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Research Paper

Comparative adsorption study of Acid Red 18 on Cocoa *(Theobroma cacao)* Shell and Commercial Activated Carbon

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Abstract *- Adsorption of Acid Red 18 (AR 18) from aqueous solution on Cocoa(Theobroma cacao) Shell Activated Carbon (CSAC) and Commercial Activated Carbon (CAC) have been studied comparatively. The influence of various factors such as pH (2.0-10.0), initial concentration (20, 40, 60,80mg/lt) and contact time were investigated for CSAC and optimal experimental conditions was ascertained. The effect of adsorption data were modeled using Langmuir and Freundlich adsorption isotherms for CAC and CSAC. Adsorption kinetics was verified by pseudo-first order and pseudo-second models and adsorption capacities have been compared with that of CAC. Results indicated that CSAC could be employed as low cost alternative to CAC in dye removal from aqueous solution.*

Keywords: Cocoa shell, Activated carbon, Acid Red 18, Kinetics, Isotherm; Adsorption etc.

Introduction

The extensive use of dyes in the textile, paper, rubber, plastic, cosmetics, food and pharmaceutical industries poses pollution problems in the form of colored wastewater discharge into environmental water bodies. Intense colors of dye effluent have an adverse aesthetic effect which reduces aquatic diversity by blocking the passage of light through the water, therefore, reduces photosynthetic activity [1]. Industrially, the methods employed for treating dye wastewaters include coagulation and flocculation [2], photodegradation [3], ultrafilteration [4], adsorption [5] and reverse osmosis [6]. Due to economic advantage of these technologies, adsorption using activated carbon was successfully employed for color removal from wastewater. Activated carbon is effective but expensive due to its high cost of manufacturing [7]. Many natural adsorbents have been tested for reducing the dye concentrations. Among these, agricultural waste products are considered to be low-cost product for dye removal from aqueous solutions [8]. The preparation of activated carbon from agricultural solid waste would not only be economical but also solve the solid waste disposal problem. Some of the agricultural waste materials used for the production of activated carbon are sugarcane bagasse pith [9], peanut shell [10], tamarind fruit shell [11], pongam seed shell [12], walnut shell [13], groundnut shell [14], etc. The objective of this study was to investigate the feasibility of using agricultural solid waste cocoa shell for the removal of AR 18 as a probe molecule from aqueous solution by adsorption method. The adsorption capacity of CSAC was compared with that of CAC to assess its suitability as a cost effective substitute for dye removal.

Material and Methods

Adsorbent preparation: Cocoa shell collected from local agricultural field was air–dried and allowed to chemical activation, by the addition of 50% sulfuric acid with constant stirring (w/v). The resulting black product obtained was kept in muffle furnace maintained at 550°C for 7 hours. The carbon obtained was washed with double distilled water and soaked in 10% sodium bicarbonate solution and allowed to stand overnight to remove the residual acid from pores of the carbon. The material was washed with distilled water, until the pH of the adsorbent reached 7.0. Then it was dried in a hot air oven at 100±5 ºC for 12 hours. The dried material was grounded and sieved to get the particle size of 150µm and stored in an airtight container. The physico-chemical characteristics of CSAC were studied as per the standard testing methods and the physico-chemical properties were reported in our earlier paper [15].Commercially available granular activated carbon was procured from Loba Chemie, India, grounded to a size of 150µm and used for adsorption tests.

Adsorbate preparation: Stock solution of Acid Red 18 (Molecular formula: $C_{20}H_{11}N_2Na_3O_{10}S_3$, M.W.: 604.47, C.I. no.16255 ,CAS: 2611-82-7) was prepared by dissolving 1gm of dye in 1000ml of double distilled water to give the concentration of 1000mg/L. The stock solutions were diluted with known initial concentrations say 20, 40, 60 and 80mg/L in accurate proportions.

Adsorption experiment: Adsorption experiments were carried out in temperature controlled orbital shaker at a constant speed of 125rpm using 250mL conical flasks containing 100mg of activated carbon with 50mL of dye solution at 35°C. All the experiments (except the study of pH effect) were carried out at pH of 7±0.5. After agitating the flasks for predetermined time intervals, samples were withdrawn from the flasks and the adsorbents were separated from the solution by centrifugation (REMI make) at 2000rpm for 10 minutes. The absorbance of the supernatant solution was estimated to determine the residual dye concentration, measured at λ_{max} = 507nm spectrophotometrically using Elico make UV-Visible spectrophotometer. The amount of adsorbate adsorbed at equilibrium condition, q_e (mg/g) was calculated using the following equation:

$$q_e = (C_o - C_e)\frac{V}{W} \qquad (1)$$

where, C_o and C_e are the initial and equilibrium adsorbate concentrations (mg/ L), respectively, V is the volume of solution (L) and W is the mass of adsorbent (g).

The dye removal percentage can be calculated as follows:

$$\% removal = \frac{C_0 - C_e}{C_0} 100 \qquad (2)$$

where, C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

Results and Discussion

Effect of Contact time and initial dye concentration

The effect of contact time on batch adsorption of initial dye concentration ranged from 20 to 80mg/L at 35°C was shown in Figure 1. The amount of adsorption increases rapidly in the beginning and then gradually increases to reach an equilibrium value in 90 minutes. The increase in uptake capacity of the adsorbent with increasing dye concentration may be due to higher probability of collision between dye ions and adsorbent particles. The variation in the extent of adsorption may also be due to the fact that initially all sites on the surface of adsorbent were vacant and the solute concentration gradient was relatively high. Consequently, the extent of dye uptake decreases significantly with the increase of contact time, which is depending on the decrease in the number of vacant sites on the surface. The results indicated that there was no change in the sorption capacity after 90 minutes, therefore 120 minutes was fixed as the agitation time for further studies.

Effect of pH: The pH of the system exerts influence on the adsorptive uptake of adsorbate molecules. The effect of solution pH was studied between 2 to 10, initial pH controlled by the addition of 0.1M HCl or 0.1M NaOH and agitated with 100mg of adsorbent for 2 hours at 35°C. The effect of initial pH of dye solution on the adsorption of AR18 for initial dye concentration of 40 mg/L was illustrated in Figure 2. From the figure, it was observed that dye sorption decreased with the increasing of pH solution. In low pH the surface of activated carbon charged with H^+ ions leads to strong electrostatic attraction between the positively charged carbon surface and anionic dye molecule that cause increasing of dye sorption. Also by increasing of pH solution, the number of negatively charged sites on the surface of activated carbon increased. On the other hand the number of the positively charged sites decreased. Activated carbon with negatively charged sites due to electrostatic repulsion cannot adsorb the anionic dye, therefore by increasing of pH, dye removal would been decreased [16].

Adsorption Isotherms

Adsorption data explain the performance of adsorbent and adsorption isotherms and the equilibrium distribution of solute between adsorbent and solution, which will provide the ability to estimate the adsorbent efficiency and costs. Two most common isotherm equations namely, Langmuir and Freundlich were tested in this work.

Langmuir isotherm: Langmuir adsorption isotherm model was usually adopted for homogenous adsorption and it is used successfully in monomolecular adsorption processes [17]. Linear form of Langmuir model was expressed by

$$\frac{C_e}{q_e} = \frac{1}{b} Q_0 = \frac{C_e}{Q_o} \qquad (3)$$

where, C_e is equilibrium constant of dye (mg/L), q_e is amount of dye adsorbed at equilibrium (mg/g), Q_0 is Langmuir constant related to adsorption capacity (mg/g), b is Langmuir constant related to energy of adsorption capacity (L/mg). The linear plot of C_e/q_e versus C_e for adsorption of AR 18 onto CSAC and CAC were shown in Figure 3. The constants Q_0 and b can be calculated from slope and intercept of the plot and the values are tabulated in Table 1. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption [18]. R_L was calculated as follows:

$$R_L = \frac{1}{1+bC_0} \qquad (4)$$

where, C_o is the initial dye concentration(mg/L). R_L indicates the type of isotherm to be irreversible (R_L= 0), favorable (0 < R_L< 1), linear (R_L = 1) (or) unfavorable (R_L > 1). In the present investigation, the R_L values for CSAC and CAC were less than one, showing favorable adsorption.

Freundlich isotherm: Freundlich isotherm model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface [19]. Linear form of Freundlich model was expressed by

$$\log C_e = \log k_f + \frac{1}{n}\log C_e \qquad (5)$$

where, q_e is dye concentration in solid at equilibrium (mg/g), C_e is dye concentration in solution at equilibrium (mg/L), k_f is the Freundlich isotherm constant related to adsorption capacity(L/mg) and n is the Freundlich isotherm constant related to adsorption intensity. The linear plot of logq_e versus logC_e for adsorption of AR 18 onto CSAC and CAC were shown in Figure 4 and the values of n and k_f calculated from the slope and intercept are given in Table 1. The values of n were greater than one indicating the favorable adsorption.

For AR 18 dye, adsorption onto both adsorbents confirms the Langmuir and Freundlich models. Based on the correlation coefficients (r^2 values) of the isotherms studied, it was found that Langmuir isotherm was the most suitable isotherm than Freundlich isotherm for the experimental data. The Langmuir maximum adsorption capacity of CSAC was 42.1 mg/g which was similar to that of CAC (43.4 mg/g) for adsorptive removal of AR 18 dye. The fitness of Langmuir's model indicated the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent.

Adsorption kinetics

In order to investigate the mechanism of adsorption, the pseudo-first order and the pseudo-second order kinetic models were used to test dynamical experimental data.

Pseudo-first order kinetic model: This model was suggested for the adsorption of solid/liquid systems [20]. The integrated linear form of the model is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (6)$$

A plot of log (q_e-q_t) versus t gives a linear line (Figure 5&6) from which the values of k_1 and q_e were determined from the slope and intercept respectively and presented in Table 2.

Pseudo-second order kinetic model: The adsorption mechanism over a complete range of the contact time is explained by the pseudo – second order kinetic model [21]. The integrated linear form of the model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (7)$$

The initial adsorption rate, h (mg/g min), as t → 0 can be defined as

$$h = k_2 {q_e}^2 \qquad (8)$$

A plot of t/q_t versus t gives a linear relationship (Figure 7&8), from which q_e and k_2 were determined from the slope and intercept of the plot respectively and presented in Table 2. For all the systems studied, good correlation coefficients were obtained ($r^2 \approx 1$) by fitting the experimental data to pseudo-second order kinetics than that for the pseudo-first order kinetic model. The q_e values calculated from the pseudo-second order model system are in good agreement with the experimental q_e values. It was observed that the k_2 value decreases with increasing dye concentration. Therefore, the sorption was more favorably by pseudo-second order kinetic model, which was based on the assumption that the rate limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate [22].

Conclusion

The present study was carried out to compare the adsorption capacity of AR18 dye from aqueous solution using Cocoa shell and Commercial activated carbon. The adsorption characteristics of CSAC have been examined by initial pH, initial concentration and contact time. The maximum removal of AR 18 was observed at pH 2.0. Kinetics and isotherm studies have been studied and compared with CAC. The adsorption followed pseudo-second order kinetics and fitted well with Langmuir isotherm for CSAC and CAC. The fitness of Langmuir's model indicated the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent. Moreover the Langmuir adsorption capacities for both carbons were similar in removal of dye from aqueous solution. With the experimental data obtained, it is possible to optimize CSAC as an alternative for dye removal in economical industrial effluent treatment process.

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Table 1: Isotherm parameters for adsorption of AR 18 onto CSAC and CAC at 35°C

Langmuir	**CSAC**	**CAC**
Q_m(mg/g)	42.1	43.4
b(L/mg)	0.024	0.019
R_L	0.2066-0.4098	0.2411-0.4586
r^2	0.997	0.996
Freundlich		
k_f(mg/g)	5.26	4.21
n	2.71	2.43
r^2	0.970	0.971

Table 2: Kinetic parameters for adsorption of AR 18 onto CSAC and CAC at 35°C

Concentration (mg/L)	**20**	**40**	**60**	**80**	**20**	**40**	**60**	**80**
Pseudo-first order kinetics	**CSAC**				**CAC**			
k_1 x 10^{-2}(1/min)	3.0	2.76	2.76	2.53	4.14	2.53	2.53	2.53
$q_e$exp(mg/g)	9.43	18.46	27.46	36.26	9.63	18.87	27.27	35.73
$q_e$cal(mg/g)	8.45	16.07	24.21	30.97	10.89	17.7	25.18	33.81
r^2	0.980	0.978	0.970	0.969	0.978	0.983	0.988	0.971
Pseudo-second order kinetics								
k_2 x10^{-3}(g/mg min)	3.37	1.6	0.1	0.07	3.03	1.1	0.68	0.51
$q_e$cal (mg/g)	10.58	19.23	30.30	38.41	10.52	19.60	28.54	37.03
h	0.46	0.85	1.22	1.5	0.45	0.66	0.94	1.2
r^2	0.993	0.990	0.989	0.986	0.994	0.992	0.993	0.992

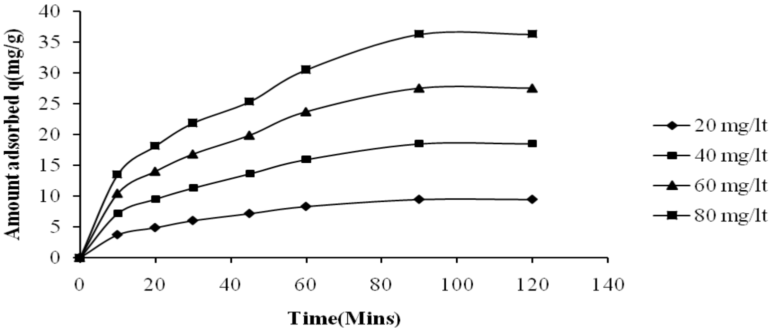

Figure 1: Effect of agitation time on adsorption of AR 18 onto CSA-Initial Concentration variation

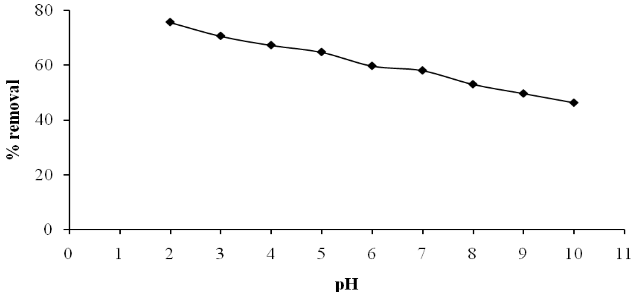

Figure 2: Effect of pH on removal of AR 18 onto CSAC

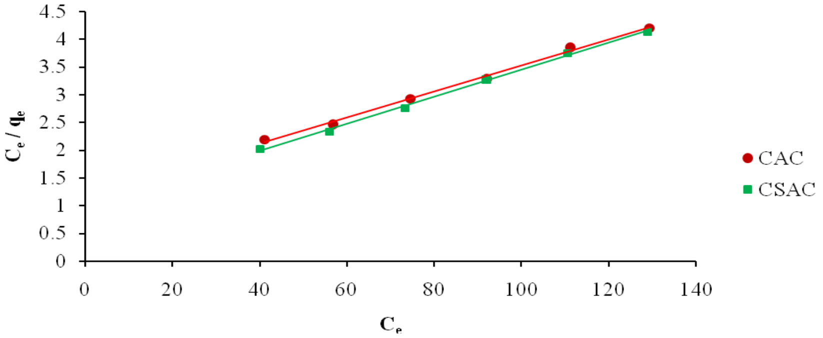

Figure 3: Langmuir isotherm plot for adsorption of AR 18 onto CAC and CSAC

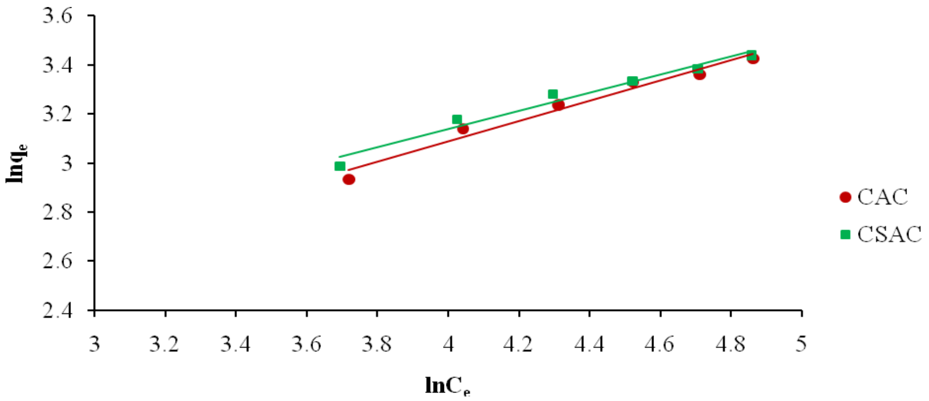

Figure 4: Freundlich isotherm plot for adsorption of AR 18 onto CAC and CSAC

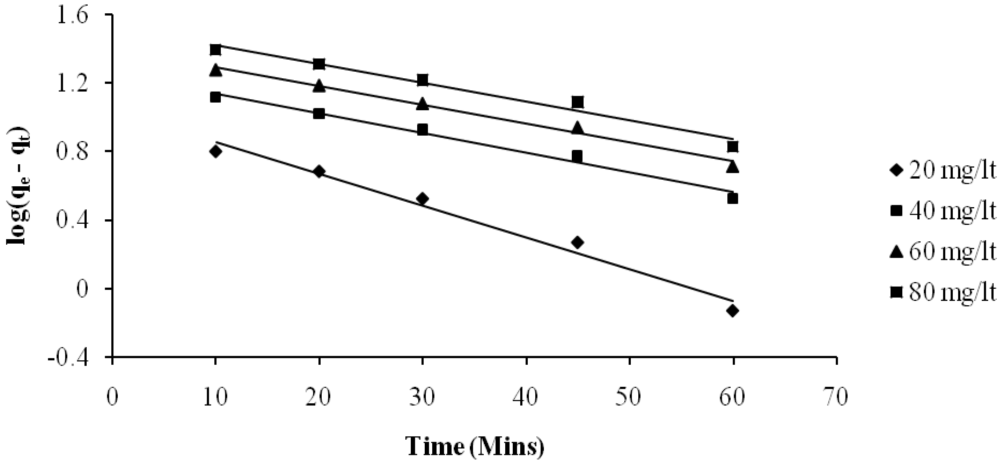

Figure 5: Pseudo-first order plot for adsorption of AR 18 onto CAC

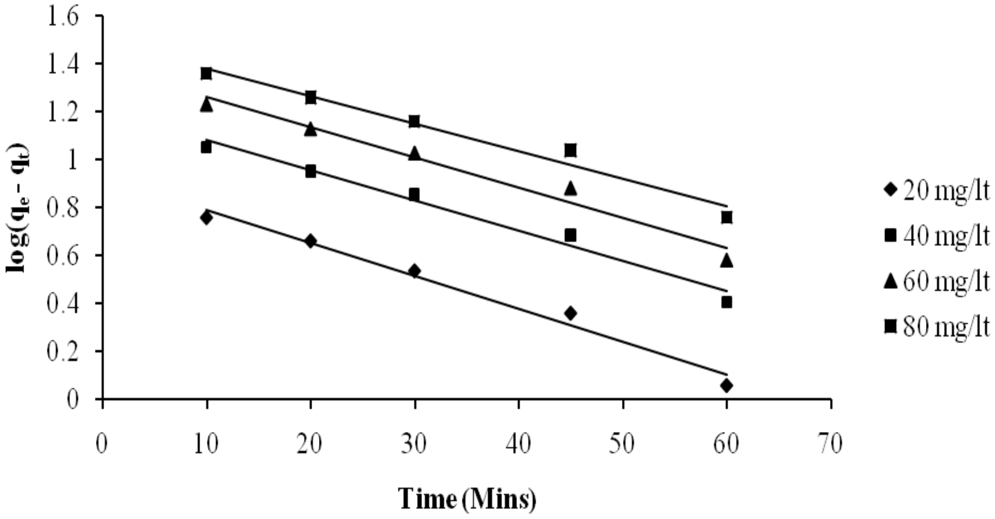

Figure 6: Pseudo-first order plot for adsorption of AR 18 onto CSAC

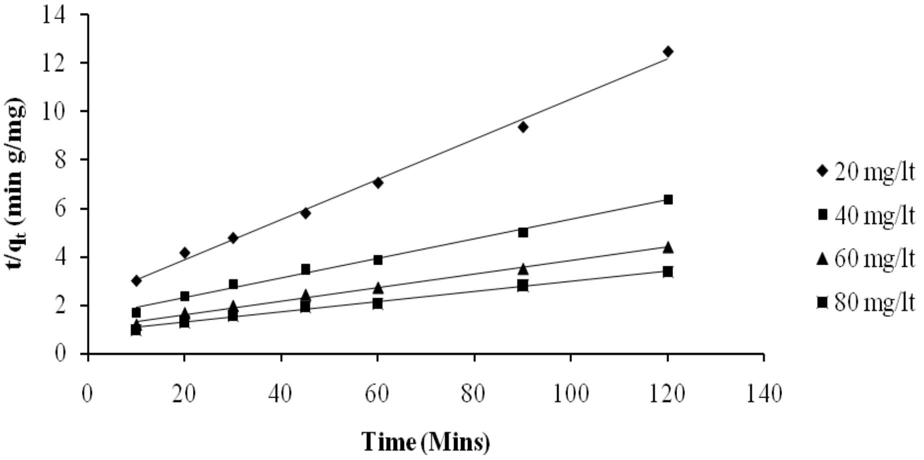

Figure 7: Pseudo-second order plot for adsorption of AR 18 onto CAC

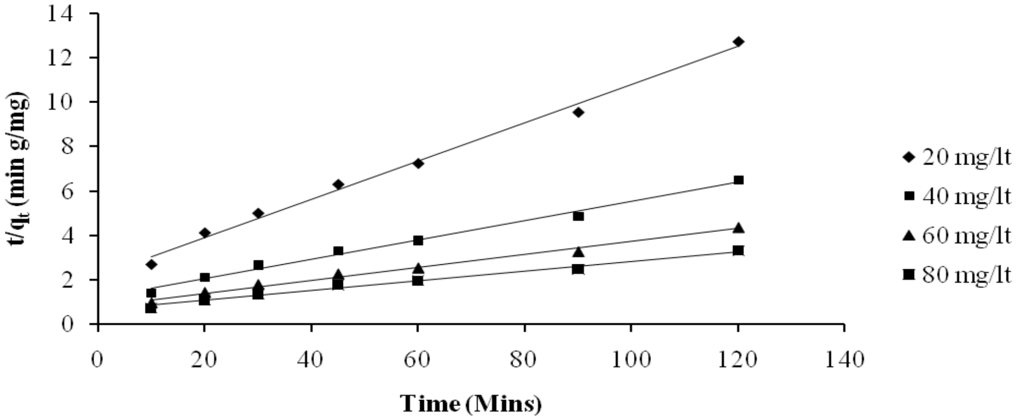

Figure 8: Pseudo-second order plot for adsorption of AR 18 onto CSAC