ADSORPTION KINETICS, ISOTHERMS, THERMODYNAMICS STUDIES ON THE REMOVAL OF CONGO RED DYE USING *ANNONA SQUAMOSA* (CUSTARD APPLE) PEEL

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Abstract: The present study evaluates the feasibility of an adsorbent prepared from *Annona squamosa* (custard apple) peel, in removing Congo red dye from its aqueous solution. Batch experiments were carried out to study the effect of various parameters like pH (2-8), adsorbent dose (0.005-0.5 g/100mL), contact time (5-120 min), initial dye concentration (25-200 mgL^{-1}) and temperature (298-308 K) to determine its effectiveness as an adsorbent. Maximum dye removal was attained at pH 2, adsorbent dose 0.1 g/100 mL in equilibrium time of 45 min at 308K. Adsorption kinetics using pseudo-first order and pseudo-second order models, and adsorption isotherm using Langmuir and Freundlich models were studied. The adsorption process was found to follow pseudo-second order kinetic model and it more favorably described the Langmuir isotherm model. Removal of Congo red dye from its aqueous solution by custard apple peel was an endothermic process with negative Gibbs free energy signifying its spontaneous nature. The results of the present study suggest that custard apple can be effectively used as an adsorbent to remove Congo red dye from aqueous solution.

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INTRODUCTION

Globally, widespread increase in industrialization and urbanization have led to contamination of air, water and land that has caused environmental imbalance. There is also a rapid demand of water for residential, industrial and agricultural use that had left the existing resources polluted and contaminated. Therefore, it is of utmost importance to treat the contaminants to avoid further water pollution.

The textile industry is one of largest pollution creating industries in the world. Textile industry contributes nearly 14% of the total industrial production in India. There are about 10,000 garment manufacturers and 2100 bleaching and dyeing industries in India (CETeDDD, 2014). Moreover, textile industry is second largest employment generating industry in India, after agriculture. Spreading across many states, textile sector is one of the most important source of water pollution in India. Million litres of textile wastewater are discharged into the rivers and water bodies. Many dyes and their break down products may be toxic for living organisms, and dyes even in low concentrations affect the aquatic life. These dyes can significantly affect the photosynthetic activity of the aquatic lives due to reduced light penetration (Patil & Shrivastava, 2010).

Dyes in general fall in broad distinct categories based on their properties: (a) acid dyes which are generally water soluble and are used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food, and cosmetics; (b) basic dyes also called as cationic dyes that are water soluble and yield coloured cations in solution and originally used for silk, wool, and tannin-mordant cotton; (c) disperse dyes which are substantially water-insoluble non-ionic dyes used mainly for polyester and to some extent on nylon, cellulose, cellulose acetate, and acrylic fibres; (d) direct dyes are used in the dyeing of cotton and rayon, paper, leather, and they are generally water-soluble anionic dyes and when dyed from aqueous solution in the presence of electrolytes it have high affinity for cellulosic fibres; (e) reactive dyes, whose chemical structures are simpler and provide brightness which makes them advantageous over direct dyes. These dyes generally used for cotton and other cellulosics. (f) solvent dyes are soluble in solvent (water insoluble) and generally non polar or little polar as they lack polar solubilising groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. This dyes are used mainly for plastics, gasoline, lubricants, oils, and waxes; (g) sulphur dyes chiefly used for cotton and rayon. The low cost and good wash fastness properties make this class of dyes important from an economic point of view; and (h) vat dyes used for cotton mainly to cellulosic fibres (Christie, 2007). Among these dyes, Congo red dye, a benzedene based acid dye, which cause an allergic reaction and metabolized to Benzedrine, this decomposition results in carcinogenic products. It acts as a skin, eye and gastrointestinal irritant and impresses blood factors such as clotting and induces drowsiness and respiratory problems (Abbas *et al.*, 2012). The enormous utilization of Congo red dyes in industries and its uncontrolled discharge to the water bodies have arisen alarming concern, which necessitates its effective removal.

Dyes have been in use for hundreds of years and for a long time in history, there have been no consideration of its effects on the flowing water bodies. Later with the realization of its harmful effects, the treatment began with few physical methods including sedimentation, and equalization followed by secondary treatment techniques using filter beds, activated sludge process and other such process. Presently, there are several techniques including ozonation, adsorption, ion- exchange etc. for treating textile effluent (Robinson *et al.*, 2001). Considering the economics and eco- friendliness of the different processes available, adsorption stands- alone.

Adsorption is a process in which a material (usually pollutant) is concentrated at a solid surface (adsorbent) from its liquid or gaseous state. Dyes that usually not removed by biodegradation and other physical process can be removed with adsorption. Various commercially used adsorbents are silica gel, zeolites, alumina and activated carbon. But due to their high cost, cheaper alternatives are being developed, most of which are prepared from agricultural and other bio wastes, thus treating dyes in cost- effective and environmental friendly way. A number of adsorbents, prepared from agricultural waste such as rice husk (Low & Lee, 1997), banana pith (Namasivayam & Kanchana, 1992; Namasivayam *et al.*, 1993), orange peel (Namasivayam *et al.*, 1996), castor seed (Howlader *et al.*, 1999), sagaun sawdust (Khattri & Singh, 1999), coir pith (Crini, 2006), *Magnifera indica* seed powder (Singh *et al.*, 2018),and *Chrysanthanum indicum* powder and microparticles (Chukki et al., 2016, 2018) have been used for removal of dyes from wastewater.

Among the different agricultural wastes, the peel of *Annona squamosa* fruit is considered in this study. *Annona squamosa* commonly is an evergreen fruit producing plant, grown in large parts of tropical and sub-tropical India. It bears fruits, commonly known as custard apple, which is generally round shaped and pulpy. In India, custard apple is a popular fruit grown in almost all plains of the country and cultivated in around 550,000 hectares of the cultivable land. Such widespread cultivation of custard apple trees makes it readily available all over the country. Considering its immense presence and the absence of any direct beneficial use of the custard apple peel, it was used as the adsorbent in this study. Thus, the objective of this study is to determine the adsorption potential of custard apple peel for removal of Congo red dye from aqueous solution.

MATERIALS AND METHODS

Adsorbent preparation

Custard apple peel was collected from local fruit juice vendors in Vellore, Tamil Nadu. The peel was washed properly 3-4 times using double distilled water to remove fruit pulp and other impurities adhered to it. It was then dried in hot air oven at 80°C for 12 hours and then grinded using a domestic mixer. The powder passing through 150μm sieve was used for further studies. **Table 1** presents the physical properties of the adsorbent.

Preparation of stock solution

Stock solution of 1000 mg L^{-1} concentration of dye solution was prepared by dissolving 1g of Congo red dye in 1000 mL of distilled water. All working solutions of other concentrations were obtained from the above stock solution by successive dilution. The pH of the dye solution was adjusted using 0.1 M H_2SO_4 and 0.1 M NaOH to the desired value. All chemicals used in this study were used without any further purification and were of analytical reagent grade.

Adsorption experiments

Batch adsorption experiments were carried out to examine the effect of initial pH, adsorbent dose, initial dye concentration, contact time and temperature on the adsorption of Congo red dye onto custard apple peel. 250 mL conical flasks were used to carry out batch experiments in which 100 mL Congo red dye solution of desired concentration and required adsorbent dose were added. Solution was then stirred at 120 rpm in orbital shaker (REMI, CSI 24BL). Each batch experiment for the study of effect of pH, contact time, adsorbent dose and temperature were carried out. The samples were taken from the shaker at pre-determined time intervals and the dye solution was then separated from the adsorbent by centrifugation using a centrifuge (REMI- R24 Research Centrifuge) at 8000 rpm for 10 minutes. Dye concentration was then calculated by finding the absorbance at 497 nm using a UV spectrophotometer (Cyberlab-UV 100). The dye removal (in %) was estimated using the following **Eq. (1)**:

$$\% \ Removal \ = \frac{(C_i - C_f)}{C_i} * 100 \qquad (1)$$

where, C_i and C_f are the initial and final concentrations of dye (mgL^{-1}) in aqueous solution respectively.

Adsorbent characterization

Scanning electron microscopy (SEM) was employed to study the surface morphology of the raw and dye loaded adsorbent. The FTIR spectroscopy was employed to determine the functional groups present in both raw and

Table 1: Physical properties of Custard apple peel

| Parameter	Value
Moisture content (%)	8.0
Volatile matter (%)	63.6
Ash content (%)	4.0
Fixed carbon (%)	24.4

dye loaded adsorbent. The infrared spectrum of the adsorbent was recorded as KBr discs in the range of 4000-400 cm^{-1}.

RESULTS AND DISCUSSION

Characterization of Custard apple peel

FTIR Analysis

FTIR spectra of raw and dye adsorbed custard apple peel are presented in **Fig. 1(a)** and **Fig. 1(b)**, respectively. It can be noted from Fig. 1 (a) that the wide peak at 3267.41 cm^{-1} assigned to stretching vibration of O-H groups. The peak at 2920.23 cm^{-1} corresponds to C-H stretching vibration, whereas the band at 1600.92 indicates that the stretching vibration of C=C present in the adsorbent. The band observed at 1228.66 cm^{-1} assigned to the stretching
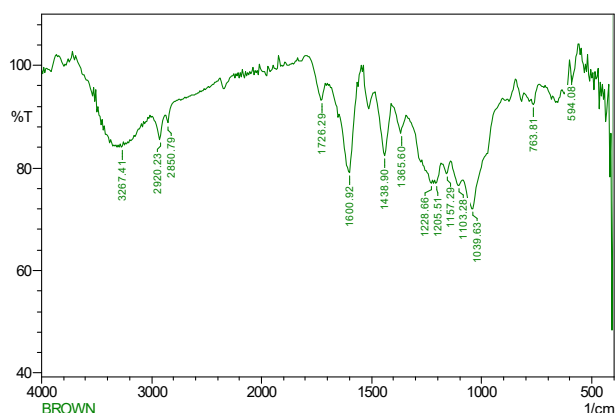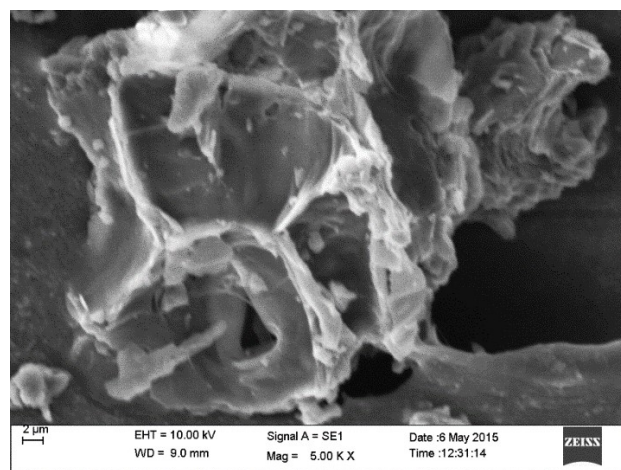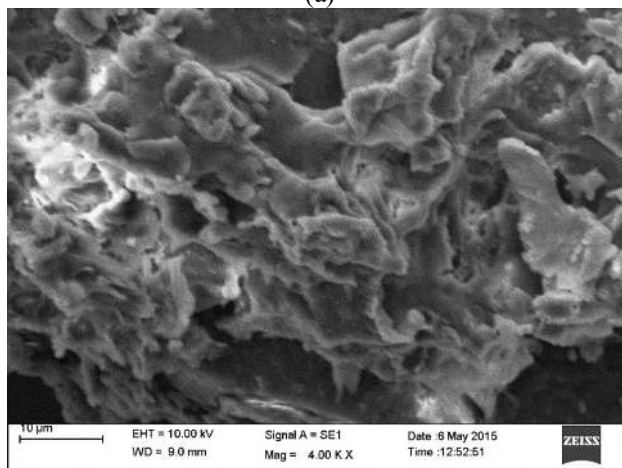

(a)
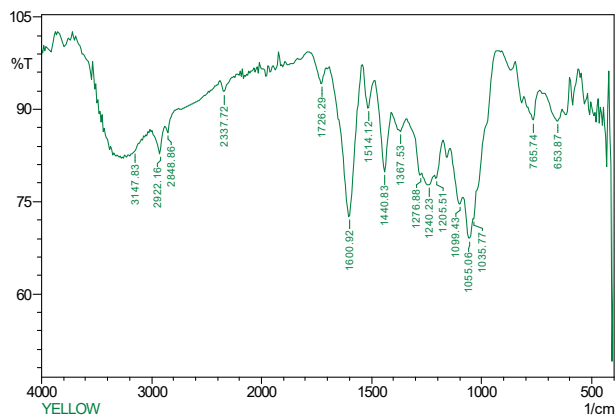
(b)

Fig. 1 FTIR Spectra of (a) raw and (b) dye adsorbed custard apple peel

(a)

(b)

Fig. 2 SEM images of (a) raw and (b) dye adsorbed custard apple peel

Fig. 3 Effect of initial pH on adsorption of Congo red onto custard apple peel (Working conditions: adsorbent dose 0.1g/100mL; initial dye conc. 50 mgL–1; contact time 60 min; temp 30°C; stirring speed 120 rpm)

vibration of O-C groups and the peak at 1039.63 corresponds to the deformation of CH_3 groups. After the adsorption of Congo red dye (Fig. 1b), the downshift of the band from 3267.41 cm^{-1} to 3147.83 cm^{-1} is attributed to –NH stretching. Further, the upshift of wave number from 1039.63 cm^{-1} to 1055.06 cm^{-1} shows that C-O is involved in the adsorption of Congo red dye.

SEM Analysis

Surface structure and morphology of the raw adsorbent (**Fig. 2a**) and dye loaded adsorbent (**Fig. 2b**) were studied by employing Scanning Electron Microscopy (SEM) technique. It can be noted from the figure that the surface of raw adsorbent is heterogeneous in nature and has significant pores, which act as binding, sites for adsorption of dye. Further, Fig. 2b depicts the Congo red dye adsorbed to the pores of custard apple peel.

Effect of initial pH

Batch experiments for observing the effect of pH on adsorption were carried out in the pH range 2.0 to 8.0 (**Fig.3**). It can be noted from the figure that, as the pH
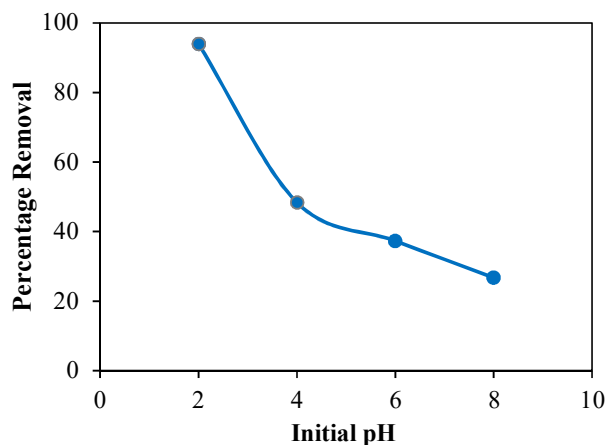
increases, the percentage removal decreases. For a change of pH from 2 to 8, the removal dropped from 94 % at pH 2 to 26.75 % at pH 8. High electrostatic attraction between excess H^+ ions at low pH and the anionic Congo red dye is the main reason that at pH 2, there is high percentage removal. With increase in pH, there is decrease in H^+ ions and increase in OH^- ions. Due to presence of excess negative ions OH^- at alkaline pH competing with dye anions for adsorbent sites, there is lower adsorption. Thus, an optimum pH of 2.0 for which, there is an observed higher percentage dye removal was taken for all further studies.

Effect of adsorbent dosage

To determine the effect of adsorbent dose on dye removal, batch process was carried out at 50 mgL^{-1} dye concentration at the optimum pH of 2.0 for an adsorbent dose range of 0.005-0.5 g $100mL^{-1}$ of dye solution (**Fig. 4**). For 0.005g of adsorbent dose, 61.16% dye removal was observed which kept on increasing until 0.1 g adsorbent dose. Considering the trend of dye removal for adsorbent dose, it can be seen that increase in adsorbent dose increased removal of dye until 0.1 g, which could be due to more active sites with increasing adsorbent dose. The percentage removal almost remained a constant at higher dose, which may be due to the attainment of equilibrium in the adsorption system. Thus, at $0.1g100mL^{-1}$ at which there is a maximum dye removal was taken as the optimum adsorbent dose for further adsorption studies.

Effect of initial dye concentration with contact time

Effect of initial dye concentrations of 25, 50, 100, 150, 200 mg L^{-1} was studied for a range of contact time of 5 to 120 min. It can be observed (**Fig. 5**) that the percentage
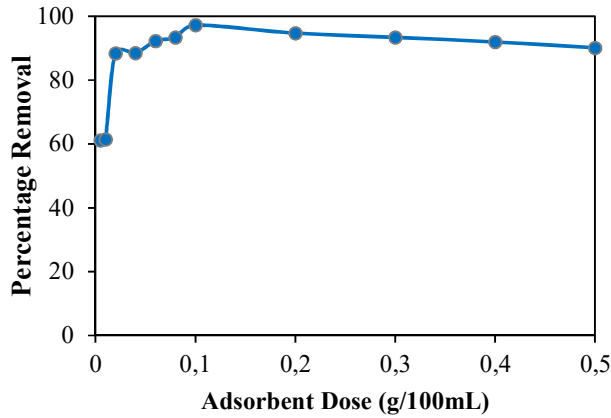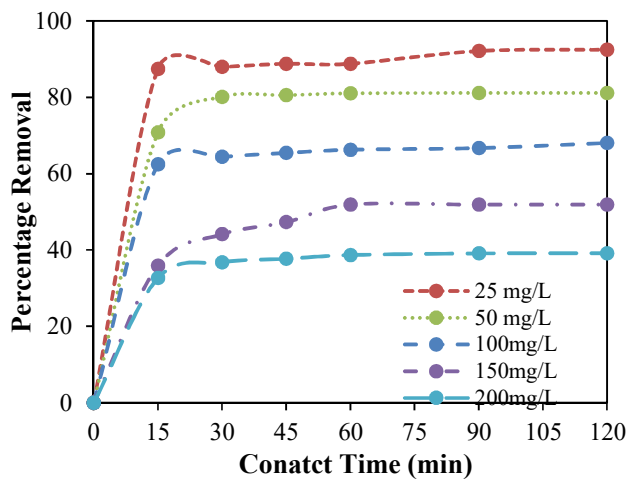
Fig. 4 Effect of adsorbent dose on adsorption of Congo red onto custard apple peel (Working conditions: pH 2.0; initial dye conc. 50 mgL–1; contact time 60 min; temp 30°C; stirring speed 120 rpm)

removal decreases with increasing initial dye concentration. This may be due to the fact that at low dye concentration, the ratio of available surface binding sites to the initial dye concentration is large, and it enhances removal. The amount of dye adsorbed shows increasing trend with increase in contact time and for the dye concentrations 25, 50, 100, 150, 200 mg L^{-1} reached equilibrium after 45 min.

Adsorption kinetics

Adsorption kinetics reveals the mechanism of adsorption and its potential rate-limiting step that include mass transfer and surface reaction processes (Chatterjee & Schiewer, 2014). The adsorption kinetics of Congo red dye on custard apple peel was explored as a function of contact time at different initial dye concentrations (25, 50, 100, 150, 200 mgL^{-1}). In the study, pseudo-first order model and pseudo-second order model have been studied to understand the adsorption kinetics and to measure the rate of adsorption.

Fig. 5 Effect of initial dye concentration with contact time on adsorption of Congo red onto custard apple peel (Working conditions: pH 2.0; adsorbent dose 0.1 g/100mL; temp 30°C; stirring speed 120 rpm)

Pseudo-first order model

The rate constant of adsorption is determined from the first order rate expression (**Eq. 2**) given by Lagergren (Namasivayam & Ranganathan, 1994):

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303\, t} \qquad (2)$$

where Qe and Qt are the amounts of dye adsorbed (mg/g) at equilibrium and at time t (min), respectively, and K_1 is the rate constant of adsorption (L/ min). Values of K_1 and Qe $_{(cal)}$ were calculated from the slope and intercept from the plots of log (Qe-Qt) versus t, for different concentrations of the dye. The experimental Qe values do not agree with the calculated ones (Table 2), obtained from the linear plots, and hence, the adsorption process does not follow the pseudo-first order model.

Pseudo-second order model

The pseudo-second order kinetic rate equation (**Eq. 3**) is expressed as (Mckay & Ho, 1999):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \qquad (3)$$

where K_2 is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The values of Qe $_{(cal)}$ and K_2 were calculated from the slope and intercept of the linear plot of t/Qt versus time. The values of pseudo-second order kinetic constants along with the corresponding correlation coefficients (R$_2$) are presented in Table 2. It can be noted from **Table 2** that the theoretical values Qe$_{(cal)}$ agree well with the experimental values Qe$_{(exp)}$. Further, the correlation coefficient values (R$_2$) were observed as $\cong$0.99, suggesting that the adsorption process can be more favourably described by pseudo-second order kinetic model.

Adsorption isotherm

Isothermal modelling data was used to determine if custard apple peel actively adsorbs Congo red dye from its aqueous solution. For developing isotherm models, the adsorption of Congo red dye on adsorbent was carried out at different temperatures (298-308 K) for different dye concentrations (25–200 mg L^{-1}) at 120 rpm for equilibrium time, adsorbent dose and optimum pH. Analysis of isotherm data was carried out to study and to design adsorption models. In this study, the isotherm data was analyzed with Langmuir and Freundlich isotherm equations.

Langmuir isotherm

Langmuir isotherm is represented by the following equation (**Eq. 4**):

Table 2. Adsorption kinetics of Congo red dye adsorption onto custard apple peel

Dye Conc. (mg L^{-1})	$Q_{e(exp)}$ (mg g^{-1})	Pseudo-first order model			Pseudo-second order model		
		K_1 (min^{-1})	$Q_{e(cal)}$ (mg g^{-1})	R^2	K_2 (min^{-1})	$Q_{e(cal)}$ (mg g^{-1})	R^2
25	22.210	0.151	2.739	0.799	0.021	22.208	0.999
50	40.290	0.183	7.448	0.913	0.004	40.292	0.985
100	65.460	0.148	5.869	0.899	0.003	65.458	0.990
150	71.000	0.088	6.139	0.992	0.002	71.000	0.998
200	75.460	0.095	4.982	0.870	0.004	75.458	1.000

Table 3. Adsorption isotherm of Congo red adsorption onto custard apple peel

Temperature (K)	Langmuir Isotherm				Freundlich Isotherm		
	Q_m (mg g^{-1})	K_l (L mg^{-1})	R^2	R_L	n	K_f (mg g^{-1})	R^2
298	71.480	0.134	0.983	0.035	3.912	20.948	0.874
303	80.602	0.132	0.993	0.036	3.963	23.711	0.950
308	80.536	0.136	0.994	0.035	3.955	23.770	0.951

$$\frac{C_e}{Q_e} = \frac{1}{K_1 \cdot Q_m} + \frac{C_e}{Q_m} \qquad (4)$$

where Q_e is the amount of Congo red dye adsorbed per unit weight of adsorbent (mg g^{-1}), C_e is the concentration of dye in the solution at equilibrium (mg L^{-1}), Q_m signifies adsorption capacity (mg g^{-1}) and K_1 is the related to the energy of adsorption.

Values of the Langmuir constants, K_1 and Q_m were calculated from the intercept and slope of the plot of C/Q_e versus C_e (Table 3). The maximum adsorption capacity ($Q_{m)}$ of 80.602 mg g^{-1} was obtained at 303 K for the adsorption of Congo red dye by custard apple peel powder as seen from **Table 3**. The correlation coefficient (R^2) obtained have high values, which suggests that the Langmuir isotherm model can satisfactorily describe the adsorption process.

Langmuir isotherm's viability is also described in terms of separation factor (R_L). R_L is calculated using the following expression (**Eq. 5**):

$$R_L = 1 + \frac{1}{K_1 C_o} \qquad (5)$$

As R_L values lay between 0 and 1, we can assert that adsorption is favourable.

Freundlich isotherm

Freundlich isotherm is represented by the following equation (**Eq. 6**):

$$\log Q_e = \log K_f + \frac{1}{n} \cdot \log C_e \qquad (6)$$

where C_e is concentration of dye in solution at equilibrium (mg L^{-1}), K_f indicates the relative adsorption capacity of the adsorbent (mg g^{-1}) and n is a parameter indicating adsorption intensity. Values of K_f and n are obtained by plotting log Q_e versus log C_e. High values of

R^2 indicate that adsorption process also follows Freundlich model. As the value of K_f increases, the adsorption capacity also increases, as indicated by values of K_f and R^2 (**Table 3**).

Adsorption Thermodynamics

The effect of temperature on adsorption of Congo red dye on custard apple peel were studied at different temperatures (298, 303, 308 K). Percentage removal of Congo red dye increased with increase in temperature and decreased with increasing initial dye concentration. Gibbs free energy change ($\Delta G°$), the standard enthalpy ($\Delta H°$) and the standard entropy ($\Delta S°$) are different thermodynamic parameters that were calculated for understanding the adsorption process. The Gibbs free energy change was calculated using the following equation (**Eq. 7**):

$$\Delta G° = -RT \ln K_c \qquad (7)$$

where R (8.314 J (mol^{-1} K^{-1})) is the universal gas constant, T is the absolute temperature in Kelvin and K_c (L g^{-1}) is obtained by multiplying the Q_m and K_1 (Langmuir constants).

The values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the plot of lnK versus 1/T. The negative values of $\Delta G°$ (**Table 4**) indicate the spontaneous nature and feasibility of the adsorption process in the study (Namasivayam & Ranganathan, 1994). Endothermic nature of adsorption is ensured by positive value of $\Delta H°$ and increase in attraction of the adsorbent at the solution/solid interface is indicated by positive value of $\Delta S°$ (**Table 4**).

CONCLUSION

The results obtained from the present study through a series of batch experiments suggest that the adsorben

Table 4. Thermodynamics of congo red adsorption on custard apple peel

Thermodynamic Parameters			
Temperature (K)	-$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1}K^{-1})	$\Delta H°$(kJ mol^{-1})
298	5.614		
303	5.958	52.539	10.016
308	6.137		

prepared from custard apple peel waste is effective towards removing Congo red dye from aqueous solution. The adsorption process follows pseudo- second order kinetics and is endothermic in nature and the Langmuir isotherm model best represents the experimental isotherm data. The thermodynamic studies further confirmed the adsorption process to be spontaneous and feasible.

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