dyes. In batch type adsorption process monolayer of adsorbate is generally formed on the surface of adsorbent and removal rate of adsorbate species from aqueous

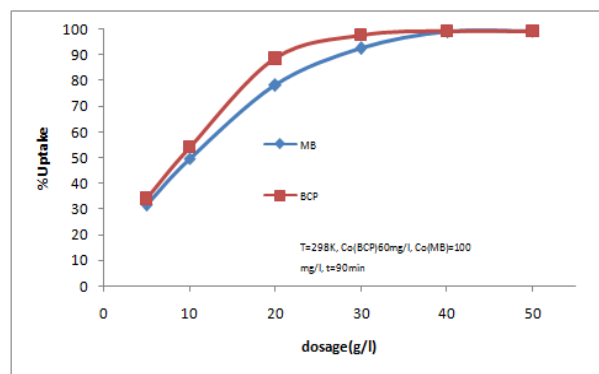
solution is controlled especially by the rate of transport of the adsorbate species from the outer sites to interior sites of the adsorbent particulars [17].



Fig(2): Effect of contact time on the uptake of the two dyes

3.3 Effect of Adsorbent Dose

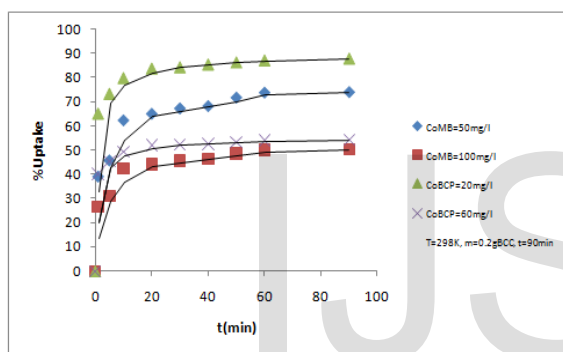
The effect of BCC dosage (m) on the percent uptake of the dyes (BCP, and MB) by BCC at $C_{0BCP}=60 \text{ mg.L}^{-1}$, $C_{0MB}=100 \text{ mg.L}^{-1}$ and $T=298\text{K}$ is carried out and the percent uptake of the dye from aqueous solutions was found to increase to a certain limit 30 and 40 g.L^{-1} (for BCP, and MB respectively) and then it remained almost constant (shown in Fig.(3)). This is due to the availability of more binding sites as the dose of BCC increases [18]. However the removal will grow up to certain limit and then remains constant, the limit in each case is still related to the effect of adsorbate on adsorption [19].



Fig(3): Effect of the dosage 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 percent uptake of the BCP, and MB dyes by BCC was investigated using dyes concentrations ranging between 20 – 60 mg.L⁻¹ for BCP and 50 – 100 mg.L⁻¹ for MB. Although the C_0 increased from 20 to 60 mg.L⁻¹, the percent uptake decreased from 87.88% to 54.1% for BCP also decreased from 74% to 50% for MB although the C_0 increased from 50 to 100mg.L⁻¹ (shown in Fig.(4)). The C_0 provides the driving force to overcome the resistances to the mass transfer of dyes between the aqueous and the solid phases. Therefore, an increase in C_0 of the dyes enhances the adsorption uptake due to increase in the driving force [20].



Fig(4): Effect of varying initial dye concentration on the uptake of the two dy

3.5 Adsorption kinetics

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

3.5.1 Pseudo-first-order model

The pseudo-first-order equation is given by equation (4)

$$\log(Q_e - Q_t) = \log Q_e - (k_f/2.303)t \quad (4)$$

Where Q_t is the amount of dye (adsorbate) adsorbed at time t per unit mass of adsorbent (mg.g⁻¹), Q_e the adsorption capacity at equilibrium (mg.g⁻¹), k_f the pseudo-first-order rate constant (min⁻¹), and t the contact time (min).

The values of the adsorption rate constant (k_f) for BCP, and MB dye adsorption on BCC were determined from the plot of $\log(Q_e - Q_t)$ versus t [20]. Table (3) shows the kinetic parameters for BCP, and MB dyes.

3.5.2 Pseudo-second-order model

The pseudo-second-order model [21] is represented by equation (5)

$$Q_t = t / ((1/h) + (1/Q_e)t) \quad (5)$$

$$h = k_s \cdot Q_e^2 \quad (6)$$

Where k_s is the pseudo-second-order rate constant (g.mg⁻¹.min⁻¹). The initial sorption rate, h (mg.g⁻¹.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 (3) for BCP, and MB dyes. The Q_e values for the pseudo-first-order model and pseudo-second-order models are also shown in Table (3) for BCP, and MB 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 BCP, and MB dyes.

3.5.3 Bangham's equation

Bangham's equation [20] is given as

$$\log \log (C_0 / (C_0 - Q_t \cdot m)) = \log (k_0 m / 2.303V) + \alpha \log(t) \quad (7)$$

Where V is the volume of the solution (ml), α (<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 BCP, and MB dyes. The calculated correlation coefficients, R^2 (linear) (shown in Table (3)) are closer to unity for the

TABLE 3: Kinetic parameters calculated for the removal of BCP and MB dye using BCC ($T = 298K$, $Co_{BCP} = 20$ and $60mg.L^{-1}$, $Co_{MB} = 50$ and $100mg.L^{-1}$, $m = 0.2$ g) where R^2 is the correlation coefficient

Dye	Conc (mg/L)	Pseudo-first-order			Pseudo-second-order				Intra-particle Diffusion			Bangham		
		K_f (min^{-1})	Q_e (mg/g)	R^2	K_s ($g mg^{-1} min^{-1}$)	Q_e (mg/g)	h ($mg g^{-1} min^{-1}$)	R^2	K_{id} ($m g g^{-1} min^{-0.5}$)	I (mg/g)	R^2	k_o ($mL L^{-1} g^{-1}$)	α	R^2
BCP	20	0.048	0.0138	0.94	13.107	0.0708	0.0657	0.999	0.002	0.054	0.808	0.053	0.068	0.962
	60	0.062	0.029	0.899	7.738	0.1309	0.1326	0.999	0.003	0.101	0.792	0.032	0.071	0.952
MB	50	0.0691	0.0839	0.849	2.301	0.1578	0.0573	0.998	0.008	0.086	0.831	0.0316	0.152	0.933
	100	0.0691	0.1074	0.85	1.778	0.205	0.0747	0.998	0.011	0.112	0.83	0.0213	0.152	0.935

adsorption of BCP, and MB 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.

3.5.4 Intra-particle diffusion study

The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intra-particle diffusion model [20] as

$$Q_t = k_{id} t^{1/2} + I, \quad (8)$$

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 [22]. From, (Table (3)), it may be seen that there is one single straight line for each concentration (C_0), i.e. an initial linear portion or rapid adsorption stage takes place, so intraparticle diffusion is one of the rate determining step [23].

3.6 Adsorption isotherm models

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.

3.6.1 Freundlich isotherm

The Freundlich isotherm [20] 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

$$\log Q_e = \log K_f + (1/n) \log C_e, \quad (9)$$

Where K_f is the Freundlich constant ($L.mg^{-1}$), 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 BCP, and MB dyes respectively. The correlation coefficients for the Freundlich isotherms are higher at low temperatures for both dyes.

3.6.2 Langmuir isotherm

In the Langmuir theory [20], the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent.

Langmuir equation [24] is given as

$$C_e/Q_e = (C_e/Q_m) + (1/K_L Q_m), \quad (10)$$

Where K_L is the Langmuir adsorption constant ($L.mg^{-1}$) related to the energy of adsorption and Q_m signifies adsorption capacity ($mg.g^{-1}$). 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 by [25] as:

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

TABLE 4: Isotherm parameters for the removal of BCP and MB dyes by BCC (t=90min, and m = 0.2 g) and values of R².

Dye	Tem p K	Freundlich isotherm			Langmuir isotherm				Temkin Isotherm		
		1/n (mg/L)	K _f (K mg/g)	R ²	Q _m (mg/g)	K _L (L/mg)	R _L	R ²	A (L/mg)	B	R ²
BCP	298	3.086	55.463	0.954	0.1409	0.6541	0.0485	0.995	12.856	0.055	0.966
	305	4.149	55.976	0.931	0.1281	0.6094	0.0519	0.997	21.163	0.043	0.973
	313	3.322	49.659	0.953	0.1463	0.3496	0.087	0.995	7.197	0.056	0.961
MB	298	0.293	0.1905	0.972	0.901	0.0605	0.412	0.995	1.725	0.338	0.990
	305	0.401	0.1038	0.974	0.943	0.0285	0.259	0.989	0.385	0.437	0.968
	313	0.174	0.2178	0.951	0.522	0.1109	0.0827	0.999	398.1	0.105	0.926

$$R_L = 1 / (1 + C_0 K_L) \quad (11)$$

where C₀ is the higher value of initial dye concentration (mg/L). 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 for BCP, and MB dyes. From Table (4) it is found that the determination coefficients values for the Langmuir isotherm are higher than the values obtained for the Freundlich isotherm for BCP, and MB dyes

3.6.3 Temkin isotherm

The Temkin isotherm is given as

$$Q_e = RT / b \ln(AC_e), \quad (12)$$

$$Q_e = B \ln A + B \ln C_e \quad (13)$$

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

lnC_e enables the determination of the isotherm constants B₁ and K_T from the slope and the intercept, respectively. A is the equilibrium binding constant corresponding to the maximum binding energy and constant B₁ 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 Langmuir isotherm (for BCP, and MB dyes at almost all temperatures), so the Temkin isotherm cannot be used for adsorption of BCP, and MB dyes on BCC.

3.6.4 Thermodynamic studies

Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy

(ΔS°) are calculated using the following equations

$$\Delta G^\circ = -RT \ln K_L \quad (14)$$

$$\Delta G^\circ / T = \Delta H^\circ / T - \Delta S^\circ \quad (15)$$

where R is the universal gas constant (8.314 kJ·kmol⁻¹·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 [27] from eq.(15).

of BCP, and MB from aqueous solutions polluted by them.

TABLE 5: Thermodynamic parameters for BCP and MB removal using BCC.

Dye	ΔH° (kJ/mol)	ΔS° (kJ/mol. K)	ΔG° (kJ/mol)		
			298 °K	305 °K	313 °K
BCP	29.307	200.3	-59.66×10^{-3}	-61.1×10^{-3}	-62.66×10^{-3}
MB	31.685	187.65	-55.89×10^{-3}	-57.2×10^{-3}	-58.7×10^{-3}

From Table (5) the negative values of ΔG° indicate spontaneous adsorption of BCP, and MB on BCC.

4 CONCLUSIONS

The present study shows that the bentonite carbon composite material used is an effective adsorbent for the removal of Bromocresol Purple (BCP), and Methylene Blue (MB) dyes from aqueous solution.

1. The percent uptake for both BCP, and MB was nearly 100% at all pH values.
2. The optimum adsorbent dose was $\approx 30\text{g.L}^{-1}$ for BCP dye and 40g.L^{-1} for MB dye.
3. The equilibrium between the adsorbate in the solution and the adsorbent surface was practically achieved in 60min for both BCP and MB dyes.
4. Adsorption kinetics were found to follow a pseudo-second-order rate expression for BCP, and MB dyes.
5. Equilibrium adsorption data of BCP, and MB dyes on BCC were best represented by the Langmuir isotherm.
6. The negative values of ΔG° indicate spontaneous adsorption of BCP, and MB on BCC.

As an overall conclusion, the used bentonite – carbon black composite material showed excellent adsorptive characteristics for removal

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