



# Application of Adsorption Thermodynamics and Column Studies for $Pb^{2+}$ , $Cd^{2+}$ and $Mn^{2+}$ Ions Removal in Multicomponents Model Solution Using Low-Cost Bentonite Clay Adsorbent

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**Abstract:** The presence of heavy metal contaminants in wastewater effluents has become a great threat to living creatures and the environment. In this study, the application of thermodynamics and column studies for  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Mn^{2+}$  metal ions removal in multicomponent aqueous solution using low-cost bentonite clay was investigated. Evaluation of enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ) and Gibbs free energy ( $\Delta G^\circ$ ) revealed that heavy metals adsorption was endothermic and spontaneous as temperature increased from 30 to 65 °C. The column performance was determined at 0.05m adsorbent bed depth, 0.023 and 0.04 mL/s flow rates. The influent concentration was 10 and 50 ppm while the breakthrough time was between 0.83 and 8 hr. The maximum uptake of metal ions was 2.2 mg/g for  $Pb(II)$ ,  $Mn(II)$  was 0.4 mg/g and 1.7 mg/g for  $Cd(II)$ . The result showed the potential of bentonite clay as a candidate for toxic metal ions adsorption in wastewater.

**Keywords:** Uptake, toxic metals, clay, column, bentonite

## 1. INTRODUCTION

The occurrences of toxic heavy metals in contaminated water creates serious danger to humans and the environment. Bentonite clay is available in most part of the world at low cost and the health risk associated with heavy metal ions cannot be over emphasised. The discharge of these poisonous metals ions into the environment has been in the increased due to technological advancement and industrial activities. Industrial processes such as metal plating, smelting, battery, fertilizer, mining, paint and pigments, are considered as major sources of toxic metals [1].

Metal ions, like manganese, arsenic, lead, chromium and cadmium, are defined by their high atomic weight. The types and exposure pathways that a heavy metal is exposed to determine its toxicity.  $Cd(II)$  is extremely toxic, causing permanent damage to the brain, kidneys, and liver.  $Mn(II)$  exposure could lead to neurological abnormalities and brain damage, while  $Pb(II)$  exposure can cause hypertension, unfavorable pregnancy outcomes, cardiovascular diseases, reduced renal function, and infertility. According to the World Health Organization, the permissible levels for manganese (II), lead (II) and cadmium in drinking water are 0.4, 0.01 and 0.003 mg/L, respectively. [2].

Instead of single-metal pollution, the majority of the pollution of heavy metals in wastewater and contaminated sites is multi-metal composite pollution. The result influences the transit and fate of these heavy metal ions as well as human and animal toxicity. [3].

There are various wastewater treatment techniques that have been introduced to control water pollution and amongst which are chemical precipitation, electro-dialysis, reverse osmosis, membrane filtration, ion exchange, irradiation, precipitation, ozonation, and adsorption. The adsorption procedure has gotten significant consideration in light of its convenience, ease of operation and simplicity of design [4].

The process of adsorption is used for the treatment of wastewater contaminated with heavy metals, using a different adsorbent. These include low-cost materials such as peat, limestones, and rice husk ash, as well as activated carbon, zeolites, activated alumina, and clay minerals. Activated carbon is the most commonly used adsorbent because it is an amorphous, microcrystalline, non-graphic solid with unique properties such as good thermal and mechanical stability. It has a high surface-to-volume ratio, is porous and extremely pure [5]. However, there are many drawbacks to using activated carbon as an adsorbent, including its high price, the difficulty, and the cost of renewal. Clays are therefore

regarded as inexpensive adsorbents. Clays are a viable substitute for activated carbon for the adsorption of heavy metals since they are accessible, affordable, and have adsorption properties. To remove contaminants from wastewater, a variety of natural clays are employed. They consist of zeolite, bentonite, and kaolin [6].

Potential adsorbents for metal ions include the clays kaolin and bentonite. This is as a result of its numerous financial benefits as well as inherent qualities like accessibility, affordability, and superior surface and textural qualities. They also provide a more affordable option for wastewater treatment than the traditional methods because they are physically and chemically durable in tough conditions. A layered phyllosilicate, bentonite clay serves as a scavenger for pollutants. It is widely accessible everywhere and has a porous structure that may be divided into macro, meso, and micropores. The presence of micro and mesopores determines the uptake of metal ions. [7].

This research focused on the application of low-cost clay adsorbent for the removal of manganese(II), lead(II) and cadmium(II) multi-components form from wastewater. The adsorption process was monitored through thermodynamics and continuous column studies. These metal ions are poisonous and their direct exposure may affect human health as well as aquatic and livestock. The choice for Dijah Monkin bentonite is because no work has been reported on its application as an adsorbent for heavy metal removal. In addition, the clay is readily available and inexpensive.

## 2. MATERIALS AND METHODS

### 2.1 Sample Collection

The clay sample was collected from Dijah-Monkin, Zing Local Government Area, Taraba State, Nigeria on 8°00'N latitude and 10°30' E longitude. The location of the sample collection site is shown Figure 1.

Crushed raw clay was placed in water and let to soak for 24 hours. The siliceous quartz impurities were permitted to sink to the bottom of the clay-water combination after it had been shaken continuously for 30 minutes, while the colloidal clay solution and suspended particles floated to the top. Colloidal clay and quartz sediments were gathered and sorted. The clay solution was sieved through a 230 mesh (63  $\mu$ m sieve opening) Tyler sieve to further remove coarse contaminants and organic particles. The clay slurry was put in a filter cloth and heavily squeezed to extract the water. After being sun dried, the finished cake was oven dried at 110°C to a constant weight. A 125  $\mu$ m mesh was used for sieving and grinding the dry clay [8]. An analysis of the textural, chemical, and mineralogical characteristics of the beneficiated clay was conducted. Additionally, research on column adsorption and thermodynamics were conducted using clay as an adsorbent.

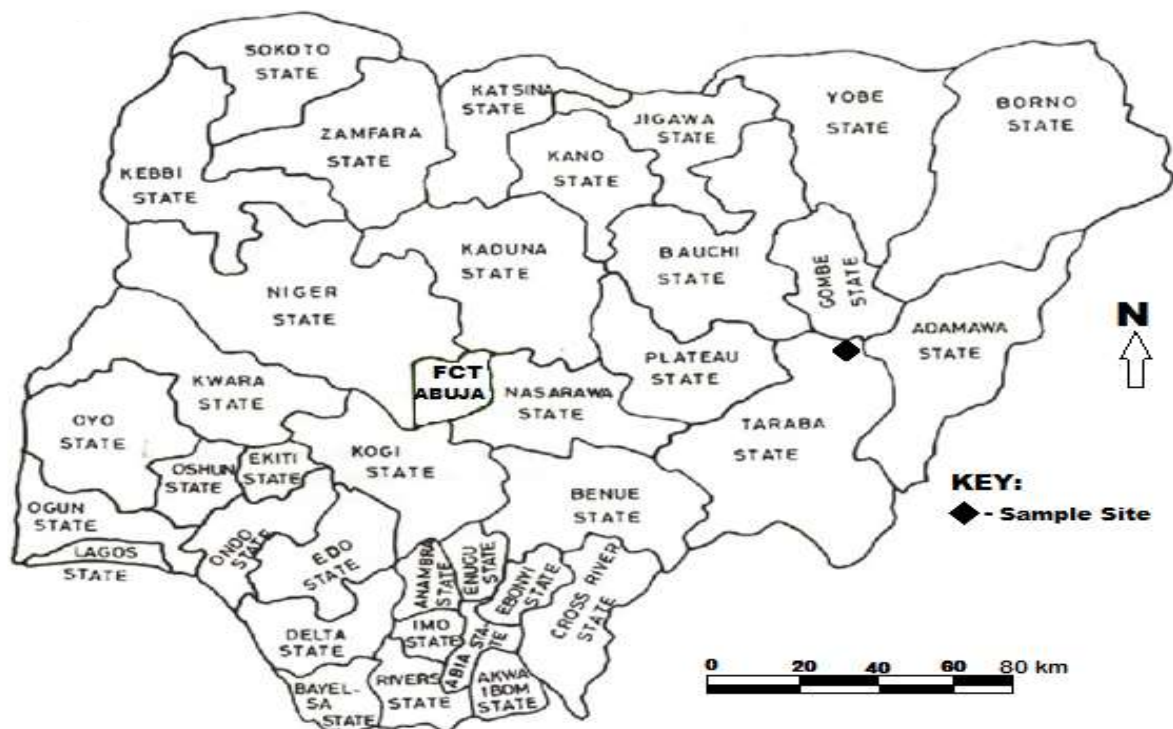


Figure 1: Location of the sample site (Dijah-Monkin) on Nigeria map

### 2.2 Bentonite Characterization

XRF was used to do a chemical analysis of the bentonite clay, and a Surfer Thermo Scientific device based on nitrogen adsorption and desorption isotherms at a temperature of -196°C in liquid nitrogen was used to determine the textural

qualities. The ammonium acetate method was used to calculate the bentonite's cation exchange capacity (CEC) [9]. A pH meter was used to evaluate the clay's pH, and an X-ray diffraction (XRD) device was used to determine the clay's mineralogical makeup.

### 2.3 Adsorption Studies

- 1) **Stock solution and analytical method:** All chemicals used are of high purity.  $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{MnO}_2$ —representing lead(II), cadmium(II), and manganese(II), respectively—were used to create a model multicomponent metal ion solution. During the preparation of the stock solution, the mass of each metal salt required was calculated and dissolved in equal volume of distilled water. The model solution of each metal (lead, cadmium and manganese ions) was then mixed together in equal volume. In the multicomponent solution, the concentration of each of the cations in the mixture was the same [10, 11]. The stock solution was diluted with distilled water to create the desired working solutions. The residual metal ion concentrations were measured using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).
- 2) **Thermodynamics studies:** Thermodynamics experiments performed in a batch mode were carried out by varying the adsorption temperature between 30 and 65°C. Fifty milligrams of bentonite were added to 50 mL of multi-metal solution of known concentration in 250 mL beakers. The mixtures were shaken in a water bath at 110 rpm for 72 h after which the residual metal ions concentrations were measured.
- 3) **Column adsorption studies:** Continuous flow bench-scale adsorption was conducted using a glass column of length and diameter 0.35 m and 0.006 m respectively. Figure 2 displays a schematic diagram of the experimental set-up employed for the column investigation. According to Renu et al. [12], the trials were carried out by altering the influent concentration and flow rate. The column was packed with 1.0 g of clay placed in the middle of the glass column. The bed depth measured as 0.05 m was supported at top and bottom with a layer of cotton wool. The feed prepared at 10 and 50 ppm were pumped upward using a peristaltic pump at desired flow rates of 0.023 and 0.04 mL/s. Metal ions concentrations in the treated feed collected at the outlet of the column were determined using ICP-OES.

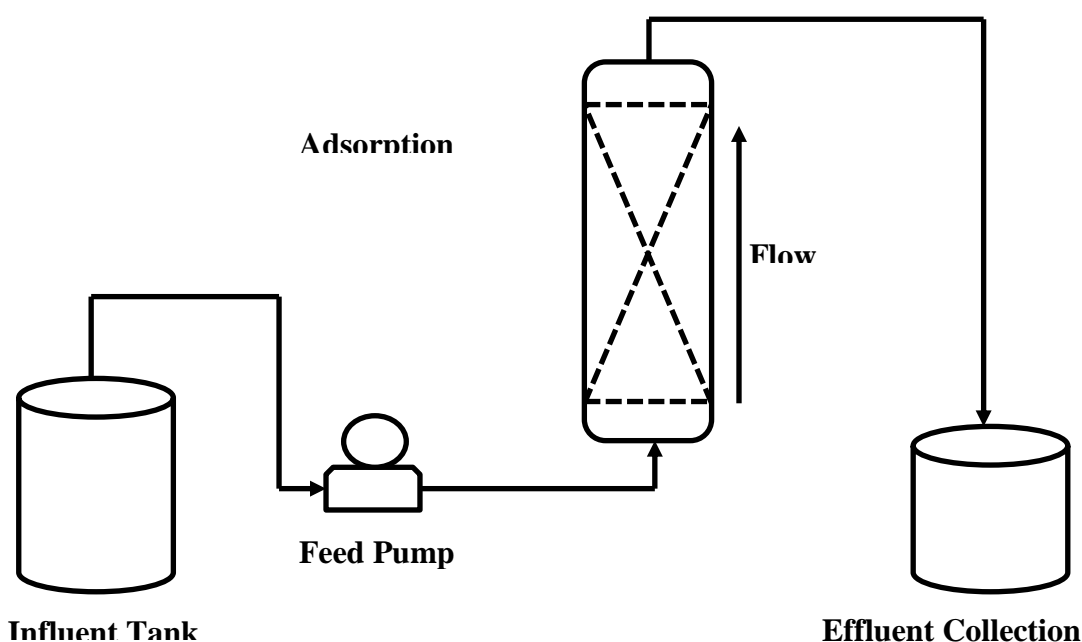


Figure 2: Experimental set-up for fixed-bed continuous flow operation.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Bentonite Clay Characterization

The physicochemical properties of the bentonite clay sample are presented in Table 1. The XRF analysis revealed the presence of oxides of Si and Al as major components in the clay. Other metal oxides appearing in minor quantity were Fe, K, Ca and Ti. The abundance of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the clay showed the basic oxides of smectite clay group. The presence of  $\text{Ca}^{2+}$  and  $\text{K}^+$  cations confirmed that the clay can be designated as polycationic bentonite [13,14].

The bentonite pH value of 6.6 (Table 1) depicts that the bentonite is acidic. Specific surface area of bentonite was 24.0  $\text{m}^2/\text{g}$ , 0.07  $\text{cm}^3/\text{g}$  total pore volume and 77.5% mesoporosity, indicates that the clay is porous. Similarly, the clay CEC determined was 48.0  $\text{mEq}/100 \text{ g}$  and this value is within the range for calcium montmorillonite, 40 to 70  $\text{mEq}/100 \text{ g}$  [15].

The diffractogram of the sample is presented in Figure 3. The major minerals revealed by XRD were montmorillonite (M), and quartz (Q). Kaolinite, muscovite and illite were also observed in the clay. The presence of montmorillonite suggests that the clay is bentonitic [16].

Table 1: Physico-chemical properties of bentonite clay.

Chemical composition (%)						Textural characteristics				Cation Exchange Capacity (mEq/100 g)	pH
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	TiO <sub>2</sub>	Specific area (m <sup>2</sup> /g)	Micropore volume (cm <sup>3</sup> /g)	Total volume (cm <sup>3</sup> /g)	Mesopore content (%)		
62.3	21.0	8.20	1.17	4.59	1.22	24.0	0.06	0.07	77.5	48.0	6.6

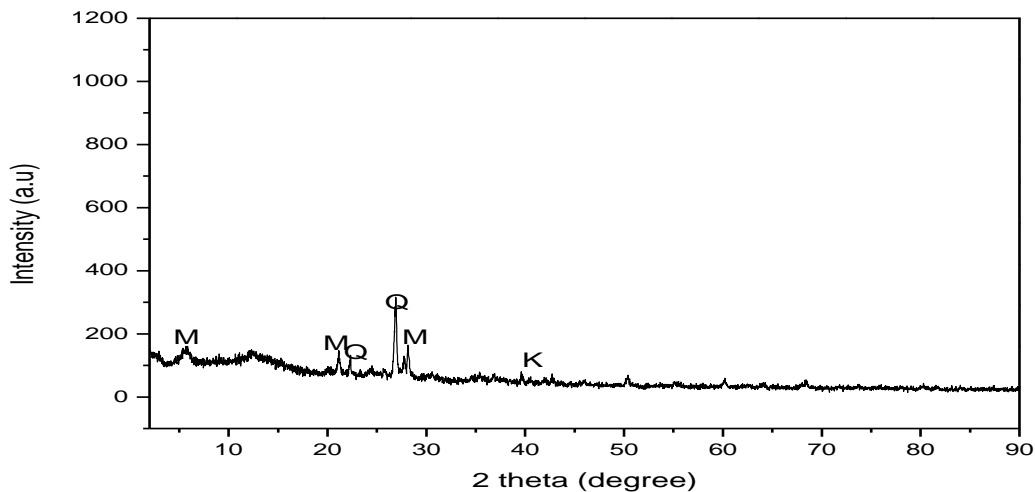


Figure 3: XRD pattern of bentonite

### 3.2 Thermodynamics Studies

Temperature effect on heavy metals adsorption in multicomponent solution was investigated at 30, 45, 55 and 65°C. The thermodynamics parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) were determined using Equation 1-3.

$$k_c = \frac{q_e}{C_e} \quad (1)$$

$$\Delta G^\circ = -RT \ln k_c \quad (2)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

where  $k_c$  is equilibrium constant,  $q_e$  and  $C_e$  are equilibrium and solid-phase concentrations at equilibrium respectively.  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are Gibbs free energy, enthalpy and entropy respectively. R is gas constant and T, temperature. Thermodynamics parameters calculated are presented in Table 2.

The heavy metals adsorption slightly increased as the temperature increased from 30 to 65 °C. This could be due to increasing random movement of the metallic ions toward the clay surface with the rise in temperature. It implies that preferential adsorption occurred at high temperature. Accordingly, the increase in metal ions adsorption with increasing temperature shows that the metal uptake is endothermic and appeared to be favoured at higher temperature. Similarly, positive values of  $\Delta S^\circ$  depicts the randomness at solid/solution interface during metal ions uptake.  $\Delta H^\circ$  and  $\Delta S^\circ$  values for the metal's adsorption ranged from 13.00 to 54.00 kJ/mol and 0.007 to 0.180 kJ/mol respectively. It can also be observed that,  $\Delta H^\circ$  for individual metals adsorption onto the bentonite clay decreased with increasing concentration (Table 2).

$\Delta G^\circ$  decreases with increased in temperature and also increased with increasing concentration. Decrease in  $\Delta G^\circ$  with increasing temperature suggests that the spontaneity of metal ions uptake increases when temperature is increased. Positive and higher  $\Delta G^\circ$  values indicate that adsorption is less spontaneous. The adsorption of lead (II) in multi metals solution is highly spontaneous (negative  $\Delta G^\circ$  value) at lower concentration (10 ppm) as presented in Table 2. The adsorption of these metal ions at all concentrations and temperatures studied showed same increasing order of  $\Delta G^\circ$ : Mn (II) > Cd (II) > Pb (II) This shows that the adsorption of Pb (II) is more feasible and spontaneous than Cd (II) and Mn (II). This finding is similar to the work performed by [16].

Table 2: Thermodynamics properties for multicomponent heavy metals adsorption

Metals	$C_o$ (ppm)	Temperature (°C)	$\ln k_c$	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol K)
Pb(II)	10	30	-0.17	0.44	54.08	0.180
		45	0.88	-2.33		
		55	1.51	-4.11		
		65	2.02	-5.67		
Pb(II)	30	30	-1.59	3.99	26.85	0.075
		45	-1.38	3.66		
		55	-0.90	2.46		
		65	-0.49	1.38		
Pb(II)	50	30	-2.01	5.07	17.83	0.042
		45	-1.84	4.86		
		55	-1.52	4.14		
		65	-1.30	3.65		
Cd(II)	10	30	-2.62	6.60	14.16	0.024
		45	-2.53	6.70		
		55	-2.27	6.20		
		65	-2.04	5.75		
Cd(II)	30	30	-4.25	10.70	13.00	0.007
		45	-4.09	10.81		
		55	-3.91	10.67		
		65	-3.71	10.42		
Cd(II)	50	30	-5.87	14.79	51.78	0.120
		45	-4.56	12.06		
		55	-4.18	11.41		
		65	-3.75	10.54		
Mn(II)	10	30	-2.71	6.84	14.85	0.026
		45	-2.62	6.92		
		55	-2.29	6.25		
		65	-2.13	5.98		
Mn(II)	30	30	-4.54	11.44	26.14	0.049
		45	-4.05	10.71		
		55	-3.67	10.01		
		65	-3.51	9.87		
Mn(II)	50	30	-4.80	12.09	26.78	0.049
		45	-4.25	11.23		
		55	-4.07	11.11		
		65	-3.67	10.31		

### 3.3 Column Studies

The metal ion uptake in the continuous column,  $q_T$  (mg/g) can be evaluated using Equation 4 and 5,

$$q_T = \frac{FA}{1000} = \frac{F}{1000} \int_{t=0}^{t=T} C_s dt \quad (4)$$

$$C_s = C_o - C \quad (5)$$

where  $t_T$  and  $F$  are time of flow and wastewater flow rate into the column respectively.  $A$  is the breakthrough Area while  $C_s$  concentration of solute at exhaust point (ppm).  $C_o$  and  $C$  are initial concentration and effluent concentration at any time  $t$  (ppm) respectively.

Calculated breakthrough time,  $t_b$  at  $C/C_o = 0.1$  for the column study with 10 and 50 ppm solutions at 0.023 and 0.04 l/s flow rates were summarized in Table 3. The breakthrough curves of S-shaped were obtained and this shows that adsorption was favourable. It was also observed that the breakthrough increases with increasing time and stabilized at 0.9. The breakthrough times and the exhaust times for all metal ions adsorption corresponds to  $C/C_o = 0.1$  and 0.9, respectively [17, 18].

Similar to this, Table 3 shows that higher metal ions were taken up at higher concentrations and lower flow rates. This may be because there are more metal ions present and the adsorbent and solution have been in touch with each other for longer. Better metal uptake was seen in the developed column at a lower rate of inlet solution flow (0.023 mL/s).. The adsorption of Pb (II), Cd (II) and Mn (II) in multi-components metal solution onto the bentonite clay might have been

prompted by the functional groups through ion-exchange occurring between the active sites of the bentonite clay and the heavy metal ions ( $M^{2+}$ ) in solution [10, 19, 20].

Table 3: Column parameters for Pb (II), Cd (II) and Mn (II) Ions adsorption at 30°C

Heavy metal	Initial metal ion concentration, $C_o$ (ppm)	Rate of flow, $F$ (mL/s)	Breakthrough time, $t_b$ (hr)	Metal ion uptake	
				$q$ (mg/g)	$q$ (mmol/g)
Pb(II)	10	0.023	7.5	1.83	0.0088
	10	0.04	4.17	1.53	0.0074
	50	0.023	3.33	2.22	0.0107
	50	0.04	-	1.77	0.0085
Cd(II)	10	0.023	8.0	1.58	0.0141
	10	0.04	5.33	1.44	0.0128
	50	0.023	5.0	1.71	0.0153
	50	0.04	2.5	1.64	0.0146
Mn(II)	10	0.023	5.0	0.28	0.0051
	10	0.04	3.33	0.10	0.0018
	50	0.023	2.5	0.37	0.0067
	50	0.04	2.0	0.35	0.0064

#### 4. CONCLUSIONS

Thermodynamic and column studies of bentonite clay adsorbent for Cd(II), Mn(II) and (Pb(II) uptake in a multi-component model solution was conducted. It was observed that heavy metal adsorption depends on the influent concentration and rate of flow. It was observed that the breakthrough time and metal ions adsorption decreased with increasing rate of flow and at lower inlet concentration. Lead (II) ion adsorption was favoured in all the concentrations by the bentonite clay. The metal ions adsorption was endothermic and more spontaneous at high temperature. Similarly, better uptake was observed at lower rate of flow and higher concentration. The adsorption of the metal ions by bentonite adsorbent was in the order; Pb (II)>Cd (II)>Mn (II). This finding revealed that the bentonite adsorbent was a promising candidate for treatment of wastewater loaded with heavy metals.

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