

## Adsorption of Cadmium (II) by Chitin

CHUNHUA XIONG

Department of Applied Chemistry, Zhejiang Gongshang University,  
Hangzhou Zhejiang 310012, China.

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**Summary:** The feasibility of using chitin as an adsorbent for cadmium (II) was examined. The adsorption characteristics were studied as a function of solution pH, temperature, contact time *et. al.*. Maximum uptake amount of cadmium (II) was estimated to 93.9 mg/g • chitin by saturated capacity method at pH 5.41 in the HAc-NaAc system. The isotherm data for cadmium (II) at pH 5.41 fitted well to a Langmuir equation with a sorption capacity of 94.3 mg/g • chitin which was in accordance with the maximum uptake amount by means of the saturation method. The apparent adsorption rate constant was  $k_{298K} = 3.34 \times 10^{-5} s^{-1}$ ,  $k_{298K} = 4.60 \times 10^{-5} s^{-1}$ ,  $k_{308K} = 6.35 \times 10^{-5} s^{-1}$  and  $k_{318K} = 9.89 \times 10^{-5} s^{-1}$ . The apparent activation energy was 63.1 kJ/mol. Thermodynamic parameters,  $\Delta G_{298K}$  was calculated to be -19.5 kJ/mol,  $\Delta H$  and  $\Delta S$  were found to be 10.6 kJ/mol and 101 J/mol·K, respectively. Adsorption mechanism was also proposed using infrared spectroscopy technique (IR).

### Introduction

Cadmium was discovered in 1817, in Germany, by F Stromeyer. Now, it has been well recognized for its negative effect on the environment where it accumulates readily in living systems. Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans *et. al.*, [1, 2]. Conventional methods employed for the removal of heavy metal ions from industrial effluents include chemical precipitation, filtration, electrochemical treatment, and ion exchange. Most of these methods are expensive and incapable of removing trace levels of heavy metal ions [3]. In recent years this situation has led to a growing interest in the application of biomaterials technology for the removal of trace amounts of toxic metals from dilute aqueous wastes. Biomaterials including algae, bacteria, fungi, higher plants, and products derived from these organisms, have been demonstrated to remove certain chemicals species [4]. As environmental friendly materials, natural polymers are biodegradable and biocompatible, therefore, they can be expected as potential suitable materials and have attracted much attention.

The chitin, a polymer composed of *N*-acetyl-d-glucosamine residues, is a natural polysaccharide of major importance, first identified in 1884 [5]. Meanwhile, chitin is an inexpensive biological material and can be obtained from seafood

such as the shells of crab, shrimp. Additionally, it is worth remembering that chitin extraction does not cause any disturbance to the ecosystem. Chitin exhibits numerous interesting physico-chemical, biological, and mechanical properties with great potential applications. It carries one -NHCO- group per glucose ring, thus allowing excellent complexation capacity with metal ions, particularly transition and post-transition metals [6, 7]. The formation of a coordination complex between the metal and the chitin nitrogen or oxygen has been reported [8]. Consequently, chitin has been used in water treatment for the removal of Cd (II) ions, but the adsorption amount just was 14 mg/g chitin [4]. It was considered as a small amount.

The aim of this paper was to conduct and improve the basic information for the design of adsorption equipment. Then, the batch method was used to determine the equilibrium data. The optimum experimental conditions and mechanism of adsorption such as pH were investigated for the quantitative recovery of cadmium on chitin.

### Results and Discussion

#### *Effect of pH on the Adsorption of Cd (II) onto Chitin*

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process [9]. It has been regarded as master

variable in most processes governed by adsorptive separation.

Fig. 1 shows that, when pH was less than 5.41, the uptake of Cd (II) increased with increasing initial pH and was the greatest at pH 5.41. Whereas, with the increasing of pH, uptake of Cd (II) decreased. Based on the findings before [10], it is assumed to be that in acidic solution, although functional groups may contribute to metal chelation, their protonation significantly reduces their ability to react with Cd (II). Adsorbent is likely a net positive charge in the adsorption system due to  $H^+$ . In such system,  $H^+$  compete with metal ions resulting in active sites to become protonated to the virtual exclusion of metal binding on the adsorbent surface. This means that at higher  $H^+$  concentration, the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal cations. As pH increases, interactions between  $H^+$  and chitin are destabilized, leading to an improvement of the adsorption of Cd (II) onto chitin because more ligands groups would be exposed and the biosorption of the metal ions with positive charge Cd (II) process was reached maximum. However, above the threshold pH, decrease in biosorption is due to the precipitation of some Cd (II) ions. The optimal pH value was 5.41. Therefore, pH 5.41 was selected for further experiments.

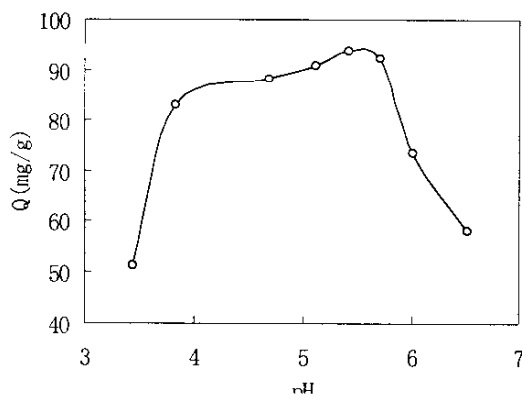


Fig. 1: Influence of pH on adsorption capacity Chitin 30.0 mg  $[Cd^{2+}]_0 = 0.1$  g/mL  $T=298$  K  $r = 100$  r/min.

As shown in Fig. 1, we also can see the maximum sorption amount of cadmium is 93.9 mg/g chitin. This is an important parameter because it

determines how much sorbent is required to quantitatively concentrate the metal from a solution.

#### Adsorption Isotherms

Sorption isotherms describe how adsorbates interact with adsorbents. In order to successfully represent the equilibrium adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Two kinds of several isotherms equations were tested [11]:

$$\text{Langmuir equation: } C_e/Q = C_e/Q^\circ + 1/(Q^\circ b)$$

$$\text{Freundlich equation: } \lg Q = 1/n (\lg C_e) + \lg k$$

where  $Q$  is the amount adsorbed at equilibrium (mg/g) and  $C_e$  is the equilibrium concentration of metal ions in solution (g/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In the Langmuir equation,  $Q^\circ$  is saturated sorbing amount and  $b$  is a constant related to the energy of adsorption (mL/mg). Freundlich treatment gives the parameters,  $n$ , indicative of bond energies between metal ion and the adsorbent and  $K$ , related to bond strength.  $n = 1$  indicates the adsorption is linear with homogeneous adsorption sites and there is no interaction between the adsorbed metals.  $1/n < 1$  shows that the adsorption is favorable, new adsorption sites are available and the adsorption amount increases.  $1/n > 1$  indicates that the adsorption bonds are weak, adsorption capacities decrease and unfavorable [12].

The Langmuir and Freundlich parameters are being listed in Table-1. It is evident from these data that the adsorption of Cd (II) ions onto chitin is fitted well to the Langmuir isotherm model than that of the Freundlich isotherm models, as indicated by the  $R^2$  values. The Langmuir model is the best-known isotherm for describing adsorption from aqueous solution. It assumes that there is no interaction between the adsorbate molecules. The adsorption is localized in a monolayer. The maximum adsorption capacity ( $Q^\circ$ ) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorbent for Cd (II) ions. The adsorption capacity increased with an increase in the temperature. The highest value of  $Q^\circ$  obtained at 298 K is 94.3 mg/g.

Table-1: Langmuir isotherm equations and Freundlich isotherm equations in various temperatures.

T(K)	Langmuir isotherm equations	R <sup>2</sup>	Q <sup>0</sup> (mg/g)	b(J/mg)
288	Ce/Q=0.0111Ce+0.0002	0.9903	90.1	55.5
298	Ce/Q=0.0106Ce+0.0001	0.9946	93.9	107
308	Ce/Q=0.0105Ce+0.00008	0.9927	95.2	131
318	Ce/Q=0.0102Ce+0.00006	0.9923	98.0	170
	Freundlich isotherm equations	R <sup>2</sup>	n	
288	lgQ=0.4912lgCe+2.5324	0.9903	2.04	
298	lgQ=0.4869lgCe+2.5943	0.9954	2.05	
308	lgQ=0.4484lgCe+2.5824	0.9747	2.23	
318	lgQ=0.3781lgCe+2.5217	0.9676	2.64	

#### Determination of Adsorption Rate Constant

The time-dependent behavior of Cd (II) adsorption was studied by varying the contact time between the chitin and Cd (II). As our investigations, the Brykina method was used to test adsorption kinetics data to investigate the mechanism of biosorption. The equation was  $-\ln(1-F) = kt$  [13], where F is the fractional attainment of equilibrium ( $F = Q_t/Q_e$ ), where  $Q_e$  and  $Q_t$  are the amounts of Cd (II) ions adsorbed on the adsorbent at equilibrium and at various times t (mg/g); k is the adsorption rate constant. A linear plot of  $-\ln(1-F)$  vs t with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbents.

The sorption rate curves (Fig. 2) of the chitin towards Cd (II) were obtained by plotting the sorption amount against the sorption time allowed. And, the sorption rate constant k ( $k_{288K} = 3.34 \times 10^{-5} s^{-1}$ ,  $k_{298K} = 4.60 \times 10^{-5} s^{-1}$ ,  $k_{308K} = 6.35 \times 10^{-5} s^{-1}$ ,  $k_{318K} = 9.89 \times 10^{-5} s^{-1}$ ) can be found from the slope of the straight line (Fig. 3). The rather high correlation coefficient ( $R^2_{288K} = 0.988$ ,  $R^2_{298K} = 0.997$ ,  $R^2_{308K} = 0.999$ ,  $R^2_{318K} = 0.991$ ) were obtained via linear fitting. According to G. E. Boyd [14], if the beeline accord with the linear relationship of  $-\ln(1-F) \sim t$ , it can be deduced that the liquid film spreading is the predominating step of the sorption process.

According to the formula of Arrhenius  $\lg k = -E_a/RT + \text{Constant}$ , the slope of straight line, which is made by plotting  $-\lg k$  versus  $1/T$  can be obtained. Then,  $E_a = 63.1$  kJ/mol. The magnitude of activation energy gives an idea about the type of sorption, which is mainly physical or chemical. Low activation

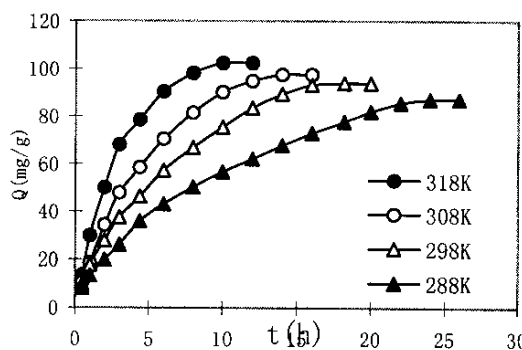


Fig. 2: Adsorption curves Chitin 30.0 mg,  $[Cd^{2+}]_0 = 0.1$  g/mL pH = 5.41 r = 100 r/min.

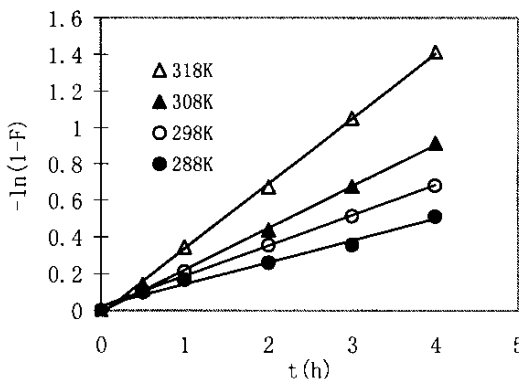


Fig. 3: Determination of adsorption rate constant  $[Cd^{2+}]_0 = 0.1$  g/mL Chitin 30.0 mg pH = 5.41 r = 100 r/min.

energies (5–40 kJ/mol) are characteristics for physisorption, while higher activation energies (40–800 kJ/mol) suggest chemisorption [15]. The obtained result (63.1 kJ/mol) for the adsorption of Cd (II) by chitin indicates that the adsorption corresponds to chemisorption.

#### Effect of Temperature

In any adsorption procedure, both energy and entropy considerations should be taken into account in order to determine which process will take place spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The effect of temperature on the Cd (II) adsorption experiment has been investigated at four different temperatures (288 K,

298 K, 308 K and 318 K). The temperature of the adsorption medium could be important for energy dependent mechanisms in metal adsorption by chitin. For an increase in temperature from 288 K to 318 K, an increase in the adsorption of Cd (II) was observed (87.1 mg/g at 288 K to 102 mg/g at 318 K at experimental conditions). The results indicated that an increase of the temperature deals induce an increase in the amount of sorption. Meena *et al.*, [16], reported that the increase in sorption with temperature may be attributed to either increase in the number of active surface sites available for sorption on the adsorbent or due to the decrease in the boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of adsorbate in the boundary layer decreased.

The free energy change  $\Delta G$ , enthalpy change  $\Delta H$  and entropy change  $\Delta S$  for adsorption process were calculated using following equations:

$$\lg D = - \frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R}$$

$$\Delta G = \Delta H - T\Delta S$$

The result was shown in Table-2. The Gibbs free energy change,  $\Delta G$ , is the fundamental criterion of spontaneity, reaction occurring spontaneously at a given temperature if it is a negative value. Negative  $\Delta G_{298K}$  values indicate that the sorption process led to a decrease in Gibbs free energy and confirmed the feasibility of the process and spontaneous nature of the sorption under the experimental condition [17]. If sorption decreases with increasing temperature, it may be indicative of physical sorption, and the reverse frequently assumed as chemical sorption [18]. In addition, the values of  $\Delta S$  were found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process.

Table-2: Thermodynamic parameters for Cd (II) on chitin.

$\Delta H$ (kJ/mol)	$\Delta S$ (J/ mol·K)	$\Delta G$ (kJ/mol)			
		T = 288 K	T = 298 K	T = 308 K	T = 318 K
10.6	101	-18.5	-19.5	-20.5	-21.5

#### IR Analyses

IR spectra are a useful tool to identify functional groups in a molecule, as each specific

chemical bond often has a unique energy absorption band, and can obtain structural and bond information on a complex to study the strength and the fraction of hydrogen bonding and miscibility. The IR spectra (400–4000  $\text{cm}^{-1}$ ) of the chitin and metal-loaded chitin are shown in Fig. 4. The IR spectrum of  $\alpha$ -chitin exhibited major peaks at 3452.17  $\text{cm}^{-1}$  for –OH stretching vibration. In addition, for  $\alpha$ -chitin, the amide I band is split at 1661.92 and 1626.69  $\text{cm}^{-1}$ , the amide II band is unique at 1556.23  $\text{cm}^{-1}$ . The absorption peaks of 1373.67 and 1310.12  $\text{cm}^{-1}$  were the  $\delta$  ( $\text{CH}_3$ ) and  $\nu$  (C-N) of the acetylamino. A comparison of the spectra for chitin with that of Cd-loaded reveals characteristic changes of acetyl groups,  $\delta$  ( $\text{CH}_3$ ) and  $\nu$  (C-N), which shift from 3452.17, 1661.92, 1556.23, 1373.67 and 1310.12  $\text{cm}^{-1}$  before  $\text{Cd}^{2+}$  adsorption to 3433.10, 1652.31, 1560.03, 1378.33 and 1319.22  $\text{cm}^{-1}$  after  $\text{Cd}^{2+}$  adsorption. At the same time, the infrared absorption band of 1626.69  $\text{cm}^{-1}$  disappeared. The spectral analysis indicated that the complex reactions took place between the acetylamino (–CONH–), the hydroxyl group (–OH) and  $\text{Cd}^{2+}$ .

## Experimental

### Apparatus

The cadmium was determined with Shimadzu UV-2550 UV-Visible spectrophotometer. Chitin dosage was measured by electronic balance of METTLER TOLEDO AL204. Mettler toledo delta 320 pH meter was used for measuring pH. The sample was shaken in the DSHZ- 300A temperature constant shaking machine. The water used in the present work was purified using Molresearch analysis-type ultra-pure water machine.

### Reagents and Solutions

Chitin was supplied by ZheJiang University. The structure of chitin was shown in Fig. 5. Standard solutions of metal ions were prepared by dissolving appropriate amounts of analytical grade  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  in purified water, and further diluted prior to use. HAc-NaAc with pH 3.44-6.50 and HCl- $\text{Na}_2\text{B}_4\text{O}_7$  with pH 9.00 buffer solutions were prepared from the NaAc, HAc, HCl and  $\text{Na}_2\text{B}_4\text{O}_7$  solutions. The color reagent of 0.1% PAR-ethanol solution was obtained by dissolving 0.1 g PAR

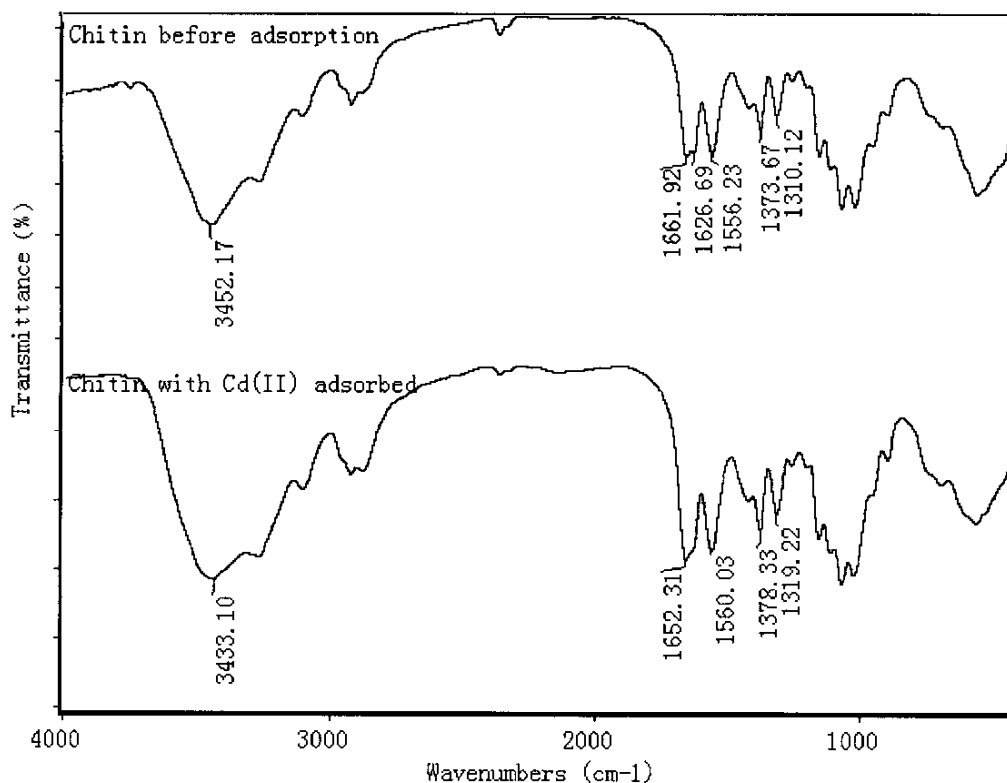


Fig. 4 IR analyse.

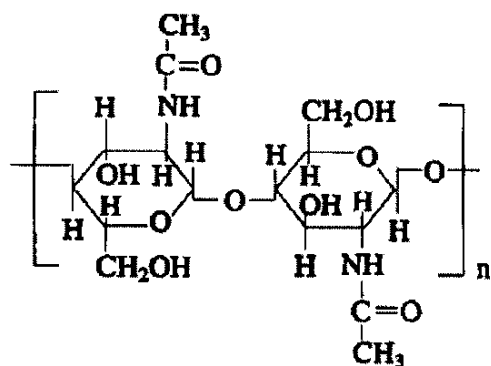


Fig. 5: Structure of Chitin.

( $C_{11}H_{19}N_3O_2$ ) powder into 100 mL 95% ethanol solution. All other chemicals were of analytical grade and purified water was used throughout.

#### Adsorption Experiments and Analytical Methods

The amount of absorbed metal ( $Q$ ) and distribution coefficient ( $D$ ) were determined as a

difference of metal ions concentration before and after adsorption based on the equation:

$$Q = (C_0 - C_e)V/W, D = Q/C_e$$

where  $C_0$  is initial concentration of  $Cd^{2+}$  in solution (g/L),  $C_e$  is equilibrium concentration of  $Cd^{2+}$  in solution (g/L),  $V$  is total volume of solution (mL),  $W$  is chitin weight (g).

#### Measurement of Heavy Metal Ions

The concentration of unadsorbed  $Cd^{2+}$  ions in the sorption medium was determined spectrophotometrically. A solution containing lower than  $75 \mu g$  of  $Cd^{2+}$  was accurately added into a 25 mL colorimetric tube, and then 1 mL colour reagent of 0.1% PAR-ethanol solution and 10 mL pH 9.00  $HCl-Na_2B_4O_7$  buffer solutions were added. After the addition of purified water to the mark of colorimetric tube, the absorbency was determined in a 1cm colorimetric vessel at wavelength of 497 nm and compared with the blank test.

### Analytical Procedure

The factors that affect the adsorption of the chitin were examined in a batch system. The effect of the initial pH of the solution, adsorption isotherms, kinetics and temperature were investigated to determine the optimum conditions for  $\text{Cd}^{2+}$  adsorption.

### pH Studies

The static adsorption experiments with known concentration of  $\text{Cd}^{2+}$  solutions at 0.1 g/L were conducted to determine optimal pH. The effect of pH was investigated at a constant speed of 100 r/min at 298 K. The pH values of solutions containing cadmium ion were adjusted to 3.44-6.51 by using buffer solutions.

### Adsorption Isotherm Studies

Freundlich isotherm was studied by varying the chitin dosage in the range of 40.0 mg-85.0 mg at 30 mL  $[\text{Cd}^{2+}]_0 = 0.1$  g/L, pH 5.41, 100 r/min.

Langmuir isotherm was studied by varying the initial  $\text{Cd}^{2+}$  concentration in the range of 0.05 g/L - 0.1 g/L with 40.0 mg chitin at pH 5.41, 100 r/min.

### Kinetics and Thermodynamic Studies

For kinetics studies, 30.0 mg of chitin was contacted with 50 mL of 0.1 g/L metal solutions stirred vigorously in a shaker of 100 r/min, maintained at a constant temperature. At appropriate time intervals, stirring was briefly interrupted while 0.2 mL volumes of supernatant solutions were pipetted from the reactor and were analyzed to determine the residual metal concentration in the aqueous solution.

Thermodynamic parameters of adsorption have been determined using classical thermodynamic equations at the condition of 30.0 mg chitin and 30 mL  $[\text{Cd}^{2+}]_0 = 0.1$  g/L at pH 5.41, 100 r/min, in the range of 288 K-318 K.

### IR Studies

The samples for IR spectroscopy were prepared according to the following procedure. The

chitin was saturated with  $\text{Cd}^{2+}$  ions (under static). Then, the samples were dried. The chitin tableting was carried out with KBr (0.3 mg of chitin to 200 mg KBr). The IR spectra were detected on IR spectrometer and identified.

### Conclusions

In this study, the effects of parameters such as the initial pH of the solution, adsorption isotherms, kinetics and temperature were investigated. More and better results are further improved on the base of former researchers. The maximum adsorption amount of cadmium (II) was estimated to 93.9 mg/g by saturated capacity method which is much bigger than the 14 mg/g by former researcher. From the results, we can know the adsorption was feasible, spontaneous and endothermic under examined conditions. Adsorption mechanism was also proposed that the complex reactions took place between the acetylamino (-CONH-), the hydroxyl group (-OH) and  $\text{Cd}^{2+}$ .

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