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## ADSORPTION OF AN ANIONIC DYE ONTO NATIVE AND CHEMICALLY MODIFIED AGRICULTURAL WASTE

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### Abstract

The native and surface modified adsorbents from agricultural waste, such as Psyllium stalks (PS) were investigated for their ability to remove the Coomassie Brilliant Blue (CBB) dye from aqueous media. The native and surface modified adsorbents were characterized by the Fourier Transform Infrared spectroscopy (FTIR). The results show that the Sodium Bicarbonate Treated Carbon (SBTC) has good surface properties for the removal of the CBB dye from aqueous media. The SBTC was analyzed by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectrometry (EDX) and Brunauer, Emmett and Teller (BET) analysis. Batch adsorption experiments were carried out using all the adsorbents, by varying the adsorption parameters such as, solution pH, adsorbent dose, contact time, initial dye concentration, and temperature. The maximum percentage of dye removal was observed for the solution pH of 7.0 and an adsorbent dose of 0.4 g/L for SBTC. The adsorption kinetics for the SBTC reveals that the equilibrium was attained in 90 min. The kinetics of dye adsorption onto the adsorbents follows the pseudo-second order model. The external mass transfer controls the dye removal during the earlier stages of adsorption, and intraparticle diffusion during the later stages of adsorption. The percentage removal of the dye decreases with an increase in the dye concentration. The Langmuir maximum monolayer adsorption capacity value of SBTC for the CBB dye is found to be 237.2 mg/g. The thermodynamic study shows that the adsorption of the dye onto the adsorbents was spontaneous and exothermic in nature.

*Key words:* adsorption, anionic dye, kinetics, adsorption isotherms, thermodynamics

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### 1. Introduction

Deterioration of the natural resources is the major threat to the environmental sustainability. Development in agriculture, medicine, energy sources, and all chemical industries is necessary in order to fulfill the needs and demands of the overgrowing human population. Almost all processes employed by man for the production of goods and services lead to the accumulation of environmental pollutants. These pollutants released into the air, water and soil have detrimental effects on the health of

humans, plants, animals and microbes. Current research is focused on ways for the eradication and reduction of the existing environmental pollution. We need green chemistry and environmental remediation for the sustenance of human society. Over the last two decades, there has been a tremendous increase in the awareness of the toxic and carcinogenic effects of many chemical pollutants, which were not considered hazardous in the past (King et al., 1997).

Water pollution is one of the major environmental pollutions. Most of the manmade chemicals are having complex organic structures and

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highly resistant to biodegradation (Fernando and Aust, 1994). The colored effluent treatment remains a continuing problem for dye manufactures, dyers, finishers and water purifiers, because of the enforcement of stringent color consent standards by regulatory bodies.

Triphenylmethane dyes are aromatic xenobiotic compounds that are used extensively in many industrial processes such as, textile dyeing, leather, pharmaceutical, paper printing, food colorants and cosmetic manufacturers and also in laboratories (Hessel et al., 2007). These dyes are highly toxic, mutagenic and carcinogenic to mammalian cells and also elicit a major threat to the aquatic ecosystem, causing severe environmental problems worldwide (Fernandes, 1991). Coomassie Brilliant Blue (CBB) belonging to the class of triphenylmethane dyes, originally developed for various applications in the textile industry. It also has wide application in analytical biochemistry for staining proteins. CBB G-250 differs from CBB R-250 because of the presence of methyl groups. 'R' in CBB R-250 represents the slight reddish tint in the blue color of the dye. 'G' in CBB – G250 represents the greenish tint in the blue color. The 250 denotes the purity of the dye. Extinction coefficient of the dye is  $43,000 \text{ M}^{-1}\text{cm}^{-1}$  at pH 7 (Chial, 1993). CBB G-250 has many industrial applications in textile industries, and it is applied specifically in basic and applied biological research.

Various physical, chemical and biological methods for treating dye wastewater have some drawbacks such as, being economically unfeasible; incompetent to treat the complex organic dyes and metabolites because of the color fastness; stability and the resistance of dyes to degradation; engendering a substantial amount of slurry that may lead to secondary pollution; considerably raising the economic value of the treatments with complex processes (Dermentzis et al., 2011; Eichlerova et al., 2007; Forgacs et al., 2004; Tawfik et al., 2017; Zhang et al., 2004).

Adsorption is the exchange of materials at the interface between two immiscible phases in contact with one another. Adsorption may be either physical or chemical. It can be explained as, when a solid surface is in contact with a solution, solute molecules from the later have the tendency to accumulate on the solid surface as a layer. Adsorption results in the formation of an adsorbate monolayer on the surface of the adsorbent. The rate of adsorption is defined as the speed at which the adsorbates are transferred from the liquid phase to the solid phase.

From the available literature, the advantages of adsorption when compared to the other available wastewater treatment methods are as follows: requirement of less land area, comparatively lesser sensitivity to daylight variation, less impact of toxic chemicals on the system, flexible design, operation and superior removal of organic contaminants (Jaycock and Parfitt, 1981; Kitinya et al., 2017).

Conventional industries use activated carbon as adsorbents for wastewater treatment. Because of high

cost, researchers all around the world are in search for an efficient, low cost and readily available adsorbent. Many of them succeeded in their endeavor, and found plenty of low cost adsorbents. In the last few decades, a lot of research has been carried out on finding low cost adsorbents and the search is still going on. The major drawbacks of their low cost adsorbents are low adsorption capacity and high adsorbent dosage for complete color removal.

The present study objective is to develop a new low-cost and effective adsorbent from an agricultural waste. Adsorbent used in this present study are the stalks of the psyllium plant *Plantago ovata*. India is the largest producer and exporter of this crop in the world for Isabgol (dietary fiber) production. The psyllium stalks are the major agricultural waste in the Isabgol production. Almost no significant advancements have been made for the utilization of the psyllium stalk as an adsorbent. There is hardly any literature available, particularly with regard to the utilization of psyllium waste for the treatment of wastewater containing dyes, either directly or in its modified form. Those stalks are activated by various methods in order to adsorb an anionic dye (CBB G – 250) from aqueous media.

## 2. Material and methods

Coomassie Brilliant Blue (CBB G – 250) dye was obtained from Sigma chemical Co., St Louis, USA. Double distilled water was used for preparing the dye solution throughout the study. For chemical modification of the waste, Hydrochloric acid (HCl), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ), sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium bicarbonate ( $\text{NaHCO}_3$ ) were purchased from Hi-media India private limited, Mumbai, India. The chemicals utilized for this study are pure and of an analytical grade.

All pH measurements were carried out with a microprocessor based pH meter model number HI 98107, Hanna Equipments Private Limited, Mumbai, India. The experimental studies were conceded by stirring the reaction mixture in a horizontal bench shaker (Orbitek Private Limited, Chennai, India). The kinetic studies of the adsorption of dyes onto all the prepared adsorbents were carried out by stirring the reaction mixture by means of a mechanical agitator RQ – 124A (REMI Motors, Mumbai, India). The samples were centrifuged at 10000 rpm by using a density gradient centrifuge (REMI Motors, Mumbai, India) to separate the adsorbents. The residual concentration of the CBB dye in the solution was estimated, using absorbance at 610 nm recorded on the Shimadzu UV-1800 spectrophotometer model number (Tokyo, Japan).

### 2.1. Preparation of adsorbent

Powdered Psyllium Stalks (PS) was modified using various chemical treatments for the preparation of adsorbents. This precursor was provided by the

Isabgol producing factory, Gujarat, India. The characteristics of the initial material are shown in Table 1.

The stalks were thoroughly rinsed with distilled water to wash out the impurities and dried at room temperature. The dried stalks were ground to powder in a flour mill and were charred in muffle furnace at 200 °C. The charred stalks were activated using three different bases and acids respectively to obtain six different activated carbons. The charred stalks were treated with sulphuric acid, nitric acid, hydrochloric acid, sodium hydroxide, potassium hydroxide and sodium bicarbonate of unimolar concentration in the ratio of 1:2 for 24 h respectively. The treated materials were washed with double distilled water, until the pH of the supernatants remained constant at 7.0. This material was dried at 80°C for 3 h. The dried materials were ground into a fine powder in still mill and after that it was sieved to get the average particle size of 0.354 mm. The prepared carbons were abbreviated in the following order as, STC (Sulphuric acid Treated Carbon), HTC (Hydrochloric Treated Carbon), NTC (Nitric acid Treated Carbon), SHTC (Sodium Hydroxide Treated Carbon), SBTC (Sodium Bicarbonate Treated Carbon) and PHTC (Potassium Hydroxide Treated Carbon).

## 2.2. Preparation of dye solution

An amount of 500 mg of the Coomassie Brilliant Blue G-250 dye was dissolved in 1L of distilled water to prepare the stock solution and it was diluted to various required concentrations according to the study. Stock dye solution was stored in the dark at room temperature. 0.1 M NaOH or 0.1 M HCl was added to the dye solution to adjust the pH according to the requirement of the particular study. 1. The chemical structure of the CBB dye is shown in Fig. 1.

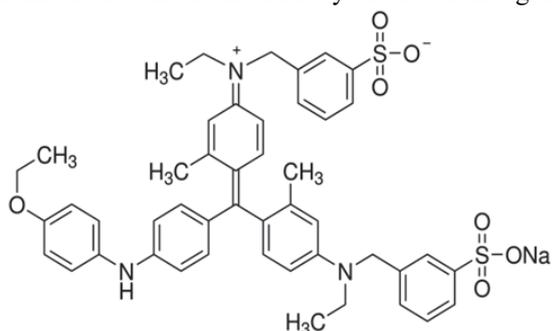


Fig. 1. Chemical structure of the CBB G-250 dye

## 2.3. Adsorbent characterization

The different chemical functional groups present on the surface of adsorbent could be identified by the Fourier Transform Infrared Spectroscopy (FT-IR) analysis. KBr is used within the spectral range varying from 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$  for this analysis.

Quanta 200 FEG Scanning Electron Microscope (SEM) is utilized for the surface morphology studies of the adsorbents with the working distance of 50 $\mu\text{m}$  at an accelerating voltage of 10 kV. The SEM coupled with Energy Dispersive X-ray spectrometry (EDX) used for elemental analysis. The surface area of the adsorbent was measured using the nitrogen gas adsorption technique with an ASAP 2010 micro pore analyzer at 77 K liquid nitrogen. The Brunauer, Emmer and Teller (BET) method is used to study the surface area of the adsorbents before and after the modification (Brunauer et al., 1938; Barret et al., 1951).

## 2.4. Batch adsorption experiments

Several set of experiments were carried out by varying the adsorption parameters such as, solution pH, adsorbent dose, contact time, initial dye concentration and temperature in order to optimize them for better results. For all the analysis of various parameters mentioned above, precisely weighed adsorbents was added to the dye solution taken in a 250 mL conical flask according to the analysis. The flasks containing the required amount of adsorbents and dye solution was stirred at 180 rpm in a shaker. 0.1 M NaOH or 0.1 M HCl was added to the dye solution to adjust the pH according to the requirement of the particular study. pH meter is used for monitoring the pH of the solution before and after the experiments and also during the course of the analyses. Once the system approaches the equilibrium condition, the adsorbent were separated by centrifugation and then the supernatant was subjected for the UV-Visible spectroscopic analyses to record the concentration of dyes present in the sample after adsorption. The percentage of dye removal was calculated by using the following mass balance relationship (Eq. 1):

$$\% \text{ dye removal} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where  $C_i$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of the dye solution respectively.

### 2.4.1. Effect of the solution pH on dye adsorption

A volume of 50 mL of 100 mg/L dye solution has been taken for the pH studies in the pH range of 3.0-10.0 with respective adsorbents at 30°C. Experiments could not be performed at other pH values due to the instability of dye molecule at those pH ranges.

The solutions with 100 mg of the respective adsorbents at different pH were subjected for agitation in the horizontal bench shaker at 180 rpm for 200 min and then the adsorbent were separated by centrifuge. The supernatants were analyzed using the UV-Vis Spectrophotometer.

**Table 1.** Characteristics of the powdered PS

Powdered PS	Moisture (%)	Ash (%)	Extractable ratio (%)	Lignin (%)	Cellulose (%)	Hemicellulose (%)
	5.60	7.60	13.38	12.95	21.65	25.37

#### 2.4.2. Effect of the adsorbent dose on dye adsorption

In order to optimize the adsorbent dosage for the effective removal of dyes, the experiments were carried out with different adsorbent doses. The adsorbent dose was added in the range of 10 to 100 mg to the 100 mL of CBB (100 mg/L) dye solution at the optimized pH for a contact time of 2 h, at 30°C. The reaction mixtures were centrifuged and the supernatants were subjected for UV-Visible Spectroscopic analyses.

#### 2.4.3. Effect of contact time and kinetic studies on dye adsorption

In order to analyze the effect of the contact time on the adsorption of CBB dye onto the various adsorbents prepared, experiments were performed and samples were withdrawn at different time intervals which is utilized for adsorption kinetic studies. Various kinetic models were adapted for this study to map the experimental data obtained from the contact time analyses to understand the mechanism of adsorption and to determine the rate controlling step. The parameters were maintained for this study as pH 7, 1 g/L of adsorbent dosage, 500 mg/L dye concentration and at room temperature. Samples were withdrawn for every 10 minutes and analysed until the adsorption system reached equilibrium. The mixture was continuously stirred at 180 rpm by the mechanical agitator (REMI), throughout the experiment.

Various kinetic models like pseudo-first order equation (Lagergren, 1898), pseudo-second order equation (Ho and McKay, 1999) and intraparticle diffusion model (Weber and Morris, 1963) were adapted to study the adsorption mechanism and to determine the rate limiting step. The amount of dye adsorbed onto the adsorbent at various time intervals was calculated, using Eq. (2) (Zhang et al., 2004):

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

where,  $q_t$  is the amount of dye adsorbed onto the adsorbent at any time  $t$  (mg/g),  $C_0$  is the concentration of the dye solution at time  $t = 0$  (mg/L),  $C_t$  is the concentration of the dye solution at any time  $t$  (mg/L),  $V$  is the volume of the dye solution (L) and  $m$  is the mass of the adsorbent used (g).

#### 2.4.4. Effect of the initial dye concentration and adsorption isotherms

In order to study the effect of the initial dye concentration on the adsorption of CBB dye onto the adsorbents, experiments were performed with an optimum adsorbent dose in 100 mL of the CBB dye solution of varying initial concentrations (20-160 mg/L). The adsorption isotherm models, such as the Langmuir, Freundlich and Redlich-Peterson

(Freundlich, 1906; Langmuir, 1918; Redlich, 1959) were adapted to analyse the experimental data obtained in this study. The amount of dye adsorbed,  $q_e$  (mg/g), was determined by using the following mass balance relationship (Zhang et al., 2004) (Eq. 3):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (3)$$

where  $C_i$  and  $C_e$  represents the initial and equilibrium concentrations (mg/L) of the dye solution respectively;  $V$  is the volume of the dye solution (L) and  $m$  is the mass (g) of the adsorbent.

#### 2.4.5. Effect of temperature and thermodynamic studies

Batch adsorption experiments were performed with adsorbents (PS, HTC, STC, NTC, SHTC, PHTC and SBTC) in the temperature range of 30-65 °C at a fixed initial CBB dye concentration with their respective optimum adsorbent dose and at the optimum pH. The reaction mixtures were agitated at 180 rpm in the horizontal bench shaker for their respective contact times. The reaction mixtures were centrifuged and the supernatants were analyzed using UV-Visible spectrophotometer. The thermodynamic parameters such as, Gibbs free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated using the data from this study.

### 3. Results and discussion

#### 3.1. Characteristics of activated carbon

##### 3.1.1. Fourier Transform Infrared spectroscopy (FT-IR) studies

The FT-IR spectrum of PS is shown in Fig. 2 and the discussions were referred from Coates, 2000. The broad band in the 3500-3700  $\text{cm}^{-1}$  range indicates O-H stretching vibrations of alcoholic groups on the surface of PS. The vibrations at 1700-1725  $\text{cm}^{-1}$  and 1735-1750  $\text{cm}^{-1}$  range indicates the C=O stretching vibrations of acid and ester groups on the surface of the carbon respectively. The band range between 1300-1470  $\text{cm}^{-1}$  indicates the -CH<sub>2</sub> bending vibrations and -COO vibrations of the ester groups present on the surface of the PS. The C-O stretching vibrations appeared in the range of 1120-1260  $\text{cm}^{-1}$ . Hence the PS might carry not only the strongly hydrogen bonded residual O-H groups but also the ester and ether groups. The broadening of the bands is a confirmatory proof of the existence of strong hydrogen bonds.

The FT-IR spectra of acid and base activated carbons are shown in Fig. 2 and Fig. 3, respectively. The FT-IR spectra of both acid and base activated carbons displayed nearly similar features as those of PS. But the vibrations at 2850-2952  $\text{cm}^{-1}$  represent the

-CH<sub>2</sub> vibrations of the alkyl groups present on the surface of both acid and base activated carbons, but not on the surface of PS. The FT-IR spectra of acid and base activated carbons after dye adsorption are shown in Figs. 4 and 5, respectively.

When compared to the FT-IR spectra of both acid and base activated carbons, the O-H stretching vibrations of the alcoholic groups shifted to a lower wavelength in the spectra of the dye adsorbed activated carbons. The C=O stretching vibrations of the acid and ester groups are completely absent in the spectra of the dye adsorbed activated carbons.

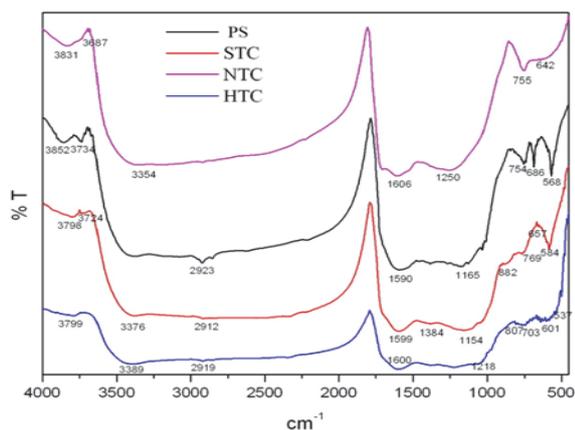


Fig. 2. FT-IR spectra of PS, HTC, STC and NTC

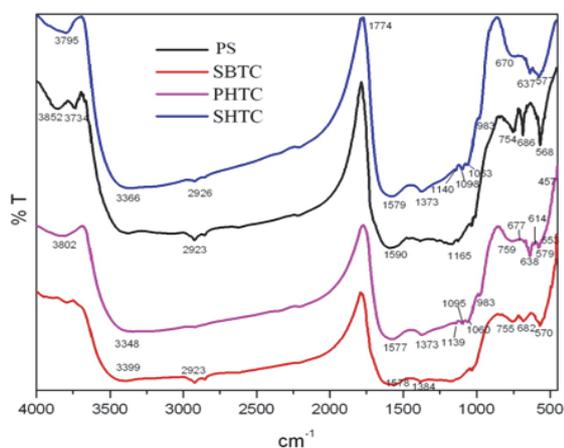


Fig. 3. FT-IR spectra of PS, SHTC, SBTC and PHTC

The -CH<sub>2</sub> vibrations of the alkyl groups also shifted in the spectra of the dye adsorbed activated carbons. Since the presence of the carboxyl groups is suggested, base treated carbon could be expected to have a high level of dye adsorption, compared to the acid activated carbon. Hydrogen bonding and dipole-dipole interaction between the carbon surface and the dye might be the reason for the strong adsorption in the base treated carbons.

### 3.1.2. Scanning Electron Microscopy (SEM) analysis

The SEM images of PS and SBTC are shown in Fig. 6 (a) and (b) respectively. The presence of the pores in the SBTC is clearly evident by comparing the SEM images of the PS Fig. 6(a) and the SBTC Fig.

6(b). The nonporous surface of the PS had been chemically modified by sodium carbonate and hence pores are produced on the surface of the SBTC which contributes to adsorption applications as it increases the surface area. Based on this observation, it is clearly evident that the SBTC has an adequate morphology for CBB adsorption.

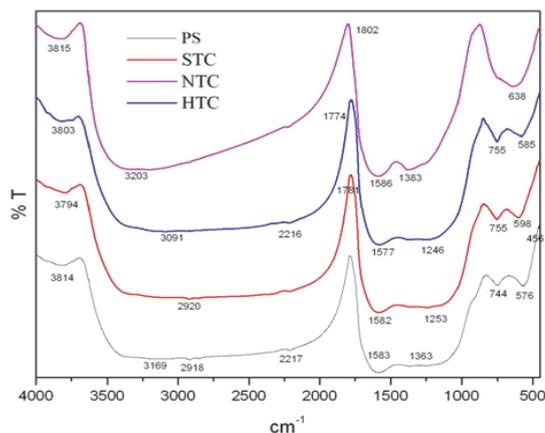


Fig. 4. FT-IR spectra of PS, HTC, STC and NTC after CBB adsorption

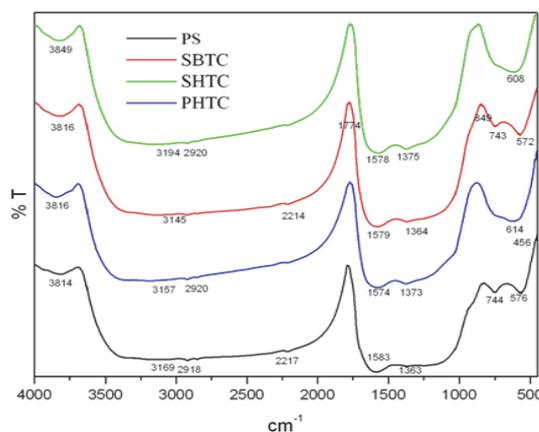


Fig. 5. FT-IR spectra of PS, SHTC, SBTC and PHTC after CBB adsorption

### 3.1.3. Energy Dispersive X-ray spectrometry (EDX) Studies

The EDX spectra of PS, SBTC and SBTC after dye adsorption are shown in Fig. 7(a), Figs. 7(b) and 7(c) respectively. The weight and atomic percentage of the organic and inorganic materials present in the PS, SBTC and dye adsorbed SBTC are tabulated in Table 2. The carbon weight percentage of the PS was increased from 54.11 to 79.26 and the carbon atomic percentage increased from 71.01 to 85.08, after the sodium bicarbonate treatment. This clearly shows that the material becomes more carbonaceous because of the chemical activation. Potassium, magnesium, calcium, silica and aluminum are the inorganic materials present in trace amounts along with carbon in raw as well as treated carbon (Fig. 7(a) and Fig. 7(b)). From the EDX spectra, it is clearly inferred that the sodium content is increased in the SBTC after dye adsorption (Fig. 7(c)).

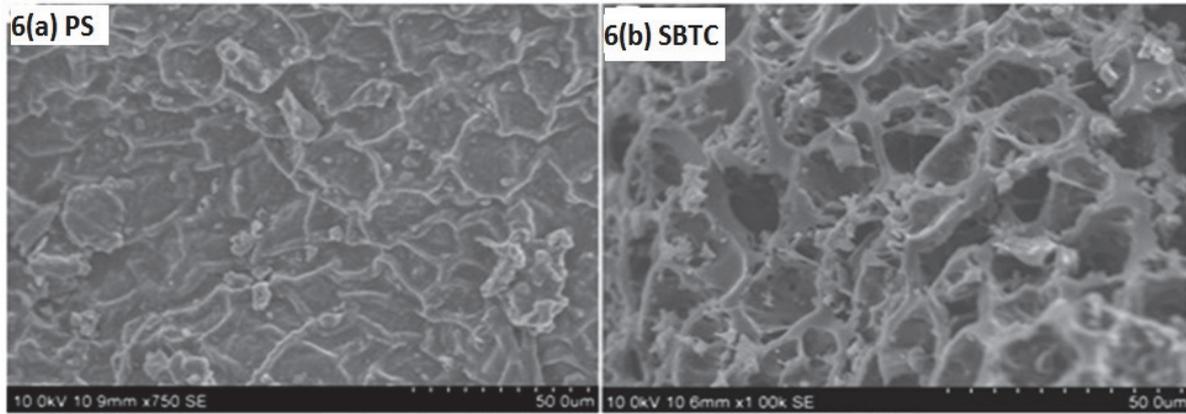


Fig. 6. (a) SEM image of PS and 6(b) SEM image of SBTC

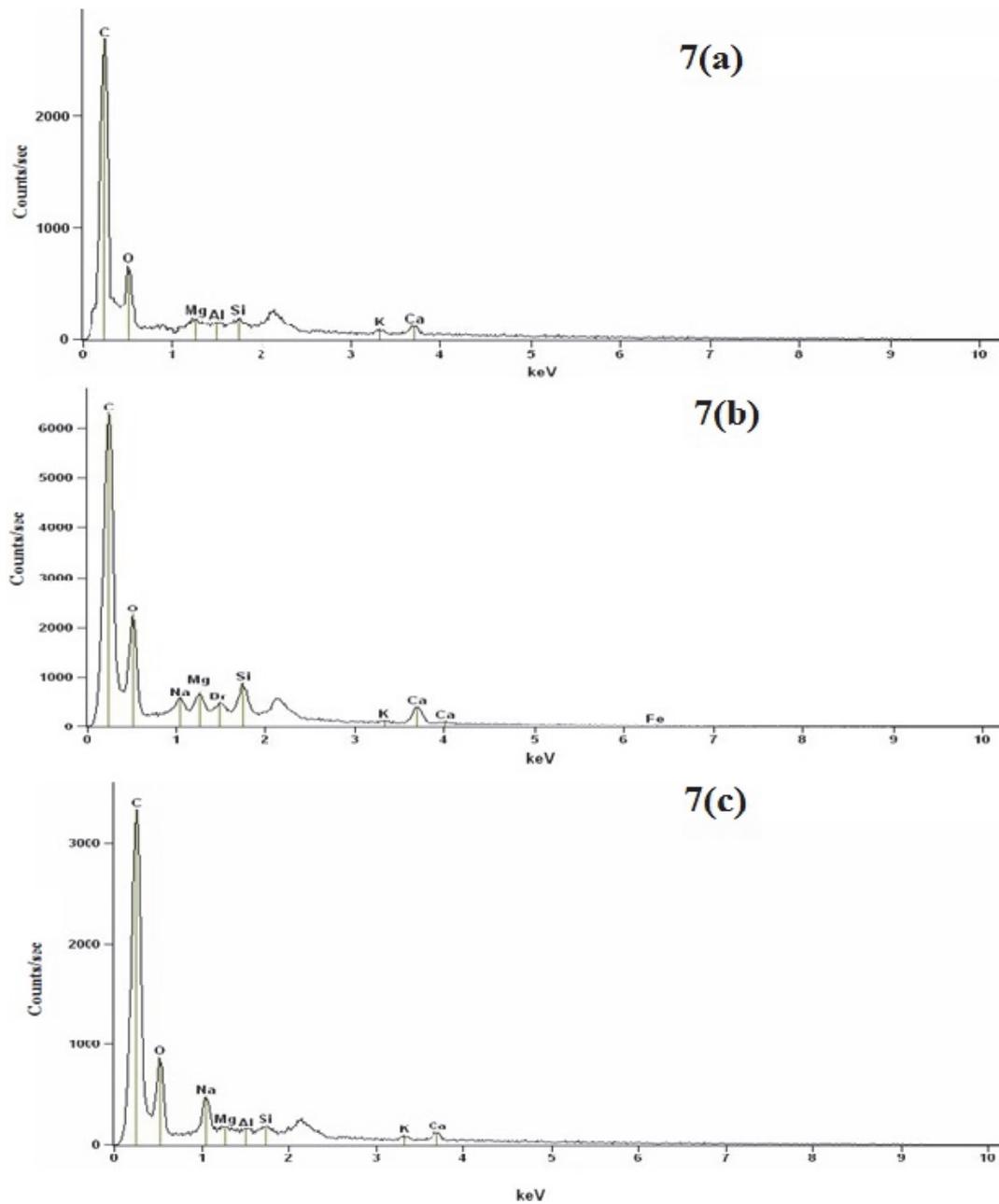


Fig. 7. (a) EDX spectra of PS, (b) EDX spectra of SBTC and (c) EDX spectra of SBTC after CBB dye adsorption

**Table 2.** EDX analysis for PS, SBTC and SBTC after dye adsorption

Element	Weight %			Atom %		
	PS	SBTC	Dye adsorbed SBTC	PS	SBTC	Dye adsorbed SBTC
C	54.11	79.26	73.67	71.01	85.08	81.60
O	23.17	15.47	18.50	19.26	12.47	15.38
Na	0.13	0.87	2.60	0.07	0.50	1.46
Mg	0.86	0.21	0.58	0.56	0.11	0.32
Al	-	0.10	-	-	0.05	-
Si	3.14	0.52	1.86	2.54	0.24	0.88
K	0.73	0.65	0.23	0.23	0.21	0.08
Ca	1.89	1.18	2.94	0.67	0.38	0.98
Fe	0.67	-	0.49	0.19	-	0.12
Total	100	100.00	100.00	100	100.00	100.00

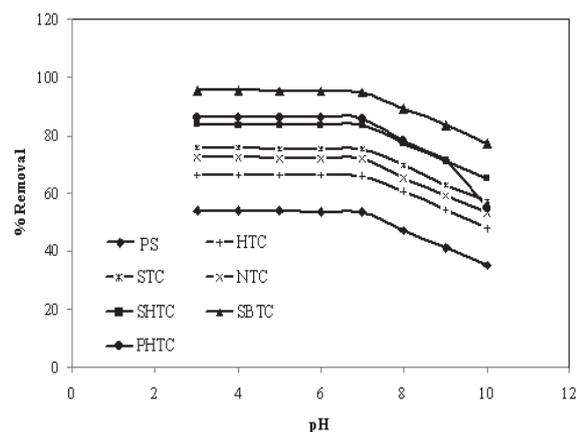
3.1.4. Brauner, Emmet and Teller (BET) analysis

The evolution of the BET surface area with PS and SBTC are 119 and 910 m<sup>2</sup> g<sup>-1</sup>, respectively. It can be clearly seen that the BET surface area is influenced by both charring and the activation of sodium bicarbonate, and it reaches a value of 910 m<sup>2</sup> g<sup>-1</sup> for SBTC.

3.2. Batch adsorption experiments

3.2.1. Effect of the solution pH on dye adsorption

One of the significant parameters in the adsorption studies is the solution pH. The pH value affects the surface charge of the adsorbent, the degree of ionizing property of the adsorbate during the adsorption process (Kumar et al., 2010). Hence, the effect of the H<sup>+</sup> ion concentration in the aqueous solutions on the percentage removal of the CBB was studied using PS and the acid and base treated carbons as adsorbents at different pH values ranging from 3.0 to 10.0. The experimental results are shown in Fig. 8.



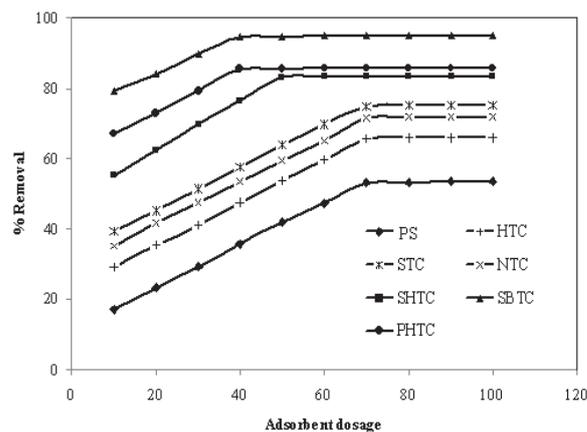
**Fig. 8.** Effect of solution pH on CBB adsorption onto PS, HTC, STC, NTC, SHTC, SBTC and PHTC.

The abundant H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> ions in the solution at low pH values, upholds the the alkyl groups on the surface of the acid and base treated carbon, to acquire a positive charge, by absorbing the H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> ions. Resilient electrostatic attraction appears between the positively charged carbon surface and the anionic dye CBB as the carbon surface gets positively charged,

which results in maximum adsorption. Because of the competition between the CBB and negative ions beyond pH 7.0, the percentage of the CBB dye removal decreases. But as the pH increases from 3.0 to 7.0, there is no profound decrease in the percentage of the dye removal. Optimum pH for the maximum removal of the CBB dye is found to be pH 7.0 from this study. The maximum removal of the CBB using the PS, and modified carbons was found to be 53.6% for PS, 66.1% for HTC, 75.2% for STC, 71.95% for NTC, 83.5% for SHTC, 95% for SBTC and 85.9 % for PHTC at the optimum pH of 7.0.

3.2.2. Effect of the adsorbent dose on dye adsorption

The adsorbent dose is an important parameter, as it helps in the determination of the amount of the adsorbent for a given initial dye concentration. The experimental data obtained from this study is presented in Fig. 9.



**Fig. 9.** Effect of adsorbent dosage on CBB adsorption onto PS, HTC, STC, NTC, SHTC, SBTC and PHTC

It is clearly evident from Figure that there is an increase in the percentage of dye removal as the adsorbent dose increases. The percentage of dye removal increases from 17.1% to 53.6% for PS, from 29.2% to 66.1% for HTC, from 39.4% to 75.2% for STC, from 35.3% to 71.95% for NTC, from 55.4% to 83.5% for SHTC, from 79.2% to 95% for SBTC and from 67.3% to 85.9% for PHTC respectively. Rapid superficial adsorption onto the adsorbent surface

occurred with higher adsorbent to dye concentration ratios, which results in a lower dye concentration in the solution when compared with low adsorbent to dye concentration ratios. There would be no dye molecules in the solution to be adsorbed as the adsorbent dose increases; this results in more vacant adsorption sites causes the decrease in percentage of dye removal. From this study it is clearly evident that the SBTC acquired higher percentage removal (94.5%) with the requirement of less adsorbent dosage (40 mg), compared to the other adsorbents studied.

### 3.2.3. Effect of contact time on dye adsorption

For an economical wastewater treatment plant, the equilibrium time is one of the most important parameters. The effect of the contact time on the percentage removal of the CBB dye from an aqueous solution by the adsorbents is shown in Fig. 10.

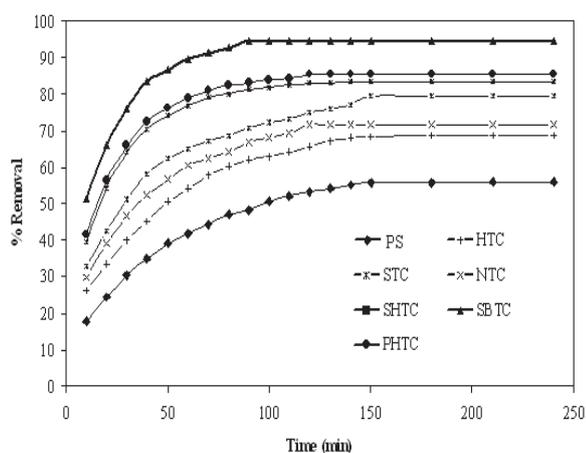


Fig. 10. Effect of contact time on CBB adsorption onto PS, HTC, STC, NTC, SHTC, SBTC and PHTC

It is clearly evident from Figure that the removal of dyes increases with the increase in the contact time, at which the equilibrium is reached; 150 min for the HTC, STC as well as PS, 140 min for the NTC, 120 min for the SHTC as well as PHTC and 90 min for the SBTC under study. This is mainly due to the rapid adsorption of dyes that takes place during the initial stages on the external surface of the adsorbents. Further experiments were conducted for the respective contact times only. There is a higher possibility for monolayer adsorption of the dye molecules onto the adsorbents chosen in this study; because the curves obtained are smooth, single and continuous, and saturates at equilibrium. From this study it is clearly evident that the SBTC acquired equilibrium in 90 min, with the maximum high percentage removal of 94.5% as compared with the other adsorbents.

### 3.2.4. Kinetic studies

Pseudo-first order, pseudo-second order kinetic equations and the Intraparticle diffusion model were used to test the experimental data obtained from the effect of the contact time studies on the CBB adsorption in order to examine the controlling mechanism of the adsorption process.

#### 3.2.4.1. Pseudo-first order kinetic model

The pseudo-first order kinetic model was suggested by Lagergren. The pseudo-first order equation is given by Lagergren (1898) (Eq. 4):

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

where  $q_t$  is the adsorption capacity at time  $t$  (mg/g) and  $k_{ad}$  ( $\text{min}^{-1}$ ) is the rate constant of the pseudo-first order kinetic equation. The rate constant ( $k_{ad}$ ), adsorption equilibrium capacity ( $q_e$ ) and coefficient of determination ( $R^2$ ) values of the CBB dye adsorption onto the adsorbents in the pseudo-first order kinetic model were calculated from the linear plots of  $\log(q_e - q_t)$  versus  $t$  (Fig. 11) and the values have been listed in Table 3.

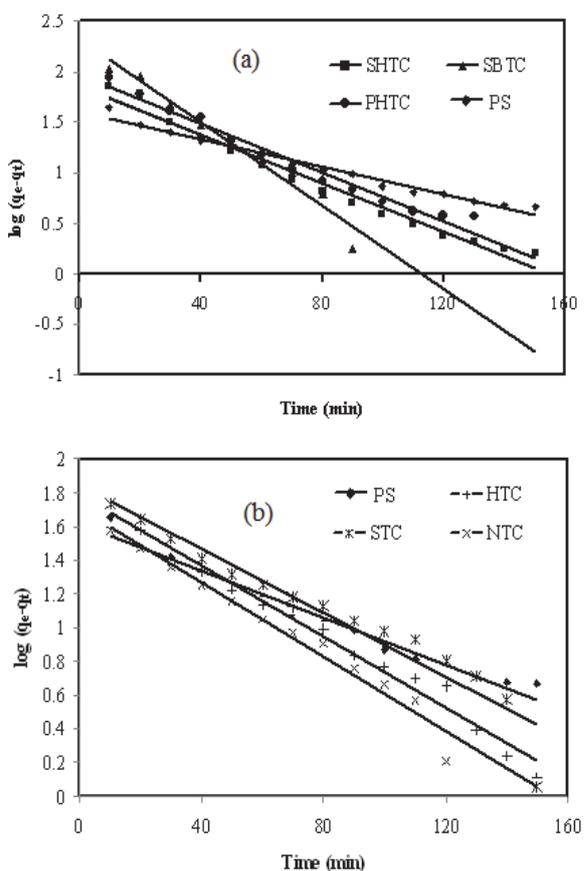


Fig. 11. Pseudo-first order kinetic plots on the CBB adsorption (a) PS, SHTC, SBTC and PHTC and (b) PS, HTC, STC and NTC

#### 3.2.4.2. Pseudo-second order kinetic model

The kinetic data were further analyzed using Ho's pseudo-second order kinetics model. It can be expressed as (Ho and McKay, 1999) (Eq. 5):

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{1}{q_e} t \quad (5)$$

where  $k$  is the pseudo-second order kinetic rate constant ( $\text{g/mg}\cdot\text{min}$ ). The slope and intercept derived

from the linear plot of  $t/q_t$  versus  $t$  yields the values of  $q_e$  and  $k$  (Fig. 12) and they are listed in Table 3.

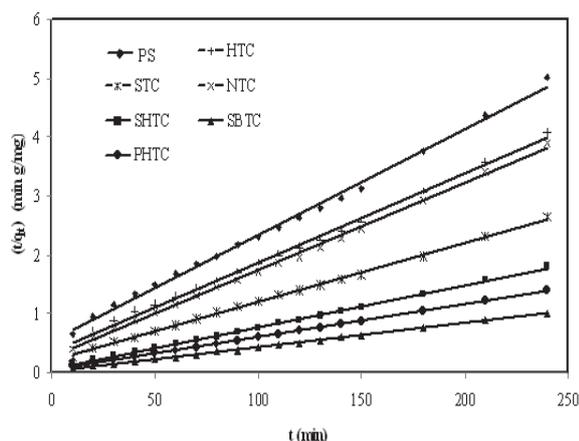


Fig. 12. Pseudo-second order kinetic plots on CBB adsorption onto PS, HTC, STC, NTC, SHTC, SBTC and PHTC

### 3.2.4.3. Intraparticle diffusion model

In order to gain an insight into the adsorption mechanism, the experimental data should be fitted to the mass transfer kinetic model such as Weber's intraparticle diffusion model. This model is expressed as (Weber and Morris, 1963) (Eq. 6):

$$q_t = k_p t^{1/2} + C \quad (6)$$

where  $C$  is the intercept and  $k_p$  is the intraparticle diffusion rate constant ( $\text{mg/gmin}^{1/2}$ ), which can be evaluated from the slope of the linear plot of  $q_t$  versus  $t^{1/2}$ , (Fig. 13).

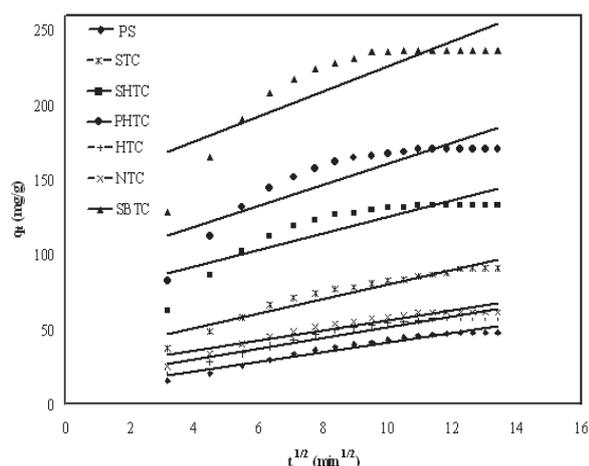


Fig. 13. Intraparticle diffusion kinetic plots on the CBB adsorption onto PS, HTC, STC, NTC, SHTC, SBTC and PHTC

The calculated intraparticle diffusion coefficient  $k_p$ ,  $C$  and  $R^2$  values of the CBB dye adsorption onto the adsorbents are listed in Table 3. The intercept of the plot reflects the boundary layer effect. The larger the intercept the greater will be the

contribution of the surface adsorption to the rate controlling step.

Though the  $R^2$  values were found to be high in both the pseudo-first order and pseudo-second order kinetic model, the  $q_e$  experimental values are close to the  $q_e$  calculated values in the pseudo-second order model. Therefore, the adsorption of the CBB dye onto the adsorbents follows the pseudo-second order kinetic model. In the diffusion model, if the plot of  $q_t$  versus  $t^{1/2}$  is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots for the CBB dye did not pass through the origin. This indicates that the intraparticle diffusion was not the only rate controlling step. Hence, it is concluded that the rate limiting step for the adsorption of CBB dye on the adsorbents may be due to both adsorption and intraparticle diffusion.

### 3.2.5. Effect of the initial dye concentration on dye adsorption

The effect of the initial dye concentration on the adsorption of the CBB dye onto the adsorbents was investigated in the range of 20 to 160 mg/L and the result is shown in Fig. 14.

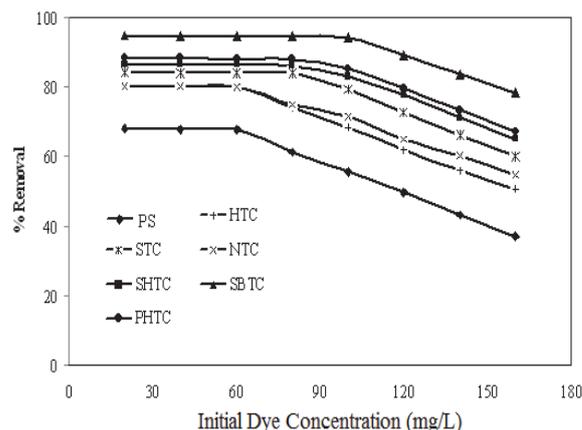


Fig. 14. Effect of the initial dye concentration on the CBB adsorption onto PS, HTC, STC, NTC, SHTC, SBTC and PHTC

From Fig. 14 it is evident that the percentage dye removal of the CBB decreased from 68.15% to 37.1% for PS, 80.45% to 50.7% for HTC, 84.3 to 60.1% for STC, 80.4% to 54.8% for NTC, 86.7% to 65.2% for SHTC, 94.9% to 78.4% for SBTC and 88.4% to 88.2% respectively, for the increase in initial dye concentration from 20 mg/L to 160 mg/L. This may be due to the adsorption of available active sites on the adsorbent, beyond a certain concentration of the dye solution. At a fixed adsorbent dose for a low concentration of the dye solution, the adsorption process proceeds faster due to the less number of dye molecules in the solution of CBB. If the dye concentration is increased then the number of dye molecules in the solution increases against a fixed amount of available active sites. Therefore, there is a decrease in the percentage dye removal with an increase in the initial dye concentration.

**Table 3.** Kinetic parameters for the adsorption of the CBB onto the acid and base treated adsorbents

Kinetic model	Parameters	Adsorbents						
		PS	HTC	STC	NTC	SHTC	SBTC	PHTC
Pseudo-first order equation	$k_{ad}$ (min <sup>-1</sup> )	0.0665	0.140	0.136	0.115	0.084	0.2907	0.1175
	$q_{e,cal}$ (mg/g)	49.22	46.72	77.74	42.43	96.56	111.3	212.4
	$q_{e,exp}$ (mg/g)	58.11	58.77	90.85	61.47	138.24	236.25	176.4
	R <sup>2</sup>	0.9538	0.975	0.929	0.959	0.949	0.9247	0.9547
Pseudo-second order equation	$k$ (g/mg.min)	1.066	1.08	0.9857	0.8627	2.404	1.536	0.9854
	$q_{e,cal}$ (mg/g)	52.4	53.24	87.87	59.27	134.44	234.22	173.2
	$q_{e,exp}$ (mg/g)	58.11	58.77	90.85	61.47	138.24	236.25	176.4
	R <sup>2</sup>	0.998	0.998	0.998	0.99	0.998	0.998	0.998
Intraparticle diffusion	$k_p$ (mg/g.min <sup>1/2</sup> )	2.751	2.256	2.671	2.715	2.465	2.641	2.454
	$C$	50.11	52.21	72.44	42.44	97.22	111.4	72.4
	R <sup>2</sup>	0.73	0.773	0.724	0.714	0.728	0.714	0.74

The results show that the percentage of the CBB dye removal decreases with the increase in the initial dye concentration. In order to overcome the mass transfer resistance of the dye between the aqueous phase and the solid phase, the initial dye concentration provides the necessary driving force. The interaction between the dye and the adsorbent is enhanced by the increase in the initial dye concentration. Hence the adsorption of the dye enhances due to an increase in the concentration gradient of the initial dye concentration.

### 3.2.6. Adsorption equilibrium study

Various adsorption isotherm models were adapted to fit the data obtained from the study on the effect of the initial dye concentration in order to understand the mechanism of adsorption of CBB dye onto the adsorbents. The maximum adsorption capacity of the adsorbent could be determined from the adsorption isotherm studies. This analyses provides a clear view of the efficiency of the adsorption of CBB dye onto the adsorbent and also to estimate the economic viability of the adsorbents for commercial applications. The well-established adsorption isotherm models such as the Langmuir, Freundlich and Redlich-Peterson adsorption models were used to fit the experimental data obtained from the effect of the initial dye concentration study.

#### 3.2.6.1. Langmuir adsorption isotherm

The theoretical Langmuir adsorption isotherm is based on three assumptions, namely: Equivalent active sites present on the surface of the adsorbent, and can adsorb minimum one atom; the adsorption of the adsorbate molecules at a given site does not depend on the adsorption of other adsorbate molecules onto the neighboring active sites, and adsorption of the molecules follows a monolayer trend. The Langmuir isotherm model can be expressed as the non-linear equation as follows (Langmuir, 1918) (Eq. 7):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where  $C_e$  is the dye concentration at the equilibrium state of the system (mg/L),  $q_m$  (mg/g) represents the

maximum monolayer adsorption capacity of the adsorbent and  $K_L$  (L/mg) is the energy constant related to the heat of adsorption .

#### 3.2.6.2. Freundlich adsorption isotherm

The adsorption process could be explained well by Freundlich isotherm model. The assumptions of this model are: adsorption occurs on heterogeneous surfaces with an interface between the adsorbed molecules, and the adsorption energy exponentially decreases, on sustaining the adsorption centers of the given adsorbent. This empirical equation of this isotherm is expressed by Eq. (8) (Freundlich, 1906):

$$q_e = K_F C_e^{1/n} \quad (8)$$

where  $K_F$  is the Freundlich constant ((mg/g)(L/mg)<sup>(1/n)</sup>) related to the bonding energy. The adsorption or distribution coefficient,  $K_F$  is defined as the quantity of the dye adsorbed for unit equilibrium concentration. The heterogeneity factor  $1/n$ , and  $n$  is the gauge of the deviation from the linearity of adsorption which indicates the degree of non-linearity between the solution concentration and adsorption as follows: if  $n=1$ , the adsorption is linear; if  $n<1$ , it implies that the adsorption process is favored by chemisorption and if  $n>1$ , the adsorption process is favored by physisorption.

#### 3.2.6.3. Redlich - Peterson adsorption isotherm

The Redlich - Peterson isotherm is a blend of the Langmuir-Freundlich model. The equation is given as (Eq. 9) (Redlich 1959):

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^\beta} \quad (9)$$

where  $K_R$  is the Redlich - Peterson isotherm constant (L/g),  $\alpha_R$  is the Redlich - Peterson isotherm constant (L/mg), and  $\beta$  is the exponent which lies between 0 and 1. The constant  $\beta$  can characterize the isotherm; if  $\beta = 1$ , the Langmuir will be the preferable isotherm, while if  $\beta = 0$ , the Freundlich isotherm will be the preferable isotherm.

The graphical representations of the above mentioned adsorption isotherm models for the PS and the other adsorbents HTC, STC, NTC, SHTC, SBTC and PHTC respectively are presented in Fig. 15 and Fig. 16. The parameters and R<sup>2</sup> values for the respective adsorption isotherms were calculated, and are provided in Table 4.

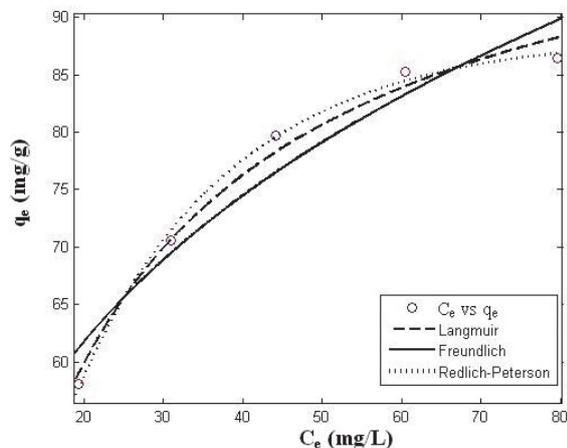


Fig. 15. Nonlinear adsorption isotherm for the CBB dye onto the PS

From Table 4, it was inferred that the Langmuir and Redlich-Peterson adsorption isotherm model best

fits the experimental data based on its R<sup>2</sup> values, as compared with the Freundlich adsorption isotherm models. This confirms that the saturated monolayer of the dye molecules was adsorbed onto the adsorbent surface. From the Freundlich adsorption isotherm model, it was found that the value of n is less than unity which indicates that the adsorption of the CBB dye onto the adsorbents is a favorable chemical process.

The Redlich – Peterson exponent  $\beta$  approaches closer to 1. From the Redlich exponent data it was inferred that the adsorption of the CBB dye onto the adsorbents follows the Langmuir isotherm model preferably. SBTC has a high adsorption capacity compared to other adsorbents, due to the presence of more active sites. The maximum monolayer adsorption capacity of the adsorbents for the removal dyes were given in Table 5. From Table 3, it is clearly evident that the SBTS has the highest maximum monolayer adsorption capacity for the removal of dyes from the aqueous solution.

3.2.7. Effect of temperature and thermodynamic studies

The effect of temperature on the percentage of the CBB dye removal by the adsorbents was investigated in the temperature range of 30 - 60 °C and the result is shown in Fig. 17.

Table 4. Adsorption isotherm constants for the removal of the CBB by acid and base treated adsorbents

Isotherm Model	Adsorbents							
	Parameters	PS	HTC	STC	NTC	SHTC	SBTC	PHTC
Langmuir	$q_m$ (mg/g)	58.11	58.77	90.85	61.47	138.2	237.2	176.4
	$K_L$ (L/mg)	0.06658	0.0887	0.09857	0.06827	0.08403	0.2907	0.1175
	R <sup>2</sup>	0.9862	0.998	0.9592	0.9952	0.9634	0.9247	0.9657
Freundlich	$K_F((\text{mg/g})(\text{L/mg})^{(1/n)})$	27.41	34.92	40.75	30.15	45.87	125.8	80.08
	n (g/L)	0.691	0.456	0.168	0.856	0.404	0.536	0.991
	R <sup>2</sup>	0.9146	0.9805	0.9267	0.9767	0.93	0.9447	0.9049
Redlich-Peterson	$\alpha_R$ (L/mg)	0.0175	0.1287	0.0167	0.0712	0.0077	0.0775	0.0208
	$\beta$	0.785	0.732	0.815	0.899	0.725	0.812	0.887
	$K_R$ (L/g)	4.847	13.55	10.75	10.52	15.32	66.7	25.67
	R <sup>2</sup>	0.9941	0.9988	0.9797	0.9952	0.9895	0.9487	0.9854

Table 5. Comparison of maximum monolayer adsorption capacity of the adsorbents for the removal of anionic dyes

Adsorbents	Adsorbate	$q_m$ (mg/g)	Reference
Ethylenediamine modified chitosan	Eosin Y	294.12	Huang et al. (2011)
SBTC	Coomassie Brilliant Blue G-250	237.2	Present study
Methylene dimethylamine hydrochloride modified starch	Reactive brilliant red	209	Jiang et al. (2010)
PHTC	Coomassie Brilliant Blue G	176.4	Present study
SHTC	Coomassie Brilliant Blue G	138.2	Present study
Crosslinked poly(acrylamidopropyl trimethylammonium) grafted pullulan	Azocarmine B	113.6	Constantin et al. (2013)
STC	Coomassie Brilliant Blue G	90.85	Present study
NTC	Coomassie Brilliant Blue G	61.47	Present study
HTC	Coomassie Brilliant Blue G	58.77	Present study
PS	Coomassie Brilliant Blue G	58.11	Present study
Neem saw dust carbon	Congo red	45.23	Kumar (2010)
Cashew nut shell	Congo red	5.184	Kumar et al. (2010)

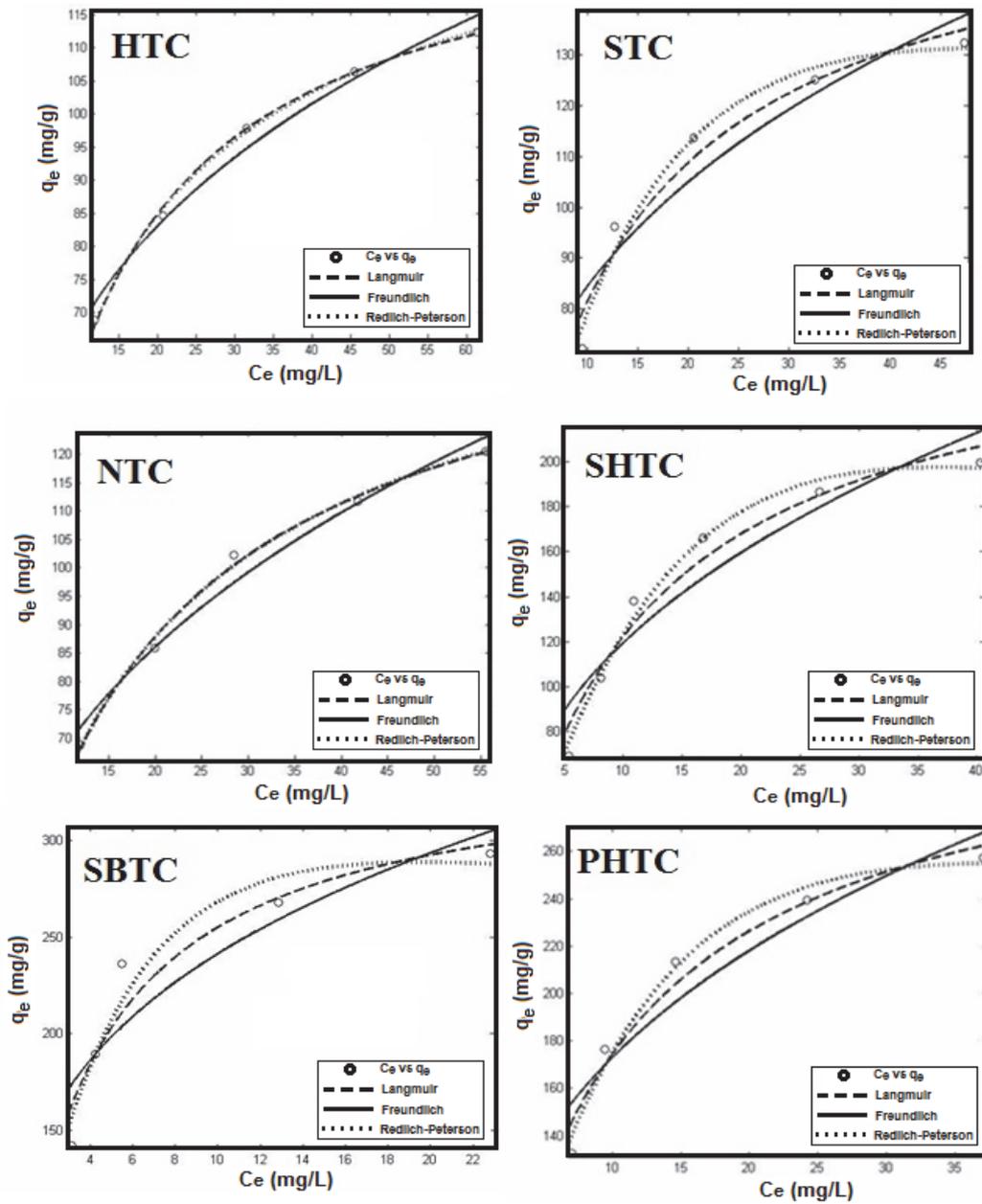


Fig. 16. The nonlinear adsorption isotherm for the CBB dye onto the HTC, STC, NTC, SHTC, SBTC and PHTC

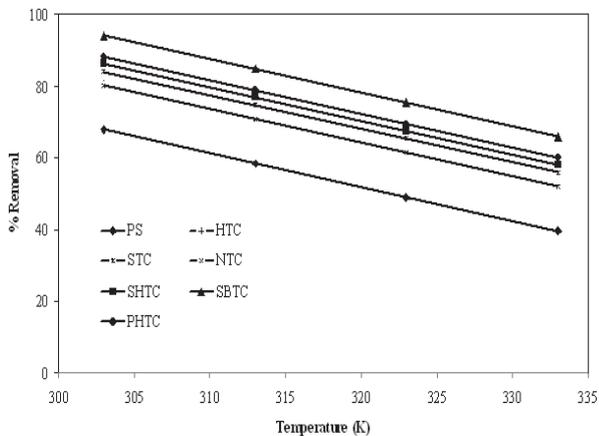


Fig. 17. Effect of temperature on the CBB adsorption onto PS, HTC, STC, NTC, SHTC, SBTC and PHTC

The results show that the adsorption of dyes onto the adsorbent is highly dependent on the temperature. The maximum adsorption of dyes onto the adsorbent was observed at 30°C. The percentage removal of the CBB dye decreases sharply with an increase in the temperature. This is mainly due to the decrease in the surface activity, suggesting that the adsorption between the dyes and the adsorbent is an exothermic process.

The thermodynamic parameters, such as Gibbs free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated from the following equations (Eichlerova et al., 2007) (Eq. 10, Eq. 11 and Eq. 12):

$$K_c = \frac{C_{Ae}}{C_e} \tag{10}$$

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

$$\log K_c = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (12)$$

where  $K_c$  is the equilibrium constant,  $C_e$  is the equilibrium dye concentration in the solution (mg/L),  $C_{Ae}$  is the amount of dyes adsorbed on the adsorbent per liter of solution at equilibrium (mg/L),  $R$  is the gas constant (8.314 J/mol.K) and  $T$  is the temperature (K). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slope and the intercept from the plot of  $\log K_c$  versus  $1/T$  (Fig. 18). The calculated thermodynamic properties are listed in Table 6.

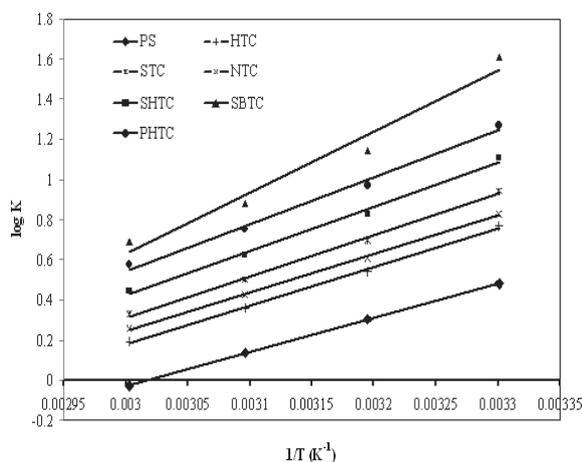


Fig. 18. Thermodynamic plots for the adsorption of the CBB onto PS, HTC, STC, NTC, SHTC, SBTC and PHTC

The thermodynamic parameters are used to evaluate the feasibility and nature of the adsorption process. The negative  $\Delta G^\circ$  value indicates that the nature of adsorption process is feasible and spontaneous. The decrease in  $\Delta G^\circ$  values with the increase in temperature which indicates that the adsorption process was more favorable at lower temperature. The increase in temperature may enhance the movement of the dyes adsorbed already which creates a trend of desorbing dyes from the adsorbent surface. The importance of  $\Delta G^\circ$  is as follows: -20 to 0 kJ/mol (physical adsorption) and -80 to -400 kJ/mol (chemical adsorption) (Jaycock and Parfitt, 1981). For the present adsorption process, the value of  $\Delta G^\circ$  was appeared between -20 and 0 which indicates that the

adsorption process may be of physical type. The negative values of  $\Delta H^\circ$  for the adsorption indicate that the adsorption of the CBB dye onto the adsorbent is an exothermic process in nature. The change in entropy ( $\Delta S^\circ$ ) reveals the randomness at the adsorbent-solution interface during the adsorption of dyes.

#### 4. Conclusions

The present investigation shows that psyllium stalks, in their native and modified forms, can be utilized as an effective adsorbent for the removal of CBB dye. The FTIR spectrum of modified adsorbents as compared to that of PS is different, which confirms the modification. The SEM image of the SBTC shows an irregular pattern and a more porous surface than the PS image, which shows that the SBTC has a more desired surface morphology for dye adsorption than the other adsorbents.

The EDX analysis on SBTC shows that this material is made more carbonaceous and adsorbs the CBB dye. The maximum removal of the CBB using the modified adsorbents was obtained at the optimum pH of 7.0. As the adsorbent dose increases, it was clearly evident that the dye removal also increases. Dye removals were increased with the increase in the contact time; the SBTC acquired equilibrium in 90 min with a high percentage removal (94.5%). The adsorption kinetics of the CBB dye onto both the native and modified adsorbents shows that both adsorption and intraparticle diffusion are the rate controlling step for the removal of the CBB dye by adsorption onto the adsorbents.

As the initial dye concentration increases, it was observed that the percentage of dye removal decreases. From the Redlich exponent data, it was inferred that adsorption of the CBB dye onto the adsorbents follows the Langmuir isotherm model preferably. The Langmuir monolayer adsorption capacity value of SBTC for the CBB dye is found to be 237.2 mg/g. The percentage removal of the CBB dye decreases with an increase in the temperature and the negative value of  $\Delta H^\circ$  reveal the exothermic nature of adsorption.

Based on the above observations, it can be concluded that among the modified adsorbents, SBTC is found to possess the maximum adsorption capacity to treat wastewater containing a high concentration of the CBB dye.

Table 6. Thermodynamic parameters for the adsorption of the CBB onto the acid and base treated adsorbents

Adsorbents	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (kJ/mol)			
			303 K	313 K	323 K	333 K
PS	-1.343	-36.379	-2.7742	-1.8109	-0.8503	-0.18129
HTC	-1.141	-23.3211	-4.43829	-3.24558	-2.2156	-1.22017
STC	-1.459	-30.194	-5.48295	-4.16053	-3.0815	-2.08192
NTC	-1.4	-30.329	-4.81072	-3.63413	-2.6182	-1.63586
SHTC	-1.572	-30.941	-6.40382	-4.94813	-3.8363	-2.83538
SBTC	-1.835	-30.309	-9.33053	-6.85777	-5.4684	-4.37318
PHTC	-1.6112	-29.256	-7.37554	-5.80101	-4.6596	-3.65936

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