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Agriculture Byproducts Derived Indigenously Prepared Activated Carbons to Remove Safranin (SF) Dyes from Aqueous Solution – A Comparative Study

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ABSTRACT

Agricultural byproducts or wastes disposal has become a major problem in world, either it has to be disposed safely or used for the recovery of valuable materials. In the present investigation, various agriculture byproducts (rice husk, sugarcane baggasse, wheat husk, jackfruit tree bark) were utilized for the preparation of activated carbons by physico-chemical method were effectively used to remove safranin (SF) dyes from aqueous solution by batch adsorption technique. The as prepared activated carbons possess excellent improvement in the surface textural and functional group characteristics. The effect of adsorbents dose, initial pH, initial dye concentration, and contact time and particle size on SF dye removal have been studied. The linearity of curve and correlation coefficient value of isotherms such as Freundlich and Langmuir shows that the system covered monolayer adsorption. The R_L value indicates that the process is favourable. The adsorption capacity value Q_0 is in the order: CAC > JFBC > RHC> WHC > SBC. The pseudo first order kinetic equations such as Natarajan – Khalaf, Bhattacharya – Venkobachar and Lagergren were found to be applicable.

Key words**:** Low-cost adsorbents, Adsorption, Dye, Kinetic, Isotherm studies

Activated carbons are extremely versatile adsorbents with major industrial significance. The world consumption of activated carbons is steadily increasing and new applications are always emerging, particularly those concerning environmental pollution remediation, which should help to sustain demand for them. Important applications are related to their use in water treatment for the removal of flavor, color, odor and other undesirable organic impurities from water [1-2]. Activated carbon (AC) is also used in industrial wastewater and gas treatment due to the necessity for environment protection and also for material recovery purposes. Agricultural wastes or by-products are considered good alternative source materials for production of activated carbons (ACs) because of their abundance, high carbon content and cheap availability. In general, an adsorbent can be termed as of low cost if its source requires limited processing, is abundant in nature, or is a by-product or a waste material from another industry. Considering the aforementioned aspects, there has been a switch of interest from the use of traditional raw materials to agricultural by-products as precursors for activated carbon. Production of activated carbons from agricultural waste and by-products has potential economic and environmental advantages especially for countries like India where agriculture is the main economic activity [3-4].

Recently, growing research interest in the production of carbon based has been focused on agricultural by-products [2]. The main aim of this study was to investigate the potentiality of adsorbents derived from Rice husk, Sugarcane baggasse, Wheat husk, Jackfruit bark towards the removal of Safranin (SF) dye.

MATERIALS AND METHODS

Chemicals and reagents

All the chemicals and reagents are analytical grade used without any further purification.

Preparation of adsorbent materials

Four different kind of agricultural by-products including rice husk, sugarcane baggasse, wheat husk, jackfruit tree bark wereused as raw materials for the preparation of activated carbons. These wastes were selected as precursors because of their availability and desirable physical characteristics. The dried raw materials were physically activated by carbonization in a muffle furnace in the absence of air by placing the sample in a well-sealed stainless-steel tube. For each adsorbent

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preparation, different conditions (temperature and time duration) was maintained. Sugarcane bagasse was carbonized at 300°C for 30 min., Rice husk was carbonized at 300°C for 75 min., Wheat husk was carbonized at 300°C for 90 min. and Jackfruit bark was carbonized at 400° C for 120 minutes [5]. The carbonized raw materials were then powdered well, sieved by molecular sieves and labeled as rice husk carbon (RHC), sugarcane bagasse carbon (SBC), wheat husk carbon (WHC), jackfruit tree bark (JFBC) and commercial activated carbon (CAC).

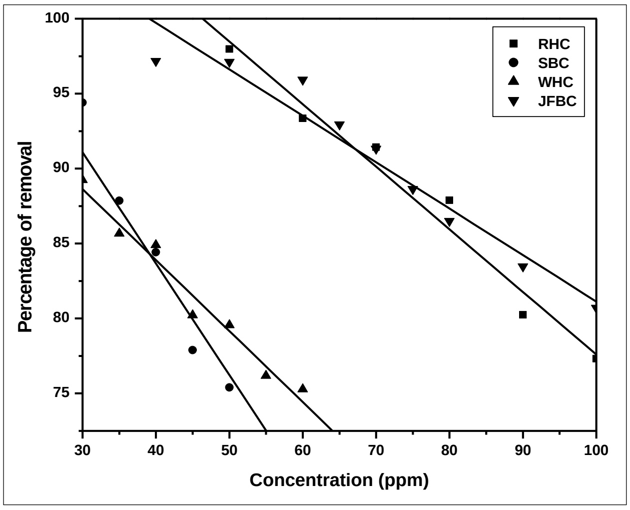

Fig 1 Effect of initial concentration on the removal of SF dye on CAC, RHC, JFBC, WHC and SBC

RESULTS AND DISCUSSION

Effect of initial SF dye concentration and adsorption isotherm studies

Effect of Initial concentration provides an important driving force for alleviating mass transfer resistances of dye molecules between the aqueous solution and solid phases. (Fig 1) shows that the effect of initial SF dye concentration on adsorption capacity over the adsorbents CAC, RHC, SBC, WHC and JFBC at different range of initial concentration (270-320 mg L^{-1} for CAC 40-100 mg L^{-1} for JFBC, 50-100mg L^{-1} for RHC, 20-60 mg L^{-1} for SBC & WHC), keeping contact time as 30 minutes. The dose of adsorbent for CAC is 2g L^{-1} and 10 g L^{-1} for IPACs. pH is initial basic pH and particle size is fixed as 90 micron.

The result shows that percentage removal of dye decreases exponentially with increase in concentration. It is also been noted that, rate of removal is greater at lower concentration. This indicates that there exists a reduction in immediate solute adsorption owing to the lack of available active sites required for high initial concentration of dye [5, 6-8]. The observation could be explained by the theory that, in the process of adsorption initially dye molecules have to first encounter the boundary layer and diffuse from the boundary layer film onto the adsorbent surface and then finally, have to diffuse into the porous surface of the adsorbent [5].

The Langmuir and Freundlich adsorption isotherm plots on the removal of SF dye on CAC, RHC, JFBC, WHC and SBC were shown in (Fig 2). The Langmuir model assumes that uptake of adsorbate ions occurs on the homogeneous surface by monolayer adsorption. A basic assumption is that sorption takes place at specific homogenous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir equation is expressed as follows:

$$C_e/q_e = 1/Q_0b + C_e/Q_o$$

The Langmuir adsorption isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions.

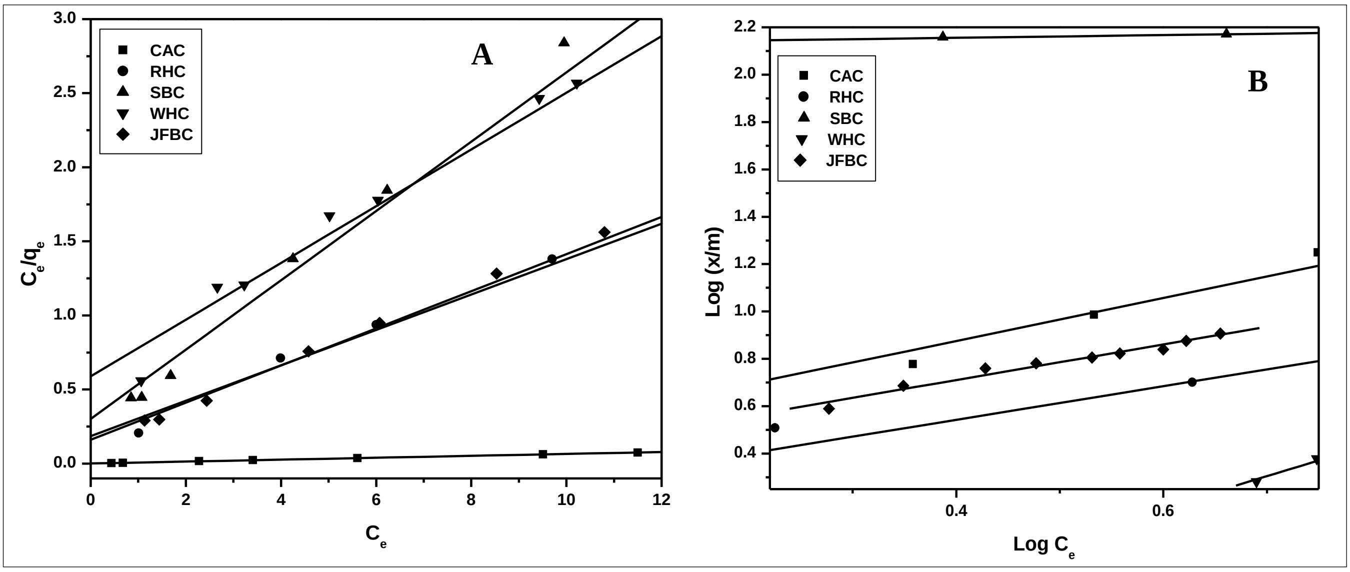

Fig 2 (A) Langmuir adsorption isotherm plot and (B) Freundlich adsorption isothermplot on the removal of SF dye on CAC, RHC, JFBC, WHC and SBC

The equilibrium isotherms in this study have been described using Freundlich isotherm as one of the isotherms. The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of Safranin dye at equilibrium. The adsorption data were also fitted with Freundlich adsorption isotherm. A linear form of Freundlich equation is generally expressed as follows:

$$log\left(\frac{x}{m}\right) = log\ k + \frac{1}{n}\ log\ C_e$$

The linearity of the graph indicates the applicability of Freundlich isotherm to the experimental data. The values of k and n are calculated from intercept and slope of the straight line. Values of n >1 represent favourable adsorption condition [6-10]. The correlation analysis of Freundlich and Langmuir isotherms are presented in (Table 1). The Langmuir constants

Q_o (mg g^{-1}) and b (L mg^{-1}), related to the adsorption capacity and energy of adsorption are obtained from slope and intercept of the straight line. The applicability of the isotherm equation is compared by judging correlation coefficient, r. The results conclude that Langmuir isotherm is best fitted compared to Freundlich, confirming the monolayer adsorption [5, 9-10].

Table 1 Result of various adsorption isotherms

Isotherm	CAC	RHC	SBC	WHC	JFBC
		Freundlich			
Slope (1/n)	0.039	0.148	0.208	0.340	0.214
Intercept (Log K)	2.147	0.682	0.354	0.247	0.631
Correlation Coefficient (r)	0.973	0.961	0.927	0.976	0.925
K	140.2814	4.8084	2.2594	1.7660	4.2756
n	25.6410	6.7568	4.8077	2.9412	4.6729
		Langmuir			
Intercept ($1/Q_0b$)	0.002	0.161	0.301	0.588	0.185
Slope	0.006	0.125	0.233	0.191	0.119
Correlation Coefficient (r)	0.999	0.996	0.991	0.984	0.992
Q_0 (mg g^{-1})	166.67	8.000	4.2918	5.2356	8.4034
b (L mg^{-1})	2.9999	0.7760	0.7740	0.3248	0.6432
R_L	0.0014	0.0127	0.0211	0.0488	0.0153

The monolayer adsorption capacity of adsorbents is in the order CAC>JFBC>RHC>WHC>SBC

Effect of contact time on the removal of SF dye

Generally, adsorption capacity and dye removal efficiency increase with prolonging the contact time. In order to find out the equilibrium time for maximum adsorption, the adsorption of Safranin on CAC, RHC, JFBC, WHC and SBC were studied as a function of time and the plot is shown in (Fig 3). Adsorption experiments were carried out at different contact time (5-120 min.,) at optimum initial concentration (50ppm for RHC, JFBC and 25ppm SBC, WHC) of the dye and initial pH of dye solution, dose (2g L^{-1} for CAC and 10g L^{-1}) and particle size (90 micron) of adsorbents kept constant. The adsorption process increases with increasing contact time.

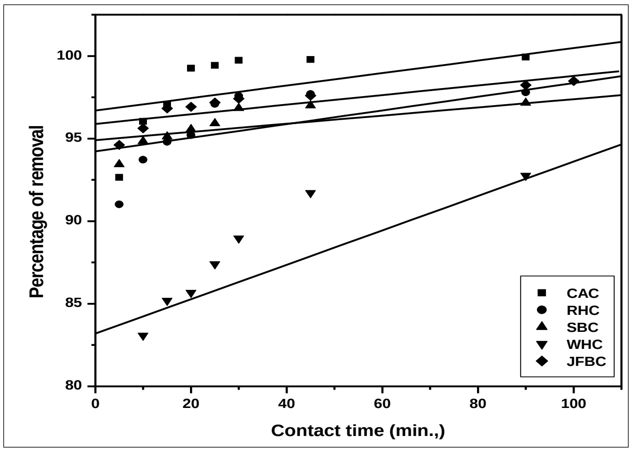

Fig 3 Effect of contact time on the removal of SF dye on CAC, RHC, JFBC, WHC and SBC

Initially the amount of dye adsorbed onto the carbon surface increases rapidly, and at some point, of time, the process slows down and reaches a plateau (constant value). At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the activated carbons. This phenomenon is attributed to reduction in immediate solute adsorption due to the lack available open sites for dye adsorption (saturation), which in turn supported film diffusion. Three consecutive mass transport steps are associated with the adsorption of solute from solution by porous adsorbent. Initially the dye molecules have to first encounter the boundary layer effect, migrates through the solution (film diffusion), followed by solute movement from particle surface into interior site by pore diffusion and finally the adsorbate is adsorbed into the active sites (porous structure) at the interior of the adsorbent particle. The amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions [5, 11-12].

Kinetic modeling on the removal of SF dye by various carbons

The kinetic models are used to determine the rate of adsorption process [1, 5, 8, 10]. The experimental data are fitted to the following kinetic models.

Natarajan and Khalafequation

$$\mathrm{Log}\ (C_i/C_t) = kt / 2.303$$

Bhattacharya and Venkobacharequation

$$\mathrm{Log}\ [1 - U(t)] = -kt / 2.303$$

Lagergren Pseudo first order kinetic equation

$$\mathrm{Log}\ (q_e - q_t) = \log q_e - kt/2.303$$

The graph of Time Vs Log C_i/C_t (Natarajan Khalaf Kinetic plot), Time Vs5+Log [1–U(t)] (Bhattacharya and Venkobachar) and Time Vs2+Log (q_e-q_t) (Lagergren kinetic plot) were shown in the (Fig 4).

Table 2 Results of various kinetic equations on the removal SF

Isotherm	CAC	RHC	SBC	WHC	JFBC
		Natrajan and Khalaf			
Correlation coefficient (r)	0.933	0.796	0.804	0. 899	0.919
K (min^{-1})	0.0467	0.0113	0.0062	0.0092	0.0106
		Bhattacharya and Venkobachar			
Correlation coefficient(R^2)	0.885	0.934	0.925	0.963	0.887
K (min^{-1})	0.1060	0.1146	0.0816	0.0622	0.0431
		Lagergren			
Correlation Coefficient(R^2)	0.885	0.934	0.925	0.962	0.887
K (min^{-1})	0.10594	0.11467	0.08164	0.0621	0.0431

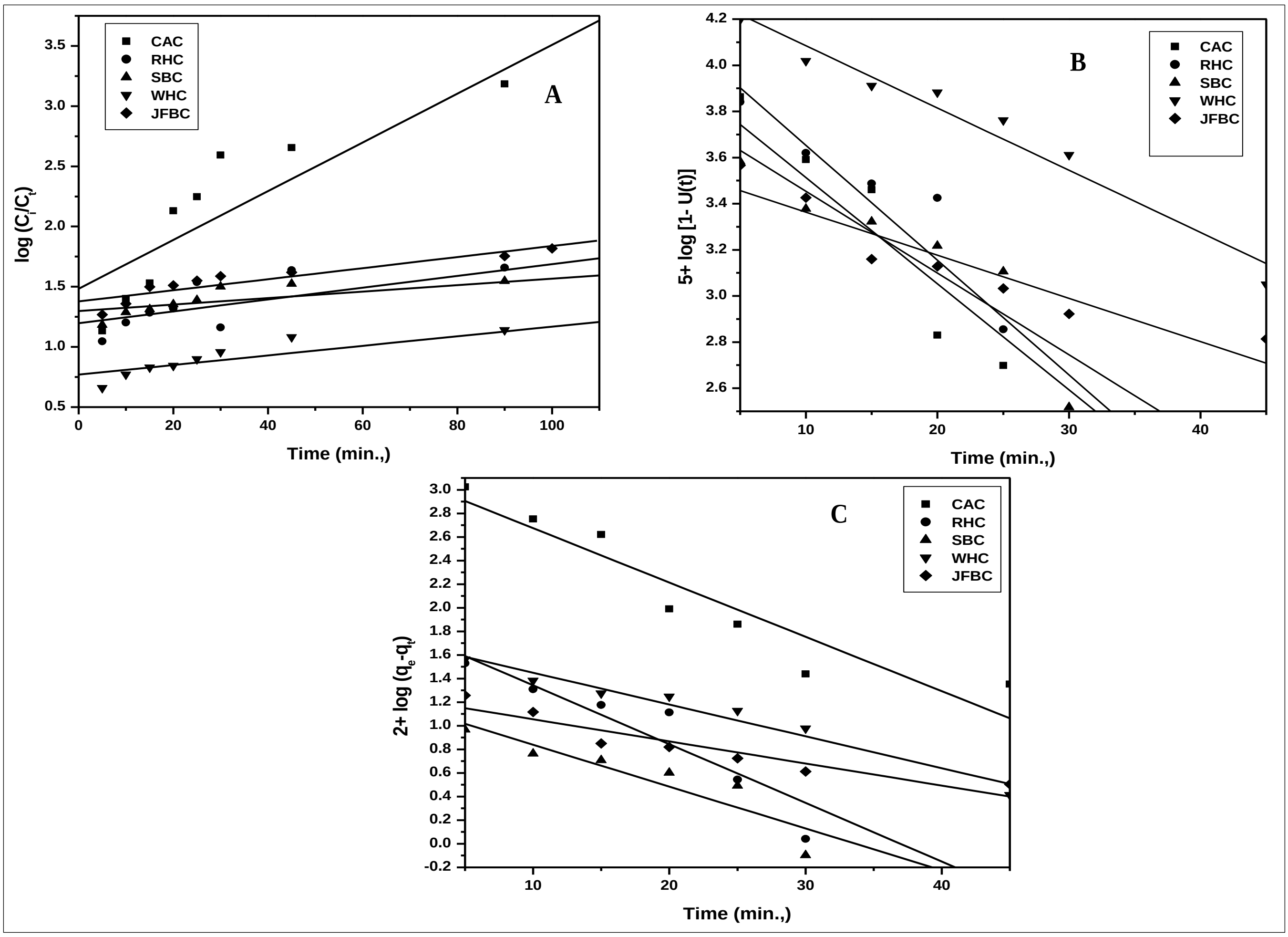

Fig 4 Kinetic Models of (A) Natarajan Khalafplot; (B) Bhattacharya and Venkobachar plot and (C) Lagergren kinetic plot for the removal of SF dye on CAC, RHC, JFBC, WHC and SBC

All the linear correlations were found to be statistically significant (as evidenced by r values close to unity) and indicate that applicability of kinetic equations. The values of 'K' calculated from the Bhattacharya and Venkobachar equation are found to be close to that computed from Lagergren equation for any given adsorbent. The rate of adsorbent 'K' is found to be high in RHC (0.115 min^{-1}) and low in JFBC (0.0431 min^{-1}) [5, 13-15].

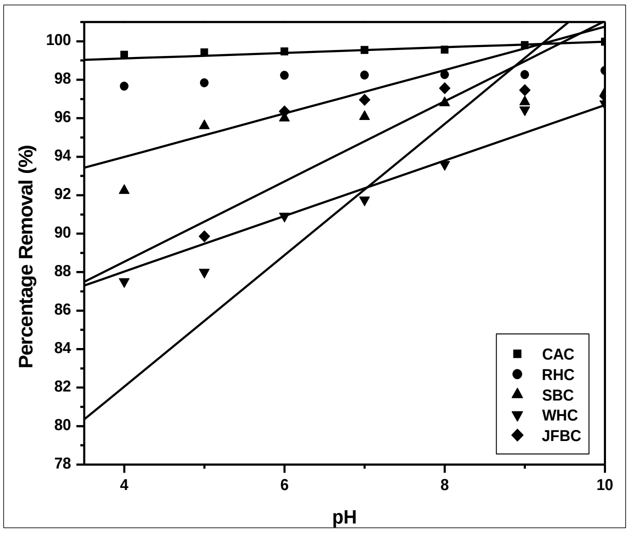

Fig 5 Effect of initial pH on the removal of SF dye on CAC, RHC, JFBC, WHC and SBC

Effect of initial pH of dye solution on the removal of SF dye

In general, pH of the dye solution may affect adsorption by regulating the adsorbents surface charge as well as the degree of ionization of constituents present in the solution. The initial pH value may enhance or depress the dyes uptake rate, inter-correlated to the changes of adsorbent surface and dye chemistry. Figure 5 shows that the relationship between the pH value and the % Removal of safranin dye. It can see from the figure that the solution pH increases, the adsorption capacity increases. Increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enhances the attraction between dye and adsorbent surface. The net positive charge decreases with increasing pH value lead in the decrease in the repulsion between the adsorbent surface and the dye thus, improving the adsorption capacity. From the observed results it is concluded that the basic medium is favourable for the maximum removal of the dye SF [5, 15-19].

CONCLUSION

The concentration of dye solution and particle size of adsorbent increases, the percentage of colour removal decreases. The percentage of colour removal increases with increase in agitation time and dose of adsorbents. The linearity of curve and correlation coefficient value of isotherms such as Freundlich and Langmuir shows that the system covered monolayer adsorption. The R_L value indicates that the process is favourable. The adsorption capacity value Q_0 is in the order: CAC > JFBC > RHC> WHC > SBC. The pseudo first order kinetic equations such as Natarajan – Khalaf, Bhattacharya – Venkobachar and Lagergren were found to be applicable.

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