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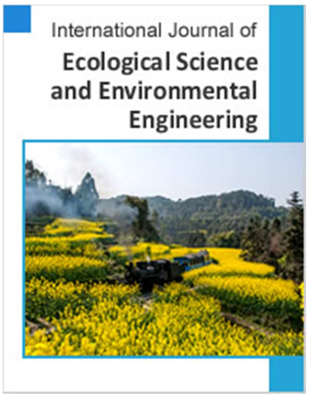

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Equilibrium and Isotherm Studies on the Adsorption of Methylene Blue and Malachite Green by Activated Carbon Prepared from *Irvingia Gabonensis* Seed Shells

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Abstract
Irvingia gabonensis seed shells were converted into activated carbon using $ZnCl_2$ as the activating agent and used for the adsorption of methylene blue (MB) and malachite green (MG) from aqueous solution. Batch adsorption experiments were conducted to investigate the effects of adsorbate concentration (50 – 250 mg/l), adsorbent particle size (0.05 – 1.0 mm), adsorbent dosage (0.1-0.5g), and adsorption time (30 – 120 min.). The results revealed that the activated carbon prepared from this plant shell was able to remove MB more that MG at all adsorption conditions. Results also showed that adsorption efficiency increase with decrease in adsorbate concentration, decrease in adsorbent particle size, increase in adsorbent dosage and increase in contact time of adsorption. Isotherm studies showed that the adsorption of MB follow Langmuir and Freundlich isotherm but fitted better with Freundlich isotherm why adsorption of malachite green fitted better with Langmuir isotherm.

1. Introduction

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate) [1]. Adsorption occurs when the attractive forces at the carbon surface overcomes the attractive forces of the liquid or gas. It is an important technique used in the separation and purification of gas and liquid. It is widely used in many industrial applications. Adsorption is currently considered to be very effective for wastewater treatment because of its simplicity and cost effectiveness [2- 3].

Among many types of adsorbents, activated carbons are the most widely used, because of their high adsorptive capacity and cost efficiency [2]. Activated carbon is known to be a solid, porous, tasteless, black carbonaceous material. Their adsorptive properties are linked to their great surface area, high microporosity, and the presence of surface functional groups [2]. Adsorption is applied widely in the purification of liquids and gases in the processing industries such as edible oil, sugars, pharmaceuticals, starch making and gas masking [5 - 6].

A large number of materials of animal, vegetable or mineral origin can be converted into activated carbon if properly treated [7].

Irvingia gabonensis is a species of African tree in the family Irivngiaceae and genusirvingia, sometimes known by the common name wild mango, African mango or bush mango. They bear edible mango- like fruits and are especially valued for their fat and protein rich nuts. *Irvingia gobonensis* is indigenous to the humid forest zones of some West African and Central African countries. The fruit can be eaten fresh or processed into jelly, jam, juice or wine. The pulp has also been used to prepare black dye for cloth colouration. The tree starts yielding fruit after 15 years from planting. The seed coat has to be cracked open to get to the seed which is used to prepare soup and could also be pressed to produce edible oil used for cooking. The oil can also be further processed to make soap or cosmetic, but the seed shell has not been used for any industrial purpose. They are always discarded as waste materials and used only as domestic fuel.

This study involved the preparation of activated carbon from the seed shell of *Irvingia gabonesis*, and applies in the removal of methylene blue, and malachite green from aqueous solution. The structure of methylene blue and malachite green are shown below.

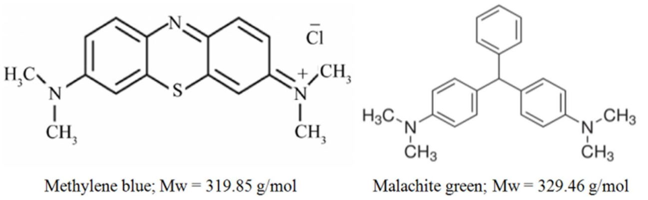

Figure 1. *Structure of Methylene blue and Malachite green.*

2. Experimental

2.1. Sample Collection and Treatment

The *Irvingia gabonensis* seed shells were collected from Ikot Akpaden, Mkpat Enin L. G. A. Akwa Ibom in Nigeria, as waste materials after the seed have been removed. It was dried and the husk and debris were removed from the seed shell. It was further reduced to chips of sizes between 6.0mm and 10.0mm, which were used for this study.

2.2. Preparation of Activated Carbon

The activated carbon was prepared by chemical activation method as it has been observed to produce better results [9]. This was carried out by weighing 100g of the chipped seed shells into a beaker. 1M $ZnCl_2$ solution was then introduced into the beaker containing the raw sample in a sample to liquor ratio of 1:20 and heated on a heating mantle set at 100°C till the sample absorbed all the activating chemical and formed a paste.

The sample paste was then removed and dried in a laboratory oven calibrated to 100°C. The dried sample was then carbonized in a muffle furnace at a temperature of 500°C for 2 hours. The furnace was hermetically sealed to provide an almost air-tight environment, after which the crucible and its content was removed and cooled in a dessicator. The carbonized sample was then washed with distilled water and dried at a temperature of 100°C in the oven for 2 hours. The resulting activated carbon was further ground and sieved to different particle sizes (0.05 - 1.0mm) and kept in air tight container.

2.3. Adsorption Study

The adsorption potentials of the activated carbon prepared from *Irvingia gabonensis* seed shells were determined following the work reported by Odebunmi and Okeola [6]. In this method, batch adsorption experiments were carried out at room temperature using a mechanical shaker. The adsorbate solutions were methylene blue (MB) and malachite green (MG). Effect of adsorbent dosage, concentration of adsorbate, particle size of the adsorbent and adsorbent – adsorbate contact time were evaluated as follows:

2.3.1. Effect of Concentration of Adsorbate

Adsorption experiments were carried out by contacting 100 ml of 50mg/l – 250mg/l solution of MB and MG differently with 0.25gactivated carbon with particle size 0.1mm. The above experiments were carried out simultaneously for the two dye solutions. The mixtures were well shaken with mechanical shaker for 1 hour, and filtered using whatmann filter paper. The post adsorption concentration was measured by taking the absorbance of the solutions at previously determined wavelength of maximum absorbance (λ_{max}) for the solution (650nm for MB and 616nm for MG). The post adsorption concentration was calculated from the absorbance of each solution at equilibrium point using Beer's Lambert law. The adsorption efficiency was determined following the work of Nsi *et al*., [10], Ogbonnaya, [11] and Nameni *et al*., [12].

$$\text{Adsorption efficiency (\%)} = \frac{(Co-Ce)}{Co} X\ 100$$

The quantity of dye adsorbed q_e (mg/g) at equilibrium was calculated using the formula

$$q_e = \frac{(Co-Ce)V}{m}\ X\ 100$$

Where: C_o (mg/l) = Initial concentration of dye
C_e (mg/l) = Post-adsorption concentration of dye
m (g) = mass of the adsorbent
V (L) = volume of solution used

The same procedures above were used to evaluate the following:

2.3.2. Effect of Particle Size of Adsorbent

To evaluate effect of the particle size, activated carbon with varying particle sizes ranging from 0.05mm - 1.00mm were used. Other parameters were kept constant; dye concentration 100 mg/l, adsorbent dosage 0.25 mg and contact time of 60 min

2.3.3. Effect of Adsorbent Dosage

Determination of this effect was done using varying masses of activated carbon ranging from 0.1-0.5 g. Other parameters were kept constant; dye concentration 100 mg/l, particle size of adsorbent 0.1mm and contact time of 60 min

2.3.4. Effect of Contact Time

The effect of contact time was determined by varying the time of contact between the adsorbent and adsorbate. Contact time used were 30min, 45min, 60min, 90min, 120min. Other parameters were kept constant; dye concentration 100 mg/l, particle size of adsorbent 0.1mm and adsorbent dosage 0.25g.

In each experiment, the post adsorption concentration, and adsorption efficiency and quantity of dye adsorbed q_e (mg/g) at equilibrium were determined.

2.4. Equilibrium Isotherm Modeling

Equilibrium adsorption isotherms are used to investigate the relationship that exists between the adsorbate concentration in solution and amount of the adsorbent at equilibrium [13]. Isotherm models provide fundamental information on the sorption mechanism, heterogeneity of the adsorbent surface and the affinity of the adsorbent. The thermodynamic isotherms determined in this work are Langmuir and Freundlich isotherm.

2.4.1. Langmuir Isotherm

This isotherm model describes monolayer adsorption onto the surface of an adsorbent with a finite number of identical adsorption sites. It assumes that adsorption occurs at specific homogeneous site within the adsorbent and no interaction between the adsorbent sites. The model is expressed as

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}K_L}\frac{1}{C_e}$$

Where q_e is quantity of dye adsorbed (mg/g) at equilibrium it's correspond to complete monolayer coverage, C_e is the equilibrium concentration of the adsorbate (mg/l), K_L is the Langmuir constant related to the energy of the adsorption (l/mg), q_{max} is the maximum sorption of adsorbate from solution (mg/g), q_{max} and K_L were determined from the intercept and slope of the plot of $\frac{1}{q_e}$ against $\frac{1}{C_e}$.

From Langmuir isotherm, R_L values was obtained which is expressed as

$$R_L = \frac{1}{1+K_L C_o}$$

Adsorption is said to be favourable if $0 < R_L < 1$ and unfavourable if $R_L > 1$

2.4.2. FreundlichIsotherm

Freundlich isotherm is an empirical equation used to describe the heterogeneity of the adsorbent surface which is an indication that the binding sites are not equivalent or dependent.

The linear form of the equation is given as

$$\text{Log } q_e = \log K_f + \frac{1}{n}\log C_e$$

Where q_e is the quantity of the adsorbate adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), K_f is the empirical constant that provides an indication of the overall adsorption capacity (mg/g), $\frac{1}{n}$ is dimensionless quantity, it is the sorption intensity of the adsorbate onto adsorbent or surface heterogeneity. The value of $\frac{1}{n}$ ranges from 0 – 1, and the closer the value to zero, the more heterogeneous the adsorbent surface [14].

3. Results and Discussion

The adsorption of cationic dyes: methylene blue (MB) and malachite green (MG), by the activated carbon sample prepared from *Irvingia gabonensis* seed shells activated with $ZnCl_2$ were evaluated under the same conditions of adsorbent dosage, contact time, particle size and adsorbate concentration.

The results as presented in Table 1-4, and illustrated graphically in Figure 2-5, are in agreement with various similar works on adsorption potential and capability of fruit and seed wastes made activated carbons [8], [15]. The samples of activated carbon in the present study were able to decolourise standard solutions of methylene blue and malachite green to various extents. All the adsorption studies were carried out at room temperature.

3.1. Effect of Initial Concentration of Dyes

The effect of initial concentration of dyes on adsorption process was carried out with adsorption of methylene blue and malachite green by activated carbon. The results as presented in Table 1, show that solute adsorption efficiency for both dyes increased with decrease in concentration. This may be due to the fact that at lower concentrations almost all the dye molecules were adsorbed very quickly on the outer surface of the activated carbon, but further increase in initial dye concentrations led to fast saturation of adsorbent surface by the dye molecules, and thus most of the dye adsorption took place slowly inside the pores [16].

The adsorption efficiency of methlyene blue ranges between 97.28 – 98.56% while that of the malachite green ranges between 18.66 – 23.64%.

Table 1. *Effect of Concentration of MB and MG on adsorption efficiency.*

Pre-adsorption	Methylene	Blue	Malachite	Green
conc. (mg/l)	Post-adsorption conc. (mg/l)	Adsorption Efficiency (%)	Post-adsorption conc. (mg/l)	Adsorption Efficiency (%)
250.00	6.79	97.28	203.35	18.66
200.00	1.99	99.00	179.36	10.32
150.00	1.06	99.29	132.08	11.95
100.00	1.01	98.99	88.28	11.72
50.00	0.72	98.56	38.18	23.64

Table 2. *Effects of particle size of adsorbent on the adsorption efficiency.*

Particle size	Methylene	Blue	Malachite	Green
Adsorbent	Post-adsorption Conc. (mg/l)	Adsorption Efficiency (%)	Post-adsorption Conc. (mg/l)	Adsorption Efficiency (%)
1.00	75.15	24.85	99.49	0.51
0.50	38.42	61.58	91.34	8.66
0.10	0.87	99.13	85.93	14.07
0.05	0.67	99.33	85.89	14.11

Table 3. *Effect of adsorbent dosages on the adsorption efficiency.*

Massof	Methylene	Blue	Malachite	Green
adsorbent (g)	Post-adsorption Conc (mg/l)	Adsorption Efficiency (%)	Post-adsorption Conc. (mg/l)	Adsorption Efficiency (%)
500	3.09	96.91	73.49	26.51
400	6.58	93.42	85.83	14.17
300	10.60	89.40	86.63	13.37
200	17.26	82.74	88.38	11.62
100	53.79	46.21	91.03	8.97

Table 4. *Effect of Contact Time on the adsorption efficiency.*

Contact Time	Methylene	Blue	Malachite	Green
(min)	Post-adsorption Conc. (mg/l)	Adsorption Efficiency (%)	Post-adsorption Conc. (mg/l)	Adsorption Efficiency (%)
120	1.01	98.99	86.14	13.86
90	1.28	98.72	88.07	11.93
60	1.47	98.53	88.28	11.72
45	1.61	98.39	90.32	9.68
30	22.56	77.44	90.89	9.11

3.2. Effect of Particle Size on Adsorption

The effect of particle size of adsorbent on adsorption of MB and MG is presented in Table 2 and Figure 3. The results revealed that there is an increase in adsorption efficiency corresponding to a decrease in the particle size of the activated carbon for both MB and MG. The 0.05mm activated carbon was found to remove more of the dye. The relatively higher adsorption capacity with smaller adsorbent particle may be due to the fact that smaller particles yield large surface areas [17]. Similar result was reported by Santhi *et al*., [18].

3.3. Effect of Adsorbent Dosage

The quantity of adsorbent is an important factor in large scale industrial application of adsorbent in the removal of a desired contaminant. In order to investigate the effect of quantity of adsorbent on the adsorption of MB and MG, a series of adsorption studies were carried out with different masses of adsorbent at fixed initial solute concentration. Table 3 shows the amount of each solute adsorbed with varying amounts of activated carbon. The results indicate that adsorption efficiency increased with increase in mass of adsorbent. Thus increase in adsorbent mass increases the contact surface area of adsorbent particles which means that it will be more probable for solute molecules to be adsorbed on adsorption sites and thus adsorption efficiency is increased [12]. This result is illustrated graphically in Figure 4.

3.4. Effect of Contact Time on Adsorption

Increase in contact time results in increase in adsorption efficiency. From Table 4, when the contact time increased, there was more time for the adsorbates to adsorb on the surface of the adsorbents, thereby leading to greater adsorption efficiency (Figure 5). Comparatively, the activated carbon produced from *Irvingia gabonensis* seed shells is observed to adsorb methylene blue solution more than malachite green irrespective of the contact time. However complete removal of dye contaminant from aqueous solution should be done at longer contact time between the dye solution and the activated carbon.

3.5. Effect of Nature of Adsorbates

Different adsorbates exhibit different types of equilibrium relationship where quantity adsorbed is a function of final and equilibrium concentration [19].

The same mass of the activated carbon was made to adsorb same concentration of methylene blue and malachite green, within the same conditions. The percentage of the solute removed was found to be higher for methylene blue than malachite green. Santhi *et al*., reported that activated carbon prepared from *A. squmosa* seed activated with Conc. H_2SO_4 at moderate temperature removed malachite green more than methylene blue. This may be due to the nature of the raw material from which the activated carbon is prepared, the method of activation, activating agent used, the pH and the solubility of the dye in solutions. Also dye removal can be related to the active sites of the adsorbent and also to the chemistry of the dye in the solution [18]. Molecular weight of the dye can also affect its adsorption efficiency.

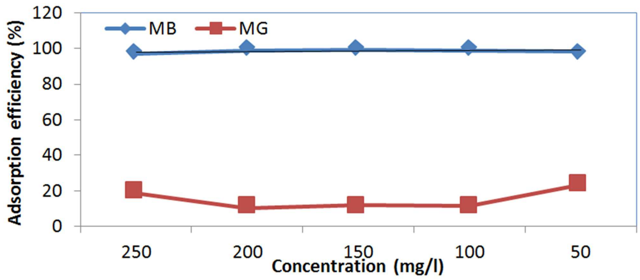

Figure 2. *Effect of concentration of adsorbate on the adsorption efficiency of MB and MG.*

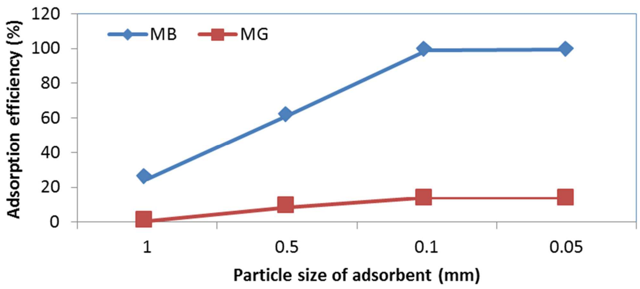

Figure 3. *Effect of particle size of adsorbent on the adsorption efficiency of MB and MG.*

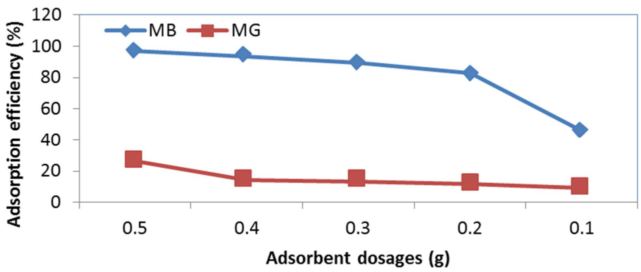

Figure 4. *Effect of adsorbent dosages on the adsorption efficiency of MB and MG.*

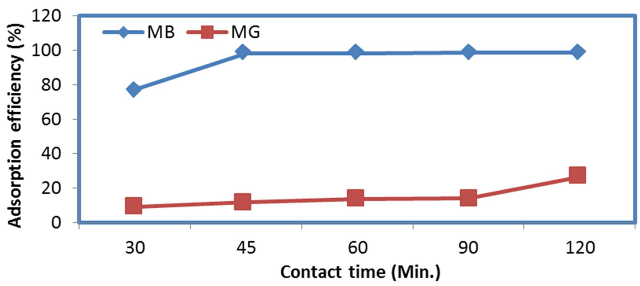

Figure 5. *Effect of contact time on the adsorption capacity of MB and MG.*

4. Isotherm Studies

Langmuir and Freundlich isotherm models were used to investigate the adsorption of methylene blue and malachite green by *Irvingia gabonensis* seed shell activated carbon. Figure 6 and 7 shows plots of the Langmuir and Freundlich isotherm models for the adsorption of methylene blue onto the activated carbon respectively and Figure 8 and 9 shows the plot of Langmuir and Freundlich isotherm model for the adsorption of malachite green unto the activated carbon respectively.

The values of the parameters obtained from each isotherm model are presented in Table 5. The value of q_{max} for MB was 90.90 while that of MG was 14.28 indicating that greater percentage of MB was removed from the aqueous solution than MG. The R_L values for the adsorption of MB and MG were 0.0063 and 0.0069 respectively indicating that the adsorption of both dyes are favourable since these values are greater than zero but less than one.

The heterogeneity factor 1/n which indicate the strength of the bond energy between the adsorbent and the adsorbate was 0.10 for MB and 0.108 for MG, indicating that the adsorbent surface was heterogeneous and the adsorption of both dyes were fair [14], [20].

The correlation coefficient R^2 for the adsorption of MB was 0.979 and 0.980 for Langmuir and Freundlich isotherm model respectively, this shows that both models fit well for the adsorption of MB. The R^2 Value for the adsorption of MG was 0.977 and 0.936 for Langmuir and Freundlich isotherm model respectively. These values show that Langmuir isotherm fits better for the adsorption of MG.

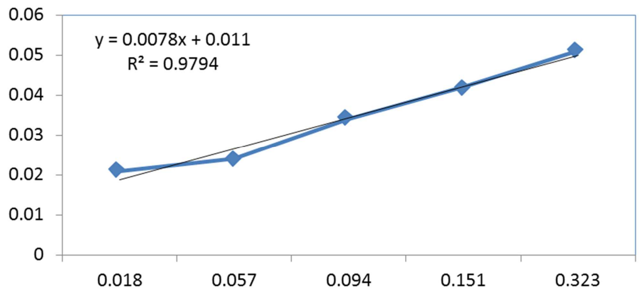

Figure 6. *Langmuir isotherm for adsorption of methylene blue by Irvingia gabonensis seeds shell activated carbon.*

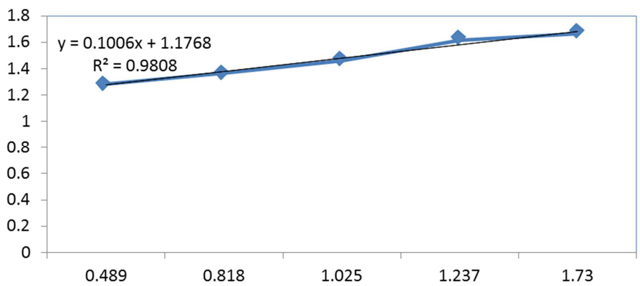

Figure 7. *Freundlich isotherm for adsorption of methylene blue by Irvingia gabonensis seeds shell activated carbon.*

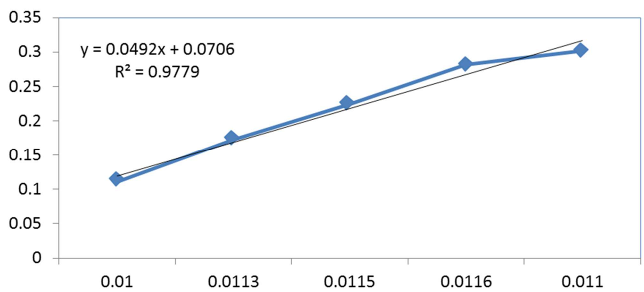

Figure 8. *Langmuir isotherm for adsorption of MG by Irvingia gabonensis seeds shell activated carbon.*

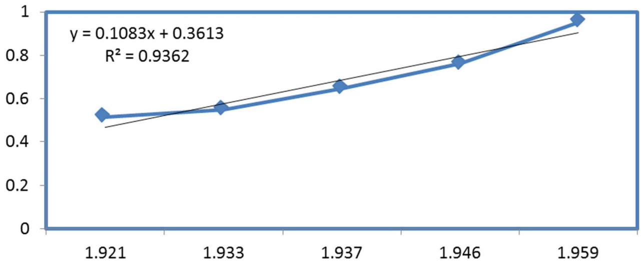

Figure 9. *Freundlich isotherm for adsorption of MG by Irvingia gabonensis seeds shell activated carbon.*

Table 5. *Langmuir and Freundlich isotherm parameters obtained for the adsorption of MB and MG onto Irvingia gabonensis seed shell activated carbon.*

Isotherm parameters	Adsorption of MB	Adsorption of MG
Langmuir		
q_{max}(mg/g)	90.90	14.28
K_L (L/mg)	1.57	1.43
R_L	0.0063	0.0069
R^2	0.979	0.977
Freundlich		
K_F(L/g)	0.07	-0.44
1/n	0.10	0.108
R^2	0.980	0.936

5. Conclusion

The use of *Irvingia gabonensis* seed shell as raw material for the preparation of activated carbon has been evaluated in this work. The results revealed that the activated carbon prepared from this material can be used as an effective adsorbent in the removal of methylene blue and malachite green contaminants from waste water. The prepared activated carbon was used for the removal of methylene blue and malachite green at various adsorption conditions and it was found that adsorption was more effective at a lower adsorbate concentration, higher activated carbon dosage, longer contact time and smaller particle size of activated carbon. Also it was found that the activated carbon was able to remove greater percentage of methylene blue than malachite green. Adsorption of methylene blue follow Langmuir and Freundlich isotherm but fitted better to Freundlich isotherm, why adsorption of malachite green fitted better with Langmuir isotherm. However *Irvingia gabonensis* seed shells which are presently discarded as waste materials can be converted to activated carbon and use as adsorbent in the treatment of effluents from textile industries.

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