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Full Length Research Paper

Modelling of the adsorption of zn^{2+} from aqueous solution by modified and unmodified tiger nut shell

Nnabuk O. Eddy[1]* and Stevens A. Odoemelam[2]

[1]Department of Chemistry, Ahmadu Bello University, Samaru Campus, Zaria, Kaduna State, Nigeria
[2]Department of Chemistry, Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria.

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Adsorption of Zn (II) ions from aqueous solutions was studied in a batch system using *Tiger nut* shells. The optimum condition for the adsorption of Zn (II) ions from aqueous solution by these shells was investigated by considering the extent of adsorption with respect to contact time, initial metal ion concentration, particle size of the adsorbent and modification of the adsorbent with H_2SO_4. The extent of metal ions removed decreased with increasing contact time but increased with increase in the initial metal ion concentration. The adsorption equilibrium data were best described by Langmuir adsorption isotherm. Although intraparticle diffusion was not the rate determining step for the adsorption of Zn (II) ions from aqueous solution by tiger nut shell, the adsorption kinetic was consistent with Weber-Morris and Lagergren pseudo second order models.

Key words: Adsorption, Zn (II), tiger nut shell, kinetics.

INTRODUCTION

Zinc is one of the heavy metals that exert its toxic effect at elevated concentrations and yet industrial effluent, domestic water and other sources of water are often enriched with elevated concentration of the metal (Eddy *et al*. 2008; Ekop and Eddy, 2005). Zinc is a divalent metal and tends to exist in a combine state. Most zinc salts are soluble in water indicating that if this metal is incidentally discharge into surface water, it may exert toxic or harmful effect. Therefore the elimination of this metal from water and waste water is important to protect public health.

Traditional technologies available for the removal of heavy metals from aqueous solutions include oxidation and reduction, chemical precipitation, filtration, electrochemical treatment, ion exchange, membrane separation, reverse osmosis, evaporation and electrolysis (Odoemelam and Eddy, 2009). However, the advantages and disadvantages of each of these methods have been extensively reviewed. Among these methods, adsorption has been found to be one of the most efficient and economic process for the removal of heavy metal ions from aqueous solution (Allen et al., 1989; Anandkumar and Mandal, 2009).Tiger nut shell is a common waste in Nigeria and other countries. Accumulation of tiger nut waste in the environment may results in land space occupation and subsequent pollution problems. Hence the recycling of tiger nut waste for use in water and waste water treatments would not only be economical but will also help to maintain the quality of the environment. Fortunately, this solid waste is available free of cost and utilizing it for adsorption purpose does not required more than carbonization or slight modification. Therefore, the main objecttive of this study is to investigate the possibility of using dried samples of tiger nut shell to develop a new low-cost adsorbent for the removal of Zn (II) ions from aqueous solution.

*Corresponding author. E-mail: nabukeddy@yahoo.com

MATERIALS AND METHODS

Biomass

Tiger nut shell was obtained from some local processors in Ikot Idem Udo village, Obot Akara, Akwa Ibom State, Nigeria. The samples were washed with distilled water. After this, they were oven dried at 105°C for 96 h and the dried tiger nut shells were milled and sieved to different particle sizes.

Modification of the sample

The dried Tiger nut shell was added in small portion to 900 ml of concentrated H_2SO_4 for 12 h and the resulting reaction mixture was kept over night at room temperature followed by refluxing for 12 h in an efficient fume hood. After cooling to room temperature, the

Table 1. Amount of Zn^{2+} adsorbed, % adsorption and amount adsorbed at equilibrium by modified (M) and unmodified (UM) Tiger nut shell at various concentrations of Zn^{2+} solution.

C (mg/L)	Amount of Zn^{2+} adsorbed (mg/L)		% sorption		x/m (mg/g)	
	UM	M	UM	M	UM	M
1.0	0.8900	0.9100	89.00	91.00	89.00	91.00
1.2	1.1885	1.1923	99.04	99.36	99.04	99.36
1.4	1.2880	1.3897	99.20	99.26	99.20	99.26
1.6	1.5893	1.5905	99.33	99.41	99.33	99.41
1.8	1.7881	1.7914	99.34	99.52	99.34	99.52
2.0	1.9878	1.9908	99.39	99.54	99.39	99.54

reaction mixture was heated in an open oven at 150°C for overnight followed by washing with 4 L of distilled water and then soaked in 1% $NaHCO_3$ solution over night to remove any remaining acid. The obtained carbon was washed with distilled water until pH of the activated carbon reached 7, dried in an oven at 150°C for 24 h in the absence of air and sieved to different particle sizes.

Preparation of solutions

A stock solution of Zn (II) ion was prepared by dissolving $ZnSO_4.7H_2SO_4$ in distilled water. The resulting solution was diluted to obtained serial concentrations of Zn (II) ion solutions.

Batch adsorption studies

Effect of concentration of Zn (II): The effect of initial concentration of Zn (II) ions on the equilibrium adsorption of Zn (II) ions from aqueous solution was studied by using various concentrations of Zn (II) ions (1.0 1.2, 1.4, 1.6, 1.8 and 2.0 mg/L). The experiment was performed by soaking known mass of the adsorbent in solutions containing various concentra-tions of Zn (II) ion for 60 min respectively.

Kinetic studies: Sorption studies were carried out in 250 ml conical flask at solution pH of 2. The adsorbent (modified and unmodified) were thoroughly mixed individually with 100 ml of solution containing 0.3 g/L of Zn (II) ions. The suspension was shaken at room temperature and the filtrate collected after 10, 30, 50, 60 and 120 min were preserved for further analysis.

Effect of particle size: Different particle size were used for the studied and in each case the batch experiment was carried out as described in section 2.4. However, the concentration of Zn (II) ion used for the experiment was 0.3 g/L.

Effect of mass of the adsorbent: Effect of adsorbent mass was studies by using different masses of the adsorbent for the batch experiment described above.

Determination of the concentration of Zn (II) ion: In each set of the experiment, the concentration of Zn (II) ion was determined using Perkin Elmer adsorption spectrophotometer.

Calculation

From the measured concentration of Zn^{2+}, percentage of Zn^{2+} adsorbed and the amount of sorption per unit mass of adsorbent (x/m) was calculated using equations 1 and 2, respectively (Odoemelam and Eddy, 2009) :

$$\%sorption = (C_i - C)/C_i \times 100 \quad \text{.....................1}$$

$$X/m = (C_i - C)/C_i \times V/m \quad \text{.....................2}$$

Where C_i and C are initial and final (outlet or effluent) concentrations of Zn^{2+}, m is the mass of the adsorbate (in g) and V (in cm^3) is the volume of solution added.

RESULTS AND DISCUSSIONS

Effect of concentration, particle size and contact period

The rate of any chemical reaction (including adsorption) has been established to be a function of reactant concentration. Therefore concentration exerts a profound influence on the rate of any reaction. Tables 1 shows the concentration of Zn^{2+} adsorbed, %sorption, and fraction of surface coverage (x/m) for the adsorption of Zn^{2+} from aqueous solution by modified (M) and unmodified (UM) tiger nut shells. Similar results were obtained when the mass of the adsorbent, period of contact and particle size of the adsorbent were varied and are presented in Tables 2, 3 and 4 respectively. From the above results, it is evident that the amount of Zn^{2+} adsorbed increases with increase in the initial Zn (II) concentration but decreases with increasing period of contact, particle size and mass of the adsorbent. These indicate that the adsorption of Zn (II) ions from aqueous solution is dependent on the initial concentration of Zn^{2+}, particle size of the adsorbent, period of contact and on the amount of the adsorbent. According to Ekop and Eddy (2005), the extent of adsorption of heavy metals from aqueous solution can be influenced by factors such as area of the adsorbent, period of contact, ionic character of the ion, pH of the solution, temperature, concentration of the electrolyte and the nature of the adsorbent/adsorbate. In this study, the pH, ionic character and temperature were held constant. Therefore the increase in %sorption with decreasing particle size may be attributed to the increase in the number of adsorption site with increasing surface area. Also, the decrease in %sorption with increasing period of contact may be attributed to competition between the forces of adsorption and desorption while the increase in percent

Table 2. Amount of Zn^{2+} adsorbed % adsorption and amount adsorbed at equilibrium by various masses of modified (M) and unmodified (UM) Tiger nut shell.

Mass (g)	Amount of Zn^{2+} adsorbed (mg/L)		(%) sorption		x/m (mg/g)	
	UM	M	UM	M	UM	M
0.2	0.7006	0.4688	70.06	46.88	70.06	46.88
0.4	0.6926	0.4624	69.26	46.24	69.26	46.24
0.6	0.6613	0.5014	66.13	50.14	66.13	50.14
0.8	0.6611	0.4473	66.11	44.73	66.11	44.73
1.0	0.6518	0.4459	65.18	44.59	65.18	44.59

Table 3. Amount of Zn^{2+} adsorbed, % adsorption and amount adsorbed at equilibrium modified (M) and unmodified (UM) Tiger nut shell at various period of contact.

Time (min)	Amount of Zn^{2+} adsorbed (mg/L)		% sorption		x/m (mg/g)	
	UM	M	UM	M	UM	M
10	0.7000	0.5101	70.00	51.01	70.00	51.01
30	0.6988	0.5000	69.88	50.00	69.88	50.00
50	0.6590	0.4890	65.90	48.90	65.90	48.90
60	0.6595	0.4786	65.95	47.86	65.95	47.86
120	0.6420	0.4700	64.20	47.00	64.20	47.00

Table 4. Amount of Zn^{2+} adsorbed % adsorption and amount adsorbed at equilibrium by various sizes of Tiger nut shell.

Size (mm)	Amount of Zn^{2+} adsorbed (mg/L)	(%) sorption	x/m (mg/g)
0.06	0.6892	68.92	68.92
2.00	0.6500	65.00	65.00
3.35	0.6496	64.96	64.96
5.60	0.6489	64.89	64.89

sorption with concentration of Zn^{2+} in the aqueous solution may be attributed to the increase in the amount of the adsorbate approaching the surface of the adsorbent.

Effect of modification of tiger nut shell

Modification of the adsorbent with H_2SO_4 implies that the organic matter content of the Tiger nut shell is removed therefore the modified Tiger nut shell has less organic matter content compared to the unmodified Tiger nut shell. From the present results, at various concentrations of Zn^{2+}, the amount of Zn^{2+} adsorbed by the modified Tiger nut shell is relatively higher than the amount adsorbed by unmodified Tiger nut shell. However, there was no significant difference between the two set of data ($P > 0.05$). However, at various masses of the adsorbent and contact time (that is, at constant concentration of the aqueous solution), significant differences were observed between the amount of Zn^{2+} adsorbed by the unmodified and modified Tiger nut shells such that the rate of adsorption can be optimised by taking advantage of time and modification.

Adsorption isotherm

Adsorption isotherms simplify the relation between the concentration of the adsorbate and the degree of surface coverage and also provide information on the mechanism of adsorption. Data obtained from the equilibrium studies were used to fit curves for different adsorption models and it was found that the adsorption of Zn^{2+} by modified (M) and unmodified (UM) Tiger nut shells can best be described by Langmuir adsorption isotherm which can be represented as follows (Baysal et al., 2009; Bojic et al., 2009);

$$C_e/Q_e = 1/Q_m b + C_e/Q_m \quad (3)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), Q_e is the amount adsorbed at equilibrium (mg/g), Q_m is Langmuir constant and is related to the adsorption efficiency while b is the equilibrium constant of adsorption and is related to the free energy of adsorption. Figure 1 shows Langmuir isotherm for the adsorption of Zn^{2+} by modified and unmodified Tiger nut shells. Values of Langmuir adsorption parameters deduced from the

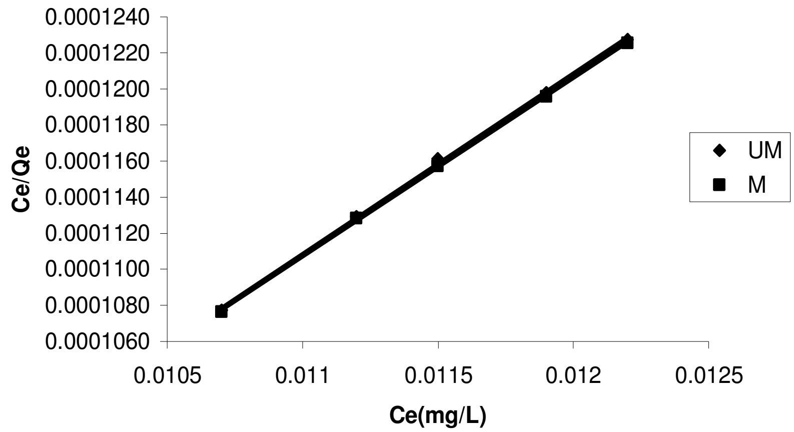

Figure 1. Langmuir isotherm for the adsorption of zinc ion by modified (M) and unmodified (UM) tiger nut shell.

Table 5. Langmuir adsorption parameters for the adsorption of Zn^{2+} by modified (M) and unmodified (UM) Tiger nut shell.

Tiger nut shell	b	Q_m	R^2
UM	1.11×10^4	100.00	0.9993
M	4.25×10^3	101.01	0.9997

slopes and intercepts of the plots are recorded in Table 5. From the results, it can be seen that values of b and Q_m for the modified Tiger nut shell are higher than those obtained for the unmodified Tiger nut shell suggesting that the adsorption efficiency of the modified Tiger nut shell is better than that of the unmodified Tiger nut shell.

Weber-Morris Intraparticle diffusion model

Adsorption kinetics is usually controlled by different mechanisms but the most limiting ones are the diffusion mechanisms, which consist of:

(1) The initial portion representing rapid external diffusion or boundary layer diffusion and surface adsorption,
(2.) The linear portion indicating a gradual adsorption state due to intra particle diffusion.
(3) A plateau to equilibrium where the intra-particles diffusion starts to decrease due to the low concentration in solution as well as fewer available adsorption sites (Ho and Mckay, 2000).

According to Weber and Morris, an intra-particle diffusion coefficient, K_{id} can be defined as follows (Choi et al., 2009);

$$K_{id} = Q_t/t^{0.5} \qquad 4$$

Where Q_t is the amount adsorbed per unit mass of adsorbent (mg/g) at time, t and K_{id} is the intra-particle diffusion constant (mg/gmin$^{0.5}$). Using equation 4, a plots of Q_t versus $t^{0.5}$ (Figure 2) were linear (for modified (M) and unmodified (UM) Tiger nut shell). However, these lines did not passed through the origin indicating that intra-particle diffusion is not the rate limiting step for the adsorption of Zn^{2+} by modified and unmodified Tiger nut shells. The plots also reveal that the intra-particle diffusion of Zn^{2+} occurred in one stage and may be attributed to macropore diffusion (Arivoli and Sadegh, 2007). Values of K_{id} and R^2 obtained from the slopes of Weber-Morris plots for unmodified and modified Tiger nut shell were 16.42 mg/gmin$^{0.5}$ ($R^2 = 1.0$) and 9.55 mg/gmin$^{0.5}$ ($R^2 = 0.8926$) respectively.

Kinetic of adsorption

The adsorption of Zn^{2+} from aqueous solution can be an equilibrium process. Thus heterogeneous equilibrium existing between the Zn^{2+} solutions and the modified/unmodified Tiger nut shell can be represented as follows;

$$A \underset{kb}{\overset{kf}{\rightleftharpoons}} B \qquad 5$$

Where k_f is the rate of adsorption while k_b is the rate of desorption. The equilibrium constant (K_0) is the ratio of the concentration of the adsorbate in adsorbent to the concentration in aqueous solution ($K_0 = k_f/k_b$). Values of K_o calculated for various concentrations of the adsorbate are recorded in Table 6. The equilibrium constant of adsorption is related to the free energy of adsorption according to equation 6;

$$\log K_o = \Delta G_{ads}/2.303RT \qquad 6$$

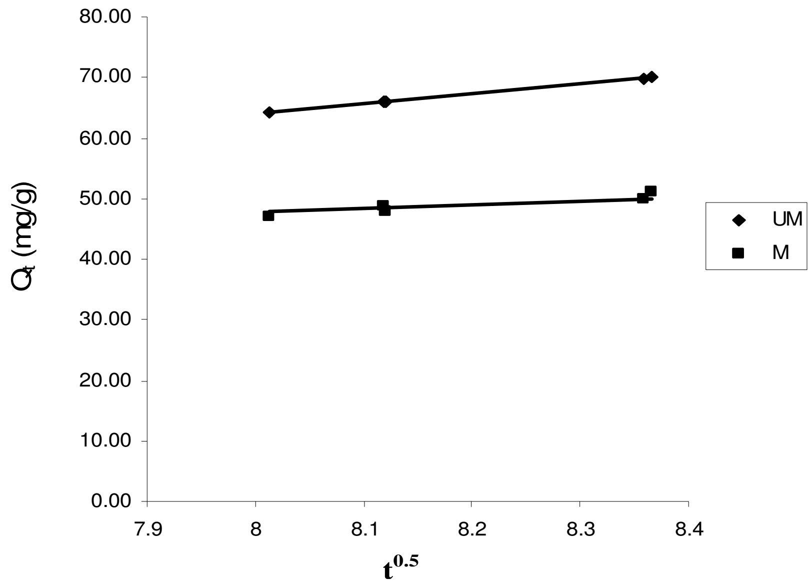

Figure 2. Weber-Moris plots for the adsorption of Zn^{2+} by modified and unmodified tiger nut shell.

Table 6. Equilibrium constant of adsorption of Zn^{2+} from aqueous solution by modified (UM) and unmodified (M) Tiger nut shell.

C (M)	K_o (UM)	K_o (M)	ΔG_{ads}(UM)	ΔG_{ads}(M)
1.0	80.90	101.11	-11.07	-11.63
1.2	103.35	154.84	-11.69	-12.70
1.4	115.00	134.92	-11.96	-12.36
1.6	148.53	167.42	-12.60	-12.90
1.8	150.26	208.30	-12.63	-13.45
2.0	162.93	216.39	-12.83	-13.55

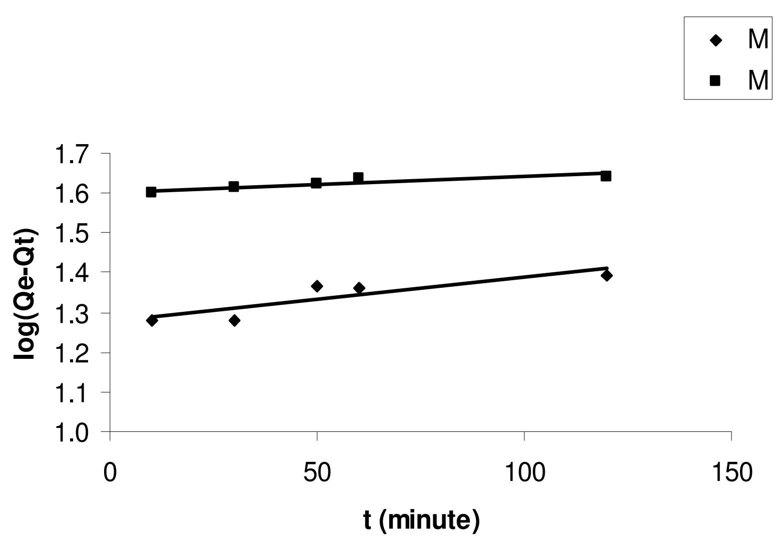

Figure 3. First order Lagergre plot for the adsorption of zinc by modified (M) and unmodified (UM) tiger nut shell.

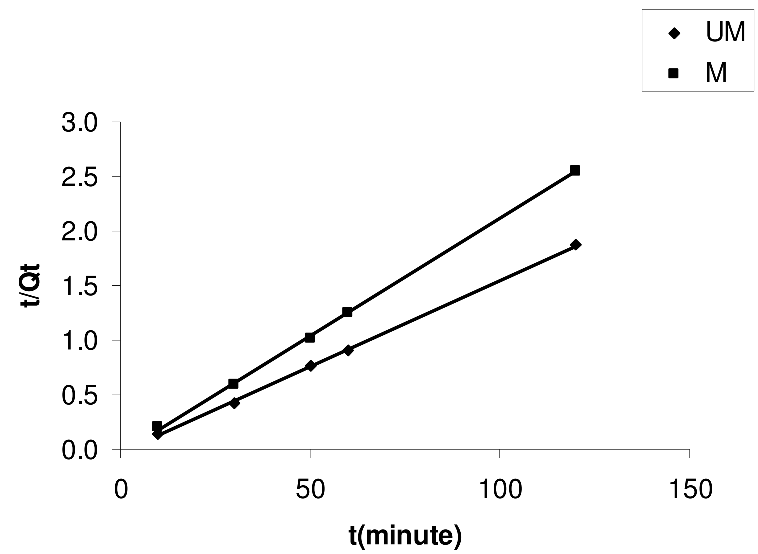

Figure 4. Pseudo second order Lageregren plot for the adsorption of zinc ion by modified (M) and unmodified (UM) tiger nut shell.

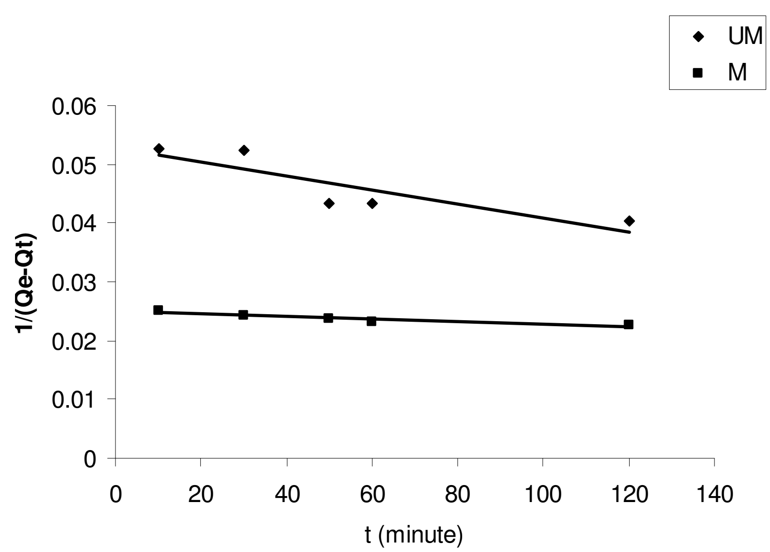

Figure 5. Second order lagergren plot for the adsorption of zinc ion by modified (M) and unmodified (UM) tiger nut shell.

Where ΔG_{ads} is the free energy of adsorption, R is the gas constant and T is the temperature. Values of the free energy computed from equation 6 (Table 6) were negatively less than the threshold value required for chemical adsorption indicating that the adsorption of Zn^{2+} from aqueous solution is spontaneous and supports the mechanism of physical adsorption.

Lagergren models were also used to further study the adsorption kinetics of Tiger nut. Lagergren first order, pseudo second order and second order kinetic can be written according to equations 7, 8 and 9 respectively (Allen et al., 1989);

$$\log(Q_e - Q_t) = \log Q_e - (K_{ad}/2.303)\, t \quad (7)$$

$$t/Q_t = 1/(K_{ad(2)} Q_e^2) + t/Q_e \quad (8)$$

$$1/(Q_e - Q_t) = 1/Q_e - K'_{ads(2)} t \quad (9)$$

Linearizing equations 7 to 9, Lagergren plots for the adsorption of Zn^{2+} from aqueous solution were developed and are presented in Figures 3 to 5. Values of rate constant for Lagergren first order, second order and pseudo second order are presented in Table 7. From the R^2 values it can be seen that the adsorption of Zn^{2+} from

Table 7. Lagergren first order, pseudo second order and second order constants for the adsorption of Zn^{2+} by modified (M) and unmodified (UM) Tiger nut shell.

	K_{ads}	R^2	$K_{ad(2)}$	R^2	$K'_{ad(2)}$	R^2
UM	0.00092	0.8736	121.37	0.9998	0.0528	0.7559
M	0.00253	0.7761	121.37	0.9997	0.0249	0.8672

aqueous solution is best described by pseudo second order Lagergren equation.

Conclusion

Modified and unmodified Tiger nut shell can be used as an adsorbent for Zn (II) ions from waste water. The adsorption process is spontaneous and can be optimised by taking advantage of contact time, concentration of the adsorbent/adsorbate and particle size of the adsorbent. Langmuir adsorption isotherm and pseudo second order Lagergreen as well as Werber-Moris models can adequately be used to explained the kinetic and mechanism of adsorption of Zn (II) ions onto tiger nut.

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