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ISOTHERMAL KINETIC AND THERMODYNAMIC STUDIES ON BASIC DYES SORPTION USING RICE HUSK CARBON

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Abstract:

Dyes are usually present in trace quantities in the treated effluents of many industries. The present study investigates the potential use of pretreated rice husk and rice husk ash for the removal of methylene blue from wastewater. A series of batch experiments were carried out to determine the influence of different system variables such as P^H, dye concentration, adsorbent dosage and temperature. The similar experiment was conducted with commercially available powdered activated carbon, in order to evaluate the performance of rice husk carbon. The adsorption capacity of both rice husk carbon and activated carbon has been tested for decolourization of waste water containing methylene blue. For equilibrium studies, two isotherm models were used which is Freundlich and Langmuir for different temperatures and it was found that both Freundlich and Langmuir, fitted in the experimental data very well. Thermodynamic studies showed that the adsorption of methylene blue from rice husk is exothermic and spontaneous in nature.

Key Words: Activated carbon, rice husk carbon, isothermal models and adsorption.

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Introduction:

There are more than 100,000 types of commercially dyes with over $7x10^5$ tonnes of dyes created yearly. Direct, reactive, acid, disperse, pre-metallized and basic dyes account for about 85% of the total dyes used in the industry. The total dye consumption of the textile industries alone is in excess of 10^7 kg/year and estimated 90% of this total endup on fabrics [1]. Consequently, approximately 106 kg/year of dyes are discharged into the waste streams by textile industries. Dyeing industry effluents constitute one of the most problematic wastewaters to be treated not only for their high chemical and biological oxygen demands but also for color. Moreover, dyeing industry effluents are harmful to fish and other aquatic organisms due to suspended solid and toxic compounds [2]. Despite these methylene blue dye causes eye burns, may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating and mental confusion [3, 4]. Hence the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters.

The conventional methods for treating dye-containing wastewaters are coagulation, flocculation, reverse osmosis, electro flotation, membrane filtration, irradiation and ozonation and active carbon adsorption [5, 6]. The most popular of these technologies is activated carbon adsorption and widely used but it is expensive. Therefore, there is a growing interest in using low-cost, easily available materials for the adsorption of dye colors. An alternative inexpensive adsorbent that is able to reduce the cost of an adsorption system has always been searched, in this regard special emphasis are given on the preparation of activated carbons from several agricultural by-products. Researchers have studied the production of activated carbon from palm-tree cobs [4], plum kernels [7], cassava peel [8], bagasse [9], jute fiber [10], olive stones [11], date pits [12], fruit stones and nutshells.[13] The advantage of using these agricultural by-products as raw materials for manufacturing of activated carbon, is that these raw materials are renewable and potentially less expensive to manufacture [9,10,12].

The focus of the research is to evaluate the adsorption potential of activated carbon derived from rice husk impregnated with 50% H_3PO_4 (Fisher Scientific AR grade) for removal of methylene dye. The kinetic data and equilibrium data of adsorption studies were processed to understand the adsorption mechanism of the dye molecules onto the rice husk carbon.

Material and methods:

Preparation of the activated carbon from rice husk:

We obtained rice husk from rice mill near Bangalore and cleaned with distilled water to remove most of the impurities like rice grains, suspended particles, dust etc, then dried in sun. Then it was activated by impregnating with orthophosphoric acid 50% (Fisher Scientific AR grade) in the ratio 2:1 of weight of rice husk carbon to acid volume. The mixture was carbonized in a furnace at 350^0C for about 20 minutes. The carbonized rice husk was washed with water then dried and crushed in a ball mill. The rice husk carbon so obtained was sieved by using 120 mesh number screen (ACME Concrete Pvt Ltd India).

Adsorption experiments:

Effect of P^H: The effect of P^H was studied by agitating rice husk carbon (0.20 g) in 50 ml of the known concentration dye solution. The experiments were conducted at different P^H values (4, 6, 7, 9.2) for 3 hrs, which was sufficient to reach equilibrium. The solutions were filtered through Whatman filter paper (No.1) and checked for absorbance in the colorimeter. The above procedure was also repeated for activated carbon.

Effect of adsorbent dosage: The effect of adsorbent dosage was studied by agitating different weights of rice husk carbon and activated carbon (0.2, 0.4, 0.6, 0.8 g) in 50 ml of the dye solution of known concentration, for 5 hrs, which was sufficient to reach equilibrium. The solutions were filtered through Whatman filter paper (No.1) and checked for absorbance in the colorimeter.

Effect of Temperature variation on sorption of methylene blue: Dye concentration (varied from10, 15, 20, 25, 30 ml/L) was measured by using standard volumetric flask (Glassco Laboratory Equipments, India) at different time interval (15, 30, 60, 90, 105 min), at different temperatures (30, 40, 50 and 60^{o}C). At the end of predetermined time intervals, mixtures were taken out and filtered through Whatman filter paper (No. 1) and checked for absorbance in the colorimeter

Results and discussion:

The effect of the initial P^H: For both powdered activated carbon and rice husk carbon, it was found that adsorption increases with increases with increase in P^H. For Rice Husk Carbon with increase in P^H, the adsorption increases from 62% - 75% & for Activated Carbon with increase in pH, the adsorption increases from 63% - 77%.

Figure 1 shows the variation of dyes removal for different adsorbents at various P^H values

The effect of adsorbent dosage: The effect of adsorbent dosage on the adsorption of methylene blue from waste water is shown in Fig 2**.** For the rice husk carbon and activated carbon, it was found that the percentage of dye removal was increased with the increment of adsorbent dosage.

The adsorption isotherm: The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [14].

Fig. 3 typically shows the adsorption isotherms of methylene blue dye at 40^0, 50^0 and 60°C on the activated carbon. Adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. Adsorption isotherm study is carried out on two well-known isotherms, Langmuir and Freundlich. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface While, Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [15].

Langmuir isotherm The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{1}{q_e} = \frac{1}{(q_m\ b)} \times \frac{1}{C_e} + \frac{1}{q_m}$$

Where *C*e is the equilibrium concentration of the adsorbate (Methylene blue) (mg/l), qe the amount of dye adsorbed per unit mass of adsorbent (mg g−1), and q_m and *b* are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When 1/*q*e was plotted against 1/*C*e, straight line with slope $1/q_m\ b$ was obtained (Fig. 3), indicating that the adsorption of Methylene blue on activated carbon follows the Langmuir isotherm. The Langmuir constants '*b*' and 'q_m' were calculated from this isotherm and their values are given in Table 1.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [16], which is defined by:

$$R_L = \frac{1}{(1 + b\ C_0)}$$

Where *b* is the Langmuir constant and C_0 the highest dye concentration (mg /l). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Values of R_L was found In between 0 and 1 and confirmed that the rice husk carbon is favorable for adsorption of Methylene blue dye

Freundlich isotherm The well-known logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (Methylene blue) and K_f and *n* are Freundlich constants, *n* giving an indication of how favorable the adsorption process and K_f is the adsorption capacity of the adsorbent.. The plot of log q_e versus log C_e gives straight lines with slope '1/*n*' (Fig. 4), which shows that the adsorption of Methylene blue also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_f and *n*) were calculated and recorded in

Table 2. As also illustrated in Table 2, the values of 1/n are found to be less than 1, which indicates favorable adsorption [17],

Thermodynamics of the adsorption process: In the present study, the adsorption studies were carried out in the temperature range 30-60^{o}C. Thermodynamic parameters were obtained by varying temperature conditions over the range 30-60^{o}C by keeping other variables constant.

Temperature affects the adsorption rate by altering the molecular interactions and the solubility. The uptake of dye increases with increase in temperature. The enthalpy of adsorption H is related with Langmuir constant b according to Vant Hoff equation

$$\boldsymbol{log\, b = log\, b^0 - \frac{\Delta H}{2.303\, RT}}$$

The graph of log b versus 1/T was plotted as shown in Fig 5 and the values of ΔH for methylene blue were calculated from the slope. The values of b for the removal of methylene blue at different temperatures by rice husk carbon and negative valves of ΔH show the exothermic nature of adsorption. The free energy ΔG and entropy ΔS changes were calculated using standard thermodynamics relationships.

$$\boldsymbol{\Delta S = \frac{(\Delta H - \Delta G)}{T}}$$

The values of ΔG and ΔS are given in Table 3. A negative ΔG would mean that the adsorption process is spontaneous with a high affinity of methylene blue dye for the adsorbent surface. The positive values of entropy reflect the affinity of the adsorbent material for dye.

Conclusions The present investigation showed that rice husk carbon could be effectively used as a raw material for the preparation of activated carbon. Activated carbon can be used effectively for removal of methylene blue dye from wastewater. The present investigation was based upon many different variables such as, adsorbent dosage and P^H.

The investigation also highlights that the rice husk carbon has more adsorption capacity. The only disadvantage is that it absorbs the moisture at room temperature, which can be prevented by keeping it in the desiccators. Adsorption isotherms like Freundlich and Langmuir isotherms were plotted and found to be favorable, Thermodynamic studies show the adsorption to be an exothermic and spontaneous.

Figures

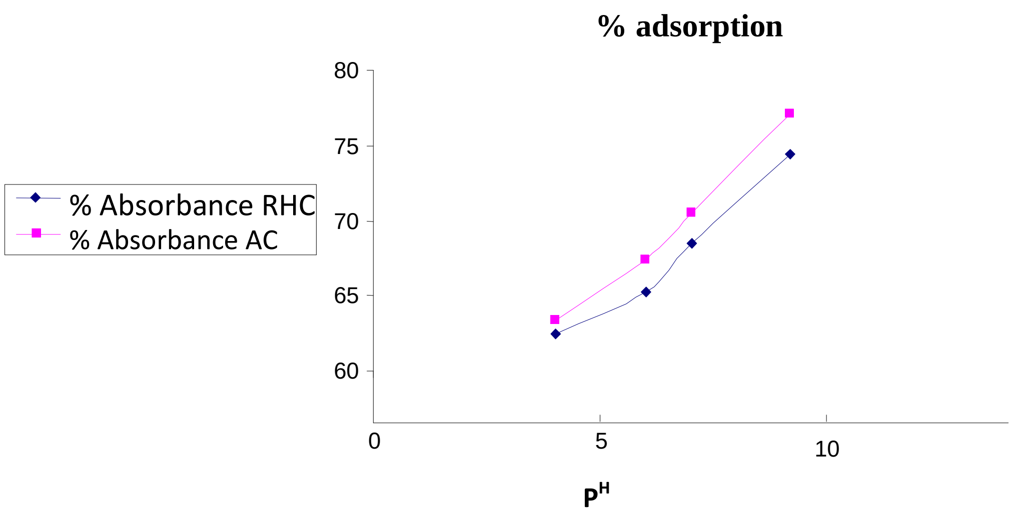

Fig 1: Effect of P^H on adsorption of dye

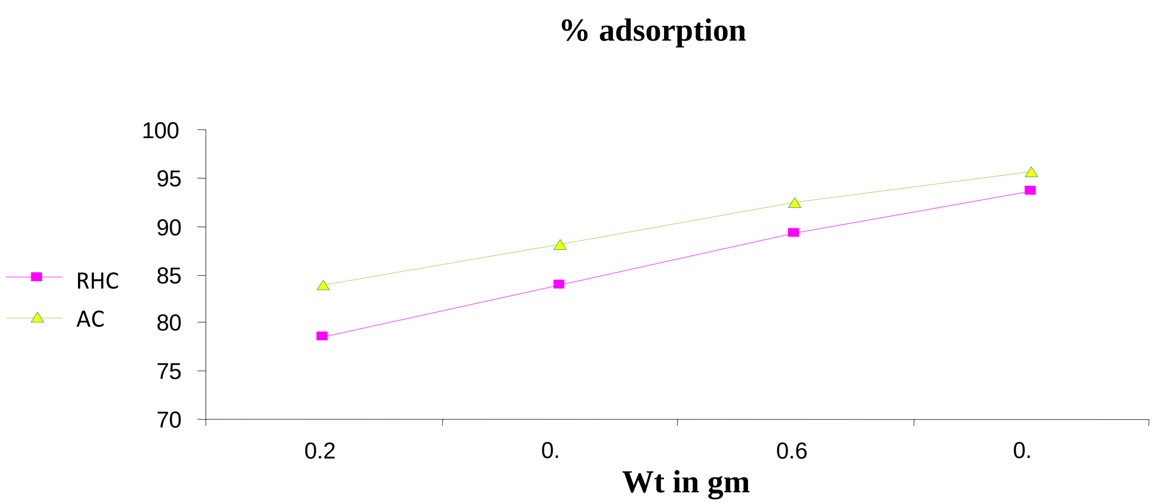

Fig 2: Effect of adsorbent dosages on adsorption

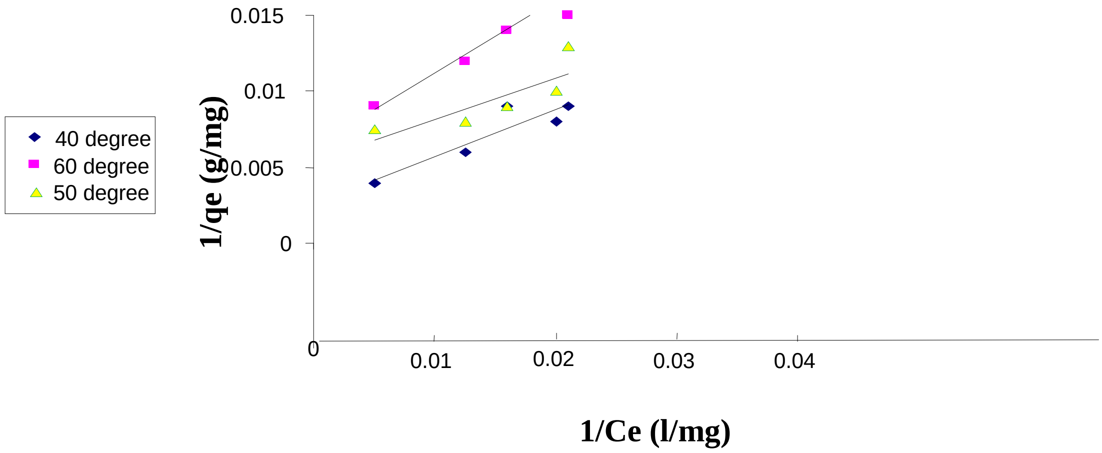

Fig 3: Langmuir adsorption isotherms for Methylene blue

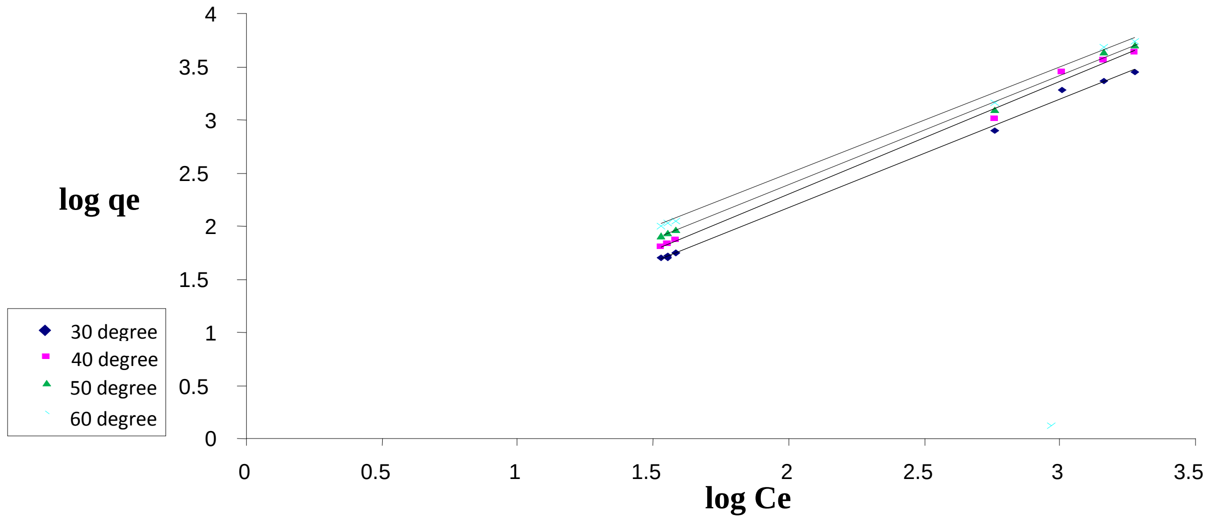

Fig 4: Freundlich adsorption isotherm for methylene blue

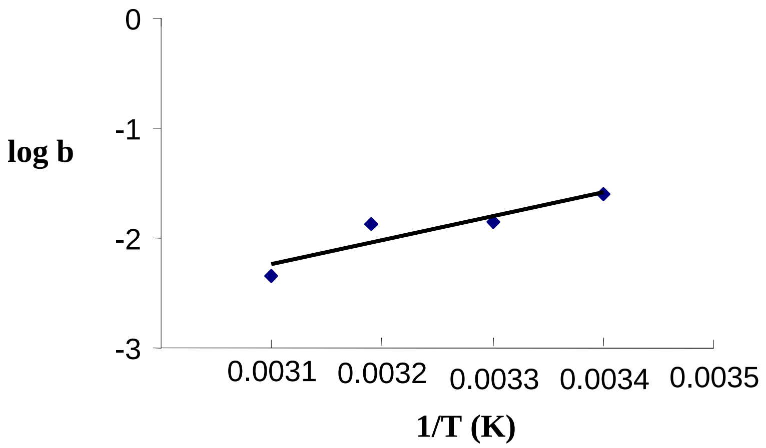

Fig 5: Thermodynamics studies

Tables

Table1. Langmuir Constants

Temp (^{0}C)	θ^0(mg/g)	b (l/mg)	R_L 10e3
40	294.11	0.01413	0.87622
50	266.67	0.01365	0.87192
60	250.00	0.00213	0.97917

Temp (^{0}C) = Temperature in degree centigrade

θ^0 and b = Langmuir constants related to the capacity mg\g and the energy of adsorption l \ mg

RL= The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter.

Table 2: Freundlich constant

Temp (^{0}C)	K_f (mg/g)	1/n
30	63.095	0.42
40	56.234	0.36
50	39.811	0.26
60	35.48	0.24

Temp (^{0}C) = Temperature in degree centigrade

K_f and 1/n = Freundlich constants related to the adsorption capacity and adsorption intensity respectively.

Table 3: Thermodynamic parameters at different temperature

Temp (^{0}K)	-Δ G (Kj/mol)	-Δ S J/mol
313	11.0795	3.2365
323	13.7825	5.2245
333	17.0268	5.7952

Temp (^{0}K) = Temperature in Kelvin

-Δ G = Free energy changes

-Δ S = Entropy changes

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