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PHENOL ADSORPTION IN WATER BY GRANULAR ACTIVATED CARBON FROM COCONUT SHELL

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ABSTRACT

Phenol adsorption by granular activated carbon from coconut shell was studied in batch experiments under various initial phenol concentrations. Adsorption equilibrium was reached within 4 hours. The characteristics of the phenol adsorption process onto granular activated carbon from coconut shell were studied by adsorption isotherm modeling, analysis that uses fluorescence spectroscopy, in addition to measuring nanoparticle size and volume distribution by a Zetasizer Nano. The Langmuir isotherm model best fits the phenol adsorption onto granular activated carbon from coconut shell, and the maximum adsorption capacities for unsterilized and sterilized types were found to be 17.54 mg/g and 13.70 mg/g, respectively. The excitation-emission matrix results showed that the humic-like substance's peaks almost completely disappear post-adsorption. It was also found that the nanoparticle size distribution shifted from ranges of 0.72–1.74 nm in raw water to 45.66–726.73 nm and 57.08–1068.47 nm post-adsorption in unsterilized and sterilized water samples, respectively, suggesting that phenol adsorption had occurred. This study shows that low-cost coconut shell-based activated carbon demonstrated good removal capability and hence can be used as a new adsorbent material on large scale.

Keywords: Adsorption; Coconut shell; EEMs; Nanoparticle; Phenol

1. INTRODUCTION

Phenolic compounds have high toxic materials in various aquatic environments. Phenols are widely used as raw materials in the manufacturing of a variety of industrial products, such as coal processing, paint, pesticides, and pharmaceuticals (Ocampo-Perez et al., 2011). They are considered one of the priority pollutants in wastewater because they are harmful to organisms, even at low concentrations (Petrie et al., 2015; Sophia & Lima, 2018). Because of phenolic compounds' toxicities, the United States Environmental Protection Agency (US EPA) and the European Union have targeted phenolic compounds as important micro pollutants in water environments.

The limit of phenol is 0.1 mg l⁻¹ in the effluent of wastewater treatment plants to defend against negative human health effects (Balasubramanian & Venkatesan, 2012). The limit of phenol concentration in drinking water is 0.001 mg l⁻¹ as regulated by the World Health Organization

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(WHO) (Rivera-Utrilla et al., 2013).

In Indonesia, especially in Padang city, water bodies also have been polluted by phenols. Research conducted by the Regional Environmental Impact Management Agency in 2011 showed that phenol levels in Kuranji River were 1 mg l^{-1} , exceeding the 0.001 ppm of phenol limit. In 2013, the phenol level had reached 2.74 mg l^{-1} , an increase of 63.5% from the previous investigation (Desmiarti et al., 2016). Therefore, the removal of phenols is a major necessity for water environmental safety.

Adsorption using activated carbon is a well-established process to remove organic pollutants, such as phenol, from water and wastewater due to its excellent adsorption abilities. Granular activated carbons are generally used due to their abilities to adsorb both organic and inorganic contaminants, especially phenolic compounds (Kowalczyk et al., 2018), nickel ions (Olufemi & Eniodunmo, 2018), lanthanide ions (Kusrini et al., 2018), and adsorbed natural gas (Alhamid et al., 2015). Activated carbon has a large surface area, micropore structure, and high adsorption capacity, rendering it an excellent adsorbent.

The adsorption of phenolic compounds from aquatic environments on activated carbons has been studied for a long period. Other adsorbents have been used, such as organoclays (Luo et al., 2015) and organomontmorillonites (Wang et al., 2017). However, some of these adsorbents could not remove all the phenol from water samples. Activated carbon, which is both lower-cost and more locally available, should be compared with other adsorbents to determine its relative performance.

In this study, granular activated carbon from coconut shell is used as an adsorbent to eliminate phenols from aqueous solutions that occur in the western coastal side of Padang city, Indonesia. Activated carbon was expected to be a cost-effective adsorbent. The objective of this study was to investigate the feasibility of activated carbon prepared from the coconut shell, an agricultural waste material, for the removal of phenol from aqueous solutions. Three types of commercial granular activated carbon were used as comparisons in this study.

2. METHODS

2.1. Materials

Water was collected from the Kuranji River in the center of Padang city, Indonesia. The river water was filtered by a $5\text{-}\mu\text{m}$ sieve with $1\text{-}\mu\text{m}$ pore size to eliminate large organic substances. Two kinds of water samples were prepared: sterilized (S type) and unsterilized (US type). The sterilization process was done with an autoclave at 126°C for 20 minutes.

The analytical-grade phenol solution used in this study was offered by Merck Co. The coconut shell used as the adsorbent was collected from the local market (GAC-1). As comparison, three types of granular activated carbon commercial were used as comparison (GAC-2, GAC-3, and GAC-4).

2.2. Adsorbent Preparation

Prior to use, the coconut shell was crushed and sieved using a 10-mesh screener. The sieved coconut shell was soaked in 5% w/w Na_2CO_3 (Sodium Carbonate). Thus, the carbon source was rapidly heated to 700°C for 4 hours and then rinsed thoroughly. Finally, the washed granular activated carbon was dried in an oven at 105°C for 24 hours and kept in a desiccator until used.

2.3. Adsorption Experiments

Batch adsorption experiments were conducted in a 500-mL glass beaker with different initial phenol concentrations (50, 150, and 200 ppm) added to the water sample. Prior to use, the water sample from the Kuranji River was filtered through a $5\text{-}\mu\text{m}$ sieve with $1\text{-}\mu\text{m}$ pore size and sterilized in an autoclave for 20 minutes. A mass of 0.5 g of activated carbon was added to 200

mL of phenol and water sample mixtures and agitated at constant speed. After equilibrium (about 4 hours), the mixing was stopped.

2.4. Analytical Measurements

The equilibrium phenol concentration was quantified using the T70 UV/VIS Spectrophotometer (Oasis Scientific, Inc). The phenol uptake loading capacity (mg/g) of granular activated carbon from coconut shell for each concentration of phenol at equilibrium was calculated using Equation 1:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

C_0 is the initial phenol concentration (mg l^{-1}), C_e is the equilibrium phenol concentration in solution (mg l^{-1}), V is the volume of the solution (liters), and m is the mass of the adsorbent in mg. The adsorption isotherm data were obtained by allowing the adsorbent to remain in contact with the solution for 4 hours to reach the equilibrium state.

The Freundlich and Langmuir isotherm models were created to analyze the adsorption equilibrium. It can be calculated using the linearized form of commonly known adsorption isotherms in the Freundlich and Langmuir equations, as shown in Table 1.

Table 1 Langmuir and Freundlich isotherm models

Isotherm	Equation	Linear Form	Plot
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$\frac{1}{q_e} = \frac{1}{b q_m C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ vs. $\ln C_e$

C_e is the equilibrium concentration of phenol in the bulk solution (mg L^{-1}), q_e is the amount of phenol adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), b is the Langmuir constant associated with the free energy of adsorption (L mg^{-1}), K_F and n are the Freundlich constants according to the capacity and intensity of adsorption, respectively.

Meanwhile, the phenol removal was characterized by three-dimensional fluorescence excitation-emission matrix (EEMs) spectroscopy. EEM spectroscopy allows characterizing the type of dissolved organic matter (DOM) in the water and phenolic compounds, and it can be easily interpreted (Bridgeman et al., 2011). Several EEMs of water samples were acquired using an RF-5300 spectrofluorometer (Shimadzu Corporation) to analyze the presence of particular fluorophores (fluorescent organic matter fractions). Furthermore, the nanoparticle size distribution and zeta potential analysis of the adsorption process were examined using a Zetasizer Nano (Malvern).

3. RESULTS AND DISCUSSION

3.1. Surface Area of the Adsorbent

The surface areas of the adsorbents were evaluated by the surface area analyzer method, and the results showed that the surface areas varied significantly, the granular activated carbon prepared in this experiments being the smallest relative to other activated carbon (GAC-1 = $494 \text{ m}^2 \text{g}^{-1}$). As for the other adsorbents—GAC-2, GAC-3, and GAC-4—the surface areas were $780 \text{ m}^2 \text{g}^{-1}$, $1200 \text{ m}^2 \text{g}^{-1}$, and $1192 \text{ m}^2 \text{g}^{-1}$, respectively. These results were expected because the physical properties of the activated carbon are dependent on the process of activation.

3.2. Phenol Removal Efficiency

Figure 1 shows the phenol removal efficiency of various adsorbent types. The maximum removal efficiency of GAC-2 = GAC-3 > GAC-4 > GAC-1. These differences in removal efficiency are related to the surface areas of the adsorbents. The maximum phenol removal efficiency by GAC-1 for both sample conditions, sterilized and unsterilized, was 92.5%. Considering that the surface area of GAC-1 is the smallest, this result shows that the granular activated carbon from coconut shell prepared in this study has superior phenol removal capability.

Furthermore, lower phenol removal in the sterilized sample shows that the phenol removal mechanism in this study was not only adsorption. Other phenol removal processes, such as phenol degradation, might have also occurred, although it was not as significant.

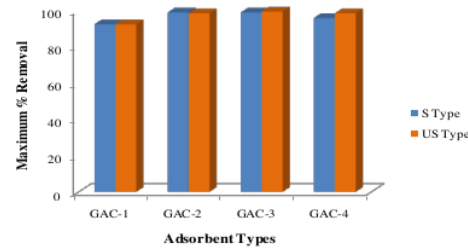


Figure 1 Removal efficiency of phenol

3.3. Adsorption Isotherms

Adsorption capacity can be studied by phenol adsorption equilibrium. Table 1 shows the isotherm constants and correlation coefficients. From Figure 2, it was detected that the equilibrium data of GAC-1 and GAC-2 adsorptions were well-characterized by the Langmuir isotherm equation; the same was true for GAC-3 and GAC-4 and the Freundlich equations.

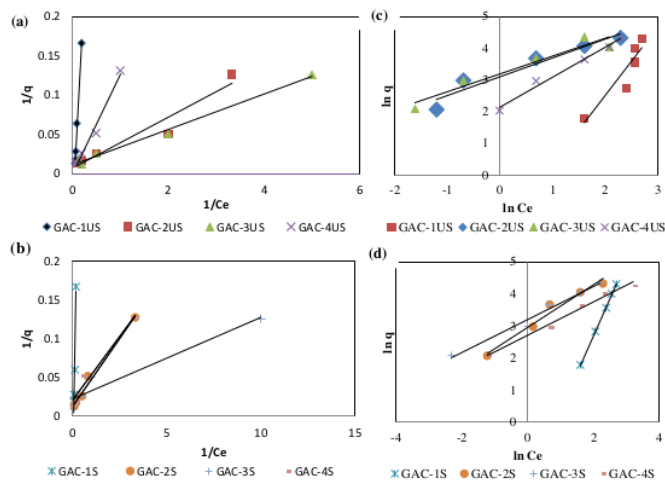


Figure 2 Langmuir isotherm for phenol adsorption on activated carbon in: (a) the unsterilized (US type); (b) the sterilized sample (S type), and the Freundlich isotherm for phenol adsorption on activated carbon in: (c) the US type; (d) the S type

The adsorption equilibrium data that fit the Langmuir isotherm assumes the monolayer coverage of phenol onto the adsorbent. The sorption capacities varied due to differences in surface area. The surface areas were 494, 780, 1200, and 1192 m^2/g for GAC-1, GAC-2, GAC-3, and GAC-

4, respectively. The granular activated carbon from coconut shell used in this study showed the lowest sorption capacity among others, as its surface area was the smallest. The maximum sorption capacities for both unsterilized and sterilized types were 17.54 mg/g and 13.70 mg/g, respectively, as can be seen in Table 2 and Table 3.

Table 2 The Langmuir and Freundlich isotherm constants for the adsorption of phenol onto activated carbon

Adsorbent Types	Langmuir Parameters			Freundlich Parameters		
	q_m (mg g ⁻¹)	b (L mg ⁻¹)	R ²	K_F	n	R ²
GAC-1 US	17.54	0.05	0.97	6.18	0.46	0.86
GAC-2 US	142.86	0.22	0.93	22.22	1.69	0.93
GAC-3 US	90.91	0.50	0.92	24.24	1.77	0.99
GAC-4 US	100.00	0.08	0.98	8.43	1.06	0.99
GAC-1 S	13.70	0.06	0.99	6.94	0.43	0.98
GAC-2 S	83.33	0.34	0.98	18.93	1.50	0.97
GAC-3 S	47.62	2.10	0.94	24.43	1.94	0.98
GAC-4 S	50.00	0.63	0.96	14.82	1.92	0.98

Table 3 Comparison of various Langmuir isotherms' adsorptions

Adsorbent Types	Sample Pre-treatment	pH	Maximum Sorption	Reference
			Capacity (mg g ⁻¹)	
Luffa cylindrica fiber	Sterilized	7	10.35	Abdelwahab and Amin (2013)
Coal fly ash	Sterilized	6.5	3.51	Singh and Nema (2015)
Modified green macro alga	Sterilized	6	230–252	Kowalczyk et al. (2018)
Zn4Al-layered double hydroxides	Sterilized	7	7.73	Lupa et al. (2018)
Organommodified montmorillonite (MT)	Sterilized	7	17.60	Li et al. (2018)
GAC-1	Unsterilized	9	17.54	This study
GAC-2			142.86	
GAC-3			90.91	
GAC-4			100.00	
GAC-1			13.70	
GAC-2			83.33	
GAC-3			47.62	
GAC-4			50.00	

Granular activated carbon from coconut shell used is not only a low-cost adsorbent but also removes phenol from water environments better than its alternatives. The maximum adsorption capacity of granular activated carbon from coconut shell used in this study (17.54) is comparable to those derived from biomasses, coal fly ash, and others. The maximum sorption capacity of GAC-1 for S type is 17.54 mg/g, higher than for US type (13.70 mg/g), because sterilized samples only undergo adsorption and unsterilized samples also undergo degradation by microorganisms.

3.4. Fluorescence Properties

The relative changes in qualitative properties of the EEMs collected for water samples and products provide useful information about phenol removal. Figure 4 shows the fluorescence EEMs of raw water and post-adsorption US type using GAC-1, GAC-3, and GAC-4.

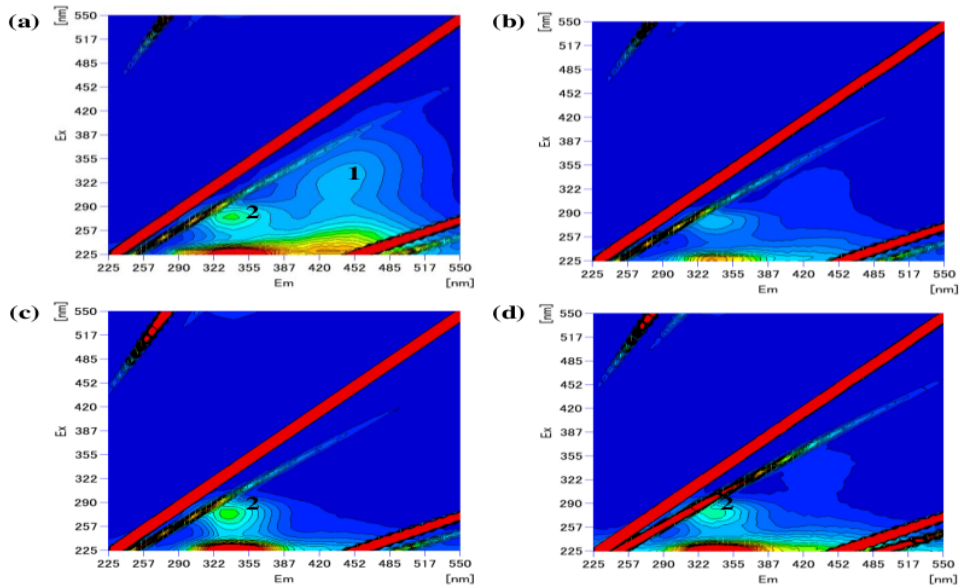


Figure 4 Fluorescence EEMs of: (a) raw water and post-adsorption of US type water using: (b) GAC-1; (c) GAC-3; and (d) GAC-4

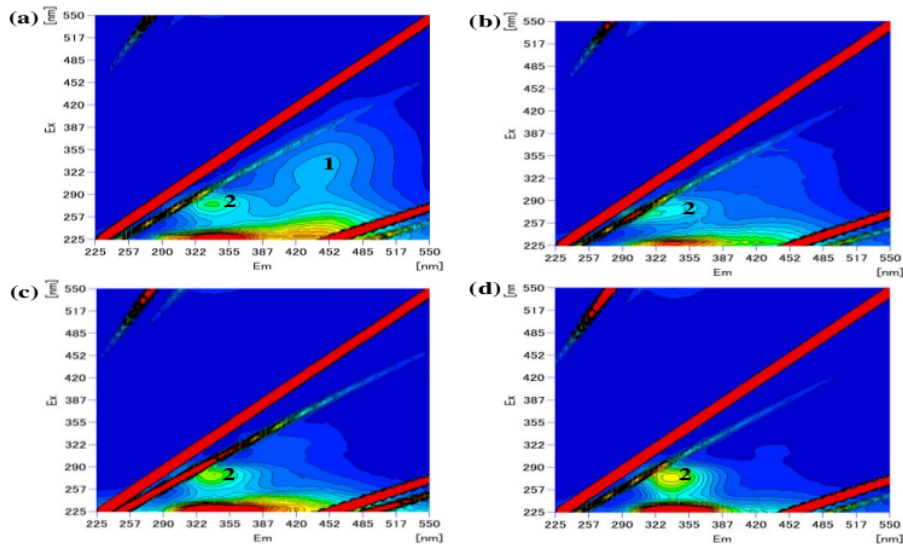


Figure 5 Fluorescence EEMs of (a) raw water and post-adsorption of S type water using (b) GAC-1, (c) GAC-3, and (d) GAC-4

The first peaks (Ex/Em, Ex: 320–350 nm; Em: 435–450 nm) in each figure represent humic-like substances, while the second peaks (Ex/Em, Ex: 260–270 nm; Em: 340–350 nm) represent

protein-like substances. The fluorescence intensities in these two post-adsorption fluorescence peak regions substantially decreased, especially within the humic-like areas, suggesting that phenolic compound removal had occurred. The highest removal was observed in the post-adsorption of GAC-3, as the peak completely disappeared.

Figure 5 displays the same pattern. Analyzing the fluorescence intensity values for the first peaks, the differences between the EEMs are clear, reflecting the effects of phenol removal through adsorption. However, no significant variations were registered in the second peaks that represent protein-like substances.

3.5. Size Distribution

Figures 6 and 7 display the nanoparticle size distribution of filtered raw water post-adsorption. Clearly, there were shifts in size distribution.

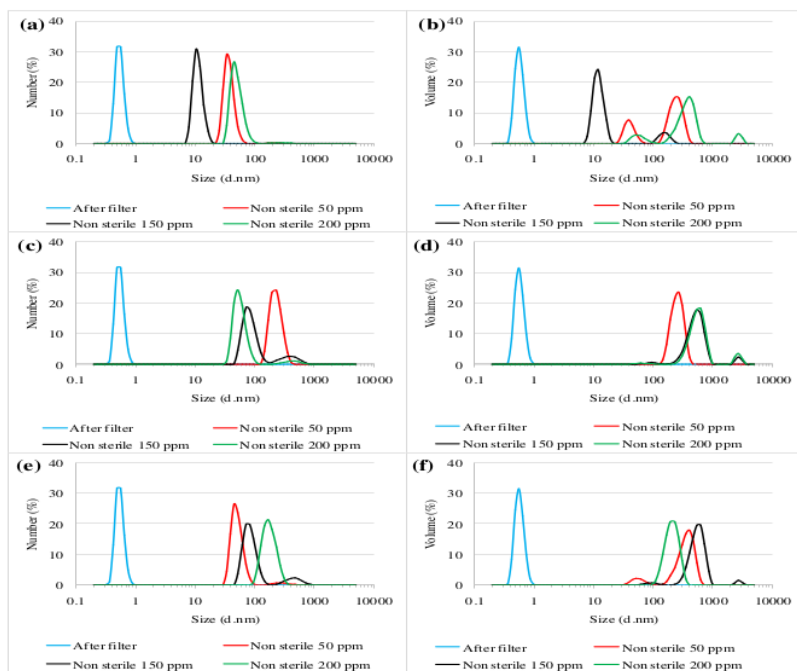


Figure 6 Nanoparticle size distribution of US type water post-adsorption of: (a) GAC-1 by number; (b) GAC-1 by volume; (c) GAC-3 by number; (d) GAC-3 by volume; (e) GAC-4 by number; and (f) GAC-4 by volume

Particles 0.72–1.74 nm in diameter represented the majority of nanoparticles in filtered raw water. However, larger nanoparticles were detected in all samples, and their number increased after equilibrium. Considering that the molecular size of phenol is about 0.7 nm (7 Å), this suggests that phenol adsorption by all three types of activated carbon had occurred. The same phenomenon was also seen on phenol adsorption of S type water shown in Figure 7, indicating that phenol adsorption also had occurred in them.

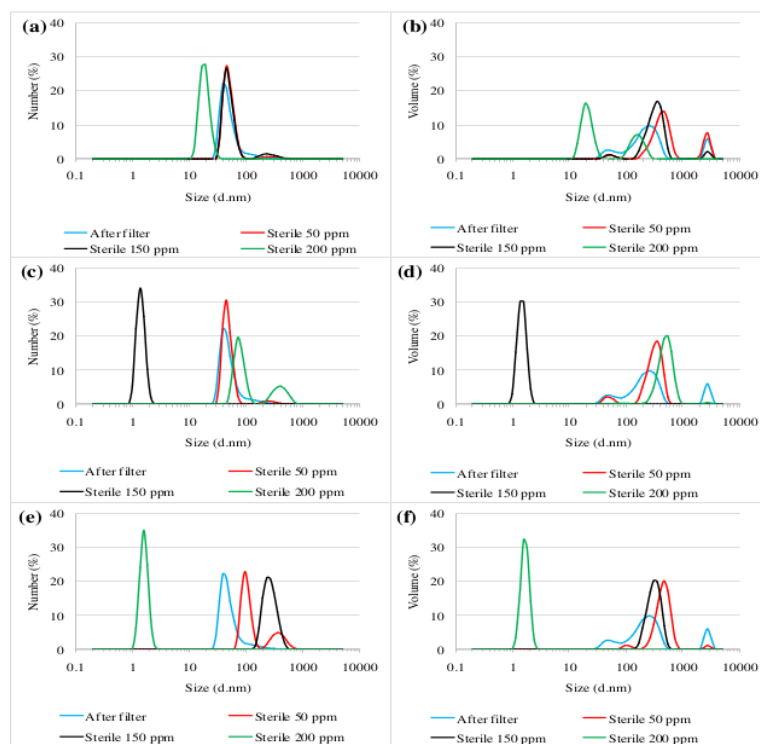


Figure 7 Nanoparticle size distribution of S type water post-adsorption of: (a) GAC-1 by number; (b) GAC-1 by volume; (c) GAC-3 by number; (d) GAC-3 by volume; (e) GAC-4 by number; and (f) GAC-4 by volume

4. CONCLUSION

Granular activated carbon from coconut shell was used to investigate the phenol-adsorption capacities of various adsorbents in batch experiments. The equilibrium adsorption data was best characterized by the Langmuir isotherm, indicating monolayer adsorption on a homogenous surface. The adsorption capacities in both US and S type was found to be 17.54 mg/g and 13.70 mg/g, respectively, at 25°C. The fluorescence spectroscopy results showed the Kuranji River DOM contained two major components: humic-like substances and protein-like substances. The maximum removal rate of 92.5% for both types of samples was obtained post-adsorption, as measured by the phenol kit. The nanoparticle size distribution also shifted from ranges of 0.72–1.74 nm in raw water to 45.66–726.73 nm and 57.08–1068.47 nm in US type and S type water, respectively. These results showed that this agricultural waste material could be used as an excellent adsorbent.

5. ACKNOWLEDGEMENT

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