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Research Paper

Adsorption of Eosin Dyes Onto Activated Carbon Prepared from Wood of *Adina cardifolia* Hook – A Kinetic and Isotherm Study

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Abstract: *The performance of activated carbon prepared from Adina cardifolia Hook has been investigated for the adsorption of using dye from aqueous solution. Eosin dye is anionic in nature and highly toxic. The effects of initial dye concentration and contact time on adsorption of eosin have been studied in batch mode. The adsorption rate data correlated with pseudo first order and pseudo second-order kinetic models using Legergren and Ho equations respectively. Present adsorption system well fitted to pseudo second order kinetic model. The intra particle diffusion was the rate determining step. Equilibrium data were fitted into Langmuir, Freundlich isotherms. The order of best describing isotherm was given based on* R^2 *value.*

Keywords: Adsorption, *Adina cardifolia* hook, Eosin Y, Kinetics, Isotherms

Introduction

Dye pollutants, emanated from the dye manufacturing, textile and leather industries, cause serious environmental problems. Colouring materials in wastewater are not only aesthetically displeasing, but also harmful for aquatic flora and fauna. Most of these dyes are poorly biodegradable. The textile industry continues to search for an economical solution to decolorize the nearly 200 billion liters of colored effluent produced annually [1].Many treatment methods have been used to remove the dyes from wastewater. Among the various methods, adsorption is a separate process which is now recognized as an effective and economical method for the removal of both organic and inorganic pollutants from wastewater [2]. The most widely used adsorbents are activated carbon because of their high surface area due to the presence of micro and meso pores. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust, buffing dust of leather industry, coir pith, crude oil, residue tropical grass, olive stone and almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater [3]. The present study is undertaken to evaluate the efficiency of activated carbon adsorbent prepared from *Adina cardifolia* Hook saw dust using sulphuric acid for the removal of Eosin dye from aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, the applicability of kinetic and mass-transfer models for the adsorption of Eosin dye onto acid activated carbon is reported.

Material and Methods

Preparation of adsorbent

Adina cardifolia Hook saw dust was soaked in concentrated H_2SO_4at 1:1 ratio (weight of raw material/volume of acid) for 24 h and activated at 160°C for 5 h. The activated carbon was repeatedly washed with distilled water until the pH of the wash water became the pH of the distilled water (nearly 7). The carbon obtained was dried at 110 ± 1°C for nearly 2h to remove the moisture. Thus prepared carbon was designated as *Adina cardifolia* Hook carbon (ACHC) Particle size in between and were taken for further study.

Preparation of Stock Solution

The stock solution of dye was prepared by dissolving appropriate amount of exactly weighed dye in double distilled water to a concentration of 1000 mg/L. The experimental solutions were prepared from the stock solution by proper dilutions.

Adsorption Experiments

The effect of parameters such as initial concentration of the dye solution and contact time was studied by batch mode technique because of its simplicity. The predetermined dose of the adsorbent was taken in 250 mL iodine flask and 50 mL of a predetermined concentration of the dye solution was poured into the flask. Then the content flask was agitated using a rotary shaker with 180 rpm for a predetermined duration. Then the aliquot was centrifuged. Concentration of the centrifuge was measured after proper dilution using Systronics Double Beam UV-visible Spectrophotometer: 2202 at the wavelength of 517 NM. The kinetics experiments were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140 and160 minutes.

Results and Discussion

Effect of Dose

The adsorption of Eosin dye onto ACHC was studied by varying the dose of the adsorbent from 10 mg/ 50 mL to70 mg/ 50 mL by taking 50 mg/ L of the adsorbate concentration which were shown in the Fig. 1.Thepercentage of removal of Eosin dye from aqueous solution increased with the increase of carbon dose. This is due to the increased carbon surface area and availability of more adsorption sites[3]. 50 mg of adsorbent per 50 mL of adsorbate solution was chosen for further studies.

Effect of Contact Time for Different Initial Concentrations

The percentage of removal of Eosin dye from aqueous solution with respect to different contact times and with different initial concentrations at different temperatures were studied and the representative graph at 302 K is shown in Figure 2.The adsorption process is characterized by a rapid uptake of the adsorbate in the initial stages as shown by the curves which is due to driving force aroused by the concentration gradient of dye between the liquid phase and solid phase. The percentage of removal decreased with the increase of initial concentration of the dye. This is because of the decrease of fraction of dye transferred from the liquid phase to solid phase.

Adsorption Dynamics

Pseudo First Order Kinetics

The pseudo first order rate constant of adsorption is determined from the following pseudo first order rate expression given by Legergren [4].

$$\text{Log}\,(q_e - q_t) = \log q_e - k_1/2.303 \times t$$

Where, q_e and q_t are the amounts of dye adsorbed (mg/g)at equilibrium and at time t (min), respectively. k_1 is the pseudo first order rate constant of adsorption. The values of $k_1$and theoretical $q_{e(th)}$were calculated from the slope and intercepts of the linear plots respectively (Fig. 3)and are presented in Table 1.

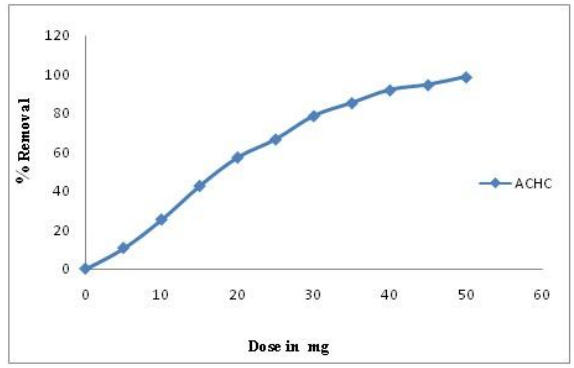

Figure 1: Effece of Dose for Eosin dye onto ACHC

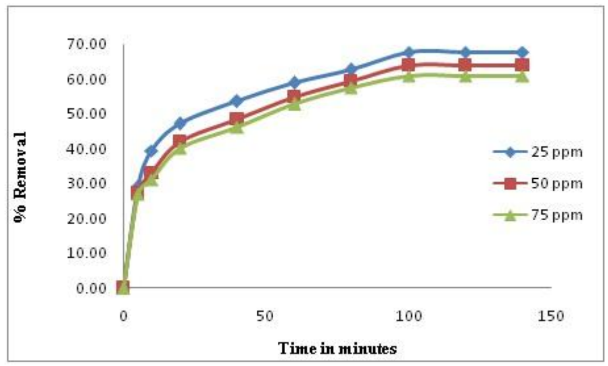

Figure 2: Effecf of contact time

Pseudo Second Order Kinetics

The rate constant of adsorption is determined from the following pseudo second order rate equation given by Ho [5] is

$$t/q_t = 1/\,k_2.qe^2 + 1/q_e\, t$$

The equilibrium adsorption capacity (q_e) and the pseudo second order constants k_2 (g/ (mg.min)) can be determined experimentally from the slope and intercept of plot of t/q_t versus t. The values calculated from the linear plots (Figure 4) are presented in Table 2.

Intra Particle Diffusion Model

The intra particle diffusion equation is given by Weber–Morris [6] is

$$q_t = k_p t^{1/2} + C$$

Where k_p is the intra-particle diffusion rate constant. Plot of q_t versus $t^{1/2}$contains multi linearity describing different steps involved in the adsorption process. The initial portion is related to mass transfer and final linear part is due to intra particle diffusion. The slope of final step gives the k_p which is the rate constant for intra particle diffusion rate constant[5]. The values of the intra particle diffusion constant KP calculated (Fig. 5) are presented in Table 3. Increase of keeping values with the increase of initial concentration infers that pore diffusion limits, the limits the overall rate of the Eosin dye adsorption.

Table 1: Pseudo first order Kinetic parameters for the removal of Eosin dyes by ACHC

Temperature (K)	Concentration (mg/L)	k_1 (min^{-1})	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	R^2
305	25	0.0470	16.94	13.22	0.948
	50	0.0345	31.94	23.34	0.949
	75	0.0292	45.65	33.37	0.932
315	25	0.0483	18.00	9.86	0.971
	50	0.0361	35.00	19.72	0.988
	75	0.0315	50.00	28.05	0.989
325	25	0.0495	20.00	12.42	0.942
	50	0.0386	39.00	23.39	0.968
	75	0.0328	55.00	33.34	0.969

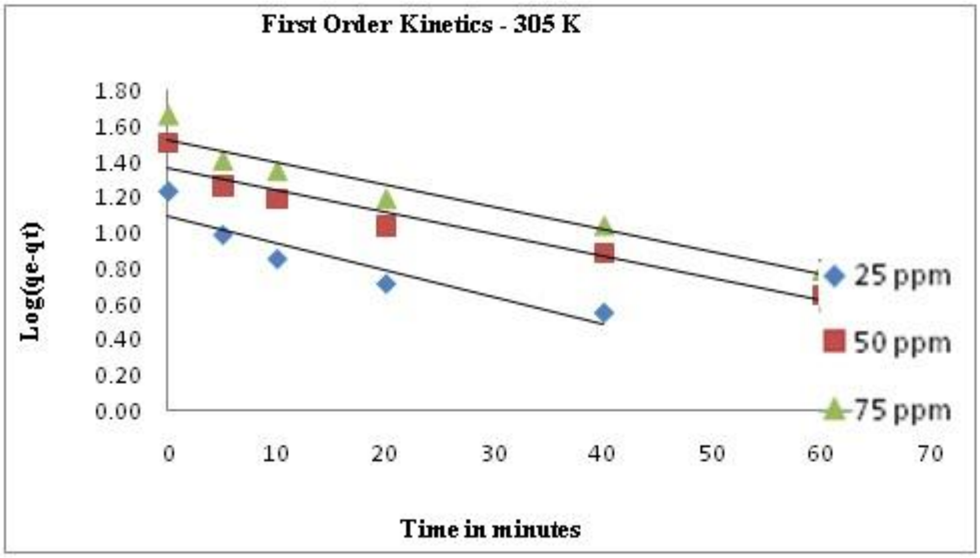

Figure 3: First Order Kinetics - 305 K

Table 2 : Pseudo second order Kinetic parameters for the removal of Eosin dyes by ACHC

Temperature (K)	Concentration (mg/L)	$k_2 \times 10^{-3}$ (g/mg.min)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	R^2
305	25	9.0	16.94	17.76	0.997
	50	8.2	31.94	33.56	0.995
	75	6.9	45.65	48.08	0.992
315	25	9.4	18.00	19.86	0.995
	50	8.6	35.00	34.72	0.993
	75	7.3	50.00	51.05	0.998
325	25	10.0	20.00	21.42	0.997
	50	9.2	39.00	38.39	0.995
	75	8.0	55.00	53.34	0.999

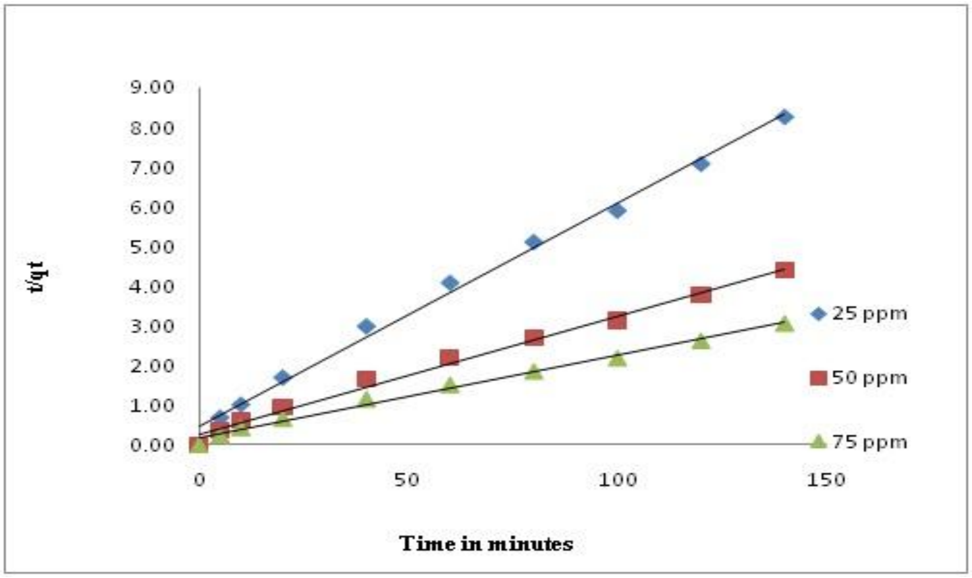

Figure 4: Second Order Kinetics - 305 K

Table 3: Intra particle diffusion parameters for the removal of Eosin dyes by ACHC

Temperature (K)	Concentration (mg/L)	k_p (mg/g.min)	R^2
305	25	1.51	0.9813
	50	2.61	0.9797
	75	3.50	0.955
315	25	2.40	0.971
	50	2.88	0.987
	75	3.73	0.987
325	25	3.50	0.978
	50	3.70	0.988
	75	3.95	0.989

Table 4: Percentage of sum of error squares for the removal of Eosin dyes by ACHC

Concentration (mg/L)	SSE %	
	First order	Second order
25	5.15	0.48
50		
75		

Sum of Error Squares

The percentage of sum of error squares is given as,

$$SSE (\%) = \sqrt{\Sigma[(q_e)exp-(q_e)cal]^2/ N}$$

Where N is the number of data points, $(q_e)_{exp}$ is the experimental q_e, $(q_e)_{cal}$ is the calculated q_e [7].The values were calculated and are presented in Table 4.

It shows that q_e (cal) of second order kinetics is close to q_e (exp). It can be seen that SSE (%) value is lower for the pseudo second order kinetic model than that of pseudo first order kinetic model. This confirms the applicability of the pseudo second order kinetic model. The determination coefficient (R^2) for pseudo first order model ranged between 0.860 and 0.989 whereas these values for the second order model were close to 1. Based on the values of regression co-efficient, the second order kinetic model was more suitable to describe the adsorption process of using dye adsorption than a pseudo first order model.

Isotherms

Langmuir Isotherm

Langmuir equation is written in the following form [7]

$$Q_e = Q_0 b\, Ce /1 + b\, C_e$$

This equation is often written in linear forms as

$$C_e/Q_e = 1/Q_0 b + C_e/Q_0$$

where Q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), Q_0 is adsorption efficiency and also called as the maximum monolayer adsorption capacity or saturation capacity (mg/g) and *b* is the adsorption energy, b is the reciprocal of the concentration at which half saturation of the adsorbent is reached.

The essential characteristics of Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation [8]

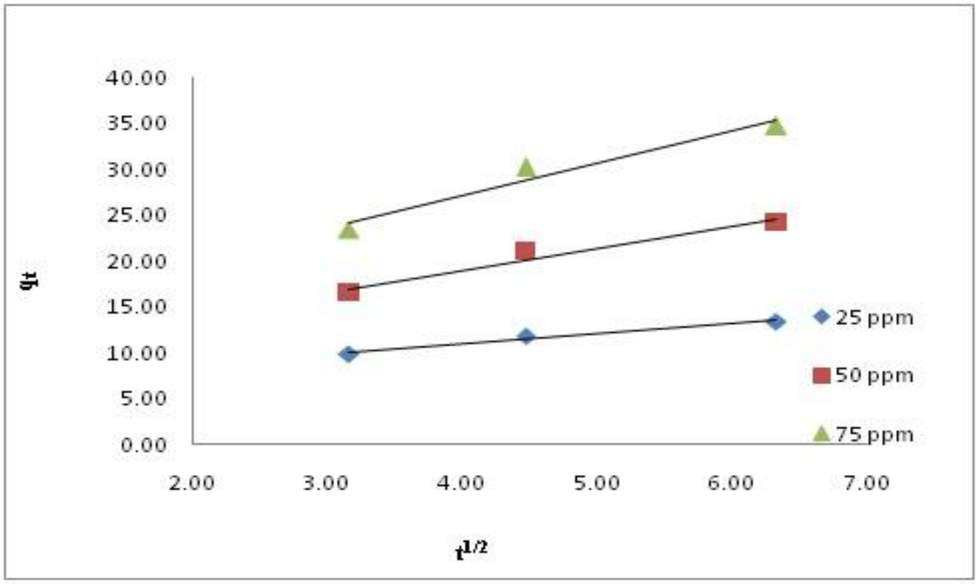

Figure 5: Intra Particle Diffusion - 305 K

Table 5: Langmuir isotherm results for the adsorption of Eosin dyes by ACHC

Temperature (K)	Q_0 (mg/g)	b (L/mg)	R_L			R^2
			25 mg/L	50 mg/L	75 mg/L	
305	330.33	0.018	0.689	0.675	0.659	0.994
315	333.33	0.019	0.525	0.510	0.492	0.992
325	339.42	0.021	0.425	0.409	0.392	0.990

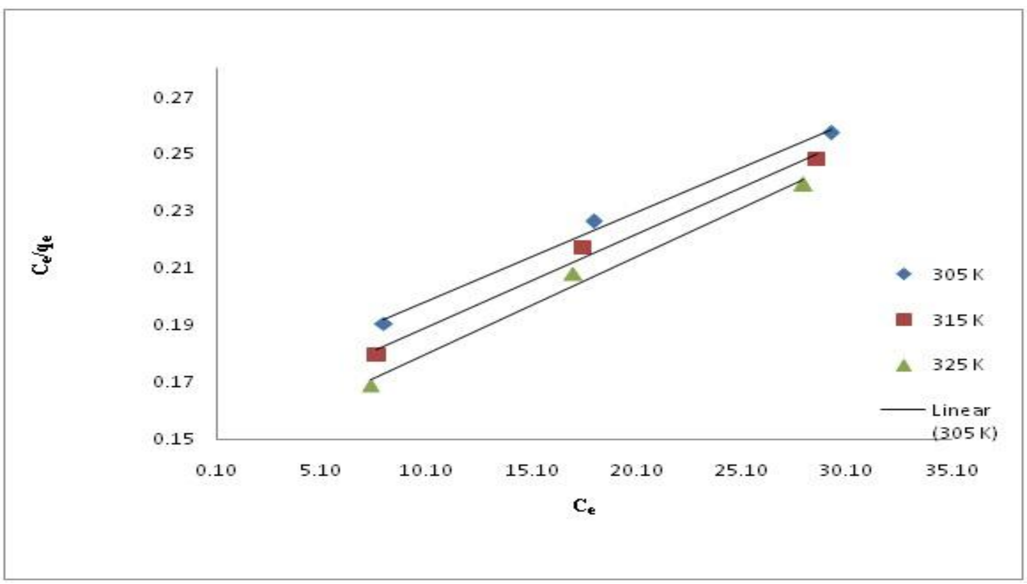

Figure 6: Langmuir Isotherm

Table 6: Freundlich isotherm results for the adsorption of Eosin dyes by ACHC

Temperature (K)	n	K_f (mg/g)	R^2
305	1.30	8.51	0.999
315	1.32	9.22	0.999
325	1.35	10.00	0.999

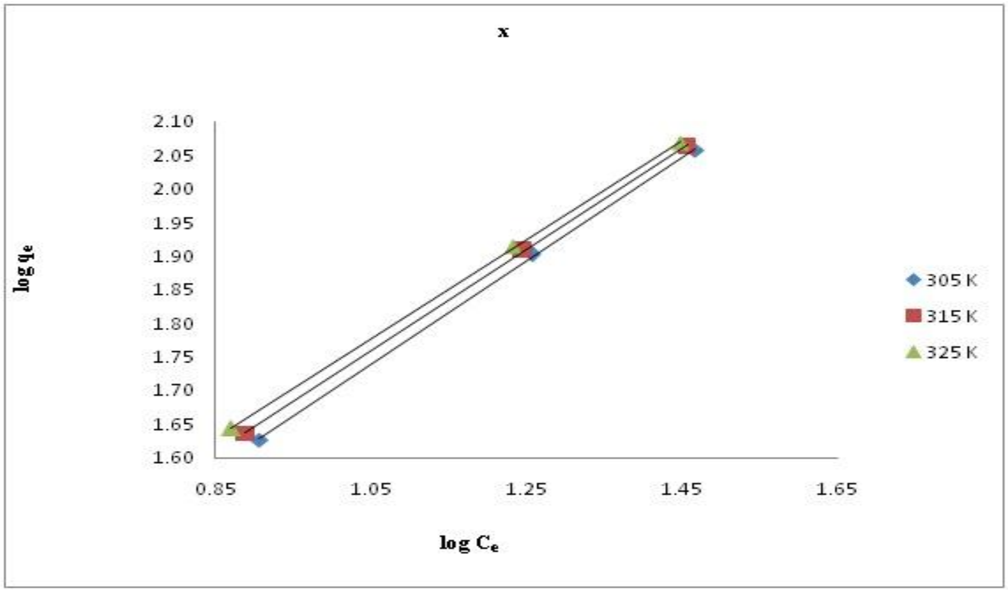

Figure 7: Freundlich Isotherm

$R_L = 1 / (1 + bC_0)$

Where, C_0 is the initial concentration of the dye solution. The separation factor, R_L, indicates the shape of the isotherm and the nature of the adsorption process which is given below,

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

The values of Q_0 and b are calculated from the intercept and slopes of linear plot of log C_e/q_e vs C_e (Fig. 6) and the results are presented in Table 5. The R_L value indicated the adsorption process is favorable, its value ranged between 0 and 1 for all the studied temperatures. The mono layer adsorption capacity Q_0 values (mg/g) are ranged from 330.33 to 339.42 for all the studied temperatures. The b values were ranged from 0.018 to 0.021 which indicate the adsorption physisorption in nature.

Freundlich Isotherm

This equation has the following form [9]

$$\log Q_e = \log K_f + 1/n \log C_e$$

Where Q_e is the amount of adsorbate adsorbed (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L) and K_f and n are the constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively.

The values of K_f and n are calculated from the intercept and slopes of linear plot of log we vs log Ce (Figure 7) and the results are presented in Table 6. The value of n is above one of all the three studied temperatures indicating that the adsorption of Eosin dyes on ACHC is favourable. It fits with the experimental data with a good correlation coefficient of 0.999.

Conclusion

The adsorption of Eosin dye onto *Adina cardifolia* Hook Carbon was studied. Adsorption experiments were carried out as a function of contact time and initial concentration in a batch mode process. Experimental data indicated that ACHC adsorbent was effective in removing Eosin dye from aqueous solution. The percentage of removal increased with an increase in contact time. Equilibrium was achieved in 100 minutes, when 50 mg ACHC was used as adsorbents for 50 mL of dye solutions for the initial concentration ranging from 25 to 75 mg/L. Adsorption capacities of ACHC were ranged from 330.33 to 339.42 mg/g for the chosen experimental condition. In the kinetic studies, R^2 value and SSE (%) revealed that the process of adsorption followed pseudo second order kinetics. Equilibrium data were fitted in the linear forms of Langmuir and Freundlich equations for the temperatures 305 K, 315 K and 325 K. The equilibrium parameter R_L values obtained in the Langmuir isotherm study were in between 0 and 1 showing the favourable adsorption process. The mono layer adsorption capacity Q_0 values (mg/g) are ranged from 330.33 to 339.42 for all the studied temperatures. The b value ranged from 0.018 to 0.021 hence is indicate the adsorption was physisorption in nature. The Freundlich isotherm constants: adsorption capacity, if values have ranged from 8.51 to 10.0 (mg/g). The values of n were found to be greater than one indicating a favourable adsorption.R^2 values indicated that Freundlich isotherm well describes the present adsorption system than Langmuir isotherm. The applicability of Freundlich isotherm suggests that the adsorption of dyes onto ACHC may be complex in nature.

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