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Activated Carbon Derived from Banana Stem Waste for Adsorption of Crystal Violet

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Abstract

The potential of activated carbon derived from banana stem waste (ACBS) and its application as a low cost adsorbent for crystal violet (CV) dye adsorption was evaluated. In this study, three types of adsorbents were prepared; ACBS treated with sodium hydroxide (ACBS-NaOH), ACBS treated with sulphuric acid (ACBS-H2SO4) and ACBS treated with distilled water (ACBS-DW). The treated adsorbents were prepared by impregnating it with the desired activated agent for at least six hours. Prior to adsorption, all the adsorbents were calcined in a furnace at 773 K for two hours. The adsorbents were characterized using Fourier transform infrared (FTIR) spectroscopy and pH_{zpc}. FTIR analysis revealed that –OH, –C=O, and –C–O functional groups were mainly responsible for the adsorption process. The study revealed that the pre-treatment with NaOH significantly enhanced the CV uptake due to the alkaline attack that affected the chemical composition of the ACBS surface by generating more O-Na sites that could bind with CV dye molecules. Fitting of the adsorption data with the non-linear Langmuir isotherms produced the maximum adsorption capacity of 268.6 mg g-1. On the other hand, the adsorption of CV onto ACBS-NaOH was mainly via physisorption process, where their activation energy was 7.9 kJ mol^{-1}. This study shows a low cost yet feasible material such as banana stem from agricultural waste , that has a huge potential as an adsorbent for the removal of CV dye ions from aqueous solution.

Keywords: Activated carbon, crystal violet, adsorption, banana stem, thermodynamics

1. Introduction

Activated carbon (AC) is a carbonaceous porous substance where it possesses a complex and contorted internal pores network that makes this material very ideal for applications for adsorption. In addition, it also possess an high surface reactivity which can be contributed by the surface functional groups and a large surface area that promotes more adsorption binding sites [1]. Activated carbon is also a popular adsorbent option because of its low cost, exceptionally high porosity, tuneable pore size and high adsorptive capacities [2].

The use of low-cost adsorbent materials has gained attention in recent years. Banana stem waste can be abundantly found in the Southeast Asia region. Thus, it is chosen as the low-cost precursor for this study. Banana stem consists of biopolymers that contains polyphenolic and aliphatic hydroxyl groups [3], which plays a huge role in the adsorption of cationic dyes [4]. However, it has a low sorption capacity and poor physical stability without any modification. Thus, converting it into activated carbon will increase the surface area and volume pore of the material that will lead to higher adsorption capacity. Activated carbon that undergoes chemical pre-treatment display significantly higher efficiencies in eliminating toxins compared with the untreated ones [5].

Crystal violet (CV) is a cationic dye with the molecular formula of $C_{25}H_{30}N_3Cl$. For medical application, CV is used for antibacterial and veterinary medicine, while nonmedical application of CV is for manufacture of printing ink, fertilizers, antifreezes, detergents, and leather. CV has been identified as a recalcitrant dye molecule, which persists in the environment for a long period of time and poses toxic environmental effects, despite its many uses. It serves as a mitotic poison, potent carcinogen and a strong clastogen that stimulates tumor development in certain fish species [6]. Correspondingly, CV is considered a biohazardous substance.

This research will emphasize on preparing activated carbon derived from banana stem waste (ACBS), characterizing the physical properties of ACBS and studying the adsorption behaviour, equilibrium isotherms and kinetics behaviour of the adsorption of CV onto ACBS. ACBS were pre-treated with alkali (NaOH), acid (H_2SO_4) and distilled water. All three variations of ACBS were compared in a preliminary experiment, and the adsorbent that displays the best adsorption capacity towards CV will be chosen, and its adsorption behaviour, equilibrium isotherm and kinetics behaviour were furthered studied.

2. Methodology

2.1. Preparation of adsorbent

The banana stem wastes (BS) were washed with distilled water to remove dust and other inorganic impurities and air-dried until it has parched. Then, the dried samples are cut into small pieces and ground. The fine powders of the ground BS were then washed with distilled water forming a sludge mixture. The sludge is then filtered out with a filter paper to remove the excess water. The remaining BS will be dried in the oven overnight at 353 K. After it had dried, the resulting BS were divided into three equal parts for further modification with the activating agents. The activating agents used in this study were sodium hydroxide (NaOH), sulphuric acid (H_2SO_4) and distilled water. The dried BS sample produced was impregnated with the activating agent at a ratio of 1:4 (3g of BS and 12g of activating agent). 250 ml of distilled water was added into the mixture and impregnated for at least 6 hours with continuous stirring. It was then filtered and dried in the oven overnight at 353 K. Once it was dried, the impregnated BS was placed in the furnace where it was calcined for 2 hours at 773 K. Once it cold down, let it dry at the oven overnight at 353 K. The resulting product is denoted as activated carbon derived from banana stem waste (ACBS-X) where X is the activating agent.

2.2. Adsorbate solution

The adsorbate, Crystal Violet (CV) dye (Molecular weight = 407.98 g.mol^{-1}) was obtained from Fluka (purity = 99%). The structure of Crystal violet is illustrated in Fig.1. Stock solution was prepared by dissolving accurately weighed quantity of dye in 1000 mg.L^{-1} of distilled water. The experimental solutions of desired concentration were prepared accordingly by diluting the stock solution with distilled water. The concentration of CV dye was measured at λ_{max} = 589 nm using UV–Visible spectrophotometer.

2.3 Adsorbent characterization

The functional groups that are involve in adsorption of CV on the ACBS were analysed by Fourier Transform Infrared Spectroscopy (FTIR) using a range sweeping wavelength 400 - 4000 cm-1.

2.4 Adsorption experiments

The removal efficiency of the ACBS were studied by batch adsorption experiments. Batch studies for CV were carried out to investigate the effect of pre-treatment and contact time, adsorbent dose, initial concentration of CV and initial pH of solution. Since the adsorption process of CV is fast, the time required for the ACBS in contact with the CV solution to achieve equilibrium was determined by preliminary experiments. Approximately, 0.02 g of the adsorbent was added to 200 mL of CV solution (10 mg L^{-1}) and the resulting suspension was shaken at ambient temperature (30 °C), at pre-determined time intervals (0-90 min) to ensure establishment of equilibrium. Residual concentration of crystal violet was determined using a UV/vis spectrophotometer at 589 nm.

Then the dose effect of ACBS was studied with different interval (0.02 g- 0.05 g), each mass of adsorbent were added to V = 200 mL of CV solution (10 mg L^{-1}) in Erlenmeyer flask at equilibrium time. The effect of initial dye concentration on equilibrium was observed by mixing 0.03 g L^{-1} (optimum mass found) of adsorbent with 200 mL of CV solutions with different initial concentrations ranges from 10 to 200 mg L^{-1}. In order to investigate the effect of initial solution pH on the adsorption property of CV, solutions of 10 mg L^{-1} with the same amount of adsorbent (0.03 g) were adjusted with a pH paper to different values by adding drops of HCl and NaOH (0.1 M) solutions and shaken at 80 rpm for 90 min at ambient temperature.

The percent removal of CV from solution was calculated by the following equation:

$$\%\,removel = \frac{Co\ - Ce}{Co} * 100 \tag{1}$$

The adsorption uptake, q_e (mg g-1), of the adsorbent is calculated using the Equation (2).

$$q_e = \frac{(Co\ - Ce)V}{m} \tag{2}$$

where, Co and Ce (mg L-1) are the concentrations of CV at the initial time and at equilibrium time, respectively, V (L) is the volume of the solution and m (g) is the mass of the adsorbent used.

2.5 Adsorption isotherm

The adsorption isotherm models generally used to design and to understand the mechanism of interaction existing between adsorbate and the adsorbent at equilibrium [7]. In this work, two isotherm models (Langmuir and Freundlich) were applied to describe the distribution of dye ions between the liquid phase and the solid phase at constant temperature.

The Langmuir model assumes monolayer adsorption on a structurally homogeneous adsorbent, where all the adsorption sites are energetically uniform. Is based on the assumptions that each active site can only react with one dye molecule, no further Adsorption can take place at that site [8]. The Freundlich model assumes heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules [9].

The non-linear form of the Langmuir and Freundlich isotherm models are given by Eq. (3) and (4) respectively.

$$q_e = \frac{q_m K_L C_e}{1 +\ K_L C_e} \tag{3}$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of dye ion adsorbed on adsorbent and the concentration of adsorbate at equilibrium while q_m (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir constants. The Freundlich isotherm can be expressed by the following equation:

$$q_e = \ K_F C_e^{\frac{1}{nF}} \tag{4}$$

where K_F is the constant of Freundlich isotherm ($L^{1/nF}$ $mg^{(1-1/nF)}$ g^{-1}), and 1/nF is the Freundlich exponent.

2.6 Adsorption kinetics

Kinetic studies are carried out to provide information about the mechanism of adsorption, two classical kinetics models, a pseudo-first order kinetic model of Lagergren Eq. (5) and a pseudo-second order kinetic model of Ho, Eq. (6) were employed to test the experimental data of dye adsorption by ACBS.

$$Pseudo-first-ord \qquad q_t = \ q_e(1 - e^{-k_1 t}) \tag{5}$$

$$Pseudo-second-ord \qquad q_t = \frac{q_{e^2} k_2 t}{1 +\ q_e k_2 t} \tag{6}$$

where, q_e and q_t are the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time, t (min) respectively. k_1/k_2 represented the pseudo-first-order rate constant and pseudo-second order equilibrium rate constant (g mg^{-1} min^{-1}) respectively. The best-fit model was chosen based on the values of the regression coefficient (R2) of the non-linear plots of pseudo- first order and pseudo-second order kinetic model equations.

3. Results and Discussion

3.1. Characterization of adsorbents

3.1.1 Functional group determination

Analyzing the FTIR spectrum helps in determine the chemical compositions of materials and the possible interactions that take place between the functional groups of ACBS and CV dye ions. Figure. 1 illustrates the FTIR spectra of all ACBS adsorbents.

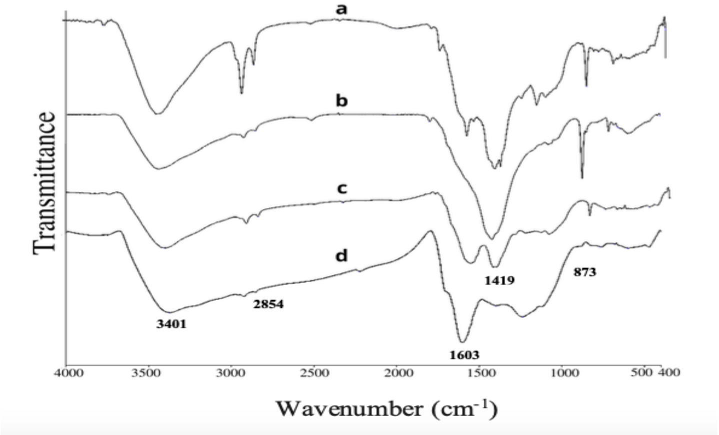

Figure 1. FTIR spectra of (a) CV adsorbed on ACBS-NaOH (b) ACBS-NaOH ,and (c) ACBS-DW and (d) ACBS-H_2SO_4.

Generally, all ACBS adsorbents shows a similar absorbance bands centered at 3405 and 2877cm^{-1} that correlate to O-H groups from the glucosidic ring of cellulose and C–H stretching of the methyl and methylene groups [9]. These peaks are present consistently before and after the chemical modifications, indicating that these groups did not participate in the chemical modification. The presence of sharp spectra at a region of 1500-1300 cm^{-1} is probably due to the detection of C=O stretching of carboxyl. The sharp peak observed at 874 cm^{-1} and assigned to the stretching and folding of the carbonate group.

It was observed that the abundance of adsorption bands pertains to the surface acidic group especially the hydroxyl and carboxyl groups are present in the ACBS composite. These functional groups are strongly electron-withdrawing because of the existence oxygen-containing surface group. The O−H, C=O and C−O bands for ACBS-NaOH shifted towards a higher transmittance which can be correlate to the increasing of level of oxidation [7]. The ACBS surface was oxidized and the functional groups containing oxygen were established. The higher oxygen content on the surfaces, the bigger influence it would have on the adsorption process. As a result, it decreases the electrons density on the carbon surface, which is a desired condition for cationic dyes adsorption

3.1.2 Surface charge determination

The surface charge of any adsorbent (in aqueous solution) can be correlated with dye adsorption and it varies with pH depending on the isoelectric pH of the adsorbent. The zero point of charge obtained for ACBS-NaOH, ACBS- DW and ACBS-H_2SO_4 were found to be at pH 5.0, 6.0 and 6.0, respectively. The zero point charge is the point at which the surface of the adsorbent has net zero charge. This is the point at which adsorbent surface exhibited amphoteric characteristics. Surface charges originate from the presence of functional groups, such as surface oxygen complexes and their interactions with the aqueous solution. Each functional group charge leads to the overall surface charge. If the solution pH is higher than the pH_{PZC}, the adsorbent surface will have an overall negative charge which promotes cationic species adsorption.

3.2 Batch adsorption studies

3.2.1 Effect of ACBS pre-treatment and contact time

Figure 2 illustrates the adsorption capacities of alkali and acid pre-treated ACBS onto Crystal Violet dye for 120 minutes. The capacity of the ACBS after treatment with acid has found to boost the adsorption process significantly compared to ACBS treated with distilled water (ACBS-DW) or acid (ACBS-H_2SO_4).

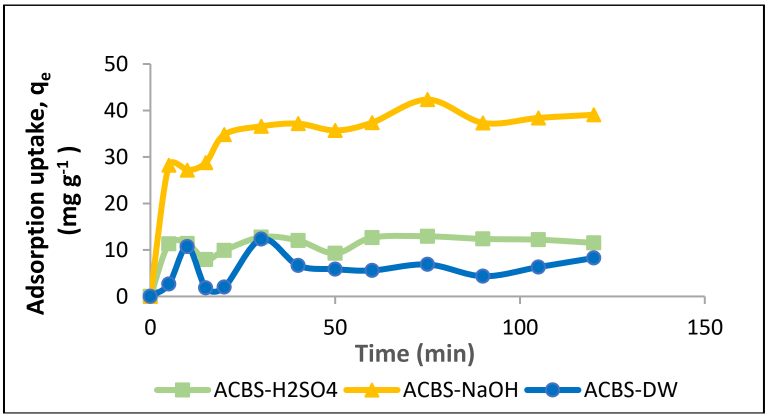

Figure 2. Adsorption capacity of ACBS-DW, ACBS-NaOH and ACBS-H2SO4 on adsorption of crystal violet.

From the plots, it can be seen that the equilibrium reached after 90 minutes. This finding indicated that in this study, for this particular condition, it only requires minimum time of crystal violet adsorption for 90 minutes. Therefore, the study was continued at contact time from 0 to 90 minutes only. It is worth mentioning that CV adsorption uptake at equilibrium for ACBS-NaOH is almost four times higher compared to the one observed for ACBS-DW and ACBS-H_2SO_4. This is attributed to the alkali attack that affected the chemical composition of the ACBS surface by generating more O-Na sites that could bind with dye molecules. Therefore, ACBS-NaOH was chosen as the most suitable adsorbent for the adsorption of Crystal Violet dyes as it displays the highest adsorption capacity compared to the other ACBS adsorbents.

3.2.2 Effect of pH

Activated carbons are compounds with amphoteric properties, such that the surface often shifts based on the solution's initial pH. Figure 3. illustrates the effect of pH (range 2–11) on the adsorption of CV by ACBS-NaOH composite.

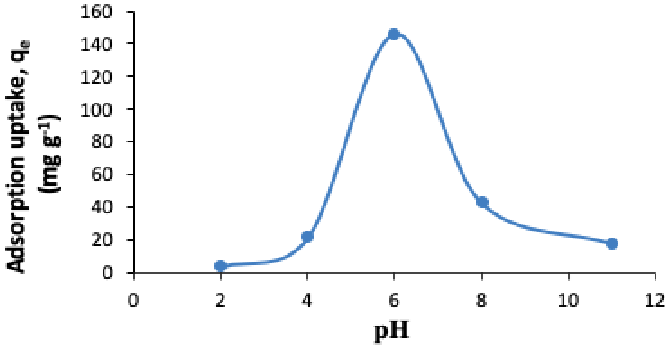

Figure 3. Effect of pH on crystal violet adsorption onto ACBS-NaOH

As shown in Figure 3, the maximum adsorption capacity achieved for CV was 43 mg g-1 at around pH 6.0. The adsorption capacity sharply increases with increase in the pH of the solution from pH 2 to pH 6 and then decreases. A similar behaviour was also reported for the adsorption of CV by Sagaun sawdust [10]. CV adsorption on the ACBS-NaOH increases with increasing the pH of solution. As the pH of the dye solution increases, the surface of the ACBS has negative charge due to the sequential deprotonation of positive charged groups on the surface of ACBS, and negative charge density on the surface increases. As a result, the electrostatic attraction takes place between the adsorbent negatively charged sites and the positively charged dye molecules (=N+(CH_3)$_2$) occurs [11].

3.2.3 Effect of adsorbent dose

The quantity of adsorbent applied in the adsorption process is crucial because it dictates the sorbent–sorbate ratio in the process and also in cost forecasting [5]. Figure 4 illustrates adsorbent dosage amount against adsorption capacity of ACBS-NaOH. Maximum adsorption capacity was reached with adsorbent dosage of 0.03 g, and the adsorption capacity started to decrease as more adsorbent dose was added.

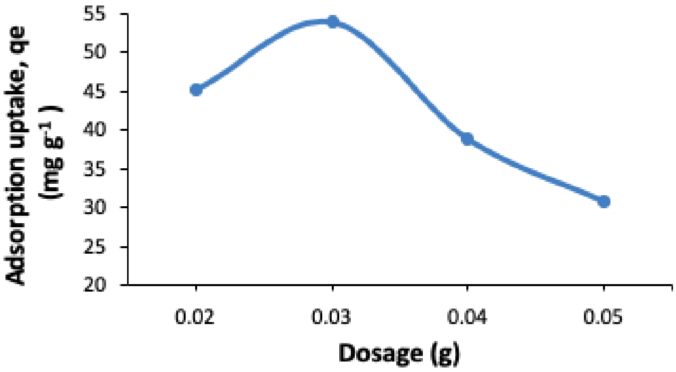

Figure 4. Effect of adsorbent dosage on crystal violet adsorption onto ACBS-NaOH

Saturation of adsorption sites due to interaction of particulate such as aggregation, causes the decrease in sorption capacity with increasing dose of adsorbent at constant dye concentration and volume [12]. This suggest that small dosages are adequate to occupy all the available surface sites dye molecules in the dye solution. Thus, the adsorbent dosage of 0.03 g was chosen as the optimum dosage for CV adsorption on ACBS-NaOH and was used for further studies.

3.2.4 Effect of initial dye concentration and Isotherm study

The results demonstrated that CV uptake increased with increasing initial concentration. This finding suggests that an increase in initial CV concentrations causes an increase in the concentration gradient acts as increasing driving force to overcome all mass transfer resistances of between the CV dye (aqueous phase) and ACBS (solid phase), leading to an increasing equilibrium sorption until sorbent saturation is achieved [10]. This may be largely due to the fact that almost all the dye molecules were adsorbed very rapidly on the outer surface at lower concentrations, however further increase in initial dye concentrations resulted in a rapid saturation of the adsorbent surface and therefore most of the dye adsorption occurred gradually within the pores [13].

Assessing the isotherms for an adsorption process are extremely important in understanding how adsorbate will interact with adsorbent. Figure 5 shows the adsorption isotherm for CV dye onto ACBS-NaOH, while the extracted isotherm information is summarized in Table 1. As observed from Table 1, the correlation coefficient values (R^2), Freundlich model exhibited a slightly better fit to the experimental equilibrium adsorption data for CV than the Langmuir model. This indicates that the adsorption process was a non-ideal and reversible adsorption which is not limited to monolayer formation. Since physisorption is caused by intermolecular forces, the binding force is weak with less adsorption heat, and the rate of adsorption and desorption is fast. The adsorbed substance is also easier to desorb, so the physical adsorption is reversible to a certain extent.

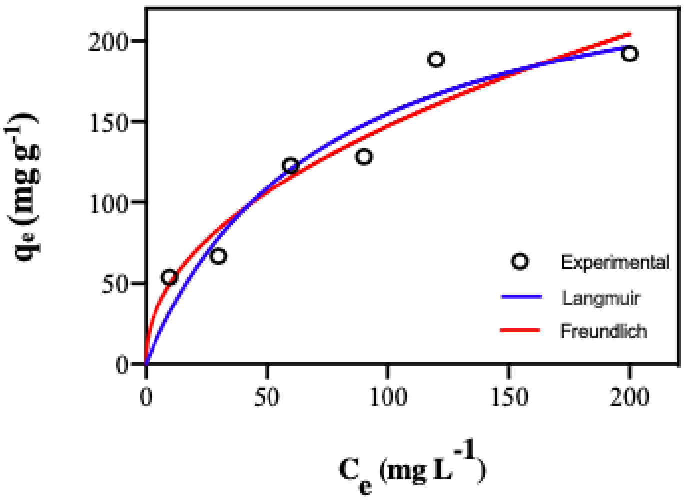

Figure 5. Effect of initial dye concentration and adsorption isotherm for crystal violet adsorption onto ACBS-NaOH.

Table 1. Parameters of isotherm study for the crystal violet adsorption on ACBS-NaOH at different crystal violet initial concentration.

Isotherm	Parameter
	ACBS-NaOH
Langmuir	q_m: 268.6mg g^{-1} R_L: 0.00136 R^2:0.9137
Freundlich	n: 0.4729 K_F: 16.69 R^2: 0.9175

3.2.5 Kinetic study

An adsorption kinetic analysis is a significant part of the analysis in order to comprehend the adsorption process mechanism and potential rate control steps, such as mass transportation or chemical reaction processes [14]. From the observation non-linear adsorption kinetics for the adsorption of CV at different temperatures (303- 333 K), pseudo-second order showed a lower correlation coefficient (R^2) over the temperature range of 303–333K than pseudo-first order equation. Additionally, the pseudo-second-order model, the theoretical adsorbed amount of CV at equilibrium ($q_{e,\ cal}$) does not fit well with the experimental data and suggested that adsorption was not conducted through a pseudo-second order (PSO) process. This finding indicates that CV removal from aqueous solution might be mainly governed by a physisorption process, where dye molecules accumulated on the surface functional sites due to weak force, known as Van der Waals forces. This data was aligned with the data obtained from the isotherm study which suggests the adsorption process is controlled by a physisorption process. The summary of the models used at four different temperatures and the kinetic information obtained from the pseudo-first and pseudo-second order plots are presented in Table 2.

Table 2. Parameters of kinetic study for the adsorption of crystal violet onto ACBS-NaOH at different temperatures.

Temp (K)	**$q_{e, exp}$ (mg/g)**	**Pseudo-first order**			**Pseudo-second order**		
		k_1 (min^{-1})	**$q_{e, calc}$ (mg/g)**	**R^2**	**k_2 (min^{-1})**	**$q_{e, calc}$ (mg/g)**	**R^2**
303	52.55	0.03414	55.22	0.9928	0.0005043	70.04	0.9850
313	42.29	0.03760	45.37	0.9632	0.0007380	56.28	0.9281
323	44.91	0.03841	48.23	0.9113	0.0007200	59.59	0.8608
333	46.5	0.03442	49.12	0.9470	0.0005664	62.43	0.9214

Conclusion

In this study, a low cost based adsorbents activated carbon derived from banana stem waste (ACBS) and pre-treated ACBS were successfully prepared and characterized for adsorption of Crystal Violet (CV). An improvement in the maximum adsorption capacity was observed for the alkali-treated ACBS (ACBS-NaOH) with an adsorption capacity almost four times higher than those exhibited by the acid treated ACBS (ACBS-H_2SO_4) and distilled water treated ACBS (ACBS-DW). The CV adsorption capacity increased in the following order: ACBS-DW < ACBS-H_2SO_4 < ACBS-NaOH. Adsorption of CV was pH-dependent and the best result was obtained at pH 6 for ACBS-NaOH. The isotherm studies showed that the Freundlich model provides the best fit to the adsorption data for ACBS-NaOH indicating the nonideal sorption on heterogeneous surfaces, as well as, multilayer sorption. The adsorption kinetics for ACBS-NaOH was best described by the pseudo-first order indicating an adsorption process mainly governed by a physisorption process. In conclusion, ACBS especially alkali-treated ACBS displays an effective and economically feasible material for the treatment of dye-containing effluents.

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