

Dye Removal from Aqueous Solution by Regenerated Spent Bleaching Earth

Ahmed I. Shehab, Sabah M. Abdel Basir, M. A. Abdel Khalek, M. H. Soliman, G. Elgemeie

Abstract—Spent bleaching earth (SBE) recycling and utilization as an adsorbent to eliminate dyes from aqueous solution was studied. Organic solvents and subsequent thermal treatment were carried out to recover and reactivate the SBE. The effect of pH, temperature, dye's initial concentration, and contact time on the dye removal using recycled spent bleaching earth (RSBE) was investigated. Recycled SBE showed better removal affinity of cationic than anionic dyes. The maximum removal was achieved at pH 2 and 8 for anionic and cationic dyes, respectively. Kinetic data matched with the pseudo second-order model. The adsorption phenomenon governing this process was identified by the Langmuir and Freundlich isotherms for anionic dye while Freundlich model represented the sorption process for cationic dye. The changes of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were computed and compared through thermodynamic study for both dyes.

Keywords—Spent bleaching earth, Regeneration, Dye removal, Thermodynamics.

I. INTRODUCTION

DYES are organic chemical compounds that are required to be stable and resist environments effects such as light, temperature and chemicals. Dyes are extensively applied in many modern technologies as textile [1], paper [2], leather tanning [3], plastics, cosmetics, rubber and dye production industries [4]-[6]. They are as well utilized in ground water tracing [7], for the purpose of specific surface area of activated sludge [8], sewage [9] and wastewater treatment [10], etc. Their discharges into the water environment possess a substantial origin of contamination due to their unmanageable nature. This will give undesirable color to the water body which will reduce sunlight penetration and resist photochemical and biological approaches to aquatic life [11]. Almost 5000 tons of dyeing materials from textile industries are released into the water environment every year [12] posing challenges to environmental researchers. Numerous techniques such as coagulation, adsorption, advanced oxidation, photo catalytic degradation, and membrane separation are used for removing from wastewater

[13], [14].

Adsorption is one of the most effective processes of wastewater treatment to diminish noxious inorganic/organic pollutants present in the effluent. Activated carbon is commonly used adsorbent for wastewater treatment and dye removal [15]. Many researchers reported the use of various low-cost adsorbents based on natural materials, industrial solid wastes, agricultural and bio-sorbents [16]-[18]. SBE is a waste that comes from the refining of edible oil plants. It usually contains 20–40% by weight of oil, fat, and colored pigments, depending upon several factors, such as process technology and oil types [19], [20]. Three methods were covered for the dealing with SBE: (1) recovery of the enclosed oil using non-polar solvents followed by steam treatment or washing with an anionic detergent and sodium tri-phenyl phosphate, (2) by burning and (3) by solvent extraction [21].

SBE was regenerated through oil extraction using hexane followed by an autoclave treatment with wet oxidation or heating in aqueous medium [22], [23]. Waldmann and Eggers [24] and King et al. [25] regenerated SBE by high-pressure supercritical CO₂ extraction. Other researchers [26], [27] extracted oil from SBE using organic solvents followed by acid and heat treatments. Boukerroui and Ouali [28] recycled and reactivated SBE by thermal treatment and subsequent washing with hydrochloric acid solution. Tsai et al. [29] regenerated SBE by pyrolysis under inert gas. Since most of the aforementioned studies only emphasize technologies rather than the economics, it is difficult to know if those technologies are financially feasible.

The goal of the present research is recycling spent bleaching earth and employing it as a dye adsorbent from aqueous solution. Determining factors such as initial dye concentration, contact time, pH and temperature will be investigated to discuss the reaction kinetics, controlling adsorption isotherm and thermodynamic parameters.

II. EXPERIMENTAL

A. Materials

Samples of SBE and virgin bleaching earth (VBE) were provided by Edible Oil-Refining Company; Cairo Company for Oil& Soap (Cairo). Acetone, n-hexane, methyl ethyl ketone (Merck) and other reagents of analytical grade were supplied by Adwick local company for chemicals. The dyes used as adsorbate in this study are cresol red (anionic dye) and brilliant cresyl blue (cationic dye), which are purchased from Merck Darmstadt Co. The molecular formulas of the dyes are displayed in Fig. 1.

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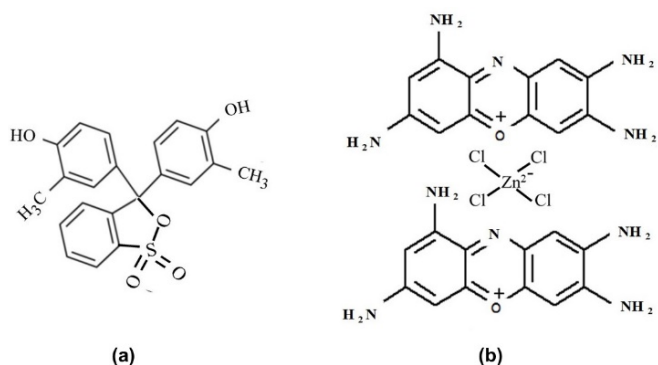


Fig. 1 Molecular formula of dyes: (a) cresol red; (b) brilliant cresyl blue

B. Oil Extraction

Oil was extracted from SBE by mixing with organic solvent (acetone, hexane or methyl ethyl ketone) of solid liquid ratio (1:4). The mixing was carried out under a reflux at the boiling point of the solvent for 2 hours. Fig. 2 displays the used system for oil extraction from SBE. The regenerated SBE was filtered off, washed using clean solvent, then dried at 105 °C for 24 hours and characterized. Fig. 3 represents a flowsheet of SBE regeneration and utilization for dye removal.

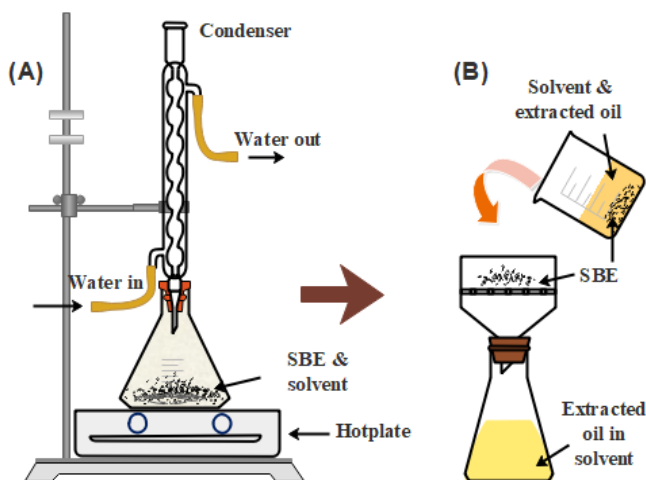


Fig. 2 Schematic diagram of (a) System of oil extraction from SBE; (b) Filtration system for oil-solvent separation from SBE

C. Dye Sorption

Synthetic dye solutions of 5000 mg/l were prepared using bi-distilled water are used in sorption study. A 0.1 g of regenerated SBE is mixed with 20 ml of dye solution for different time intervals using a water bath shaker at definite pH and temperature. The dye solution was separated from SBE using a centrifuge at 2000 rpm. Concentration of the dyes is determined by means of a UV/visible spectrophotometer (Model: U-2001; Hitachi Co., Japan) at maximum wavelength for each dye.

The removal percent and amount of eliminated dye from the solution were estimated by using (1) & (2), respectively [30]:

$$Removal(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t are the initial concentration and at time "t" of the studied dye (mg/l) at time zero and t, respectively.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where q_t is the sorption capacity of adsorbent in (mg/g), V is the volume of the solution in liter, and m is the mass of adsorbent in (g).

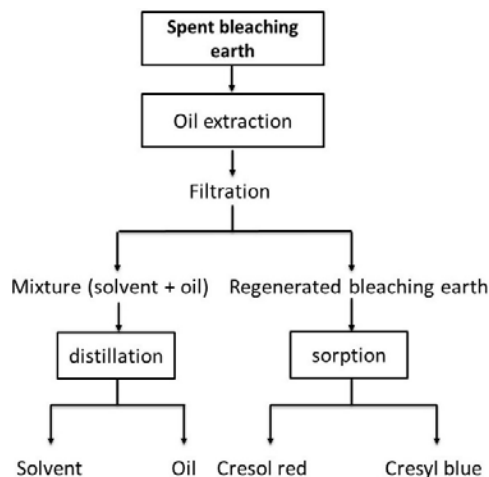


Fig. 3 Flowsheet of SBE regeneration and utilization for dye removal

D. Characterization

Scanning electron microscopy (SEM) model JEOLJSM-5400, Japan was used to determine the morphology and detailed structural formation of the samples. X-ray diffraction examination of the sample structure was made using a Philips PW 1730 powder X-ray diffractometer (Cu α $\lambda=1.5$ Å radiation). FTIR spectra of the samples were performed using a spectrophotometer model Mattson 100, made by Unicam, over the range 400-4000 cm^{-1} .

III. RESULTS AND DISCUSSION

A. Regeneration of SBE

1. Effect of Solvent Type

Three organic solvents (acetone, hexane and methyl ethyl ketone) were employed to extracted oil from SBE. Table I displays the comparative percentage of oil extracted by the three solvents. Although acetone is not the best solvent, but it gave a high oil extract, to be considered the best in economic terms compared with methyl ethyl ketone. FTIR spectra shown in Fig. 4 proved that a relative clean bleaching earth can be obtained by conducting acetone extraction using four consecutive cycles. It is noticeable that the distinctive peaks of oil have completely disappeared in the fourth cycle.

TABLE I
 PERFORMANCE OF DIFFERENT SOLVENTS FOR OIL EXTRACTION

Solvent	% Extraction Oil to SBE weight
Methyl ethyl ketone	34
Acetone	30
Hexane	22

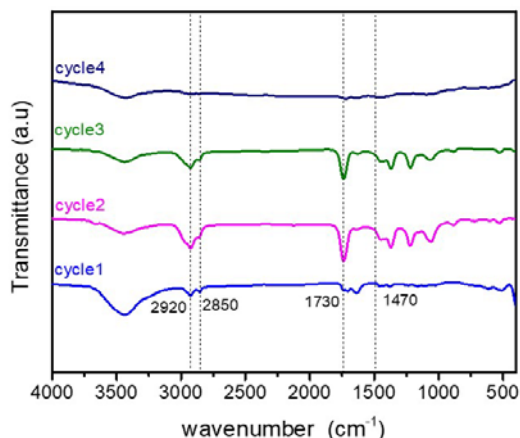


Fig. 4 FTIR spectra of regenerated SBE obtained by conducting acetone extraction using four consecutive cycles

2. Evaluation of Regenerated SBE

The X-ray diffraction patterns, in Fig. 5, of VBE, SBE and RBE show that all samples have the distinguished peaks of montmorillonite (M), and the presence of quartz impurities (Q). Thus, the primary structure of montmorillonitic clay of bleaching earth is not affected by regeneration process.

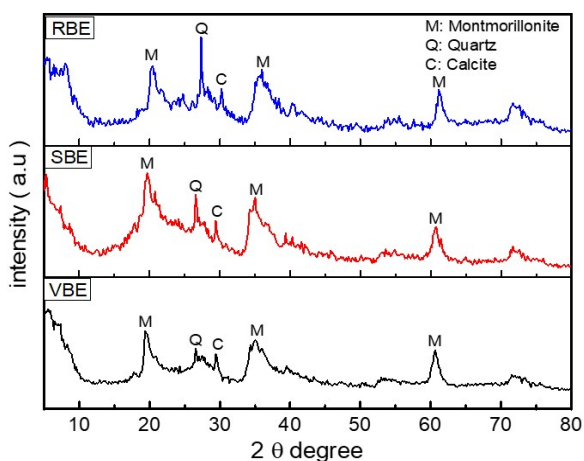


Fig. 5 XRD patterns of VBE, SBE and RSBE

FTIR spectra confirm the montmorillonite structure in VBE, SBE and RSBE samples. Fig. 6 shows peak around 3460-3650 cm^{-1} related to the stretching vibrations of the interlayer water molecules. The band at 2920-2850 cm^{-1} of FTIR spectrum of SBE corresponds to stretching vibration of C-H of saturated carbonaceous chains of oil and free fatty acids (FFA). At 1740 cm^{-1} , a band referred to strong stretching vibration of the ester carbonyl group of oil. It also refers to vibration of C-H of oil and deformation, vibration of OH of the FFA. These bands disappeared as a result of solvent treatment which implies that the organic residues adsorbed in the pores are completely eliminated by the physicochemical treatment from regeneration [31].

SEM micrographs of VBE, SBE and RSBE are shown in Fig. 7. As shown in the figure, SBE particles surface appears

covered with oil, while VBE and RSBE show a similar morphology with flattened surface and vermicular texture resulting from the solvent and thermal treatment.

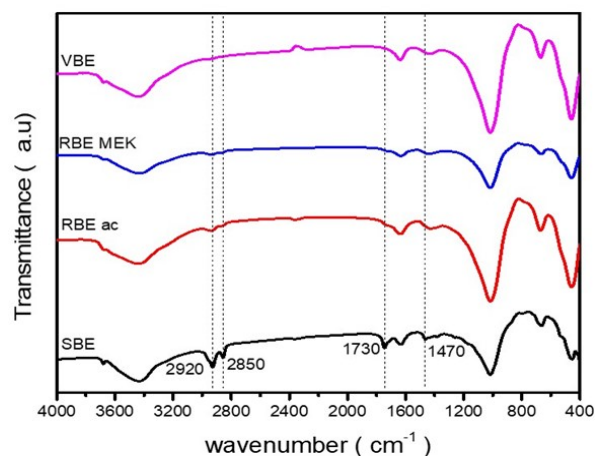


Fig. 6 FTIR spectra of VBE, SBE and RSBE (RBE ac & RBE MEK)

B. Dye Removal Study

1. Effect of pH

Sorption of brilliant cresyl blue (cationic) and cresol red (anionic) dyes by bleaching earth is highly dependent on pH solution. Fig. 8 shows the adsorption capacity values (mg/g) and removal percentage for both dyes within the pH values range of 2-10. It is observed that the maximum sorption occurred at pH 2 and 8 for anionic and cationic dyes, respectively. Basically, the presence of excess H^+ ions at low pH should compete with the cationic group of the brilliant cresyl blue dye causing a decrease in the amount of dye adsorbed. However, the presence of negative charge on the surface of RSBE at high pH should favor the adsorption of cationic dye (cresyl blue). This behavior of cresyl blue dye is inconsistent with the known fact that the adsorption increases with increasing pH for cationic dyes [32]. On the other hand, the favorable adsorption of cresol red (anionic) dye in acidic media is attributed to the electrostatic interactions between the SO_3 group of the dye and the RSBE whose surface exhibits a positive charge at low pH value.

2. Effect of Contact Time

Investigation for the contact time between dyes and RSBE adsorbent and its influence at ambient temperature was carried out and from Fig. 9, we deduced that the adsorption process included two phases. The rapid phase of them is owing to the big number of vacant active sites accessible for adsorption. However, a plateau value is reached, and that is due to the saturation of the active sites. The rate of dyes adsorption has been evaluated using the Lagergren pseudo-first order equation [33] and pseudo-second order equation based on solid phase sorption [34].

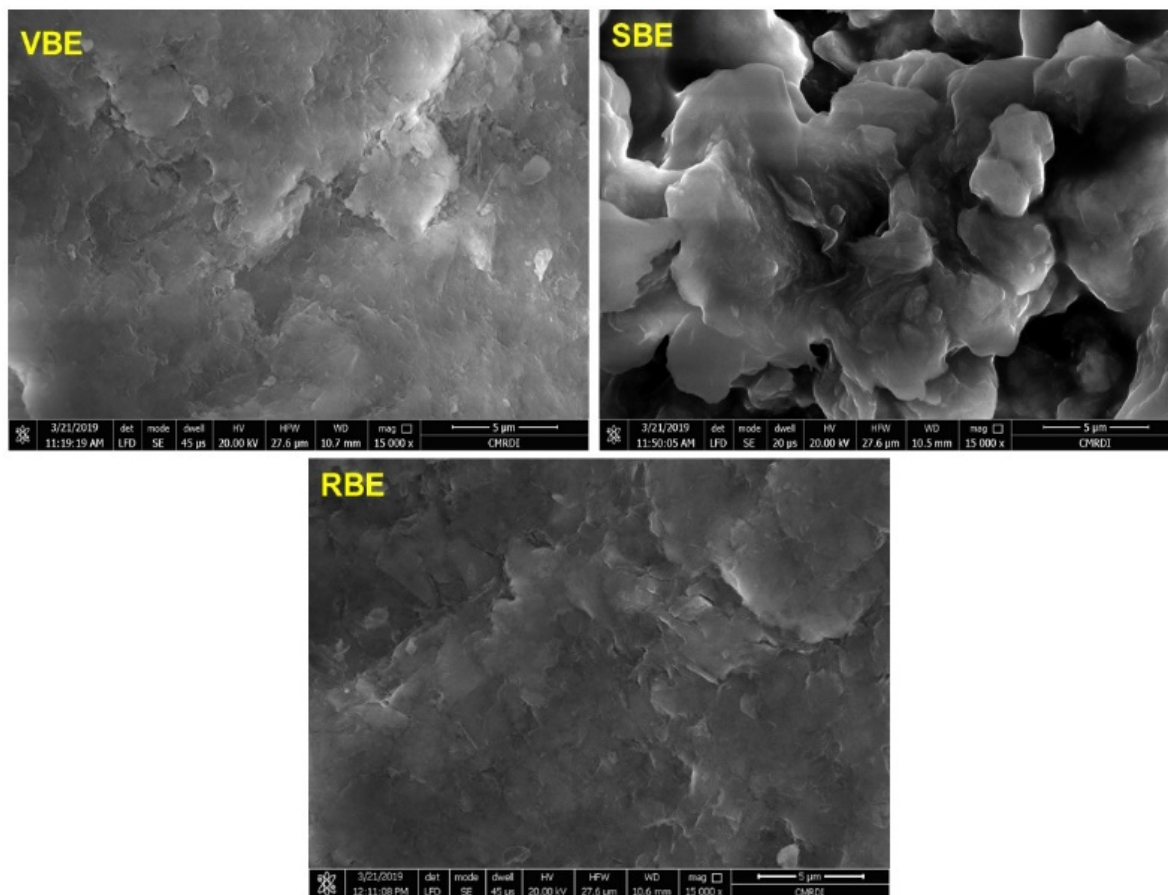


Fig. 7 SEM micrographs of VBE, SBE and RBE

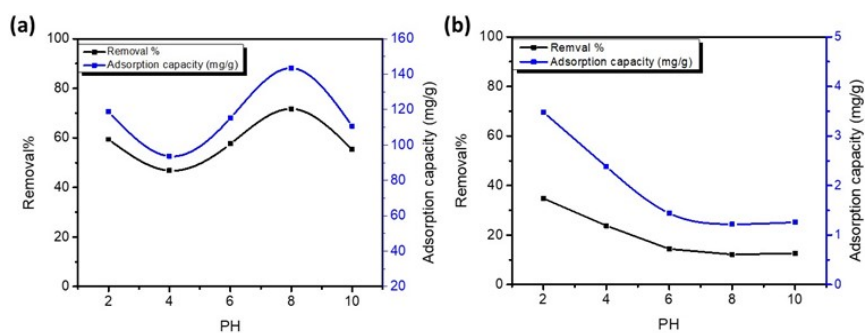


Fig. 8 Effect of pH on adsorption amount and removal percent of (a) brilliant cresyl blue; (b) cresol red dyes

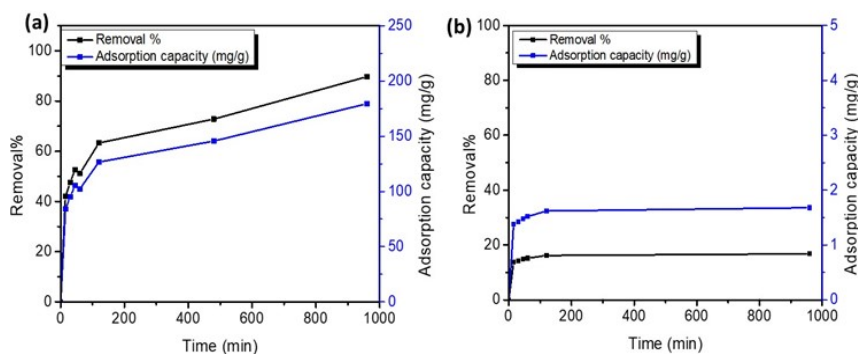


Fig. 9 Effect of contact time on adsorption amount and removal percent of (a) brilliant cresyl blue; (b) cresol red dyes

For the purpose of analyzing the adsorption kinetics of different dyes by regenerated bleaching earth, correlations between adsorbed amounts and time were looked for, by applying different mathematical expressions of various models, namely: Lagergren's equation or pseudo-first-order (3) and pseudo-second-order (4) kinetic rate models [35].

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e (mg/g) and q_t (mg/g) are the amount of dye adsorbed by RSBE at equilibrium and at different time periods, respectively. k_1 (1/min) and k_2 (g/mg min) are the corresponding rate constants for pseudo-first-order and pseudo-second-order models, respectively [36].

The adsorption data were employed to fit the kinetic models. Plots for pseudo-first and second-order models are shown in Fig. 10. The parameter values of calculated and

experimental equilibrium adsorption values estimated for the adsorption of both dyes by RSBE were summarized in Table II. Relying on the values of correlation coefficient (R^2) and reaction rate constant (k_2), the second-order kinetic model is higher and fits the data better than the first-order kinetic model.

TABLE II
CALCULATED PARAMETERS OF PSEUDO FIRST AND SECOND ORDER MODELS

Items	Brilliant cresyl blue	Cresol red
$(q_e)_{exp}$ (mg/g)	179.4	1.680
pseudo-first-order model		
R^2	0.6711	0.7888
k_1 (min ⁻¹)	-0.0025333	-0.0227997
$(q_e)_{cal}$ (mg/g)	99.3	0.70
pseudo-second-order model		
R^2	0.9900	0.9999
k_2 (g.mg ⁻¹ .min ⁻¹)	1.3×10^{-4}	1.09×10^{-1}
$(q_e)_{cal}$ (mg/g)	181.8	1.689

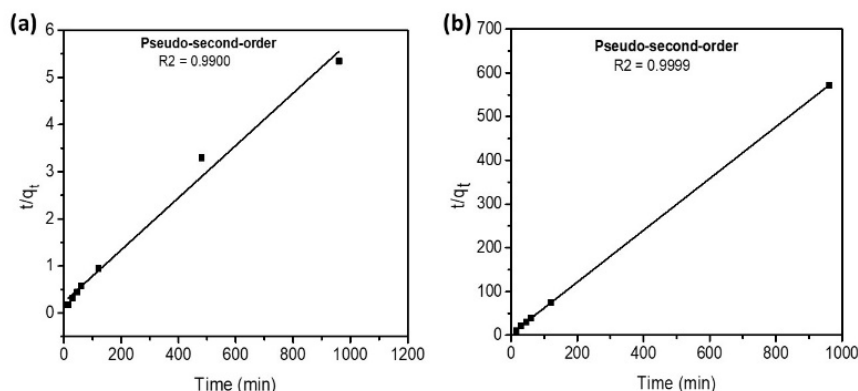


Fig. 10 Pseudo-first-order and pseudo-second-order kinetic of dyes: (a) brilliant cresylblue; (b) cresol red

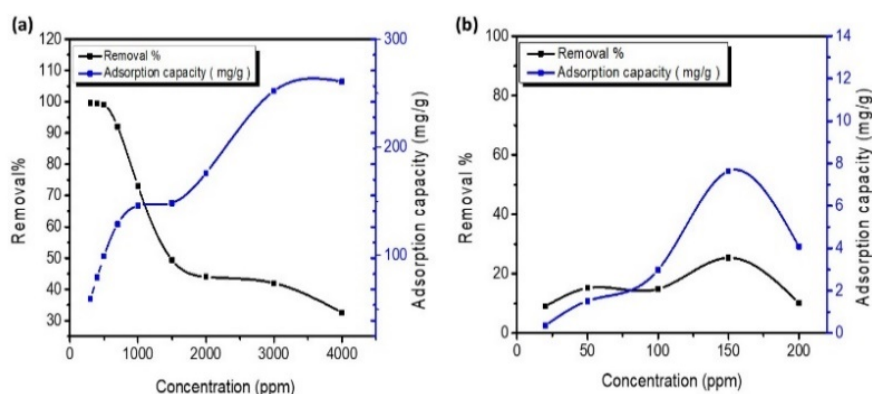


Fig. 11 Effect of initial dye concentration on adsorption amount and removal percent of (a) brilliant cresyl blue; (b) cresol red dyes

3. Effect of Initial Dye Concentration

Fig. 11 shows the effect of initial concentration on adsorption capacity and removal percent of cationic and anionic dyes by RSBE. It is clearly observed that the sorption capacity significantly increased with the initial concentration of these dyes. This increase in the sorption capacity is due to

the increase of adsorbate species which enhances the interaction probability with adsorption sites on adsorbent surface [36], [37]. On that premise, the removal percent of these dyes were found to decrease by increasing the initial concentration of these dyes. This might be for higher dye concentration or the binding capacity of the adsorbent coming

to saturation, causing a reduction of overall removal percent [38].

C. Adsorption Isotherms

The adsorption isotherm models assist the complete and precise understanding of the way of interaction between adsorbate and adsorbent. In the present study, the equilibrium adsorption data are analyzed conferring to Freundlich and Langmuir isotherm linear form models.

Langmuir isotherm model suggests a monolayer adsorption taking place at finite and definite localized sites. These adsorption sites are identical and equivalent, and there is no lateral interaction between adsorbed molecules [39]. Linear equation of Langmuir model, represented by

$$A \frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b \cdot q_{\max}} \quad (5)$$

where C_e (mg/l) is the concentration at the equilibrium, q_e (mg/g) is the amount adsorbed at equilibrium, b (L/g) is the

Langmuir isotherm constant, and q_{\max} (mg/g) is the maximum adsorption capacity of the adsorbent.

Fig. 12 displays the isotherm plots of Langmuir model for adsorption of both cationic and anionic dyes by generated bleached earth. The q_{\max} and b values were calculated from the slope and intercept obtained by plotting C_e/q_e as a function of C_e . The obtained data are summarized in Table III. The relatively high values of the correlation coefficients ($R^2 = 0.9454$) obtained from the Langmuir isotherm for brilliant cresyl blue dye indicate the inappropriateness of the application of this model. The calculated q_{\max} was much closer to that obtained experimentally. This implies that the adsorption is characterized by chemical nature (chemical adsorption) [40]. For cresol red dye, the low value of the correlation coefficients ($R^2 = 0.0128$) indicates that this model cannot apply to the system. The calculated q_{\max} was very far to that obtained experimentally. This means that the adsorption is not characterized by chemical nature (*no chemical adsorption*) [40].

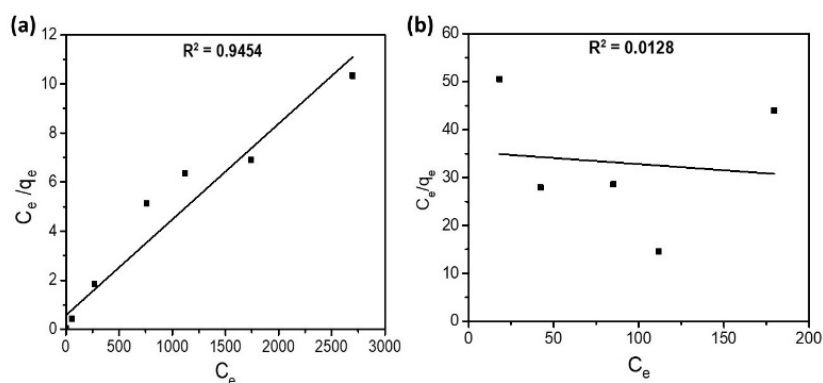


Fig. 12 Langmuir isotherm model fitting for (a) brilliant cresyl blue; (b) cresol red

TABLE III
LANGMUIR MODEL CONSTANTS FOR DIFFERENT DYES

Items	Brilliant cresyl blue	Cresol red
R^2	0.9454	0.4943
$q_{\max,cal}$ (mg/g)	256.4	-0.279
$q_{\max,exp}$ (mg/g)	260.8	7.64
b (L/mg)	0.00679	-0.07967

The all-important features of the Langmuir isotherm can be stated in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which is determined by the following relationship [41]:

$$R_L = \frac{1}{(1+bC_0)} \quad (6)$$

where C_0 (mg/L) is the initial concentration of dye and b is Langmuir constant (L/mg).

Table IV shows that the R_L is 0 – 1 for brilliant cresyl blue concentration which means that the adsorption process is favorable while, the R_L is less than 0 for cresol red concentration meaning that the adsorption process is very poor.

TABLE IV
THE DIMENSIONLESS SEPARATION FACTOR (R_L)

Brilliant cresyl blue		Cresol red	
C_0	R_L	C_0	R_L
300	0.3293	20	-1.6852
400	0.2691	50	-0.3352
500	0.2275	100	-0.1435
700	0.1738	150	-0.0913
1000	0.1284	200	-0.0670
1500	0.0894		
2000	0.0686		
3000	0.0468		
4000	0.0355		

Freundlich isotherm model is represented by (7) that can be fitted according to (8). [42]. It can be applied for both non-ideal sorption on heterogeneous surfaces and multilayer sorption.

$$q_e = K_F C_e^{1/n} \quad (7)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

where q_e is the amount of dye adsorbed per weight of sorbent at equilibrium (mg/g), C_e is the residual concentration at equilibrium in solution (mg/L), K_F is the sorption capacity (mg/g), and n the sorption intensity (unit less), n gives an evidence of the adsorbent/adsorbate system favorability [43].

The predicted equilibrium adsorption values for both dyes using Freundlich isotherm model show well fit to experimental equilibrium adsorption data as illustrated in Fig. 13, which indicated the appropriateness of this model application. It also implied that the adsorption process occurred mostly by the opposite charge attraction (*physically*

in nature) [40]. The values of K_F and $1/n$ are computed from the slope and intercept of the line as shown in Table V.

TABLE V
THE FREUNDLICH MODEL CONSTANTS FOR DIFFERENT DYES

Items	Brilliant cresyl blue	Cresol red
R^2	0.9061	0.9875
n	6.422	0.772
K_F (mg/g)	66.15	0.0095

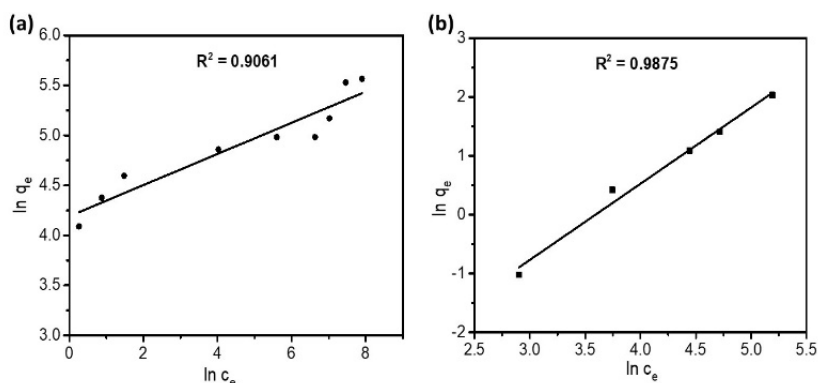


Fig. 13 Freundlich isotherm model fitting for (a) brilliant cresyl blue; (b) cresol red

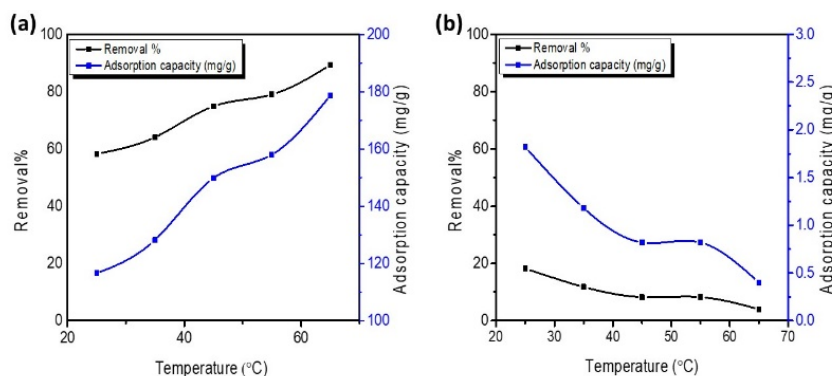


Fig. 14 Effect of temperature on adsorption amount and removal percent for (a) brilliant cresyl blue; (b) cresol red dyes

4. Effect of Temperature

The temperature effect on the adsorption capacity and removal percent is revealed in Fig. 14. The figure shows that the adsorption capacity enhanced by temperature rise from 25 to 65 °C for Brilliant cresyl blue dye. This may be ascribed to the pore size enlargement and high mobility of dye molecules in addition to the auspicious intermolecular forces between adsorbate and adsorbent stronger than those present between adsorbate and solvent [44]. This designates the chemisorption and the endothermic natures of this process [45].

For cresol red dye, the adsorption decreased with temperature increase from 25 to 65 °C. A decreasing in adsorption density with increasing temperature may be due to two factors, first due to increasing the diffusion rate of dye molecules across the exterior boundary layer and the inside

pores of the adsorbent particle. Secondly, attributable to lessening viscosity of the solution for extremely concentrated suspensions [46].

Thermodynamic parameters; Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes are calculated using van't Hoff equation to evaluate the thermodynamic feasibility and the spontaneous character of the process (Fig. 6) [47], [48]:

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

$$\ln k_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where $k_c = F/(1 - F)$, and $F = (C_0 - C_t)/C_0$, T is the temperature in degree K, and R is the gas constant [8.314 J/mol K].

From the plot of $1/T$ against $\ln K_c$, the values of ΔH° and ΔS° have been computed from the slope and the intercept of

the plot of $\ln K_c$ vs. $1/T$ which gives a straight line with acceptable coefficient of determination [$R = 8.314 \text{ J/mol K}$].

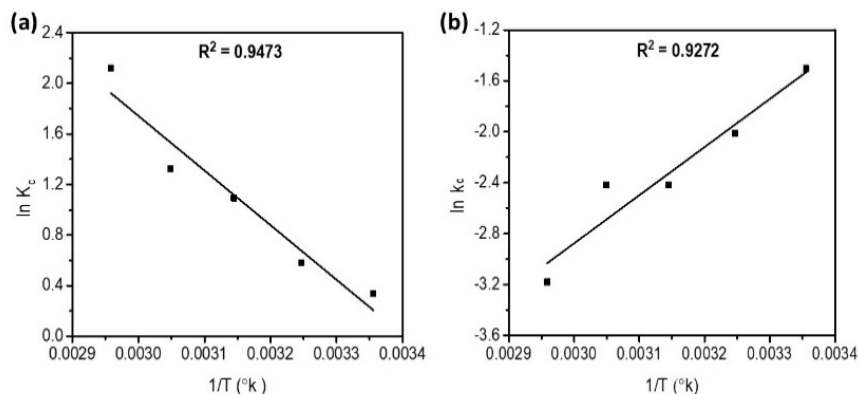


Fig. 15 Plot of ($\ln K_c$) versus ($1/T$), for (a) brilliant cresyl blue and (b) cresol red

TABLE VI
THERMODYNAMIC PARAMETERS; ENTHALPY (ΔH°), ENTROPY (ΔS°) AND GIBBS (ΔG°) CHANGES

Temp. (°C)	Brilliant cresyl blue			Cresol red		
	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
25	-0.83			3.72		
35	-1.48			5.15		
45	-2.89	41.9	122.2	6.38	-31.3	-118
55	-3.61			6.58		
65	-5.96			8.93		

The value of ΔH° is positive for brilliant cresyl blue dye suggesting the endothermic nature of the reaction and its value higher than 40 kJ/mol, indicating chemically controlled process. This is confirmed earlier by a good fitting of the data with Langmuir isotherm model (*chemical adsorption*). The values of ΔH° are negative for cresol red dye, which suggests that the adsorption processes are exothermic and its value is lower than 40 kJ/mol, indicating physically controlled processes than chemically [47].

The positive value of ΔS° for brilliant cresyl blue dye indicates an increase in randomness at the solid/solution interface during the adsorption process. For cresol red dye, the ΔS° is negative, which indicates the decreasing in randomness at the solid/liquid interface during the adsorption, indicated the adsorption was not advantageous at higher temperature [49].

For brilliant cresyl blue dye, the values of ΔG° are negative which indicate that this adsorption process is spontaneous in nature whereby no energy input from outside of the system is required. The decrease in ΔG° with increasing temperature indicates that the adsorption process becomes more favorable at high temperatures [50]. For cresol red dye, the ΔG° values were positive indicating the nonspontaneous nature of this adsorption, whereby energy input from outside of the system is required [51]. The increase in ΔG° with temperature signifies that the adsorption process becomes less advantageous at high temperatures [52].

IV. CONCLUSION

SBE was recycled to reuse as a dye adsorbent from aqueous solution. Organic solvents and thermal treatment were used to reactivate SBE. Acetone is considered the best in economic terms. X-ray diffraction proved that the structure did not affect by regeneration process. FTIR confirms the structure of montmorillonite and elimination of oil. SEM showed flattened and vermicular texture resulting from the basic and heat treatment.

Sorption of brilliant cresyl blue (cationic) and cresol red (anionic) dyes by bleaching earth is highly dependent on pH solution. The maximum removal was achieved at pH 2 and 8 for anionic and cationic dyes, respectively. The second-order kinetic model agrees with the data better than the first-order kinetic model.

Langmuir isotherm for brilliant cresyl blue dye indicates the appropriateness of the application of this model while it is not applicable for cresol red dye. Freundlich isotherm model show good suitability of experimental data, which indicated the appropriateness of the application of this model for both dyes.

Increasing temperature increased brilliant cresyl blue dye adsorption but decreased cresol red adsorption. ΔH° is positive for brilliant cresyl blue, while it is negative for cresol red, which indicated that endothermic and exothermic nature, respectively. The positive ΔS° for brilliant cresyl blue and negative for cresol red indicated increasing and decreasing in randomness at the solid/liquid interface, respectively. Negative ΔG° for brilliant cresyl blue indicated the spontaneously process, while positive ΔG° for cresol red indicated non-spontaneous nature of the process.

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