Effects of Adsorption Mechanisms on the Efficiency of ASC Whetlerite Carbon Reactor

JONG SUN LIM

School of Chemical Science and Engineering, Inha University, Incheon 402-751, Korea

CHULSUNG KIM[*],[†]

Department of Environmental Engineering, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

ckim@rrcc.mnscu.edu

YONGWOO LEE

R and D Center, Samsung Engineering Co. Ltd, Seoul, Korea

WHA-SEUNG AHN

School of Chemical Science and Engineering, Inha University, Incheon 402-751, Korea

Abstract. Dynamic adsorption equation was evaluated for its validity to characterize two different initial adsorption mechanisms with dimethyl methylphosphonate (DMMP) and cyanogen chloride (CNCl) onto ASC whetlerite carbon. Experimental results show that a linear relation between breakthrough time and the amount of carbon was occurred with high values of coefficient of correlation (0.9790–0.9993 for DMMP, 0.9979–0.9998 for CNCl) satisfying the pre-requirement for application of the adsorption equation. With initial adsorption data, as superficial flow rate increases, the dynamic adsorption capacity for DMMP increases and that for CNCl decreases which are not consistent with the earlier observation of less-relationship between dynamic adsorption and superficial flow rate. An effort was conducted to obtain numerical formulas for the dynamic adsorption capacity as a function of superficial flow rate and the calculated maximum adsorption capacities for DMMP and CNCl were 0.4291 (g/g) and 0.2500 (g/g), respectively.

For DMMP,

$$W_e = 0.3328\{1 - \exp(-0.0626V_f)\} + 0.0936$$

For CNCl

$$W_e = 0.1154\exp(-0.1387V_f) + 0.1346\exp(-2.32^{-10}V_f)$$

The rate constant for both DMMP and CNCl adsorption, has linear relation to superficial flow rate within our experimental range from 4 to 50 cm/sec. Critical bed weight which is the minimum amount of carbon to satisfy the arbitrary chosen effluent concentration, was affected by not only superficial flow rate but also rate constant.

[*]To whom correspondence should be Addressed.
[†]Present address: Department of Chemistry, Rainy River Community College, International Falls, MN 56649, USA.

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Introduction

ASC whetlerite carbons have been used for removal of toxic gas phase chemicals through physical and chemical interaction mechanisms between adsorbates and adsorbents. It has been shown that the adsorption capacity of activated carbon strongly dependent upon humidity, temperature and the concentration of adsorbate (Freemann and Reucroft, 1979; Freemann et al., 1980; Brown et al., 1989; Biron and Stavisky, 1995). Many researches have been conducted for investigating static adsorption properties of the activated carbons (Tripathi and Ramachandran, 1982; Kloubek and Medek, 1986; Sing, 1989; Korpiel and Vidic, 1997; Tessmer et al., 1997), while limited researches have been performed regarding chemical adsorption (Jonas and Rehrmann, 1972, 1973). In this present study, dynamic adsorption equation was used to explain initial adsorption characteristics of both dimethyl methylphosphonate (DMMP) and cyanogen chloride (CNCl) onto ASC whetlerite carbon. After confirming the validity of the adsorption equation for both adsorption mechanisms, we elucidated the adsorption characteristics of the ASC whetlerite carbon depending on the adsorption properties obtained with dynamic adsorption method.

Adsorption Kinetic Equation

The dynamic adsorption kinetic equation proposed by Wheeler and Robell (1969) was used for this research. The equation has been derived from the continuity equation of mass balance between the inlet amount, and the sum of adsorbed and penetrated amount in combination with the pseudo-first order adsorption reaction. The suggested equation can be shown in the form of

$$T_b = \frac{W_e W}{C_o Q} - \frac{W_e \rho \ln(C_o/C_x)}{C_o K_v} \tag{1}$$

where C_o is the influent concentration (g/cm^3); W_e is the adsorption capacity (g/g); C_x is the effluent concentration (g/cm^3); W is the adsorbent weight (g); ρ is the bulk density (g/cm^3); Q is the flow rate (cm^3/min); K_v is the adsorption rate constant (min^{-1}); T_b is the breakthrough time (min.) of the gas at the arbitrarily chosen value of C_x.

Years later, the equation was applied to several physical adsorption onto activated carbon with dynamic adsorption method (Jonas and Rehrmann, 1972, 1973; Jonas and Svirbely, 1972; Rehrmann and Jonas, 1978). In Eq. (1), parameters such as influent concentration (C_o), effluent concentration (C_x), adsorbent weight (W), and volumetric flow rate (Q) can be determined by experimental conditions. In addition, bulk density (ρ) is a constant, which is determined by shape and granular size of the activated carbon in the column. With the constant values of C_o, C_x, Q and ρ, breakthrough time variation as a function of amount of activated carbon in the column may yield straight line. From the slope and Y-axis interception, adsorption capacity (W_e), and adsorption rate constant (K_v) will be determined, respectively.

The critical bed weight (W_c) which is the minimum required amount of activated carbon in the specific column just satisfying the arbitrary chosen effluent concentration can be obtained from the X-axis intercept ($T_b = 0$) as a form of Eq. (2).

$$W = \frac{\rho Q}{K_v} \ln(C_o/C_x) = W_c \tag{2}$$

As shown in Eq. (2), critical bed weight depends on several parameters including bulk density (ρ), rate constant (K_v), influent concentration (C_o), and effluent concentration (C_x). In this present research, ρ, C_o, and C_x will be fixed as constants, such that critical bed weight (W_c) is affected primarily by adsorption rate constant (K_v) and volumetric flow rate (Q).

Adsorption Kinetics for CNCl Adsorption

Adsorption of CNCl onto ASC whetlerite carbon can be expressed as following (Jonas, 1978),

$$CNCl + H_2O \xrightarrow{Cu(II)} HOCN + HCl \tag{3}$$

$$HOCN + H_2O \xrightarrow{Cr(VI)} CO_2 \uparrow + NH_3 \uparrow \tag{4}$$

As shown in Eqs. (3) and (4), the applied CNCl vapor reacts with water in gas phase using impregnated copper as a catalyst forming HOCN and HCl. The produced HOCN reacts further with water demanding hexavalent chromium as a catalyst. From this reaction,

carbon dioxide and ammonium are produced as final products. The other product of HCl does chemical reaction with the metals such as Cu(II) and Cr(VI) loosing its toxicity. The stoichiometries for HCl reaction with each metal are shown in Eqs. (5) and (6), respectively.

$$2HCl + CuO \longrightarrow CuCl_2 + H_2O \qquad (5)$$

$$3HCl + Cr^{6+} \longrightarrow \frac{3}{2}Cl_2 + Cr^{3+} + 3H^+ \qquad (6)$$
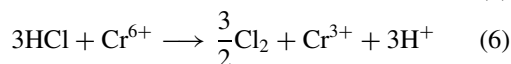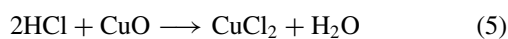
Based on the Eqs. (3)–(6), Cu(II) and Cr(VI) can work as not only catlysts but also reactants for detoxification of CNCl gas. Each 1 molar amount of Cu(II) or Cr(VI) can respond to 2 and 3 molar amounts of CNCl gas, respectively.

To apply Eq. (2) into the CNCl adsorption on the ASC whetlerite carbon, the kinetic equation should be modified as to pseudo-first order with respect to the adsorbate concentration. According to Eq. (3), reaction rate of CNCl is dependent upon the concentrations of CNCl and water. When the water vapor concentration is much higher than the CNCl concentration, the reaction rate can be assumed as pseudo-first order reaction with respect to CNCl. This assumption is agreeable with earlier experiments conducted by Zhang and Cheng (2000). They used a model based on the first order catalytic deactivation with respect to toxic gas and obtained satisfactory results comparing the experimental data.

Materials and Methods

The purity of the DMMP and CNCl vapors used for this research were 95 and 97%, respectively. The ASC whetlerite carbon (12 × 30 mesh, Grade IV) was obtained from Calgon Company with a bulk density of 0.63 g/cm^3. The surface area of the activated carbon was measured to be 850 m^2/g using BET method and the impregnated amount of metals were detected using Inductively Coupled Plasma spectrometer (Atomscan, Thermo Jarell Ash Co.). To prevent the aging of the carbon, each experiment was conducted with fresh ASC whetlerite carbons.

The experimental set up used for this research was composed of two major parts—adsorbate vapor generator and adsorption test column (I.D. 2.0 and 3.5 cm for DMMP and CNCl, respectively). Figure 1 shows the schematic description of the experimental apparatus. As shown in Fig. 1, vapor generator, mixer, container, and adsorption test column-containing ASC carbon are placed in a container where the temperature was controlled at 30 ± 1°C. Vapor generator containing either DMMP or CNCl liquid adsorbate solution was placed in a water bath where the temperature was controlled at 30°C and 1°C, respectively. The vapors were generated with aid of oxygen free nitrogen in the vapor generator followed by mixing with air containing different humidity—50% humidity for DMMP and 80% humidity for CNCl. The amount of vapor required for the adsorption experiment was extracted
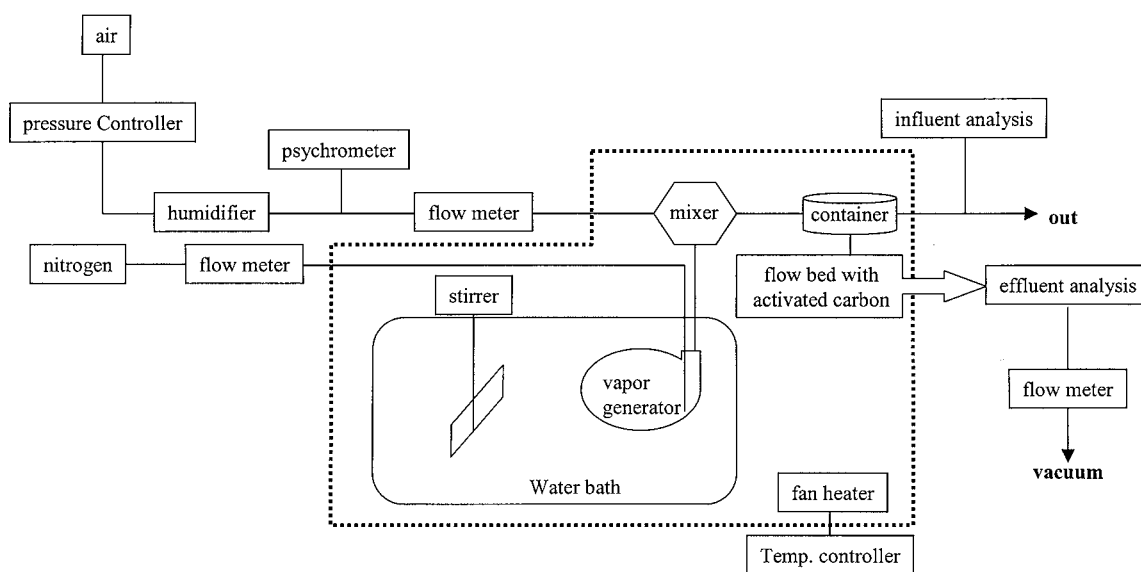

Figure 1.   Schematic description of the experimental apparatus.

using a sample pump, and the remainder was flew into a hood after passed through a series of extra activated carbon columns. Before conducting experiments, the generated vapors were collected into diethyl phthalate solvent and ethanol for DMMP and CNCl, respectively with a flow rate of 0.5 ℓ/min for 3 minutes. The concentration of DMMP was measured using Gas Chromatography (HP5890) and for CNCl, adequate amount of 35% of nitric acid was added into the solution and then the solution was titrated with 0.025 N silver nitrate standard solution using Fisher 35 automatic titrator. After achieving target concentration of 4 mg/ℓ, the vapor was directed into the adsorption test column filled over the range of 2 to 10 gram of adsorbent (ASC carbon). A vibrator was used to pile up the ASC carbons uniformly in the column. The breakthrough times were denoted as the times when the effluent vapor concentrations reached to 4.0×10^{-5} and 0.008 mg/ℓ for DMMP and CNCl, respectively.

Results and Discussion

The impregnated amount of copper and chromium were 7.8 and 2.6 weight percent, respectively and small amount of other metals such as Mg, Fe, Ca, and Al were detected.

At first, we tried to verify the validity of application of the dynamic adsorption equation (Eq. (1)) with regard to DMMP and CNCl adsorption by measuring the breakthrough time as a function of carbon weight at several different flow rates. Experimental results show the linear relation between the breakthrough time and the amounts of carbon added in the column. Table 1 shows the regression equations and coefficients of correlation for each set of experiment. As shown in Table 1, the coefficients of correlation lay over the ranges of 0.9790 to 0.9993 for DMMP and of 0.9979 to 0.9998 for CNCl. With these quite linear regression lines which
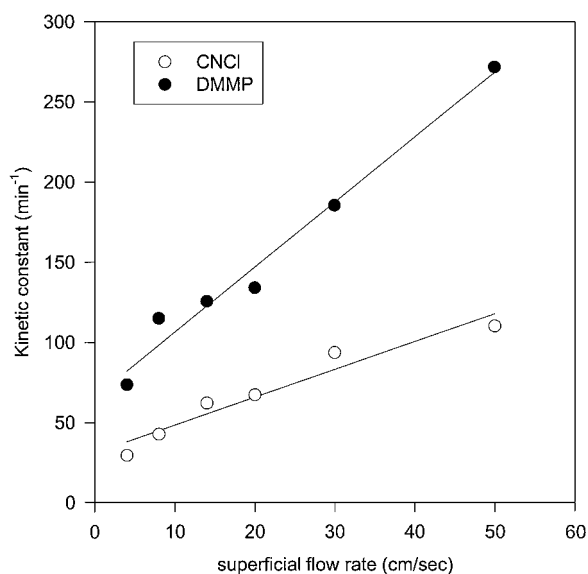

Figure 2. Rate constant as a function of superficial flow rate.

is the prerequired condition for application of the adsorption equation (Eq. (1)), we can consider that dynamic adsorption equation can be used to explain and characterize both DMMP and CNCl adsorption onto ASC whetlerite carbons.

Separate experiment was conducted using nonimpregnated carbon to confirm the requirement of Cr(VI) and Cu(II) for adsorption of CNCl using the same concentration of CNCl vapor. The results show that the breakthrough time was reached within one minute that is agreeable to the earlier result by Ehrburger et al. (1991). Therefore, Cu(II) and Cr(VI) on the ASC whetlerite should be present for detoxification of CNCl vapor on the carbon surface sites through chemical reactions.

The change of rate constant as a function of superficial flow velocity is shown in Fig. 2. It was

Table 1. Regression equations of CNCl and DMMP breakthrough times at several different flow rate.

Flow rate (cm/sec)	CNCl		DMMP	
	Regression equation	Coefficient of correlation	Regression equation	Coefficient of correlation
4	$T_b = 21.68W - 117.28$	0.9998	$T_b = 54.10W - 69.43$	0.9790
8	$T_b = 9.35W - 65.84$	0.9991	$T_b = 37.72W - 59.48$	0.9994
14	$T_b = 4.50W - 38.38$	0.9979	$T_b = 25.61W - 81.38$	0.9993
20	$T_b = 3.30W - 33.92$	0.9988	$T_b = 23.32W - 79.65$	0.9933
30	$T_b = 1.57W - 20.01$	0.9979	$T_b = 16.07 - 59.71$	0.9944
50	$T_b = 1.30W - 23.55$	0.9980	$T_b = 9.87W - 37.34$	0.9928

demonstrated that for the adsorption of DMMP, the adsorption rate constant as a function of superficial flow rate increased linearly for initial step and then the rate constant was kept steadily (Rehrmann and Jonas, 1978). However, the rate constant has a linear relation to superficial flow rate for both DMMP and CNCl adsorption within our experimental conditions. No steady condition was found in our experimental superficial flow rate range from 4 to 50 cm/sec. As shown in Fig. 2, rate constant for DMMP is much higher than the rate constant for CNCl over the range of experimental superficial flow rate. It has been suggested that the process of CNCl adsorption onto ASC whetlerite carbons includes three steps; physical adsorption followed by desorption and chemical reaction on the surface (Jonas, 1978; Zhang and Cheng, 2000). Based on our experimental data, CNCl adsorption rate is much slower than the physical adsorption process. Therefore, for CNCl adsorption process, the chemical reaction after physical adsorption may control the overall reaction rate as a rate determination step.

Dynamic adsorption capacity as a function of superficial flow rate is shown in Fig. 3. This figure shows that the adsorption mechanism may play an important role for adsorption capacity of ASC whetlerite carbon. Earlier study informed that the dynamic adsorption capacity for DMMP does not dependent on the superficial flow rate and the capacity was put in a range from 0.299 to 0.346 (g/g) depending on the carbon proper-
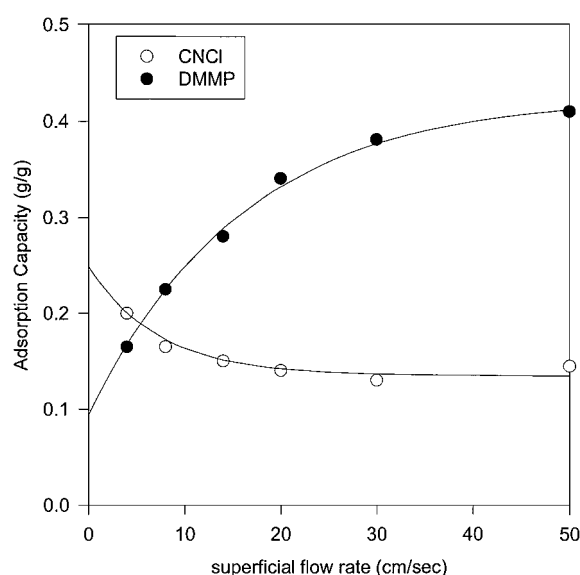
ties (Jonas and Rehrmann, 1972; Rehrmann and Jonas, 1978; Jonas et al., 1979). The obtained experimental data in this research however showed that with very initial adsorption data, as flow velocity increases, the dynamic adsorption capacity for DMMP increases and that for CNCl decreases. Within our experimental superficial flow rate area (4–50 cm/sec), the dynamic adsorption capacity has values from 0.17 to 0.41 (g/g). Most of the earlier experimental set up for physical adsorption denoted the breakthrough time (T_b) as the time when the exit gas concentration reached to 1% of the inlet gas concentration. The breakthrough time in our experiments defined as the time when the ratio of effluent to influent gas concentration get to 0.001%. Because of the very low ratio of C_x/C_o gas concentration for breakthrough time, the very limited selectively active sites responded to the incoming gas molecules showing flow dependent dynamic adsorption capacity. In addition, we cannot exclude the possibility of that due to the limited adsorption area, the obtained results might not fully explain the overall properties of the DMMP adsorption onto the ASC carbon.

For CNCl adsorption, the adsorption mechanism is totally dependent upon the chemical reaction between adsorbate and adsorbent. The incompleteness of the chemical reaction might play a role controlling the dynamic adsorption capacity. As superficial flow rate increases, therefore enough chemical reaction time may not be provided resulting in the reducing of dynamic adsorption capacity.

An effort was conducted to find numerical formulas explaining the experimental results, specifically. To derive the mathematical equations, two constraints should be solved. First constraint is the dynamic adsorption capacity (W_e) should be positive value over all range of superficial flow rate. The other is that as superficial flow rate approaches the unlimited value, the adsorption capacity also reaches to the maximum and minimum values for DMMP and CNCl, respectively. The proposed mathematical equation satisfying the two constraints for DMMP adsorption can be expressed as Eq. (7).

$$W_e = a\{1 - \exp(-bV_f)\} + c \qquad (7)$$

Where V_f is the flow velocity and W_e is the dynamic adsorption capacity. In Eq. (7), when the flow velocity approaches infinity ($\lim_{V_f \to \infty}$), dynamic adsorption capacity approaches to a value (sum of a and c). In the other way, when the flow velocity approaches zero value ($\lim_{V_f \to 0}$), the capacity also aproaches a value

Figure 3. CNCl and DMMP adsorption capacity as a function of superficial flow rate: solid line is calculated values.

of c. With positive values of c and the sum of a and c, Eq. (7) can be considered to explain the adsorption capacity under our specific experimental conditions without any conflict with both constrains. For CNCl adsorption, general two term exponential equation was applied as shown in Eq. (8). As shown in Eq. (8), the maximum adsorption capacity can be obtained when flow velocity approaches zero value as sum of A and B.

$$W_e = A \exp(-BV_f) + C \exp(-DV_f) \qquad (8)$$

With the aid of mathematical program, iterative computation was conducted for convergence of 0.0001 between theoretical and experimental values of the dependent variables. The results showed that the Eqs. (7) and (8) are reliable for the interpretation of the relation between dynamic adsorption capacity and influent flow rate (coefficient of correlation values for 0.971 and 0.927 for DMMP and CNCl, respectively). When substitute the constants with the obtained calculated values, the suggested equation of adsorption capacity as a function of flow velocity for each vapor is shown as followings,

For DMMP,

$$W_e = 0.3328\{1 - \exp(-0.0626V_f)\} + 0.0936 \quad (9)$$

For CNCl,

$$\begin{aligned} W_e = {} & 0.1154 \exp(-0.1387V_f) \\ & + 0.1346 \exp(-2.32^{-10}V_f) \end{aligned} \qquad (10)$$

According to the Eqs. (9) and (10), the maximum dynamic adsorption capacity is 0.4291 (g/g) for DMMP and 0.2500 (g/g) for CNCl. For CNCl adsorption, the maximum adsorption capacity can be calculated by chemical stoichiometry. Because 1 gram of activated carbon has 0.0779 g of copper and 0.0260 g of chromium which are 1.22×10^{-3} and 5.00×10^{-4} molar amount for copper and chromium, respectively. As shown in Eqs. (5) and (6), since 1 molar amount of copper and chromium can react with 2 and 3 molar amounts of CNCl, respectively, 1 gram of activated carbon used for this research can react with 3.94×10^{-4} molar amount of CNCl which is 0.2430 gram. This stoichiometrically calculated adsorption capacity value for CNCl is very consistent to the experimentally obtained results.

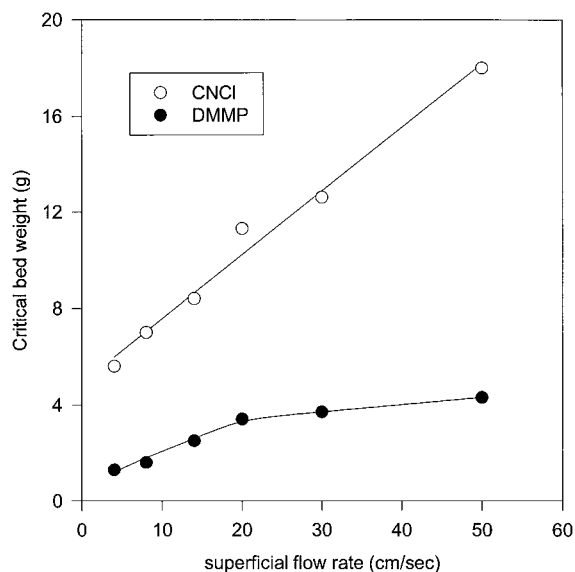Figure 4 shows the critical bed weight variation as a function of superficial flow rate. While for CNCl

Figure 4.   Critical bed weight as a function of superficial flow rate.

adsorption, it has a linear relation to superficial flow rate, for DMMP adsorption, non-linear relation occurs between critical bed weight and superficial flow rate showing a demarcation point within our experimental ranges. According to Eq. (2), critical bed weight is a function of flow rate (Q) and rate constant (K_v) in our experimental conditions. However, rate constant is also affected by flow rate. Therefore, critical bed weight may be controlled by both flow rate and rate constant at each set of experiment. Based on our experimental data, it is not clear which is the primary factor controlling the critical bed weight.

Conclusion

DMMP physical adsorption and CNCl adsorption mechanisms were characterized by dynamic adsorption equation. As flow velocity increases, adsorption capacity increases for physical adsorption while it decreases for CNCl adsorption. Linear relation between rate constant and flow rate occurs for both DMMP and CNCl adsorption mechanisms. Based on our experimental data, critical bed weight is affected by both flow rate and rate constant. However, it is not clear which is the primary factor controlling the critical bed weight.

According to our data, dynamic adsorption modeling equation might be useful tool to analyze activated carbon properties. In addition, it will enhance our

capability to better evaluate the fate and detoxification characteristics of toxic gas through both physical and CNCl adsorption mechanisms. Considering real/potential situations, the initial dynamic adsorption experimental results could provide very important insights as how to improve the design of respiratory cartridge systematically to protect human being from toxic gases as well as the efficient management.

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