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Determination of The Adsorption Kinetics for Adsorption Methylene Blue Dye with C-4-Hydroxy-3-Methoxyphenylcalix[4]resorcinarene

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ABSTRACT. Adsorption kinetics is part of adsorption and discusses the adsorption rate of an adsorbent on the adsorbate. Adsorption kinetics has an equation to determine the rate constant of adsorption, namely the pseudo-first order and pseudosecond order. In this study, methylene blue was adsorbed using a C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene (CHMFKR) adsorbent. The aim of this study to determine the effect of process parameters (concentration, pH, and processing time) on the process adsorption, with the Langmuir and Freundlich adsorption isotherm model approach, and to determine the adsorption kinetics of methylene blue with CHMFKR. Ten mL of methylene blue solution with various concentrations of 5, 6, 8, 10, and 11 ppm with a solution pH of 7 was added to as much as 0.001 gram of CHMFKR adsorbent and stirred at 600 rpm for 40 minutes. The solution was measured, and its absorbance was measured using the UV-Vis Spectrophotometer. The results show that the adsorption kinetics follow pseudo second order with an adsorption rate of 0.7217 \pm 0.4 g/mg.s. The adsorption isotherm follows the Langmuir equation, and the maximum adsorption amount is 114.94 \pm 2.04 mg/g.

Keyword: methylene blue, C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene, adsorption

INTRODUCTION

According to the World Bank in 2017, the development of the textile industry has increased significantly. Indonesia has grown from 149.88 trillion in 2010 to 151.77 trillion. This is due to the increase in the number of textile companies from 2880 to 2980, or about 3.5%. Reactive dyes are often used in the textile industry due to their different colors and textures. This increase affects the amount of waste generated. The waste from the textile industry, in particular, contains dangerous dyes and is therefore considered a potential source of pollution (Ngapa & Ika, 2020). Disposal of such dye-contaminated wastewater from the textile industry is a major problem (Karmakar et al., 2019).

Synthetic dyes are commonly used in textile dyeing processes. This is because synthetic dyes are larger and easier to use than natural dyes and have different colors. More than 700.000 tons of textile industry waste contain synthetic dyes (Adegoke & Bello, 2015). Dyes contained in textile wastewater have a complicated molecular structure and are difficult to remove by conventional wastewater treatment. They are fairly light and thermally stable and resist biodegradation, а challenge for traditional physicochemical and biological treatment methods (Sanghi & Verma, 2013).

However, the contents of the waste must be treated before they can be removed from the environment. This is because waste generally contains substances that are harmful to living organisms. One of them is the content of low-degradable organic compounds that are difficult to decompose, such as methylene blue dye in waste. The dye methylene blue is widely used in the textile industry. Methylene blue is part of the cationic dye group, which has a very strong adsorption power (Velásquez-Silva et al., 2017). In fact, only 5% was used in the methylene blue staining process, while the remaining 95% was wasted (Rizqi & Purnomo, 2014).

An easy method that can be used to treat textile waste is the adsorption method. Adsorption is a surface phenomenon due to the accumulation of chemical species at the solid-liquid surface boundary (Hadayani et al., 2015). The adsorption process is one of the most frequently used separation and purification processes, where adsorption occurs through the formation of physical or chemical bonds between a porous solid medium and a mixture of liquid or gaseous multi-component fluids. Taking into account the equilibrium data and adsorption properties of both the adsorbent and the adsorbate, the adsorption isotherm model can explain the mechanism of interaction between the adsorbent and the adsorbate at a constant temperature. Therefore, understanding the modelling of equilibrium data is a very important way to predict the adsorption mechanism of various adsorption systems (Al-Ghouti & Da'ana, 2020).

An exponential kinetics model has been proposed to model the adsorption kinetics at the solid-solution interface. This new equation is compared to the pseudo-first-order (PFO) and pseudo-second-order (PSO) equations, two well-known parametric models. It has been shown that new and pseudo-quadratic models of homogeneous solid surfaces can be used based on data points (t,q) numerically generated using the statistical velocity theory equations of homogeneous surfaces (Haerifar & Azizian, 2013).

Supramolecular chemistry is an interdisciplinary scientific discipline that covers the chemical, physical, and biological properties of species that are more complex than the molecule itself. Calixarenes/ Calixresorcinarene is a macrocyclic compound composed of "n" phenol/resorcinol units bound by a methylene bridge. These macrocycles are often used for molecular recognition. Therefore, different changes can be made at both the bottom and top, allowing the construction of well-defined multi-valued buildings (Eddaif et al., 2019a). Calixresorcinarene and calixarenes are widely used as receptors for cations, anions, and even neutral molecules (Eddaif et al., 2019b). Calix[4]resorcinarene is a calixarene derivative. Calix[4]resorcinarene can be synthesized from resorcinol or its derivative compounds and various types of aldehydes, both aliphatic and aromatic aldehydes (Handayani, et al., 2016a; Handayani et al., 2022). Calix[4]resorcinarene derivatives can be used as adsorbents. Several studies using Calix[4]resorcinarene as an adsorbent used C-Cinnamal-Calix[4]resorcinarene as an adsorbent for methanil yellow, with an optimum contact time of 150 minutes and an absorption capacity of 2.1375 mg/g (Etika et al., 2018). Another application of Calix[4]resorcinarene as an adsorbent is the adsorption of remazol yellow FG using chitosan-linked P-T-Butylcalix[4]Arene by Handayani, et al. (2016b), adsorption of sodium dodecylbenzene sulfonate (DBS) by C-3,4-di-methoxyphenylcalix[4] resorcinarene triphenylphosphonium chloride by Wulandari (2018), and adsorption of reactive blue (RB-19) dye using Calix[4]arene-based adsorbent by Junejo et al. (2019).

Based on this, it is necessary to research to determine the adsorption kinetics of the derivate Calix[4]resorcinarene as an adsorbent for methylene blue dye with varying pH and contact time.

EXPERIMENTAL SECTION

Tools and Materials

The tools used include a set of reflux equipment, 250 mL beaker, dropper, 100 mL measuring cup, watch glass, stirring rod, A&E Lab Spectrophotometer, funnel, test tube, vial bottle, magnetic stirrer, hotplate, 100 measuring flask. mL, O Hauss analytical balance, oven, Buchner funnel, thermometer, pH meter, FTIR Spectrophotometer 8201 PC Shimadzu, and ¹H-NMR Jeol JNM-ECZ500R / S1 500.1599 MHz.

Pro-analyst chemicals such as vanillin, resorcinol, hydrochloric acid, sodium hydroxide, ethanol, and methylene blue were purchased from Merck.

C-4-hydroxy-3-methoxyphenylcalyx[4]resorcinene Synthesis (Handayani et al., 2020a)

HMFKR was synthesized using the method described by (Handayani et al., 2020). Vanillin (0.04 mol) was dissolved in 50 mL ethanol, then mixed with resorcinol (0.04 mol), and 1 mL hydrochloric acid was added. The solution was refluxed at 78 °C for 24 hours. The solution was washed with distilled water and filtered using a Buchner funnel. The solid is dried in the oven. The dried solid was washed with ethanol: distilled water (1:1) and dried again. The obtained solid content yields were calculated and analyzed using an FTIR Spectrophotometer 8201 PC Shimadzu, and ¹H-NMR Jeol JNM-ECZ500R / S1 500.1599 MHz.

Determination of The Maximum Wavelength and Calibration Curve

The maximum wavelength of the methylene blue solution was determined using a 4 ppm methylene blue solution using an A&E Lab spectrophotometer in the wavelength range of 500-700 nm. Then the curve is calibrated using a solution of methylene blue at 1, 5; 2; 2.5; 3 and 3.5 ppm as measured at the maximum wavelength. Calibration curves were created by plotting concentrations and absorbances. The experiment was carried out with three repetitions.

Determination of The Optimum pH

A 10 ppm methylene blue solution was interacted with 0.01 gram of CHMFKR adsorbent at pH variations of 4, 5, 6, 7, and 8 with added amounts of hydrochloric acid 0.1 M or sodium hydroxide 0.1 M. The solution is then stirred at a rate of 600 rpm for 30 minutes. After the adsorption process is complete, the solution is filtered using filter paper, and the absorbance measured using UV-Vis is а spectrophotometer. The concentration of the solution is obtained by plotting the absorbance against the calibration curve. Percent (%) adsorption can be determined using Equation 1.

% adsorption =
$$\frac{Co-Ct}{Ct} \times 100\%$$
 (1)

Co = initial concentration (mg/L) Ct = final concentration (mg/L)

Determination of The Optimum Contact Time

A 10 ppm methylene blue solution was made at optimum pH and interacted with a 0.025 gram CHMFKR adsorbent. Then the solution is stirred for a variation of 10, 20, 25, 30, and 50 minutes at a rate of 600 rpm. After the adsorption process is complete, the solution is filtered using filter paper, and the absorbance is measured using a UV-Vis spectrophotometer. The concentration of the solution is obtained by plotting the absorbance against the calibration curve. % Adsorption can be determined using Equation 1.

Determination of The Adsorption Isotherm and Kinetics Isotherm

Methylene blue solutions with various concentrations of 5, 6, 8, 10, and 11 ppm were made at optimum pH and interacted with a 0.001 gram CHMFKR adsorbent. The solution is then stirred at the optimum time at a speed of 600 rpm. After the adsorption process is complete, the solution is filtered using filter paper, and the absorbance is measured using a UV-Vis spectrophotometer at a maximum wavelength of 664 nm.

Adsorption kinetics generally correspond to the first-order pseudo-kinetic model developed by Lagergren (Ho & Mc Kay, 1999) and the second-order pseudo-kinetic model developed by Ho (2006). The first order pseudo equation can be seen in Equation 2.

$$\ln(qe - qt) = \ln qe - \frac{kt}{2,303}$$
(2)

The values of qe and k can be known by graphing the relationship between ln(qe-qt) vs t. Meanwhile, in the pseudo-second order, the values of qe and k can be determined by plotting t/qt vs t. The pseudo second-order equation can be seen in Equation 3.

$$\frac{t}{qt} = \frac{1}{qe}t + \frac{1}{kqe^2}$$
(3)

qe = concentration at equilibrium (mg/g)

qt = concentration at time t mg/g

k = adsorption rate constant (g.mg-1min-1)

t = time (minutes)

The adsorption isotherm is a function of the concentration of the solute adsorbed on the solid to the concentration of the solution. This type of isotherm is used to study adsorption mechanisms. According to Atkins (1999), the most commonly found isotherms include the Langmuir and Freudlich isotherms. The Langmuir adsorption isotherm equation can be derived theoretically by assuming the equilibrium between the adsorbed substance molecules on the surface of the adsorbent and the non-adsorbed substance molecules as follows Equation 4:

$$q = \frac{b \cdot k \cdot Ce}{1 + k \cdot Ce}$$
(4)

The constants k and b can be determined based on the Ce/q relationship curve with the Equation 5:

$$\frac{Ce}{q} = \frac{1}{qmaks}Ce + \frac{1}{k. qmaks}$$
(5)

Information:

q = mass of adsorbed adsorbate/gram of adsorbent (mg/g), Ce = equilibrium concentration of adsorbate in solution after adsorption (mg/L), k = empirical constant.

Freundlich adsorption isotherm is adsorption where the adsorption process occurs heterogeneously

on the surface, and not all adsorbent surfaces have adsorption capacity. This model shows the adsorbate layer on the surface of the adsorbent in a multilayer manner (Husin & Rosnelly, 2007). The form of the equation on the Freundlich adsorption isotherm is as follows Equation 6:

$$\log q = \frac{1}{n} \log Ce + \log k \tag{6}$$

Information:

q = amount of adsorbed substance per gram of adsorbent (mg/g), Ce = equilibrium concentration of adsorbate in the solution phase (mg/L), k = Freundlich capacity factor (mol/g), n = Freundlich intensity factor The amount of dye adsorbed, the distribution ratio and the selectivity coefficient can be determined by the following Equation 7:

$$q = (C_{o} - C_{e}) V/W$$
(7)

Information:

q = amount of adsorbed substance (mg/g)
 Co = initial concentration before adsorption (mg/L)
 Ce = final concentration after being adsorbed (mg/L)
 W = adsorbent mass (g)

V = volume of dye solution (L) (Buhani et al., 2010).

RESULTS AND DISCUSSION

C-4-hydroxy-3-methoxyphenylcalix[4] resorcinarene Synthesis

Synthesis of C-4-hydroxy-3-methoxyphenylycalix [4]resorcinol using vanillin, resorcinol, ethanol as a solvent, and hydrochloride acid as a catalyst. Hydrochloride acid is used to allow vanillin to form its carbocation. Vanillin is electrophilic, and resorcinol acts as a nucleophile (Utomo, 2014).

The results showed CHMFKR synthesis in creamcolored solid form with a yield of 85.707% and a melting point of above 380 °C. These synthesis products are characterized using FTIR and ¹H-NMR.

Figure 1 shows the FTIR spectrum from CHMFKR. Absorption at a wave number of 3402 cm⁻¹ shows the presence of an OH group. On the other hand, the absorption in the regions 1612 cm⁻¹ and 1427 cm⁻ regions indicates an aromatic ring. There is also absorption in the of 2939 cm^{-1} , 2846 cm^{-1} and 1373 cm^{-1} ranges, corresponding to the aliphatic C_{sp3} -H range. This C_{sp3} -H derived from CH₃ of methoxy and C-H methyne formed by the cyclization process of CHMFKR (Handayani et al. 2020). Vanillin-derived methoxy groups also appeared in the 1280 cm⁻¹ and 1211 cm⁻¹ regions (Fatoni et al. 2018). During absorption of vanillin-derived that time, the aldehyde groups, which typically occurs I n the 2850 cm⁻¹ and 2750 cm⁻¹ regions is not appear. Similarly, uptake of carbonyl groups ranging from 2850 cm⁻¹ to 2750 cm⁻¹. This indicates that the aldehyde group has reacted with resorcinol to form a methylene bridge at the CHMFKR junction.







Figure 2. The ¹H-NMR spectrum of CHMFKR



Figure 3. Calibration curve solution of Methylene blue

Figure 2 shows the ¹H-NMR CHMFKR spectrum. Seven signals are displayed based on Figure 2. This signal shows that there are 7 protons from CHMFKR in different environments. Signals in the range of δ 1.3 ppm are the H₂O signal as well as H₂O soluble in the DMSO. The signals from methoxy derived from vanillin appear at the range of δ 3.5-3.8 ppm because these protons are far from the benzene ring experience the anisotropic effect (Wade, 2006). While in the region of δ 4.4 ppm, there is a signal from the methine bridge with a singlet peak. This methine bridge is one of the important groups showing the formation of CHMFKR compounds. Absorption at δ 6.1 ppm and δ 6.8 ppm is the absorption from the aromatic rings. On the other hand, the hydroxyl group appeared in the range of δ 8.5 ppm.

Calibration Curves

The calibration curve is a curve that shows the relationship between the concentration measured at the maximum wavelength and the absorbance. Methylene blue has a maximum wavelength 664 nm, On the other hand, the concentration of the methylene blue solution used is 1.5-3.5 ppm. Figure 3 shows the calibration curve of the methylene blue solution.

From Figure 3 we can see that the regression equation is y = 0.225x + 0.035 and R^2 is 0.994. The correlation coefficient (R²) value satisfies the requirements of 0.9 <r<1 so that can be used as a standard curve in measurement. The value of the correlation coefficient being close to 1 indicates a relationship between absorbance and concentration that has a linear correlation where all the points lie on one straight line. The regression equation is used to determine the concentration of the methylene blue solution before and after adsorption so that later the optimum conditions, adsorption kinetics, and adsorption isotherms can be known.

Optimum pH

The following are the results of the analysis of the methylene blue solution at various pH. The optimum

pH value is the pH condition at which the adsorbent concentration is maximized. Determining the optimum pH is important as it can affect the chemical equilibrium of the adsorbate and adsorbent. The pH value affects the charge on the surface of the absorbent, the degree of ionization and the species that can be absorbed during the adsorption process (Hasmalina et al., 2016). The variations of pH from the methylene blue solution used were 4, 5, 6, 7 and 8. The analysis results of the analysis of the methylene blue solution at various pH values are shown in **Figure 4**.

From Figure 4, we can see that the % adsorption of the methylene blue solution by the adsorbent CHMFKR increase from pH 4 to pH 7 and then decreased to pH 8. The maximum % adsorption was at pH 7, and the number of adsorptions was 98.91%. Methylene blue belongs to the group of cationic dyes. Low or acidic pH is considered saturated with excess H+ ions. This reduces the positive charge on the surface of the adsorbent and promotes the formation of hydroxyl radicals from the adsorbent (Sapawe et al., 2013). Whereas at high or alkaline pH values, there is OH that promotes OH radicals. The CHMFKR adsorbent adsorbed methylene blue at pH 7 due to the change added to the adsorbent surface. This increased the electrostatic interaction between the CHMFKR adsorbent and methylene blue (Wahyu & Dini, 2014). On the other hand, if the pH is too high, many OH ions will be present, creating a repulsive force between the hydroxy and methoxy groups of CHMFKR and the OH - ions (Atikah, 2017).

Optimum Contact Time

Contact time is an important parameter that determines the time it takes for the adsorbent and adsorbate to interact in the adsorption process. The time variations used in the adsorbing of the methylene blue solution with the CHMFKR adsorbent was 10, 20, 30, 40 and 50 minutes. **Figure 5** is a graph of % adsorption of methylene blue solution using CHMFKR at variations of time.



Figure 4. Graph % adsorption solution methylene blue using adsorbent CHMFKR at various pH



Figure 5. Graph of the adsorption of methylene blue using CHMFKR at variations of time

Figure 5 shows that the longer the interaction between the adsorbent and the adsorbate the higher the adsorption %. However, when kinetic equilibrium conditions are reached, the interaction time is 40 minutes and the adsorbent tends to remove adsorbates, which reduces adsorption (Hasmalina et al., 2016). This indicates that the CHMFKR adsorbent is saturated.

Adsorption Kinetics

The adsorption rate in this study was determined based on Equation 2 and 5. The reaction sequence and the rate of a chemical reaction are the rates at which the reaction occurs. The resulting adsorption rate data can be used to determine the dynamics of the adsorption process based on the adsorption order (Handayani et al., 2020a).

Methylene blue adsorption kinetics using the adsorbent CHMFKR determined based on a pseudo-first order and the pseudo-second order with 10, 20, 30, 40, and 50 minutes contact time variations. First-order pseudo kinetics are obtained by creating a curve between ln (qe-qt) vs t. Below is the curve of the relationship between ln (qe - qt) vs t in first order pseudo kinetics.

Based on **Figure 6**, we can obtain the regression equation of the pseudo first order adsorption kinetics: y = -0068x-0.269 and $R^2 = 0.896$. Based on the linear equation, the slope value is -0.068 and the intercept value is 0.896. The value of k_1 is determined by the expression $b = \frac{k_1}{2,303}$ and the value of q_1 is determined by the expression $\ln q_1 = a$. On the other hand, the second-order pseudo adsorption kinetics was obtained by plotting t/qt vs t. Below is the t/qt vs t relationship curve in second-order pseudo adsorption kinetics.

Based on the **Figure 7**, regression adsorption kinetics may be known. The pseudo second order is y = 0.282x + 0.110 and R² is 0.999. Based on the regression equation, we can see that the slope value is 0.282 and the intercept is 0.110. The value of k₂ can be determined by the expression $b = \frac{1}{q^2}$ and the value of q₂ can be determined by the expression $a = \frac{1}{k_2q^2}$. Based on the results of linear regression (R²), the rate constant (k) reaction, q value of the adsorption kinetics, pseudo first order and pseudo second order as shown in **Table 1**.



Figure 6. First-order pseudo adsorption kinetics



Table 1. Comparison of the instantaneous adsorption value of methylene blue adsorption using CHMFKR

I	1	, 1 0
Adsorption Kinetics	First-order pseudo	Second order pseudo
R^2	0.8965	0.9999
К	0.1575	0.7217
Q	0.7636	3.5410
0.015 0.01 0.005 0	y = 0.0087x + 0.0011 $R^2 = 0.9818$	
0	0.5 1	1.5

Figure 8. Langmuir's adsorption isotherm

Ce

The order in which they are used can be determined by examining the value of R2. When the value of R2 was close to 1, the adsorption pseudo second-order kinetics rate was 0.9999. It is amplified by the value of the second order reaction rate constant (k) of the two orders. The value of k in the pseudo second order is greater than the value of k in the pseudo first order. Therefore, the process of adsorbing

a methylene blue solution using the CHMFKR adsorbent follows the second-order pseudo equation.

Adsorption Isotherm

The adsorption isotherms can provide information about the adsorption mechanism that occurs. This adsorption isotherm can be determined based on the Freundlich isotherm equation and The Langmuir isotherm can be determined by plotting Ce/qe vs Ce. Where Ce is the equilibrium concentration of adsorbate (mg/L) and qe is the amount of adsorbate (mg/g). Equilibrium data were described using the Langmuir and Freundlich models to determine thermodynamic parameters, Gibbs free energy ΔG° , enthalpy change ΔH° , and entropy ΔS° . Negative values of ΔH indicate that the adsorption is exothermic. Positive values of ΔG° at all temperatures investigated indicate that adsorption is a spontaneous process (Alsenani, 2014). Below is the curve of the relationship between Ce/qe vs Ce in the Langmuir isotherm.

Based on the Figure 8, we can see the regression equation of Langmuir adsorption isotherm of is 0.008x + 0.001 and R^2 is 0.981. Based on the regression equation, the slope value (b) is 0.008 and the intercept value (a) is 0.001, so that the qmax value in equation $b = \frac{1}{q \text{ maks}}$ and the k 1 value (adsorption rate constant) with the equation $a = \frac{1}{k1 \times q \text{ maks}}$. So that the max q value is 114.94 mg/g and the k 1 value = 35.30 mol / g. The results of the adsorption of methylene blue using CHMFKR produce a higher max value when compared to some adsorbents. Research conducted by Baunsele and Missa (2020), using Fe₂O₃ impregnated corncob activated carbon adsorbent is available Langmuir isotherm with Langmuir constant and adsorption capacity/the maximum (gm) obtained were 0.49 and 15.38 mg/L, respectively. The research using coconut coir adsorbent showed that the adsorption of methylene blue using coconut coir adsorbent followed the model pseudo second order reaction kinetics with adsorption constant rate of 0.01 gram mg⁻¹ minute⁻¹ (Ristianingsih et al., 2020). This indicates that the absorption capacity of methylene blue by CHMFKR is greater.

The Freundlich isotherm can be determined by plotting log Ce vs log q, where Ce is the equilibrium concentration of adsorbate (mg/L) and qe is the amount of adsorbate adsorb (mg/g). Below is the graph showing the relationship between log Ce vs log q in the Freundlich isotherm.

Based on **Figure 9**, we can get the regression equation where y = 3.337x - 6.795 and R^2 is 0.911. Based on the regression equation, we can see that the gradient (b) value is 3.337 and the intercept (a) is 6.795. Therefore, the value of n (Freundlich's intensity coefficient) is given by the expression $b = \frac{1}{n}$ and k_2 with the equation log $k_2 = a$. This gives the values n =0.2996 g / L and $k_2 = 19.536$ mol / g is obtained. **Table 2** shows a comparison of the Langmuir isotherm and the Freundlich isotherm values.

Table 2 shows that the R² values for the Langmuir and Freundlich isotherms are close to one, with the R² Langmuir being greater than the R² Freundlich. This indicates that the adsorption of methylene blue by the adsorbent CHMFKR is performed according to Langmuir isotherms. Negative energy values of -87458.29 J/mol, on the other hand, indicate that the reaction process is spontaneous.



Figure 9. Freudlich's adsorption isotherm

Table 2. Comparison of adsorption isotherms on adsorption of methylene blue using CHMFKR

Parameter	lsoth	nerm
	Langmuir	Freundlich
Intercept	0.0011	- 6.7958
Slope	0.0087	3.337
R ²	0.9818	0.9114
E	- 87458.29 J/mol	- 7363.985 J/mol

CONCLUSIONS

The optimum conditions for adsorption of methylene blue using the adsorbent C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene were obtained at pH 7 with a contact time of 40 minutes. The adsorption kinetics follow pseudo-second order with an adsorption rate of 0.7217 \pm 0.4 g/mg.s. The adsorption isotherm follows the Langmuir equation, and the maximum adsorption amount is 114.94 \pm 2.04 mg/g.

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