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Comparative Study of Adsorption of Different Dyes from Aqueous Media Onto Physically Activated Carbon: Isotherm, Kinetic and Thermodynamic Parameter

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Abstract:

The present work demonstrates efficient and fast removal of different dyes namely Brilliant Green, Naphthol Blue Black-B and Alizarine Red-S from aqueous solutions by using activated carbon from coconut shell, which is prepared by the simple activation method. Batch mode experiments were carried out by varying the parameters like contact time, dosage of activated carbon, temperature, agitation speed and desorption studies. The results indicated that only carbonaceous adsorbent removed the dyes from solution to an appreciable extent compared to other adsorbents. The activated carbon as adsorbent can, therefore, be a useful material for dye removal. The adsorption isotherms of the dyes were found to conform to the Langmuir equation. The kinetic studies of the adsorption process showed it to be pseudo-second order. The thermodynamic parameters calculated indicated that the physical in nature of the adsorption.

Keywords: Adsorption, Brilliant Green, Naphthol Blue Black-B, Alizarine Red-S, Activated carbon.

INTRODUCTION

Water conservation is one of the most important environmental issues affecting both human being and the environment[1]. Dyes are the major source of contributors in water pollution[2-7]. They are used in industries like textile, leather, paper, printing and paint. Among these industries, textile industry discharges significant amount of untreated wastewater. This has prompted the development of technologies for efficient dye removal from wastewater. Over the past three decades, many physical, chemical and biological methods have been reported for dye removal. Among the available technologies for dye removal, adsorption is a selective one with a high efficiency, costless, better designed, higher degree of accessibility, etc.

In the present study, physically activated carbon was prepared and used for removal of different dyes such as Brilliant Green, Naphthol Blue Black-B and Alizarine Red-S[8]. Effect of different variables like contact time, dosage of activated carbon, temperature, agitation speed and desorption studies was investigated. Langmuir isotherm was applied to fit the adsorption of dyes on physically activated carbon. Pseudo-second kinetic models were used to estimate the adsorption mechanism. Various thermodynamic parameters have also been calculated.

MATERIALS AND METHODS

Materials

Naphthol Blue Black-B (NBB-B) was obtained from Loba Chemie Pvt. Ltd., Mumbai and Brilliant Green (BG) & Alizarine Red-S (AR-S) were procured from Hi Media Laboratory Pvt Ltd., Mumbai which are used in the adsorption studies.

Preparation of Physically Activated Carbon (PAC)

Coconut shells were collected from domestic waste and followed by washing with tap water & distilled water for removal of dust adheres to it. Then it was dried in oven and then carbonized in Bunsen burner. The carbonized substance was ground, dried at 105°C for 2 hrs and used for all adsorption experiments[8].

Adsorption Studies

The objective of the current study was to understand the adsorbing and desorbing nature of activated carbon as reusable adsorbent. The batch experiments were carried out in 250ml pyrex bottle with 100ml of these dye solution contains 0.1g of PAC, shaken in an orbital shaker at 250rpm to investigate the effects of contact time, dosage of adsorbent, temperature, agitation speed on the adsorption process and desorption studies. Before and after adsorption of these dye concentrations are measured by using Elico UV-spectrophotometer at wave length of 625, 618 and 503nm. The amount of these dyes adsorbed on the PAC(mg/g) and percentage of adsorption of dye are calculated using Eq.1 and 2 respectively[8-10]

$$q_e = \frac{(C_i - C_e)V}{M} \qquad \text{-------------------(1)}$$

and,

$$\%removal = \frac{(C_i - C_e)}{C_e} \times 100 \qquad \text{-----------------(2)}$$

where q_e is the adsorption capacity (mg/g) of PAC at equilibrium, C_i and C_e are initial and equilibrium concentration of dyes (mg/L) respectively, V is the volume of dye solution (ml) and M is the weight of PAC (g).

Kinetic and Thermodynamic Study

In order to find out the adsorption rate of the dye solutions by PAC kinetic study were carried out. Adsorption kinetic study was carried out using 100ml of the dye solution having 0.1g of PAC at 34°C. It was stirred in orbital shaker at 250rpm and concentration is measured at different time intervals (10-100min). Thermodynamic parameters were calculated by executing the experiment at different temperatures (34-40°C).

RESULTS AND DISCUSSION

Adsorption Studies

Variation of contact time

The adsorption of all the dyes at a fixed concentration using PAC was studied as a function of contact time to find an equilibration time for maximum adsorption. Fig.1 is seen that 80minutes are required for the equilibrium adsorption to be attained. It is further seen from Fig. 1 that adsorption is very fast initially, showing that 50% adsorption in all the three dyes is completed in less than 10min. After that, it slowly attains equilibrium adsorption[11].

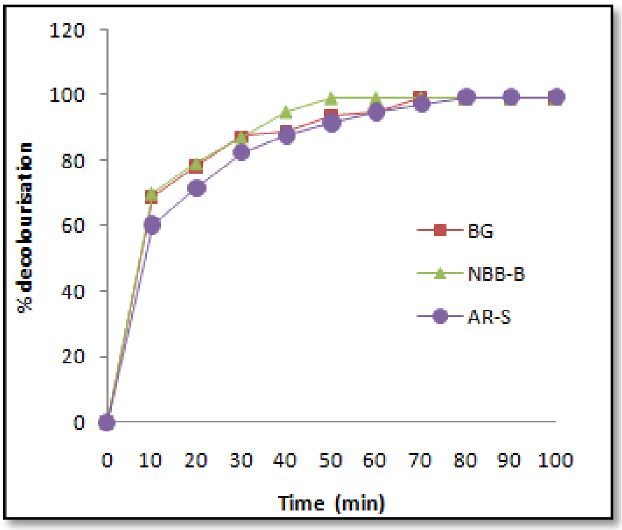

Fig. 1: Variation of contact time

Variation of PAC dosage

PAC dosage is also an important parameter because it determines the capacity of PAC for a given initial dye concentrations at suitable conditions. Fig.2 explains the influence of PAC dosage on % decolourization of these three dyes. Usually the percentage of dye removal increases with an increase in PAC dosage, where the number of sorption sites at the adsorbent surface will increase by increasing the dosage of the adsorbent and as a result increase in the % dye removal from the solution[12].

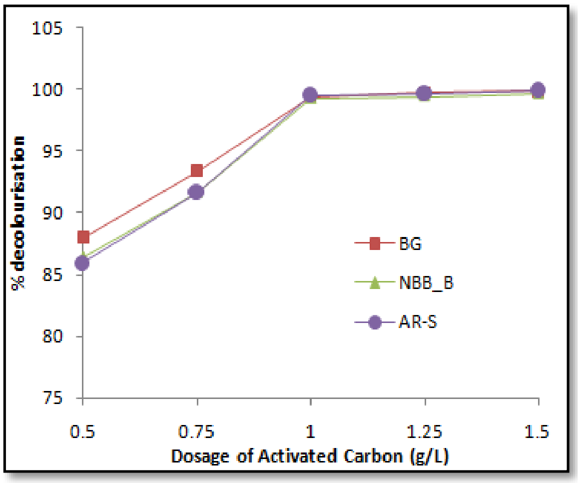

Fig. 2 : Variation of PAC dosage

Variation of temperature

The temperature influence is an important controlling factor in the proposed adsorptive dye removal process. To study the effect of temperature on the dye removal efficiency. The experiment was studied by varying the different temperatures (34, 37 and 40°C) at optimum conditions. The equilibrium data evident that % decolourisation increased with increasing temperature due to the excitation of adsorbent particles. The results are shown in Fig.3 which revealed the endothermic nature of adsorption process[13,14].

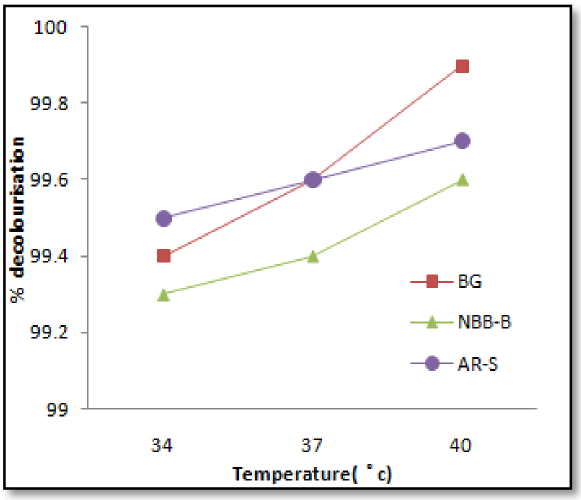

Fig. 3 : Variation of temperature

Variation of agitation speed

The effect of agitation speed of all dyes on PAC was carried out by varying the agitation speed from 50 to 250rpm, keeping the other parameters is constant. Fig.4 evident that the adsorption of dyes are found to increase with increasing agitation speed due to the fact that with the increased turbulence, there is a decrease in boundary layer thickness around the adsorbent particles.

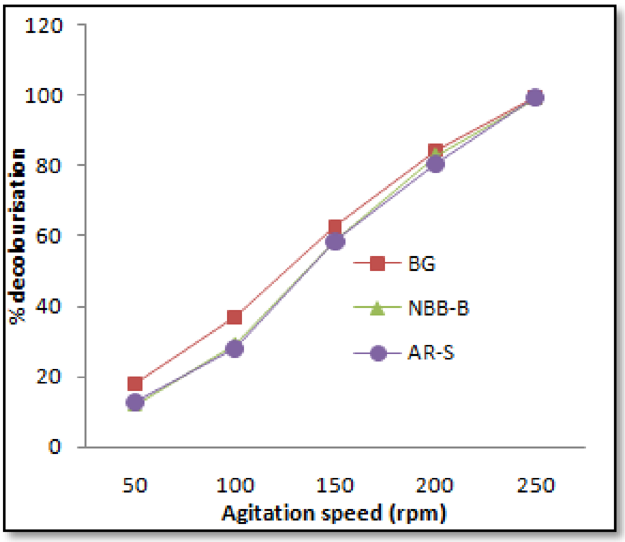

Fig. 4 : Variation of agitation speed

Desorption studies

Reusability of an adsorbent is of crucial importance in industrial practice for dye removal from wastewater. Desorption of the adsorbent dye from PAC was studied using a batch system. In this study, the ability of HCl & NaOH to desorb dye uptake by PAC was investigated. Fig.5 shows that the desorption efficiency increases with increase in strength of HCl & NaOH due to ion substitution. If the desorption of dyes by mineral acid and alkaline medium indicates that the dyes are adsorbed onto the PAC by physisorption[15].

Adsorption equilibrium

The adsorption isotherm indicates how the adsorption molecules are being distributed between the liquid phase and the solid phase when the adsorption process reaches equilibrium state. The isotherm model is an important step to find the best fitting model that can be used for design purpose.

Langmuir isotherm

Langmuir isotherm[16-18] is precise for the monolayer adsorption of a solute from a liquid on the adsorbent surface containing a definite number of identical active sites. The linear equation of Langmuir isotherm is expressed by

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad \text{----------------(3)}$$

where Q_0 and b are Langmuir constants. Langmuir isotherm can also be expressed in terms of separation factor, R_L which is referred as equilibrium parameter and expressed as

$$R_L = \frac{1}{(1+bC_i)} \qquad \text{-----------------(4)}$$

R_L value indicates the shape of the isotherm and nature of adsorption process. When, the R_L value >1 adsorption is unfavorable, $0<R_L<1$ it is favorable, if $R_L = 0$ it is irreversible. In the present study, the R_L value was found to be 0.9592, 0.0018 & 0.0250 for BG, NBB-B & AR-S respectively. This indicates that the adsorption of all dyes using PAC are a favorable process.

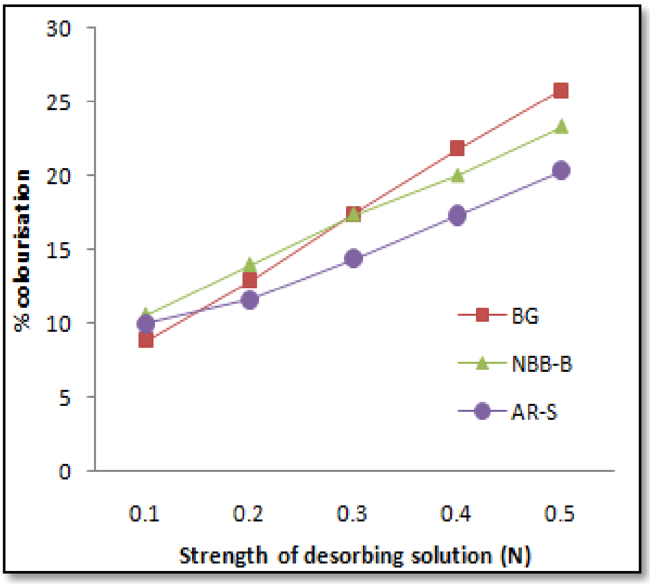

Fig. 5: Desorption studies

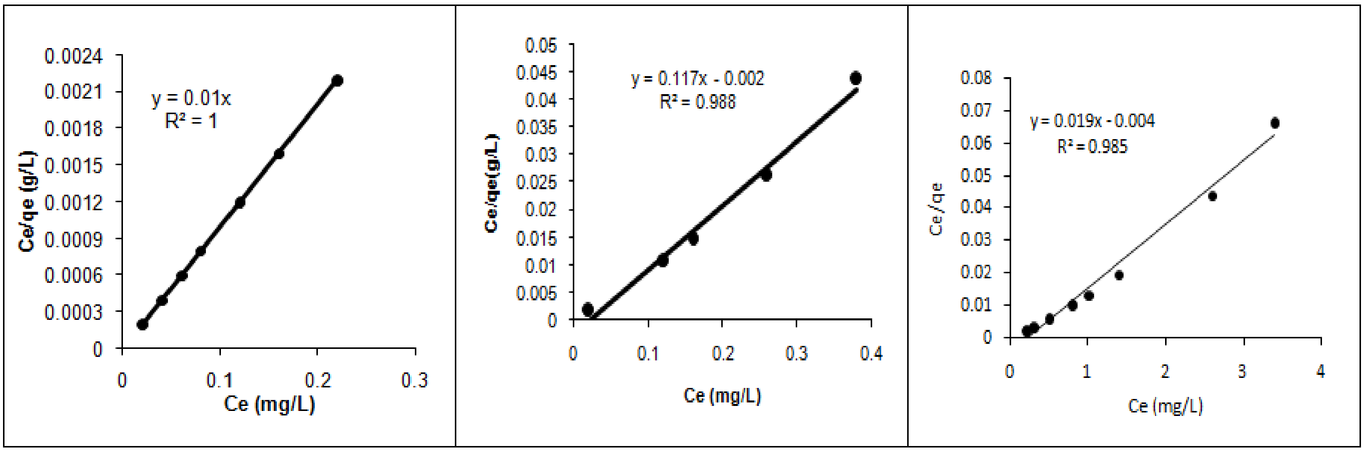

Fig.6 : Langmuir isotherm model for the three dyes

Adsorption kinetics:

The kinetics of decolourisation of all dye solutions over PAC has been studied using pseudo-first and pseudo-second order kinetic models.

Pseudo-first order kinetic model

Pseudo-first order model[19,20] is given by Lagergren as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{--------------(5)}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively, k_1 is the rate constant of the pseudo-first order adsorption.

After integration, the integrated form of the above equation becomes

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

The equilibrium data shows that the adsorption of all dyes onto PAC cannot be applied and the reaction mechanism is not a first-order reaction.

Pseudo-second order kinetic model

Pseudo-second order kinetics[19,20] is expressed as

$$\frac{dq_t}{dt} = (q_e - q_t)^2 \quad \text{--------------(7)}$$

where k_2 is the rate constant of pseudo-second order adsorption.

After integration, the form of rearranged equation is

$$\frac{t}{q_t} = \frac{1}{k_2}(q_e)^2 + \frac{t}{q_e} \quad \text{--------------(8)}$$

The plot was perfect linear (Fig.7) shows that the reaction kinetics follows pseudo-second order model. The correlation coefficients (R^2) are also confirmed that the adsorption better fitted by the pseudo-second order kinetic model than pseudo-first order kinetics.

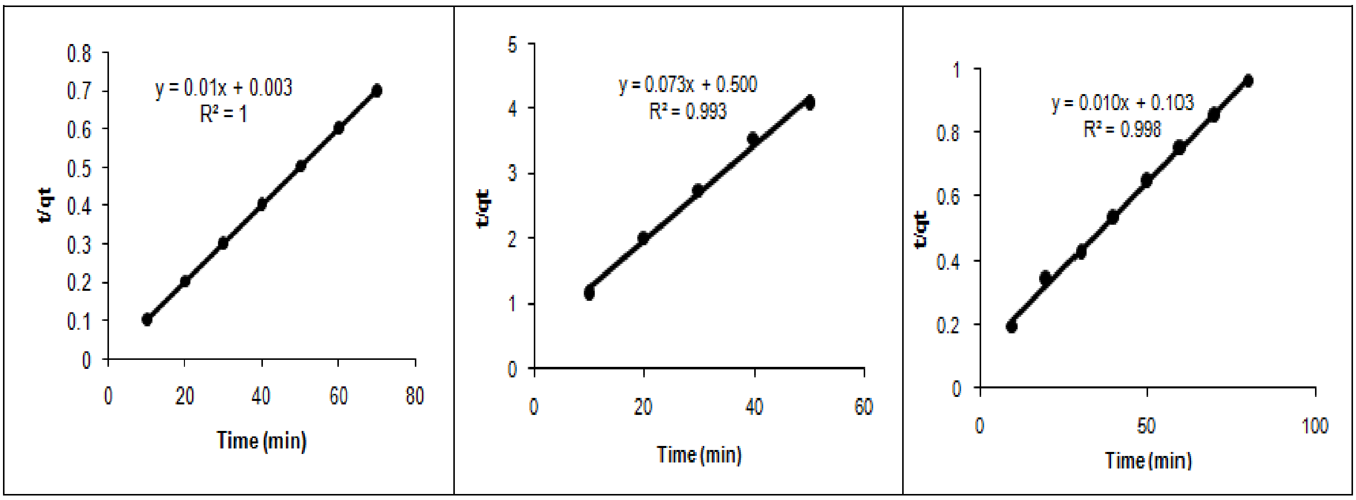

Fig.7 : Pseudo-second order kinetic model for three dyes

The constant values are listed in Table.1 for the three dyes.

Table.1: Adsorption isotherm and kinetic parameters for the adsorption of three dyes onto PAC

Name of the model	Constants		
	BG	**NBB-B**	**AR-S**
Langmuir isotherm	Q_0 = 100 b = 0.0050 R_L = 0.9592	Q_0 = 8.5324 b = 43.4074 R_L = 0.0018	Q_0 = 50.7614 b = 4.5814 R_L = 0.0250
Pseudo – second order kinetic model	K_2 = 100 q_e = 0.0294 R^2 = 1.0000	K_2 = 0.1470 q_e = 13.6054 R^2 = 0.9930	K_2 = 0.0011 q_e = 92.5926 R^2 = 0.9980

Thermodynamic study

The Gibbs free energy change[19,20] of the adsorption process is related to the equilibrium constant by the Van't Hoff equation

$$\Delta G^{\circ} = -RT \ln K_L \qquad \text{--------------(9)}$$

where K_L (L/g) is an equilibrium constant obtained by multiplying the Langmuir constants Q_0 and b, T is the absolute temperature (Kelvin), R is the gas constant (8.314J/mol/K). The graph (Fig.8) is plotted by taking ΔG°in y-axis against T in x-axis. The relationship between the changes in the Gibbs free energy, entropy(ΔS°) and enthalpy (ΔH°) can be expressed as follows

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad \text{--------------(10)}$$

ΔS° and ΔH° could be calculated from the slope and intercept of the plot respectively.

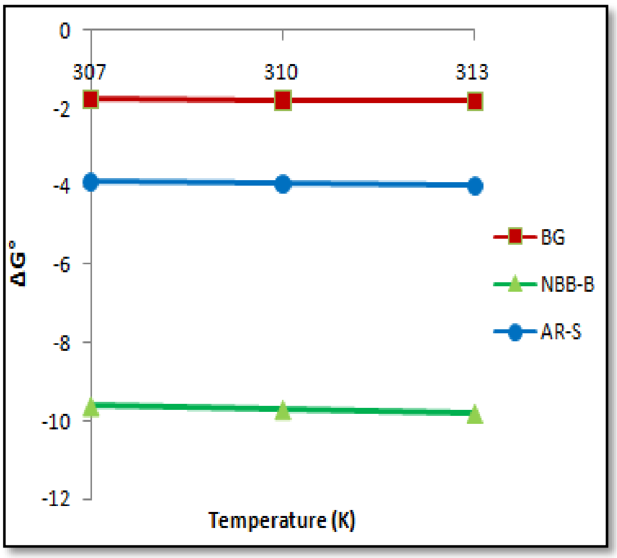

Fig.8 : Thermodynamic plot

The negative value of ΔG°(-1.7692, -9.6283 & -3.8880) indicate that the processes are spontaneous & feasible process The negative values of ΔH° (-1.7520 & $-1\text{x}10^{-13}$) indicate exothermic nature and positive value of ΔH° ($3\text{x}10^{-13}$) show endothermic nature of the adsorption. The positive value of ΔS° (+0.0314 & +0.0127) suggests that reflects the affinity of adsorbent for dye and negative value of ΔS° (-0.0173) indicate the enthalpy driven.

CONCLUSION

In this study, PAC was prepared by simple process and used for the adsorption of different dyes from aqueous solution. Adsorption efficiency of PAC for BG, NBB-B and AR-S dyes at equilibrium time of 80min was found to be 99.4, 99.3 & 99.5% for BG, NBB-B & AR-S respectively. The parameters influencing adsorption rate such as contact time, dosage of PAC, temperature, etc. were optimized. The equilibrium data were better fitted by the Langmuir isotherm and pseudo-second order kinetics model. In thermodynamic study, negative value of ΔG° and ΔH° indicate that the adsorption process is spontaneous, feasible process and exothermic in nature. The positive value of ΔS° reveals that the process reflects the affinity of adsorbent for dye. Thus, the present study has proved that PAC could be used as an efficient adsorbent for the removal of three different dyes from aqueous solution. Moreover, the use of PAC as adsorbent not only to solve the environmental pollution but also to decrease the overall cost of waste water treatment and to reduce the amount of domestic wastages.

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