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Isotherms, Kinetics And Thermodynamics Of Adsorption Study In Dye Removal Of Albizzia Lebbeck Seed Activated Carbon

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Abstract: An experimental investigation on the removal of cresol red and basic fuchsine dyes from waste water by using Albizzia lebbeck seed activated carbon (ALS AC) as low cost (cheap) adsorbent was carried out in a laboratory. Batch type experiments were conducted to study the influence of different parameter such as pH, adsorbent dosage, initial dye concentration, contact time and temperature of adsorbent. The removal data have been analyzed using Langmuir and Freundlich isotherm models. The kinetic data were used from the pseudo first order, pseudo second order and intra particle diffusion model and thermodynamic studies. The adsorption processes was in conformity demonstrated use of ALS to obtain low cost adsorbent for dye removal from aqueous solutions. The present investigation confirmed that ALS AC can be successfully employed as a good adsorbent for the removal of dye from effluent.

Keywords: Albizzia lebbeck seed activated carbon, Cresol red, Basic fuchsine

I. INTRODUCTION

Adsorption is surface phenomenon in which collection or accumulation of surface on the surface of the surface of the solid or liquid takes place. It is a physio chemical process in which dissolved molecules are attached to the surface of an adsorbent by physical and chemical forces. The substance which adsorbs another substance on its surface is called adsorbent. While the substance which itself get adsorbed on the surface of another substance is called adsorbate. One of the most important environmental problems that the industrial waste is facing today is to eliminate color from the dyes effluent into waste water. More than 10000 different dyes are used in the textile, leather, pharmaceuticals, food, paper, paint and electoplating[1]. Adsorption technique used activated carbon has been found as most effluent method used for removal dyes. However, it is used is still limited because higher the quality of activated carbon, the greater it operation costs. The need for regeneration and difficulty of major concerns associated with activated carbon [2]. Today researchers have come out with study that has been focused on the low-cost adsorbents that are mainly obtained from biomass waste and industrial by product since they required little processing and abundant in nature. From literature survey, it is revealed that a number of biological adsorbents have been investigated for removing dyes including maize cob, wood and rice hull[3] etc., it has been known that activated carbon is a versatile adsorbent because of its sufficient surface area, pore volume, high degree of surface capacities in aqueous solutions mesopores and microspores in the activated carbon help dye adsorption to increase. These are some commercially available active carbons which are expansive [4, 5].

In recent studies, plant wastes are inexpensive and they have no or very low economic value. In the present study activated carbon was prepared from cheap adsorbent as a new adsorbent for the removal of cresol red and basic fuchsine dyes from aqueous solutions. The effect of different parameters such as pH, adsorbent dosage, initial dye concentration, contact time and temperature were investigated. The kinetic data on batch adsorption studies were carried out to understand the adsorption processes.

II. MATERIAL AND METHODS

PREPARATION OF ADSORBENT

The Albizzia lebbeck seed were used as adsorbent were collected from Ennore (Tamil Nadu). The unwanted materials like impurities, soils, dust etc., were removed by extensively washed in running tap water for removing. It was followed by washing with distilled water. The washed material was dried under sun light for ten days, it was ground in mixer. This ground powder was oven dried a 50°C for 24hrs. Albizzia lebbeck seed powder weighed accurately in beaker than soak with 1:1 H_2SO_4 poured in beaker soak for 2 days then washed with distilled water pH level attain neutral. Then transferred to beaker dried in muffle furnace at 450°C for 3hrs dried well we get coal (black color powdered) obtained. It's called an activated carbon. Then used for further analysis.

PREPARATION OF ADSORBATE SOLUTION

The dyes Cresol red (Chemical formula = $C_{20}H_{19}N_3$.HCl, Formula weight = 337.86 g.mol^{-1}) and Basic fuchsine (Chemical formula = $C_{21}H_{18}O_5S$, formula weight = 382.43g.mol^{-1}) purchased from Kevin laboratories. The solution of cresol red and basic fuchsine dye were prepared by dissolving appropriate amounts (accurate weighed) of dry powdered dye in double distilled water to prepare stock solution (1000mgL^{-1}). The maximum absorbance wave length λ max for cresol red and basic fuchsine dyes were 570nm and 544nm respectively; it was measured using optima UV-visible spectrophotometer. The experimental solution was obtained by dilution were made to obtain the working solution at desired concentrations.

OTHER CHEMICALS

All other chemicals used in the study viz. 0.1N NaOH, 0.1N HCl, Buffer mixture, were supplied by Kevin laboratories India.

BATCH ADSORPTION EXPERIMENT

Batch experiments were implemented by shaking 30mL of dye solution (12 & 10) mg.L^{-1} concentration with (0.08 & 0.05) gm of Albizzia lebbeck seed activated carbon powder in 250ml conical flasks at room temperature for a predetermined contact time of 30 min for cresol dye and 60 min for basic fuchsine dye after that centrifuged at 1600 rpm for 10 minute.

The concentration of each dye in the aqueous phase was determined spectrophotometrically by UV spectrophotometer at λ max for each dye. The adsorption capacity (q) of each dye by Albizzia lebbeck seed activated carbon adsorbent (mg/g) was calculated using the following equation.

$$\text{Amount adsorbed } (q_e) = \frac{(C_0 - C_e)}{m} \times V \quad \text{...... [1]}$$

Where *Co* is the initial concentration of dye (mg/L), C_e is the concentration of dye at equilibrium (mg/L), *v* is the volume of dye solution (L) and *w* is weight of the adsorbent (g). The percentage removal of dye was determined using equation

$$\%\text{ removal} = \frac{(C_0 - C_i)}{C_0} \times 100 \quad \text{......... [2]}$$

III. RESULTS AND DISCUSSION

INFLUENCE OF THE ADSORPTION STUDY

EFFECT OF pH

The percentage of dye adsorption at different pH is shown in Fig. 1 the initial pH of dye solution plays an important role particularly on the adsorption capacity by influencing the chemistry of dye molecule and adsorbate ALS AC aqueous solution. The adsorption of cresol red and basic fuchsine dyes at pH solution range between (3 -9) was studied. The solution was adjusted by using few drops from 0.1N of (NaOH or HCl) solution to obtain the required pH. The result was shown in Fig.1 there was slight decrease in the adsorption of cresol red dye with the increase in pH solution, while slightly increase in the adsorption of basic fuchsine dye with the increase in pH solution. This behavior may be due to dyes become in an anionic form when dissolve in aqueous solution. Therefore, adsorption capacity of dyes was affected by the surface of adsorbent, which is influenced by pH solution.

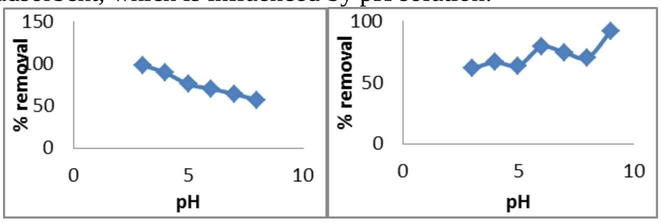

Figure 1: Effect of pH ALS AC cresol red & Basic Fuchsine dye

EFFECT OF DOSAGE

The effect of adsorbent dosage on the removal of cresol red and basic fuchsine was studied Fig 2 represents the plots of amount of adsorbent against percentage adsorption. It can be seen that as the dose of the adsorbent increases, extent of adsorption increases since there will be more active sites at higher sorbent dose before equilibrium is attained.

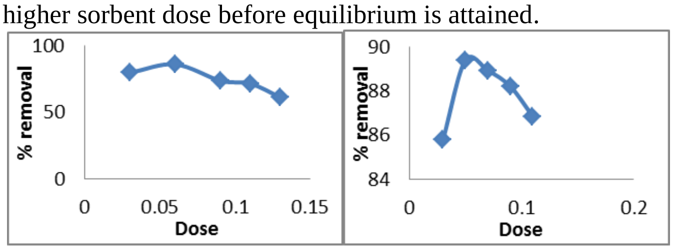

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Figure 2: Effect of Dosage ALS AC cresol red & Basic Fuchsine dye

EFFECT OF INITIAL DYE CONCENTRATION

The effect of initial dye concentration on the removal efficiency of cresol red and basic fuchsine dye was studied. Fig 3 represents the removal percentage of dyes decreased with increasing initial dye concentration, while adsorption capacity increased with increase of the dye concentration. The influence of the initial dye concentration depends on the relationship between the effective sites available on a surface of adsorbent and the dye concentration.

At low concentration there will be unoccupied effective sites on the adsorbent surface and when the initial dye concentration increases, the effective sites required for adsorption of the dye molecules will be lacking.

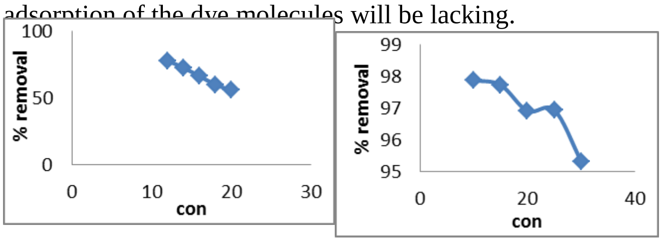

Figure 3: Effect of Initial dye concentration ALS AC cresol red & Basic Fuchsine dye

EFFECT OF CONTACT TIME

The effect of contact time on the amount of cresol red and basic fuchsine dye adsorbed was studied fig 4 represents that the percentage removal of dye increases rapidly with an increase in contact time initially. The rapid the removal of dye is observed at the beginning of the contact time due to the percentage of large number of binding sites available for adsorption.

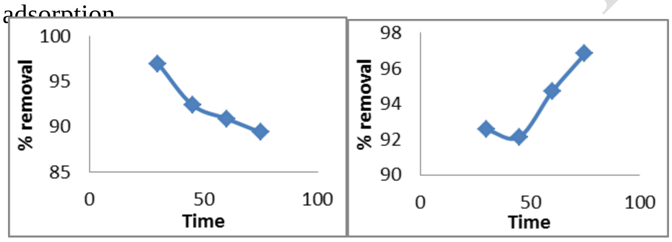

Figure 4: Effect of Contact time ALS AC cresol red & Basic Fuchsine dye

EFFECT OF TEMPERATURE

The effects of temperature on the adsorption of cresol red and basic fuchsine dye was studied fig 5 represents that the temperature is increased the removal of cresol red and basic fuchsine dye adsorption increases. An increase in temperature is expected to increase adsorption by decreasing the viscosity of the solution and increasing the mobility of the adsorbate. The results indicate that the adsorptions of cresol red are higher at low temperature suggesting exothermic processes. However, adsorption of basic fuchsine is maximal at higher temperature indicating that the endothermic process. The differences in the optimum conditions for the removal of the dyes from aqueous solution using ALS AC could be due to the nature, structure, basicity and purity of the adsorbate.

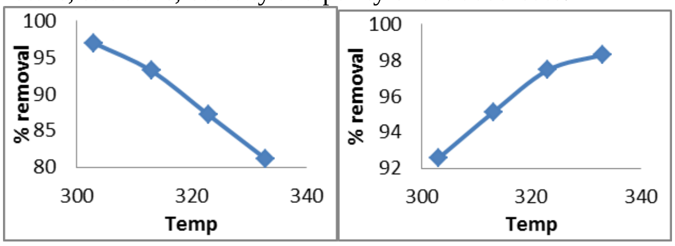

Figure 5: Effect of Temperature ALS AC cresol red & Basic Fuchsine dye

ADSORPTION ISOTHERM STUDIES

Adsorption isotherms are necessary for the characterization of how dyes concentration will interact with the surface of adsorbent and helpful to improve the adsorbent surface for the removable dyes. Adsorption isotherms are one of the basic requirements to understand adsorption systems [11]. The adsorption capacity of dye on ALS AC surface is plotted as a function of equilibrium concentrations at room temperature. It is clear that dyes can be readily removed from the polluted water by Albizzia lebbeck seed activated carbon. To characterize the adsorption of dyes on adsorbent, the equilibrium data for this study were analyzed using, Freundlich and Langmuir models.

FREUNDLICH ADSORPTION ISOTHERM

The Freundlich isotherm is an empirical model applies to heterogeneous surfaces and involves a multilayer adsorption, with clear interaction forces between the adsorbed molecules. This model suppose that when the adsorbate concentration increases, the adsorption process also increases, and accordingly, the sorption energy dramatically decreases due to completion of the sorption sites of the adsorbent. The general linear form of the Freundlich model is

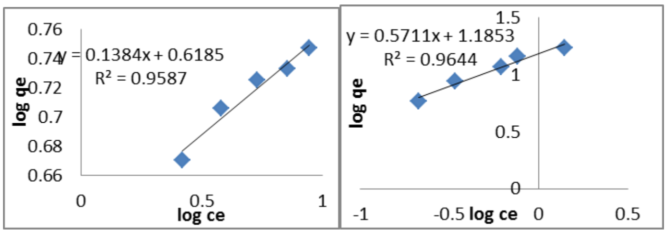

Figure 6: Freundlich adsorption isotherm for ALS AC onto Cresol red & basic fuchsine dye

$$\log q_e = \log K_f + 1/n \log Ce \quad \ldots\ldots [3]$$

Where q_e is the amount of adsorbate at equilibrium ($mg.g^{-1}$), C_e is the equilibrium concentration of adsorbate ($mg.L^{-1}$), K_F is the Freundlich constant (indicates the relative adsorption capacity) and n is constant (refers to the adsorption intensity). The values of K_F and $1/n$ can be obtained from the intercept and slope of the graph of log q_e versus log C_e. Linear relationship of Freundlich isotherm shows in fig 6 if value of $1/n<1$ it denote a natural adsorption. If $n=1$ indicates that the distribution between the two phases are not dependent on the concentration. While if $1/n>1$ denote cooperative adsorption [14]. Freundlich isotherm constant were calculated in table 1, from this data it is deduced that the Freundlich isotherm was a more fit to the adsorption of cresol red dye than the basic fuchsine dye.

LANGMUIR ADSORPTION ISOTHERM

Langmuir isotherms suppose that there are a limited number of effective sites which distributed homogeneously on the adsorbent surface. These effective sites have the same familiarity for adsorption of a unimolecular layer, and the interaction forces between molecules of adsorbed was very slight. The general linear form of the Langmuir model

$1/q_e=1/q_mK_LC_e + 1/q_m$ ……. [4]

Where K_L (L mg^{-1}) and q_m (mg g^{-1}) is Langmuir constants related to energy of adsorption and maximum adsorption capacity respectively. A graph of $1/q_e$ against $1/C_e$ results in a straight line with a slope of $(1/q_mK_L)$ and an intercept $(1/q_m)$ fig 7. The basic features of the Langmuir isotherm can be described by a constant named the separation factor R_L which is defined as

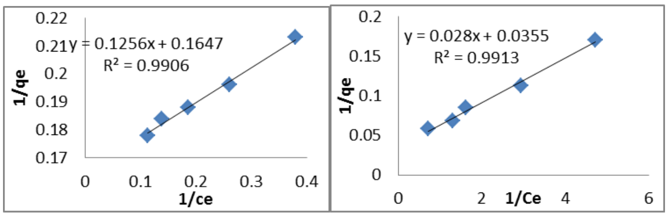

Figure 7: Langmuir adsorption isotherm for ALS AC onto Cresol red & basic fuchsine dye

$$R_L = \frac{1}{(1+K_LC_0)}$$ …….. [5]

Where C_o is the initial concentration of dye (mg L^{-1}) and K_L is the Langmuir constant (mgL^{-1}), and R_L values refer to the nature of adsorption. Values of (R_L>1) denote the adsorption is unfavorable, if (R_L=1) indicates linear, (0<R_L<1) indicates favorable adsorption while (RL=0) mean irreversible. From the data computed in table 1 the RL values for cresol red and basic fuchsine dye are (0.0985 and 0.1112) respectively i.e., (0<R_L<1)denote the adsorption was favorable for Langmuir isotherm.

ADSORPTION OF KINETICS STUDIES

To analyze the adsorption kinetics of cresol red and basic fuchsine dye onto ALS AC, there kinetic models are applied, including pseudo-first order, pseudo-second order and intra particle diffusion model.

The Pseudo First Order equation is expressed as follows,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$ ……. [6]

Where k_1 is the Lagergren's rate constant of adsorption (min^{-1}). The values of q_e and k_1 table 2 were determined from the plot of log (q_e-q_t) against t fig 8. The lower determination coefficients (R^2=0.992 and R^2=0.647) suggest that adsorption of cresol red and basic fuchsine onto ALSAC does not follow the pseudo first order model.

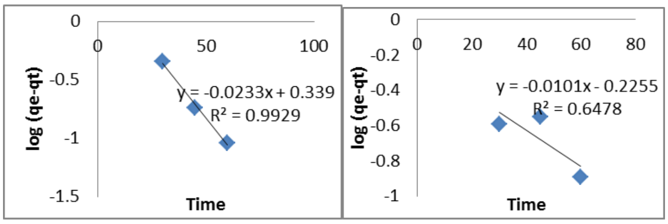

Figure 8: Pseudo first order kinetic for ALS AC onto Cresol red & basic fuchsine dye

The linearised integral form of the Pseudo Second Order model is,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} \frac{1}{q_e} t$$ ……… [7]

Where k_2 (g mg^{-1}min) is the rate constant of pseudo second order adsorption from the slopes and intercepts of straight portion of the linear plots obtained by plotting t/qt against t fig 9. The values of k_2 and q_e were calculated and listed in table 2. The higher determination coefficients (R^2=0.999 and R^2=0.998) table 2 suggest that the pseudo second order model is more likely to predict the behavior over the whole experimental range of adsorption. It also means the overall rate of cresol red and basic fuchsine adsorption process seems to be controlled by the chemical process through adsorbent and adsorbate.

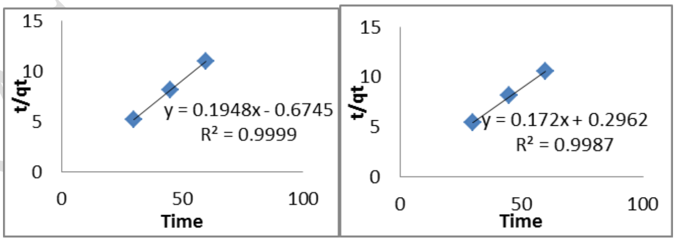

Figure 9: Pseudo second order kinetic for ALS AC onto Cresol red & basic fuchsine dye

The Intra-Particle Diffusion model is used to predict the rate controlling step

$$q_t = k_i t^{1/2} + C_i$$ …… [8]

Where q_t is the amount of cresol red and basic fuchsine adsorbed at time t, K_i (mg g^{-1}min) is intra particle diffusion constant at stage i, C_i is the intercept at stage i, and the value of C_i is related to the thickness of the boundary layer. If C_i is not equal to zero, it reveals that the adsorption involves a process and the intra-particle diffusion is not the only controlling step for the adsorption [19]. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. Fig 10 shows multi-linearity characterization by plotting qt vs. t

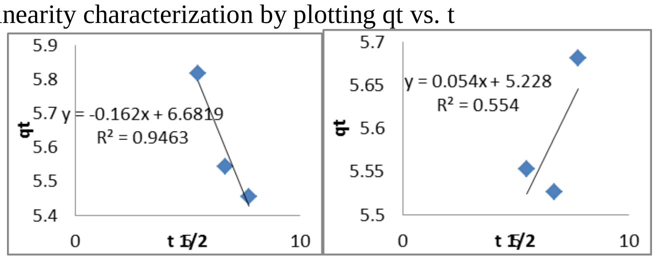

Figure 10: Intra particle diffusion model ALS AC onto Cresol red & basic fuchsine dye

Models	Parameters	ALSAC Cresol red dye	ALSAC Basic fuchsine
Pseudo-first-order	q_e (mg g^{-1})	-0.469	-0.647
	k_1 (1/min)	0.0529	0.023
	R^2	0.992	0.647
Pseudo-second-order	q_e (mg g^{-1})	5.154	5.183
	h (g $mg^{-1}min^{-1}$)	1.49	3.378
	R^2	0.991	0.998
Intra-particle diffusion	K	-0.162	0.054
	R^2	0.946	0.554
	C	6.681	5.228

Table 2: Adsorption of kinetic Parameters for the adsorption of Cresol red and basic fuchsine dyes onto Albizzia lebbeck seed activated carbon

THERMODYNAMIC STUDIES

The Thermodynamic parameters such as the adsorption standard free energy changes (ΔG°), the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) are obtained from experiments at various temperatures using the following equations

$\Delta G° = -RT \ln K$ ……… [9]

$\text{Log } K= \Delta S°/ (2.303RT) - \Delta H°/ (2.303RT)$ ……… [10]

Where *R* (8.3145 J $mol^{-1}K^{-1}$) is the gas constant, *K* (Lg^{-1}) is the Langmuir constant and T (K) is the absolute temperature (9), The values of ΔH° and ΔS° can be calculated from the slopes and the intercepts of the linear straight by plotting ln K against 1/T. according to the equation (10), the values of ΔG° can be calculated table 3 shows the values of ΔH°, ΔS° and ΔG° at different initial dye concentration and temperatures. The positive standard enthalpy change ΔH° suggests that the interaction of cresol red and basic fuchsine dye adsorbed by ALSAC is endothermic, and the positive standard entropy change ΔSo reveals the increased randomness at the adsorbate solution interface during the adsorption progress. The negative value of ΔG° at temperatures indicates the fact that the adsorption of cresol red and basic fuchsine dye is a spontaneous reaction. The increase in standard free energy changing with the rise in temperature shows an increase in feasibility of adsorption at higher temperature, which verifies the correctness of the experimental results in theory.

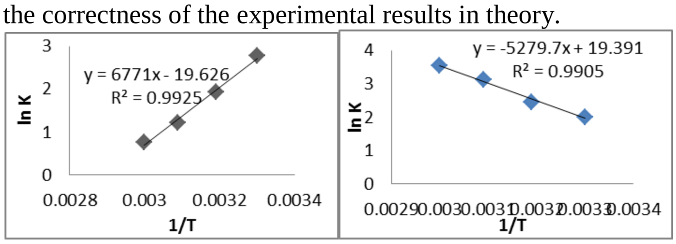

Figure 11: Thermodynamics parameter plot 1/T vs. ln K ALS AC onto Cresol red & basic fuchsine dye

Dyes	Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J $k^{-1}mol^{-1}$)	R^2
ALS AC Cresol red dye			-129.645	-375.666	0.992
	303	-6.988			
	313	-4.998			
	323	-3.27			
	333	-2.104			
ALS AC Basic fuchsine			101.077	371.263	0.99
	303	-5.06			
	313	-6.391			
	323	-8.41			
	333	-9.817			

Table 3: Thermodynamic Parameters for the adsorption of Cresol red and basic fuchsine dyes onto Albizzia lebbeck seed activated carbon

IV. CONCLUSION

Based on the results shows, Albizzia lebbeck seed activated carbon can be used as a very efficient and cheap adsorbent for the removal from waste water. The adsorption of cresol red and basic fuchsine dye was examined at different experimental conditions.

The results corrugate that adsorption increase in increase contact time, temperature, adsorbent dosage and pH. The maximum removal of cresol red and basic fuchsine dyes at (303 & 333)K was found to be 96.97% and 98.3%, (30 & 75) min-1 was found to be 96.97% and 96.81%, (12 & 10) mg/L was found to be 78.03% and 97.88%, (0.06 & 0.05)gm was found to be 86.13% and 89.40% and pH (3 & 9) was found to be 98.41% and 91.74% ALS AC at maximum percentage removal in this study. Kinetic study shows the adsorption reaction follows pseudo second order kinetic model (R^2=0.999 & R^2=0.998). Adsorption isotherm data showed that adsorption can be more fit to Langmuir adsorption isotherm model. The present research work establishes that ALSAC was excellent low-cost adsorbent for the removal of both dyes. The negative values of ΔG° and the negative value of ΔH° obtained indicated the spontaneous and exothermic nature of the adsorption processes while the negative ΔS° value obtained decreased randomness during the adsorption process. The kinetic and thermodynamic data can be further explore for the design of an adsorbed for industrial waste water treatment.

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