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THERMODYNAMICS AND ADSORPTION STUDIES OF DYE (RHODAMINE-B) ONTO NATURAL DIATOMITE

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Abstract: Thermodynamics and adsorption studies were conducted with a dye of rhodamine-B on natural diatomite. Adsorption of the dye was investigated with an initial dye concentration at pH 8±0.2, 303, 313 and 323 K. The adsorption experiments were carried out isothermally at three different temperatures. The Langmuir and Freundlich isotherm models were used to describe the equilibrium data and the results were discussed in details. The kinetic data agreed with the pseudo-first order model with rate constants (k_2) in the range of $3.05–1.59.10^{-1}$ g/mg min. The thermodynamic parameters such as standard free energy, entropy change and enthalpy were calculated for natural diatomite. These values showed that adsorption of rhodamine-B on natural diatomite was a spontaneous and endothermic process.

Keywords: *diatomite, rhodamine B, adsorption, thermodynamics, Langmuir isotherm, Freundlich isotherm*

Introduction

Synthetic dyes are widely used in many industries such as textiles, paper, plastics. Wastewater from textile is polluted by dyes. These colored effluents are known to be carcinogenic and highly toxic (Uzun, 2006; Ertas et al., 2010). The unwanted dye pollutions have to be removed from wastewaters before being discharged into the environment. For this reason, the most common methods available for color removal from waste water are coagulation and flocculation (Moi Pang, et al., 2001) and biomaterials (Papic et al., 2004). The removal of dyes from the aqueous system was a technological challenge for many decades.

A considerable research was conducted on the removal of dyes from wastewater effluent using adsorption techniques with different adsorbents such as activated carbon (Chandra et al., 2007), bentonite (Tahir and Nassem, 2007; Koyuncu, 2009), sepiolite (Dogan et al., 2006), silica (Blitz, 2007; Jesionowski, 2005), fly ash (Eren and Acar, 2006), palm-fruit bunch particles (Mamdouh and Yehiam, 1997), diatomite (Khra-

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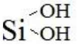
isheh, 2005; Koyuncu, 2012; Xux, 2012; Junxiong et al., 2012), TiO_2-supported diatomite (Eftekhari et al., 2010; Khraisheh et al., 2005) and other low-cost adsorbents.

Diatomite is an siliceous sedimentary rock, which has an amorphous form of silica ($SiO_2{\cdot}nH_2O$). Diatomite contains a small amount of microcrystalline material, and is available in various locations around the world. Diatomite also received attention for its unique combination of physical and chemical properties such as high permeability and porosity, small particle size, large surface area, low thermal conductivity, chemical stability, and its low-cost material for the color removal of textile wastewater (Chan et al., 2011). The silica surface contains silanol groups that spread over matrix of the silica. The silanol group is an active one, which tends to reach many polar organic compounds and various functional groups (Al-Ghouti et al., 2003; Khraisheh et al., 2005; Al-Ghouti et al., 2005). A preliminary study appointed the applicability of using diatomite as a low-cost material for removal of textile wastewater. The diatomite surface is terminated by OH groups and oxygen bridges (Si-OH,  $Si\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown OH}$), which act as adsorption sites. In the adsorption processes, it is important to know characteristic of these different adsorption sites (Khraisheh et al., 2005).

In this study, different temperatures of adsorption onto diatomite were attempted, and the effect on dye removal from the aqueous solution was investigated. The experiments were conducted at pH 8±0.2, and the initial dye concentration in the temperature range of 303–323 K was tested. The adsorption capacity and mechanisms as well as the thermodynamic parameters were investigated.

Material and methods

Materials

Diatomite samples were obtained from the Caldiran region of Van/Turkey. The chemical analysis of the diatomite obtained by a XRF technique revealed a chemical composition. The physical properties of the diatomite are given in Table 1. The natural diatomite sample, which was powdered by pounding in a porcelain mortar, was washed with distilled water and dried in an oven at 105 ºC. Rhodamine-B (Rh-B) as a dye was obtained from textile corporation (İstanbul/Turkey). The structural form of rhodamine-B is given in Fig. 1. A Rh-B has the maximum absorption wavelength at 553.7 nm. The maximum absorption wavelength of Rh-B was determined by finding out absorbance at the characteristic wavelength using a double beam UV-visible spectrophotometer.

Adsorption experiments

Adsorption was carried out on RhB by mixing 1.0 g of the natural diatomite samples with initial concentrations of 20 mg/dm^3, 40 mg/dm^3, and 60 mg/dm^3. The mixtures were shaken in a thermally controlled automatic shaker at 120 rpm, at temperatures of 303 K, 313 K, and 323 K for 15, 30, 60, 90, and 120 minutes until the equilibrium

Table 1. Chemical composition and physical properties of natural diatomite

Chemical composition	%
SiO_2	69.70
Al_2O_3	11.50
Fe_2O_3	4.40
TiO_2	0.65
Na_2O	0.80
K_2O	1.40
Loss on ignition	11.55
Physical properties	
Color: Cream	
pH 8±0,2	
Particle size 63 μm	

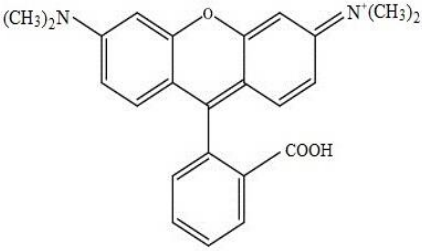


Fig. 1. Chemical structure of rhodamine B

conditions were reached. The concentration of the dye in the aqueous solutions after adsorption was measured by using a UV-vis (Shimadzu UV- Vis 1240) spectrophotometer. The measurements of the pH values of the dye solutions were determined by using a pH 211 microprocessor pH meter (HANNA Instruments). The percentage of adsorption was estimated using following equation (Xiangheng et al., 2012) :

$$\% \text{ Adsorption} = \frac{C_i - C_e}{C_e} \cdot 100 \tag{1}$$

where C_i and C_e are initial and equilibrium concentrations (mg/dm^3), respectively.

Thermodynamic parameters

The thermodynamic parameters such as standard Gibbs fee energy (ΔG^0), entropy change (ΔS^0) and enthalpy (ΔH^0) were calculated using following equations (Laidler and Meiser, 1999; Caliskan et al., 2011):

$$K_d = \frac{C_i - C_e}{C_e} \cdot \frac{V}{m} \tag{2}$$

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{3}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{4}$$

where K_d is the equilibrium constant, C_i initial concentration (mg/dm^3), C_e equilibrium concentration, V volume (cm^3), m of the diatomite (g), T (Kelvin), and R gas constant (8.314 J/mol). The changes in enthalpy (ΔH^0) and entropy (ΔS^0) were determined from the slope and intercept of the plots of lnK_d versus 1/T. The Gibbs free energy (ΔG^0) was calculated using Eq (4).

Kinetic studies

Kinetic studies were carried out using a thermostated shaker with polyethylene tubes at 303 K. A 0.1 g sample of natural diatomite was added to 10 cm^3 of RhB solution (20, 40 and 60 mg/dm^3) and at 303 K temperature between 1–150 minutes (time required to achieve an equilibrium conditions). The samples were analyzed by using the UV-vis (Shimadzu UV-Vis 1240) spectrophotometer. The adsorption experiments were conducted by using three different initial concentrations of RhB solution (20, 40 and 60 mg/dm^3). The amounts of RhB adsorbed at various time periods (q_t) were determined by:

$$q_t = \frac{(C_i - C_t)V}{m} \tag{5}$$

where C_i is the initial concentration of RhB, C_t concentration of RhB present in the aqueous solution after time t (min), V volume of solution (dm^3), and m is a mass of adsorbent (mg).

Results and discussion

Effect of initial dye concentration

The relative RhB removal by the adsorbents as a function of RhB concentration was studied (ranging from 20 to 60 mg/dm^3, at pH 8 ± 0.2, at 323 K). Figure 2 shows the effect of the initial dye concentration on adsorption. The equilibrium adsorption capacity increases with the increasing the initial RhB concentration. The RhB concentrations of 20 mg/dm^3, 40 mg/dm^3, and 60 mg/dm^3 increase the removal to 78.97%, 82.19%, and 85.51%, respectively. This increase in the proportion of adsorption may be probably due to the equilibrium shift during the adsorption process, and which may result from the increased number of ions competing for the available binding sites on the surface of diatomite (Franco, 2010; Xue et al., 2010; Calıskan et al., 2011). Adsorption of the dye was a little increase for concentrations higher than 60 mg/dm^3. It indicates that the saturation of adsorption sites was achieved. It can be seen that the rate of adsorption decreases with time and gradually reaches equilibrium. In Figure 2, where measurements were undertaken over a period of 15-120 min in all cases, the contact time of 120 min was sufficient to ensure, that the adsorption equilibrium was attained. The arithmetic mean of adsorption and standard deviation (σ) were found to be 20 mg/dm^3 73.71 and 7.57 for 20 mg/dm^3, 76.94, and 8.80 for 40 mg/dm^3, 79.26, and 8.88 for 60 mg/dm^3, respectively.

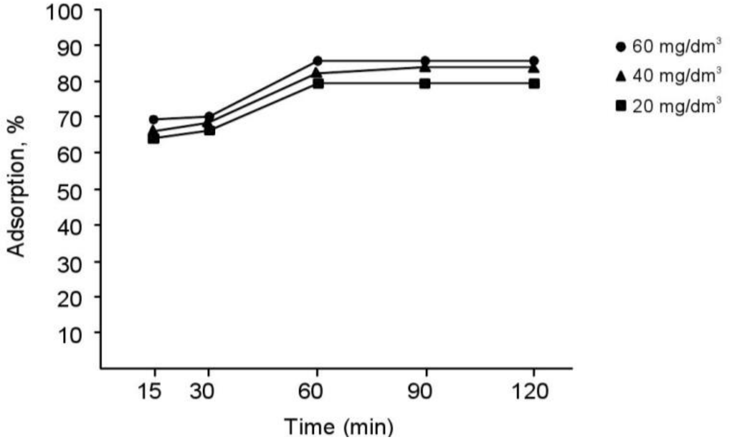


Fig. 2. Effect of contact time and initial dye concentration on dye adsorption. Natural diatomite dose 1g/ dm^3 (pH 8 ± 0.2 at 323 K)

Effect of temperature

The temperature has two major effects on the adsorption process. Higher temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to decrease in the viscosity of the solution. In addition, temperature changing will change the equilibrium capacity of the adsorbent for the particular adsorbate. In this case of study, a series of experiments was conducted at 303, 313, and 323 K to study the effect of temperature on the adsorption rate.

Adsorption of Rh-B onto diatomite at 303, 313, and 323 K is shown in Fig. 3. The results indicate that adsorption increases with the temperature. It indicates the endothermic nature of the adsorption process. Similar results were also reported for Rh-B adsorption onto acid-heat activated rectorite (Xiangheng et al., 2012), kaolinite (Khan and et al., 2012) and calcined diatomite (Yusan et al., 2012).

The standard deviations (σ) at 303, 313, and 323 K were found to be 0.55, 7.72 and 0.98, 14.23 and 1.25, and 15.12, respectively.

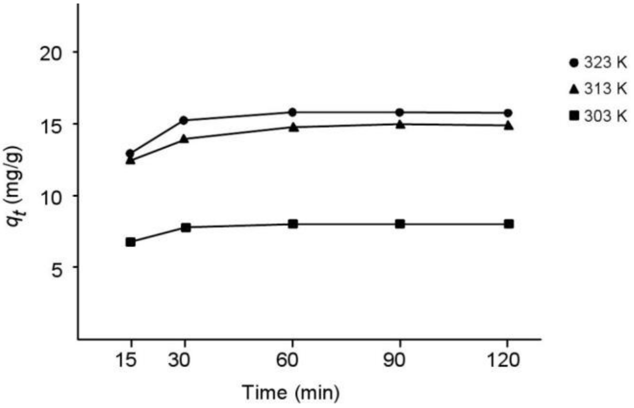


Fig. 3. Effect of temperature on adsorption of Rh-B onto natural diatomite

Adsorption isotherms

Langmuir isotherm

In the solid/liquid adsorption process, adsorption of the solute is usually characterized by either mass transfer (boundary layer diffusion) or intraparticle diffusion or even both (Ghosh and Bhattacharyya, 2002).

The adsorption data of Rh-B removal from natural diatomite was analyzed by the Freundlich and Langmuir isotherm models. The Langmuir isotherm model is valid for monolayer adsorption. The linear equation of the Langmuir isotherm is (Dogan et al., 2006):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} C_e \tag{6}$$

where, C_e is the equilibrium concentration of RhB in the solution, qe amount of Rh-B adsorbed at equilibrium, q_m Langmuir adsorption capacity, and b Langmuir constant.

Figure 4 shows the relationship between C_e/q_e and C_e for the adsorption of RhB onto the natural diatomite at 303, 313, and 323 K. The slope calculation and intercept of the linear plots give the values of q_m and b.

The values of the Langmuir constants and coefficient determination R^2 are given in Table 1. The Langmuir adsorption capacity (q_m) was found to be 8.13, 9.52, and 10.21 mg/g at different temperatures (303, 313 and 323 K). The essential characteristic of the Langmuir isotherm can be expressed by the equilibrium parameter and dimensionless constant (R_L) using equation:

$$R_L = \frac{1}{1 + bC_o} \tag{7}$$

where R_L can be $0 < R_L < 1$.

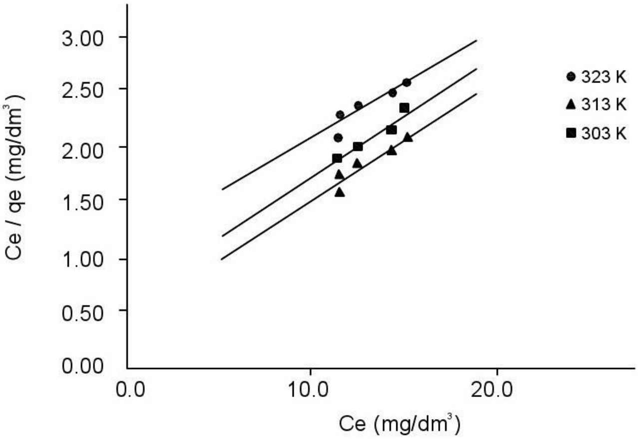


Fig. 4. Langmuir adsorption isotherm plots for adsorption of RhB onto natural diatomite at different temperatures

Table 1. Isotherm parameters for adsorption of RhB onto natural diatomite

Model	Isotherm Constants	303 K	313 K	323 K
Langmuir	q_m	8.13	9.52	10.21
	b	0.35	0.19	0.15
	R_L	0.14	0.21	0.25
	R^2	0.99	0.99	0.99
Freundlich	K_f	2.45	2.73	3.85
	n	1.61	1.48	1.44
	R^2	0.99	0.99	0.99

The dimensionless separation factor (R_L) was found to be in the range of 0 to 1, indicating that adsorption of Rhodamine-B is favorable for natural diatomite (Freundlich, 1906; Ho and Mckay, 1999; Rahchamani and Zavvar Mousavi, 2011).

The adsorption capacity (q_m) of natural diatomite was found to be 10.21 mg/g. Similar results were also reported for Rh-B adsorption, such as banana pith (Anandkumar and Madal, 2011), cellulose-based (Aksu and Dönmez, 2003) acid activated mango (Namasivayan et al., 1993) and activated carbon (Annadurai et al., 2002).

Freundlich isotherm

The Freundlich isotherm assumes an empirical equation based on the heterogeneous surface of adsorbent. The linear form of the Freundlich isotherm is expressed as (Khan et al., 2011):

$$\log q_e = \log K_f + n \log C_e \qquad (8)$$

where K_f is the Freundlich coefficient related to adsorption capacity, and n relates to adsorption intensity. The values of the Freundlich constants were obtained from the linear correlations between the values of log qe and log C_e. The values of K_f, n and coefficient determination R^2 are collected in Table 1. In the Freundlich adsorption constant, n should be between 1 and 10 for beneficial adsorption (Unuabonah et al., 2007; Vasu, 2008). Table 1 shows that n values are in the range of 1 to 10 for natural diatomite and R^2 is 0.99. It means that adsorption of Rh-B on natural diatomite can be described by the Freundlich model.

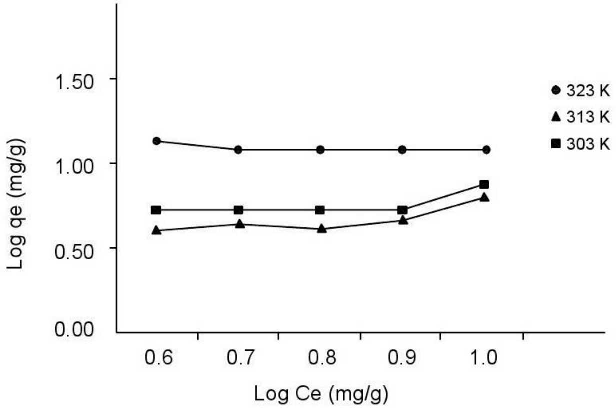


Fig. 5. Freundlich adsorption isotherm plots for adsorption of RhB onto natural diatomite at different temperatures

Thermodynamic parameters of adsorption

The thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) are presented in Table 2. The Gibbs free energy is calculated for adsorption of Rh-B on natural diatomite using Eq. (4). The values of ΔH^0 and ΔS^0 were determined from the slope and intercept from the plot of $1/T$ versus $\ln K_d$ given in Eq. (3), respectively.

The ΔG^0 value is negative for Rh-B on natural diatomite and it indicates that adsorption is spontaneous. The ΔG^0 decreases with temperature. Furthermore, better adsorption is obtained at higher temperatures (Khan et al., 2012). The positive values of the enthalpy change (ΔH^0) indicates that the adsorption process is endothermic. When ΔH^0 is lower than 40 kJ/mol the type of adsorption can be accepted to be a physical process. It indicates that adsorption is physical by nature and involves weak forces of attraction (Khan et al., 2012; Rahchamani et al., 2011). The positive value of ΔS^0 shows the increasing randomness at the solid/solution interface during adsorption of RhB on the adsorbents. The positive mean values of ΔS^0 may be due to some structural changes in the adsorbate and adsorbents during the adsorption process from the aqueous solution (Unuabonah et al., 2007).

Table 2. Thermodynamic parameters for the adsorption of rhodamine B onto natural diatomite

Initial Concentrationmg/dm^3)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)	ΔG^0 (kJ/mol)		
			303 K	313 K	323 K
20	7.68	25.81	–0.140	–0.399	–0.657
40	6.70	24.74	–0.800	–1.040	–1.290
60	7.10	25.11	–0.508	–0.759	–1.010

Adsorption kinetics

The experimental data relating to adsorption of RhB onto natural diatomite was investigated using the Lagergren pseudo-first and pseudo-second order equation (Aivalioti et al., 2010; Chan et al., 2011):

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{1}{q_e} t \tag{10}$$

where, q_e is the amount of Rh-B adsorbed at equilibrium (mg/g), q_t amount of Rh-B adsorbed at various times, t time of adsorption duration, and k_1 is a rate constant of the equation (min^{-1}).

The calculations were done for 20, 40 and 60 mg/dm^3 RhB solution initial concentration at 303 K. The $k1$ and q_e were calculated from the slope and intercept of the plots of log $(q_e - q_t)$ versus t according to the pseudo-first-order model (Fig. 6) and t/q_t versus t according to the pseudo-second-order model (Fig. 7) as well as q_e and k_2 from the slope and intercept were calculated. The kinetic parameters are given in Table 3. The the q_e values calculated from the pseudo-second-order model are match qe experimental results. The R^2 values were between 0.995 and 0.998. The linear regression correlation coefficient values for pseudo- second-order model were found to be higher than those of the first-order model. Higher R^2 values confirm that the adsorption data are well represented by the pseudo-second-order kinetics. The calculated qe values also agree very well with the experimental data in the case of pseudo-second-ordel kinetics model. Similar kinetic results were reported in adsorption of BTEX, MTBE and TAMI by natural and modified diatomite (Aivalioti et al., 2010), comparative study of lead sorption onto natural perlite, dolomite and diatomite (Irani et al., 2011), adsorption behavior of direct red 12B and rhodamine B from water onto surfactant modified coconutcoir pith (Sureshkumar and Namasivayam, 2008) and application of activated carbon derived from scrap tires for adsorption of rhomine B (Shuangxi and Tanzhu, 2010).

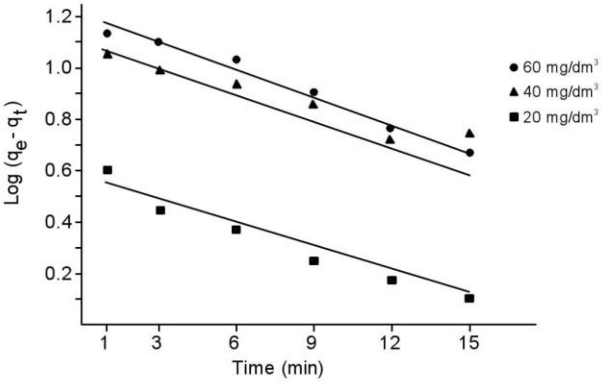


Fig. 6. Pseudo-first-order plots for adsorption of Rhodamine B onto natural diatomite

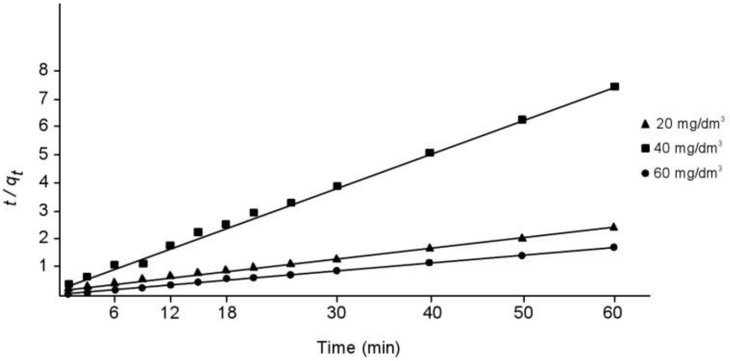


Fig. 7. Pseudo-second-order plots for adsorption of rhodamine B onto natural diatomite

Table 3. Kinetic parameters for adsorption of rhodamine B onto natural diatomite

Kinetic model	Kinetic parameters	Concentration (mg/dm^3)		
		20	40	60
Pseudo-first order	k_1	$5.68.10^{-1}$	$10.75.10^{-1}$	$12.23.10^{-1}$
	q_e (calc.)	1.32	1.09	1.07
	q_e (exp.)	8.06	24.67	34.11
	R^2	0.974	0.981	0.979
Pseudo-second order	k_2	$3.05.10^{-1}$	$1.59.10^{-1}$	$0.58.10^{-1}$
	q_e (calc.)	3.72	12.02	16.59
	q_e (exp.)	8.06	24.67	34.11
	R^2	0.998	0.992	0.995

Conclusion

The adsorption of the dye (rhodamine-B) by natural diatomite was investigated. It was found that natural diatomite is an effective adsorbent for removal of Rh-B from wastewater due to its short adsorption time and its natural pH (8.0±2). The thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) were calculated. It was shown that adsorption of Rh-B dye by natural diatomite is both endothermic and spontaneous. The removal of Rh-B by the natural diatomite was controlled by the initial dye concentration at natural pH and different temperatures. The adsorption data were well fitted by both Langmuir and Freundlich models. The maximum adsorption was found to be 10.21 mg/g (for initial concentration 20 mg/dm^3, temperature 323 K). The adsorption kinetics of Rh-B can be well described by the pseudo-second-order model. As a result, the natural diatomite can be used as a highly effective low-cost adsorbent for the removal of Rh-B from an aqueous solution.

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