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Full Length Research Article

Activated Carbons from Biomass Based *Garcinia mangostane* and *Datura stramonium* Fruit Peel for the Removal of Alizarin Cyanine Green Dye: Adsorption Isotherm and Kinetic Study

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Abstract

This study describes the preparation of activated carbons from fruit peel waste [*Garcinia mangostane* peel carbon (GMPC) and *Datura stramonium* peel carbon (DSPC)] and their application as adsorbents of synthetic alizarin cyanine green (ACG) dye. The different batch adsorption experiments were followed by varying the initial dye concentration, mass of adsorbent, contact time and pH of the medium. The equilibrium adsorption data of ACG dye on GMPC and DSPC were analyzed by Langmuir and Freundlich models. The results indicate that the Freundlich model provides the best correlation of the experimental data. The adsorption capacities of the activated GMPC and DSPC for removal of ACG dye was determined with the Langmuir equation. Adsorption data were modelled using the pseudo-first-order, pseudo-second order and intra-particle diffusion kinetics equations. It was shown that pseudo-first order kinetic equation could best describe the adsorption kinetics. The results of this work showed that indigenously prepared GMPC and DSPC are an excellent environmentally friendly adsorbent for removal of ACG dye from industrial effluents.

Key words: Biomass, Alizarin cyanine green dye, Adsorption, Kinetic and isotherm

Dyes are used by several industries, such as textile, paper, printing and plastics to colour their products. The effluent discharged from these industries is highly coloured and disposal of this coloured water into the receiving water body not only causes damage to aquatic life, but also to human beings, by producing carcinogenic and mutagenic effects [1]. There are several treatment technologies like photo degradation, biodegradation, coagulation flocculation and electrochemical oxidation available for the treatment of coloured wastewater [2]. Among the numerous techniques of colour removal, adsorption is considered to be one of the more efficient and less expensive methods. Most of the commercial industries use activated carbon as adsorbent to remove colour from waste water [3]. However, its use is often limited due to its high cost. Attempts have been made to find alternative low-cost adsorbents [4-5].

Agricultural waste materials have little or no economic value and often pose a disposal problem. So, activated carbon prepared from these wastes help to solve the waste disposal problem [6]. Recently, attentions have been focused on the development of low-cost adsorbent for the application concerning treatment of dyeing industrial waste water. Therefore, the objective of this study was to evaluate the adsorption potential of activated carbon derived from *Garcinia mangostane* and *Datura stramonium* fruit peel for ACG dye. The equilibrium and kinetic data of adsorption studies were processed to understand the adsorption mechanism of onto the activated GMPC and DSPC in aqueous solution.

MATERIALS AND METHODS

Chemicals and reagents

All the chemicals and reagents are analytical grade used without any further purification. ACG dye is used as a model pollutant (adsorbate) and the details and applications of ACG dye was given in (Table 1).

Preparation of Garcinia mangostane and Datura stramonium fruit peels carbon

The *Garcinia mangostane* and *Datura stramonium* fruit peels are used as adsorbents source material were collected

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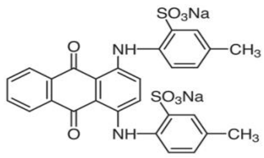
locally (local field and market) and dried in the absence of sun light. The *Garcinia mangostane* and *Datura stramonium* fruit peels are physically activated by carbonization in a muffle furnace in the absence of air by placing the sample in a well-sealed stainless-steel tube at 400 °C for 45 min. The carbonized raw materials were then subjected to acid activated as well as steam digestion. Finally, the *Garcinia mangostane* peel carbon *(GMPC)* and *Datura stramonium* peel carbon (DSPC) were thoroughly washed with distilled water until free from acid, then dried at 120°C in hot air oven, powdered well and sieved (90-micron size) by molecular sieves [7-8].

Table 1 Physico-chemical properties of ACG dye

Dye	Alizarin Cyanine green
CI No.	61570
Characteristics	Anionic, water soluble, Green Colour
Formula	$C_{28}H_{20}N_2Na_2O_8S_2$; MW: 622.58
Structure	
λ_{max}	642 nm
Applications and toxicity	Industrial uses such as plastic, paper, paint, leather industries and as basic colouring agent in textile industries and highly toxic in nature and has detrimental effect both on human and environment

RESULTS AND DISCUSSION

Effect of initial concentration on the removal of ACG dye on GMPC and DSPC

The uptake of Alizarin cyanine green over the adsorbents CAC, GMPC and DSPC were investigated at different range of initial concentration, keeping contact time, dose of adsorbent, initial pH and particle size fixed and the results are given in (Fig 1).

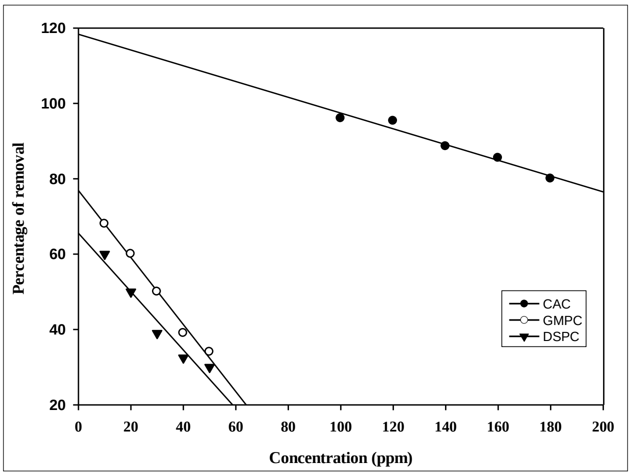


Fig 1 Effect of initial concentration on the adsorption of ACG dye

The result shows that percentage removal of ACG dye decreases exponentially with increase in concentration. It is also noted that rate of removal is faster 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. 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 [7-9].

Adsorption isotherms

The adsorption isotherms indicate how the adsorption molecules distribute between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. The adsorption data were fitted with Freundlich adsorption isotherm [10].

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

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. The Langmuir model assumes that uptake of adsorbate ions occurs on the homogeneous surface by monolayer adsorption. The Langmuir equation is expressed as follows [11]

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

Freundlich graph plotted between log C_e against log x/m and Langmuir graph plotted between C_e/q_e against C_e were shown in (Fig 2).

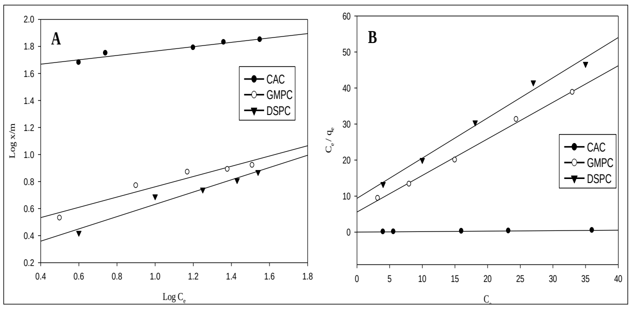


Fig 2 (A) Freundlich and (B) Langmuir adsorption isotherm

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 correlation analysis of Freundlich and Langmuir isotherms are presented in Table 2. 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.

Table 2 Results of various adsorption isotherms

Isotherm	CAC	GMPC	DSPC
Freundlich			
Slope (1/n)	0.161	0.381	0.403
Intercept (Log k)	1.604	0.379	0.245
Correlation coefficient (r)	0.931	0.926	0.976
Langmuir			
Intercept ($1/Q_ob$)	0.032	5.603	9.400
Correlation coefficient (r)	0.997	0.996	0.989
Q_o (mg g^{-1})	76.92	0.986	0.896
b (L mg^{-1})	0.406	0.180	0.118
R_L	0.012	0.020	0.027

Further the Langmuir constants are used to find the favourable or unfavourable adsorption by a dimensionless parameter R_L. $R_L = 1/(1 + bC_0)$. The value of R_L indicates the isotherm to be unfavourable, linear or favourable [12].

$R_L$value	Nature of adsorption process
R_L=1	Linear
o<R_L<1	Favourable
R_L=0	Irreversible
R_L>1	Unfavourable

In these cases R_L value is found to be less than 1. Hence the nature of adsorption is favourable. Another Langmuir constant Q_0 indicates the adsorption capacity. The monolayer adsorption capacity of adsorbents is in the order CAC>>GMPC>DSPC.

Effect of contact time on the removal of ACG dye on GMPC and DSPC

In order to find out the equilibrium time for maximum adsorption, the adsorption of alizarin cyanine green on CAC, GMPC and DSPC were studied as a function of time. Adsorption experiments were carried out at different contact time at optimum initial concentration of the dye and initial pH of dye solution, dose and particle size of adsorbents kept constant and the plots are shown in the (Fig 3). The adsorption process increases with increasing contact time [13].

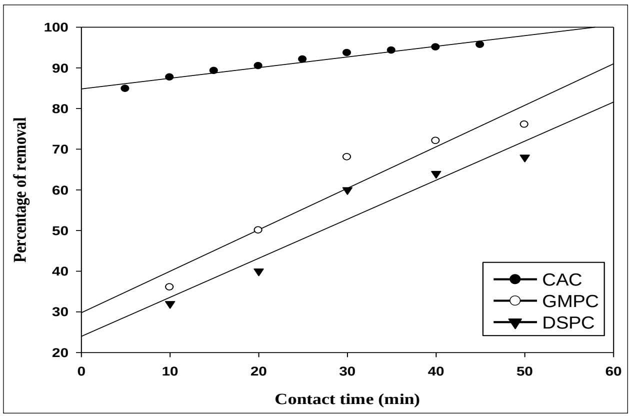


Fig 3 Effect of contact time on the adsorption of ACG dye

Kinetic modelling studies

The kinetic models are used to determine the rate of adsorption process. The experimental data are fitted to the following kinetic models.

Natarajan and Khalaf equation: $\text{Log}\ (C_i/C_t) = kt / 2.303$

Bhattacharya and Venkobachar equation: $\text{Log}\ [1 – U\ (t)] = -kt / 2.303$

Where $U\ (t) = (C_i\text{-}C_t) / (C_i\text{-}C_e)$

Lagergren equation: $\text{Log}\ (q_e\text{-}q_t) = \log q_e – kt/2.303$

The graph is plotted between $\text{Log}\ (C_i/C_t)$ against time; $\text{Log}\ [1 – U\ (t)]$ against time and $\text{Log}\ (q_e\text{-}q_t)$ against time was given in (Fig 4).

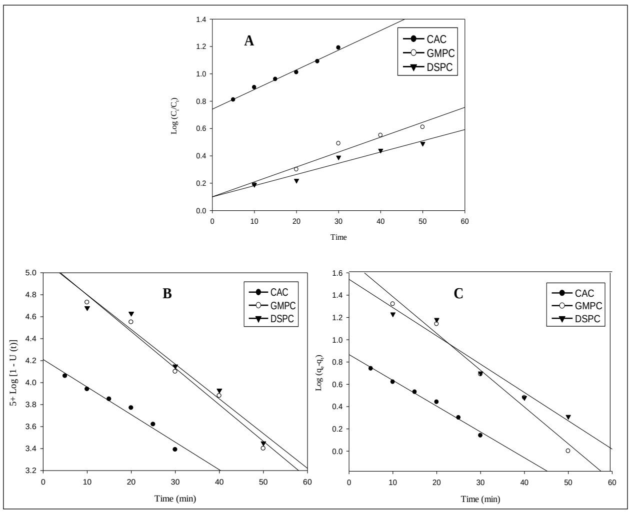


Fig 4 Kinetic Models of (A) Natarajan Khalafplot; (B) Bhattacharya and Venkobachar plot and (C) Lagergren kinetic plot for the removal of ACG dye

Various experimental parameters for the studies of kinetics of adsorption of ACG on CAC are given in the (Table 3).

Table 3 Parameters for various kinetic equations on the removal of ACG

Parameters	CAC	GMPC	DSPC
Natarajan and Khalaf			
Correlation coefficient (r)		0.989	0.951
k (min^{-1})		0.032	0.023
Bhattacharyaand Venkobachar			
Correlation coefficient (r)	0.961	0.979	0.952
k (min^{-1})	0.057	0.075	0.071
Lagergren			
Correlation coefficient (r)	0.993	0.979	0.951
k (min^{-1})	0.048	0.075	0.057

All the linear correlations are statistically significant as evidenced from the value of ‘r’. This indicates the applicability of these kinetic equation and first order of adsorption process. Among the three models, Lagergren first order kinetics yielded the highest ‘r’ value. This analysis suggests that Lagergren first order model was the most suitable equation to describe the adsorption kinetics of the dye ACG on the adsorbents CAC, GMPC and DSPC [7-9], [14-16].

Intra-particle diffusion study

The transportation of adsorbate from solution phase to the surface of the adsorbent particles may be controlled either by one or more steps: film or external diffusion: pore diffusion: surface diffusion: adsorption on the pore surface or the combination of more than one step [7-9], [18-19]. The possibility intraparticle was explored by Weber-Morris intra particle diffusion plot.

$$q_t = k_p\ t^{½} + C$$

Intra-particle diffusion plot for CAC, GMPC and DSPC is shown in the (Fig 5).

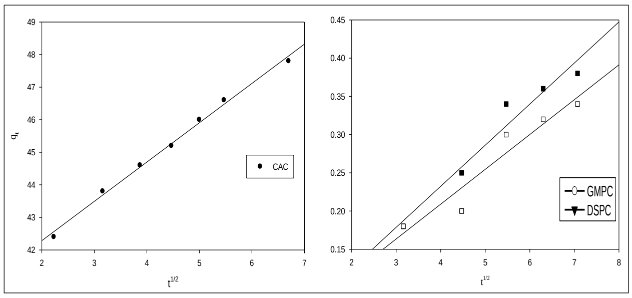


Fig 5 Intra-particle diffusion plot for CAC, GMPC and DSPC for the removal of ACG dye

Results for Intra-particle diffusion study are given in the Table 4.

Table 4 Results for Intra-particle diffusion study

Parameters	CAC	GMPC	DSPC
Correlation coefficient r	0.995	0.956	0.919
k	1.207	0.053	0.045
Intercept C	39.87	0.017	0.026

The plot of q_t against $t^{1/2}$, based on the results, gives a straight line in all the cases. This indicates that sorption process is controlled by intra-particle diffusion process [7-9], [14-15]. The values of k and C can be determined from slope and intercept of the straight line. The value of C gives an idea about the thickness of the boundary layer. Larger the intercept, greater the boundary layer effect. The value of intercept and consequently boundary layer effect is in the following order.

CAC >>> GMPC > DSPC

Effect of dose of adsorbents on the removal of ACG dye on GMPC and DSPC

The effect of dose of adsorbent was studied at optimum initial concentration, contact time and pH. The percentage removal of ACG dye on various adsorbents CAC, GMPC and DSPC are shown in (Fig 6). The percentage removal of the dye increased with increase in dose of adsorbent. This may be due to the availability of surface-active sites. The increase in the extent of removal of ACG is found to be insignificant after a dose of 2 g $L^{-1}$for CAC, 20 g L^{-1} for GMPC and DSPC. So, they are fixed as optimum dose of adsorbents for further studies. This suggests that the adsorbed dyes either block the access to internal pores or cause particles aggregate there by reducing the availabilities of active sites [20-22].

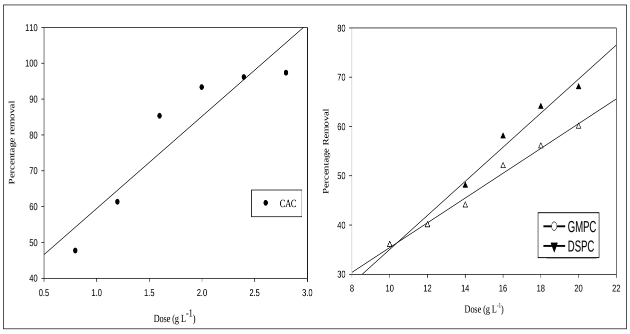


Fig 6 Effect of dose of adsorbents CAC, GMPC and DSPC for the removal of ACG dye

Effect of pH on the removal of ACG dye on GMPC and DSPC

Figure 6 shows the adsorption capacity of the adsorbents over ACG dye in the pH range 4-12. ACG being an anionic dye has shown better adsorption at lower pH i.e., in acidic medium. The analysis shows that greater increase in the percentage removal occurs in the lower pH range. This may be due to the number of positive charges on the attraction of negatively charged dye molecule and thereby increasing the adsorption. On increasing pH, deprotonation takes place, which decreases the diffusion and adsorption [17].

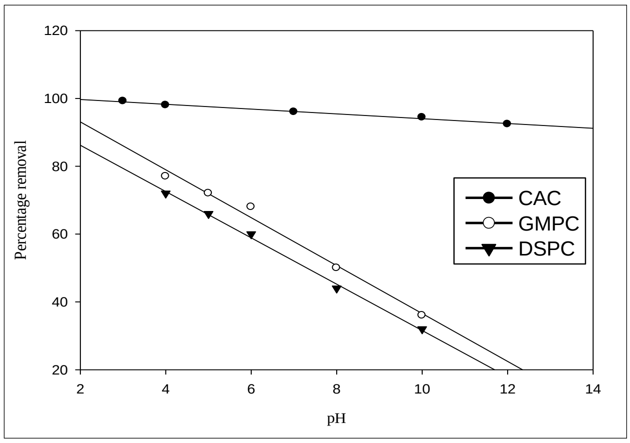


Fig 7 Effect of initial pH of dye solution

From the observed results it is concluded that the acidic medium is favourable for the maximum removal of the dye ACG [23-24].

CONCLUSION

The results of this study indicated that activated carbon prepared from fruit peel of *Garcinia mangostane* and *Datura stramonium* can be successfully used for the adsorption of alizarin cyanine green dye from aqueous solutions. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined. The *R*L values showed that GMPC and DSPC were favourable for the adsorption of ACG dye. Freundlich isotherm best-fit the equilibrium data for adsorption of ACG dye. Three simplified kinetic models, pseudo-first order, pseudo-second-order, and intra-particle diffusion were tested to investigate the adsorption mechanism. The pseudo first order kinetic model fits very well with the dynamical adsorption behaviour of ACG dye. The results of this work showed that indigenously prepared GMPC and DSPC are an excellent environmentally friendly adsorbent for removal of ACG dye from industrial effluents.

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