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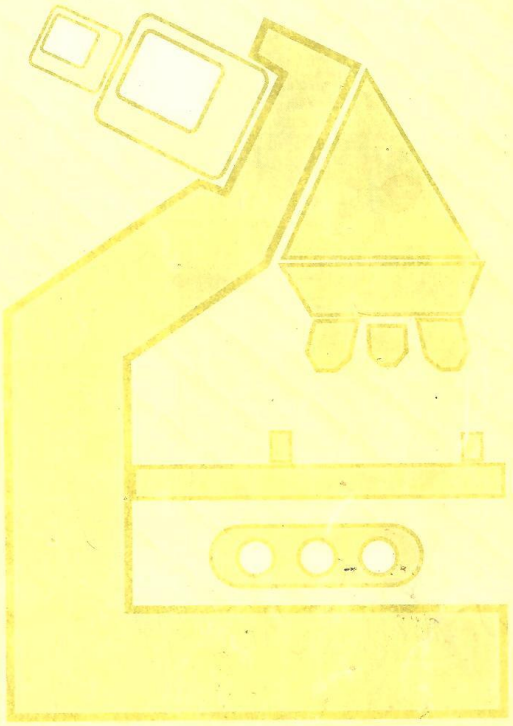

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ASSESSMENT OF SHEA NUT SHELL ACTIVATED CARBON IN BIOCHEMICAL OXYGEN DEMAND REMOVAL: A KINETIC APPROACH

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ABSTRACT

The production of activated carbons from shea nut shell, with H_3PO_4 and $ZnCl_2$ as activating agents using the two step activation process was studied. Results of physicochemical variables followed a inverse relationship between percentage burn off and yield. The highest Biochemical Oxygen Demand (BOD) removal from industrial dye wastewater were 31.79, 52.28, 14.84, 28.61, 26.85 and 28.26% for the series of sorbents labeled as SS/H_3PO_4/5, SS/H_3PO_4/10, SS/H_3PO_4/15, SS/$ZnCl_2$/5, SS/$ZnCl_2$/10 and SS/$ZnCl_2$/15 respectively and thus implies that acid catalyzed shea nut shell biosorbents are more effective than the corresponding salt modified sorbents. Evaluation of the sorption dynamics via kinetic studies revealed that BOD uptake was governed by the pseudo-second–order kinetics with more appreciable $R^2 > 0.5$, least % SSE and high precision between the calculated and experimental q_e values. Sorption rate was faster for acid catalyzed biosorbent, while the overall analysis competed favorably with those reported in literature and demonstrated the feasibility of using shea nut shell for removal of organics from textile effluent.

Keywords: Activated carbon, shea nut, dye, biochemical oxygen demand, sorbents

INTRODUCTION

Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reaction. Activated carbons are high porosity, high surface area materials manufactured by carbonization and activation of carbonaceous materials, which mixed extensive use in the industrial sector for adsorption of pollutants from gaseous and liquid streams. Activated carbon can be design for adsorption of specific adsorbates, using appropriate precursor and by optimizing the activation process conditions.

One of the effective uses of waste biomass is the production of activated carbon by thermo-chemical conversion. The activated carbon has been produced from variety of biomass, i.e. wood, rice husk, coconut shells and palm shells. There are many reports on the production of activated carbon to be used as adsorbent for removing hazardous compounds from industrial waste, or wastewater, and in catalysis as support for catalyst. To utilize agricultural by-products economically, it is proposed to use them as starting materials for the preparation of activated carbons as they have high carbon content and low ash content (Selhan *et al.,* 2008).

One way of wastewater treatment is through the use of activated carbon. Effluents discharged from dyeing industries contain large amounts of suspended solids, highly colored, low biochemical oxygen demand and greatly fluctuating pH. Disposal of this colored water into receiving water bodies could be toxic to aquatic life. The dyes may upset the biological activity in water bodies. They may also pose health problems because they may be carcinogenic (Itodo *et al.,* 2008).

The BOD test measures the ability of naturally occurring microorganisms to digest organic matter, usually in 5 days at 20°C, by analyzing the depletion of oxygen. It is used in water quality management and assessment, ecology and environmental science. The BOD test is used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters.

This work was embarked upon to test the performance of a locally made shea nut shell biosorbent in BOD removal from textile effluent.

MATER...

Experimental materials collection and preparation: The shea nut shell was obtained from Kataeregi, Katcha Local Government Area of Niger State. The industrial dye effluent was collected from Chelko Textile Limited, Kaduna. It was stored at room temperature without further purification. The chemicals used were manufactured by M & B, BDH Chemicals and Shermond Sussex of England.

The shea nut shell was pretreated as described by Omonhenles *et al.* (2006). The sample was ground and sievied with a 2 mm mesh size sieve. The less than 2 mm samples were stored in airtight container. Proximate analysis and physicochemical variables were estimated, according to the standard methods of AOAC (1990), to obtain the ash, moisture content and pH.

Activation (two step process): Activation, involving the two steps activation scheme was adopted. Firstly, 5g of blended raw sample was weighed into six different clean and pre-weighed crucibles. They were introduced into a Muffle furnace at 600°C for 5 minutes after which they were poured from the crucible into a bath of ice block. The excess water was drained off. The carbonized sample was washed, using 0.1M HCl to remove surface ash, followed by hot water wash and further washing with distilled water to remove residual acid. The sample was then sun dried, and further dried in the oven at 100°C for one hour. This process was repeated until a substantial amount of carbonized sample was obtained.

Thereafter, 5 g of already carbonized sample was mixed with 5 cm^3 of each activating agent (1M H_3PO_4 and 1M $ZnCl_2$). The sample was allowed to stand for 2 hours, after which it was introduced into a furnace and heated at 800°C for 5 minutes. The activated sample was cooled with ice – cold water, excess water was drained off and the sample dried at room temperature. The above procedure was repeated for different residual time (10 min and 15 min) until substantial amount of activated carbon was obtained. A modified version of washing method was adopted, until pH of sample solution fell within 6-7 (Rahman *et al.,* 2005; Fan *et al., 2005*).

The bulk density, activation burn off and % yield were calculated as in equation 1, 2 and 3.

Bulk density (gcm^{-3}) = $\frac{\text{weight of dry activated carbon (g)}}{\text{Volume of packed dry material } (cm^3)}$ -------1 (Rao *et al.,* 2003).

% Burn off = $\frac{W_0 - W_1}{W_0} \times 100$ ---------- 2

W_0 = Weight of char after pyrolysis, washing and drying

W_1 = Weight of carbon after activation, washing and drying.

(Ioannidou and Zabaniotu, 2006).

% Yield = $\frac{W_1}{W_0} \times 100$ --------- --- ------ --- 3

W_0 = Original mass of precursor

W_1 = Weight of carbon after activation, washing and drying (Yulu *et al.,* 2001).

Batch equilibrium experiment: Two gram of activated carbon was interacted with 40 cm^3 of industrial dye wastewater in a 50 cm^3 erlenmeyer flask and this was allowed to stand for 30 minutes. It was then filtered using Whatman Filter Paper (No.42). The filtrate was collected for further analysis. The process was repeated at pre-set times (60, 90, 120 and 150 minutes). This was continued until 400 cm^3 of each filtrate was obtained and was used for the determination of biochemical oxygen demand (BOD) (Hameed *et al.,* 2006).

Determination of Biochemical Oxygen Demand (BOD): The method reported by Udo and Ogunwale, (1986) was carefully applied. 200 cm^3 of the filtrate was measured into a conical flask. 1 cm^3 each of manganese (II) sulphate and alkali-iodide – azide solutions were added, shaken thoroughly and allowed to settle. The clear liquid above the precipitate was decanted and 2 cm^3 of concentrated H_3PO_4 and some water were added to dissolve the precipitate. The sample was titrated against 0.025 M of sodium thiosulphate. The titer value was recorded as the initial dissolved oxygen (i.e. Initial DO).

200 cm^3 of the filtrate was again measured into a blackened sample bottle. 1 cm^3 each of manganese (II) sulphate and alkali-iodide – azide solutions were added and kept for 5 days at 20°C. The clear liquid above the precipitate was decanted and 2 cm^3 of concentrated H_3PO_4 and some water added to dissolve the precipitate. This was titrated against 0.025M sodium thiosulphate. The titer value was recorded as the final dissolved oxygen (i.e. final DO).

(BOD) mg/l = Final DO – Initial DO ---------- 4 (Udo and Ogunwale, 1986).

With experimental approximations, 1cm^3 of titer value = 1mg/l dissolved oxygen (DO) (Udo and Ogunwale, 1986).

The Biochemical oxygen demand (BOD) was determined b[illegible] before and after interaction with the generated biosorbent

Batch kinetic studies: The most common models used to fit the kinetic adsorption experiments are Lagergren's pseudo – first-order and pseudo – second-order models (Hameed, 2008). The pseudo –first-order kinetic model is as simplified in equation 5.

$$\text{Log}(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \text{----------} \quad 5$$

Where K_1 = Pseudo – first – order rate constant (Min^{-1}), q_e and q_t are the amount of BOD adsorbed at equilibrium and at time, t respectively and are described as adsorption capacities of sorbent per until gram of sorbate (Hameed, 2008).

Data were also fitted into the pseudo- second –order kinetic model given as equation 6.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \text{----------} \quad 6$$

Where K_2 = Pseudo – second – order rate Constant ($g.mg^{-1}\ min^{-1}$). Fairly good values of correlation coefficient, R2 were obtained for both models and validity test was conducted using equation 7.

$$\text{SSE}\ (\%) = \sqrt{\frac{\sum(q_{e\,(exp)} - q_{e\,(cal)})^2}{N}} \quad \text{----------} \quad 7$$

Where N = Number of data point (Hameed, *et al.*, 2006)

RESULTS AND DISCUSSION

The percent ash and moisture of the precursor were determined based on dry weight as 6.67±2.89 and 9.67 ± 0.58% respectively. Table 1 presented more results on the properties of the sorbents. A pH range of 6.30 – 6.82 is an indication of removal of residual chemical through the series of washing, this rendering the carbon fit to contact consumables, including drinking water. This could also be linked to the low conductivity values (Table 1).

In line with expectations, the sample activated at high residual time (15 min) presented high value of percentage burn off, with a corresponding low yield. Some of the values include 62.67± 1.15 for $SS/H_3PO_4/15$ as against the high yield of 67.33± 3.06 for $SS/H_3PO_4/5$ (Table 2).

Table 1: The result of pH and conductivity of activated carbon after washing and removal of chemicals

Samples	pH	Conductivity (µs/cm)
$SS/H_3PO_4/5$	6.74± 0.01	7.3 ± 1.53
$SS/H_3PO_4/10$	6.71± 0.01	11.33 ± 1.15
$SS/H_3PO_4/15$	6.82± 0.01	14.33 ± 1.53
$SS/ZnCl_2/5$	6.30± 0.02	10.67 ± 1.53
$SS/ZnCl_2/10$	6.40± 0.01	5.67 ± 0.58
$SS/Zncl_2/15$	6.47± 0.01	7.33 ± 1.15

A/B/C: Sample (A) modified with chemical (B) at activation time (C)

The percentage ash and moisture content for the shea nut shell was 6.67 ± 2.89 and 9.67 ± 0.58. The percentage ash content was low which is an indication of high carbon yield. The pH of the activated carbon produced using H_3PO_4 and $ZnCl_2$ as an activating agent fall within the range of 6.74 ± 0.01 to 6.82 ± 0.01 and 6.30 ± -0.02 to 6.47 ± 0.01 respectively. This is in accordance with Ahmedna *et al.* (1997) that activated carbons produced from precursors with low ash content have been found to have low pH (less than 7.0).

Table 2: The result of activation burn off, % yield and bulk density of activated carbon .

Samples	Activation burn off (%)	%Yield	Bulk Density (g/cm^3)
$SS/H_3PO_4/5$	32.67± 3.06	67.33± 3.06	0.54± 0.01
$SS/H_3PO_4/10$	35.33± 2.31	64.00± 2.00	0.56± 0.02
$SS/H_3PO_4/15$	37.33± 1.15	62.67± 1.15	0.57± 0.01
$SS/ZnCl_2/5$	22.87± 2.53	77.13± 2.53	0.49± 0.01
$SS/ZnCl_2/10$	31.93± 2.61	68.07± 2.61	0.51± 0.01
$SS/ZnCl_2/15$	35.33± 3.06	64.67± 3.06	0.54± 0.01

A/B/C: Sample (A) modified with chemical (B) at activation time (C)

The percentage activation burn off increase with increase activation contact time regardless of the nature of the activating agent while the percentage yield decrease with increasing activation burn

off. The expected low yield for precursors with higher percentage burn off is similar to values presented by Martinez *et al.* (2006) and Itodo *et al.* (2008). It was evident that at longer dwell time, more volatiles are released from the char, thereby; resulting to a higher burn off and a corresponding lower yield (Martinez *et al.,* 2006). The bulk density (g/cm^3) increased with decrease in percentage yield of activated carbon, which is an indication that at lower percentage yield the hardness (attrition) of activated carbon is high, with a resultant high tendency for regeneration (Table 2).

The highest percentage removal of BOD by H_3P0_4 catalyzed activated carbon at 5 min dwell time (SS/ H_3P0_4/5) was obtained at short contact time (60 minutes), that is, 31.79% adsorbed (Table 3 - 5), unlike $ZnCl_2$ catalyzed activated carbon with dwell time of 5 minutes (SS/$ZnCl_2$/5) for which the highest percentage uptake of BOD was obtained at long contact time (120 minutes), that is, 28.61% adsorbed (Table 6). Activated carbon produced using H_3P0_4 as an activating agent at dwell time of 10 minutes (SS/ H_3P0_4/10) has the highest percentage uptake of BOD at 90 minutes interaction time, that is, 52.28% removed (Table 4), while the activated carbon obtained at the same dwell time with $ZnCl_2$ as an activating agent (SS/$ZnCl_2$/10) was found to have higher percentage adsorbed of BOD at a lower contact time (60 minutes), that is, 26.85% uptake (Table 7).

The activated carbon produced using H_3P0_4 as an activating agent at dwell time of 15 minutes (SS/ H_3P0_4/15) has the highest percentage of BOD adsorbed at a short time (60 minutes), that is, 14.84% removed (Table 5) unlike the activated carbon produced using $ZnCl_2$ as an activating agent at the same dwell time (SS/$ZnCl_2$/15) which was found to have the highest % BOD removal at a longer time (120 minutes), that is, 28.26% removed (Table 8) and figure I.

Table 3: The % BOD removal by SS/H_3PO_4/5 biosorbent

Time (min)	BODi (mg/l)	BOD_f (mg/l)	% Removal = $\frac{BOD_i - BOD_f}{BOD_i} \times 100$
30	28.31	23.11	18.37
60	28.31	19.31	31.79
90	28.31	21.11	25.43
120	28.31	23.01	18.72
150	28.31	22.51	20.49

Table 4: The % BOD removal by **SS/**H_3PO_4/10 biosorbent

Time (min)	BODi (mg/l)	BOD_f (mg/l)	% Removal = $\frac{BOD_i - BOD_f}{BOD_i} \times 100$
30	28.31	25.51	9.89
60	28.31	21.91	22.61
90	28.31	13.51	52.28
120	28.31	26.01	8.12
150	28.31	27.71	2.12

Table 5: The % BOD removal by **SS/**H_3PO_4/15 biosorbent

Time (min)	BODi (mg/l)	BOD_f (mg/l)	% Removal = $\frac{BOD_i - BOD_f}{BOD_i} \times 100$
30	28.31	26.91	4.95
60	28.31	24.11	14.84
90	28.31	27.71	2.12
120	28.31	27.91	1.41
150	28.31	25.81	8.83

Table 6: The % BOD removal by SS/$ZnCl_2$/5 biosorbent

Time (min)	BODi (mg/l)	BOD_f (mg/l)	% Removal = $\frac{BOD_i - BOD_f}{BOD_i} \times 100$
30	28.31	22.31	21.19
60	28.31	24.31	14.13
90	28.31	22.31	21.19
120	28.31	20.21	28.61
150	28.31	24.41	13.78

From the above, it can be clearly stated that the nature of activating agent and activation interaction time affects the removal of the BOD from industrial effluent. Similar work was reported by Kadirvelu *et al.* (2000) for the removal of BOD from dyeing industrial wastewater using carbonized cocoanut tree sawdust.

Table 7: The % BOD removal by SS/ $ZnCl_2$/10 biosorbent

Time (min)	BODi (mg/l)	BOD_f (mg/l)	% Removal $= \frac{BOD_i - BOD_f}{BOD_i} \times 100$
30	28.31	25.01	11.66
60	28.31	20.71	26.85
90	28.31	27.71	2.12
120	28.31	27.41	3.18
150	28.31	21.21	25.08

Table 8: The % BOD removal by SS/$ZnCl_2$/15 biosorbent

Time (min)	BODi (mg/l)	BOD_f (mg/l)	% Removal $= \frac{BOD_i - BOD_f}{BOD_i} \times 100$
30	28.31	22.91	19.07
60	28.31	21.11	25.43
90	28.31	21.71	23.31
120	28.31	20.31	28.26
150	28.31	27.81	1.77

Where BOD_i = Biochemical Oxygen demand of industrial effluent before interaction
BOD_f = Biochemical Oxygen demand of industrial effluent after interaction.

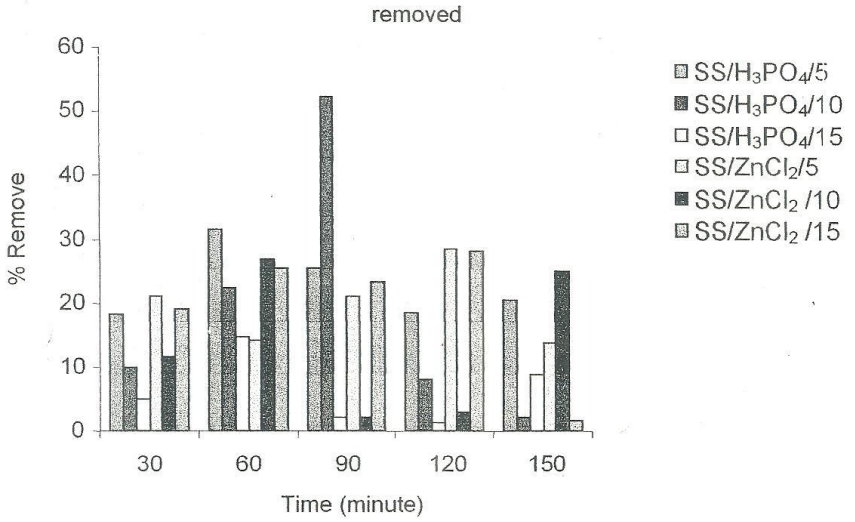

Fig. I: The percentage of the biochemical oxygen demand

Typical kinetic data were generated from experimental data. These data were separately treated as tables 9 and 10. In the evaluation of the adsorption kinetics of industrial effluent, the Lagergren Pseudo-first-order and Pseudo-second-order kinetic models were used to fit the experimental data. Sample with higher correlation coefficients R^2 ($R^2 \geq 0.5$) is accepted for a given model, while sample with values for the calculated and experimental q_e ($q_{e\ (Cal)}$ and $q_{e\ (exp)}$) nearness to each other is also accepted for a given model.
The first-order rate constant (K_1) and $q_{e(cal)}$ determined from the model with the corresponding correlation coefficients (R^2) were presented in Table 9. It was found that the correlation coefficients

(R^2) for the pseudo-first-order model were low and a wide range of variations were recorded for the calculated and experimental q_e values. This indicates that the adsorption of BOD on the adsorbent does not follow pseudo-first-order kinetics. Therefore, the experimental kinetic data were further analyzed using the pseudo-second-order model. The $q_{e(exp)}$ and the $q_{e\ (cal)}$ values along with correlation coefficients for the pseudo-second-order models were presented in Table 10.

Table 9: Pseudo first order parameters of Biochemical Oxygen Demand estimation by H_3PO_4 and $ZnCl_2$ modified SS-Carbon

Sample	R^2	K_1	q_e(cal)	q_e(exp)	%SSE
SS/H_3PO_4/5	0.35	-0.02	0.01	0.12	0.0492
SS/H_3PO_4/10	0.33	-0.02	0.03	0.01	0.0089
SS/H_3PO_4/15	0.43	-0.02	0.01	0.05	0.0179
SS/$ZnCl_2$/5	0.52	-0.03	0.01	0.08	0.0313
SS/$ZnCl_2$/10	0.55	-0.03	0.01	0.14	0.0581
SS/$ZnCl_2$/15	0.64	-0.02	0.05	0.01	0.0179

Table 10: Pseudo second order parameters of Biochemical Oxygen Demand estimation by H_3PO_4 and $ZnCl_2$ modified SS - Carbon

Sample	R^2	K_2	q_e(cal)	q_e(exp)	%SSE
SS/H_3PO_4/5	0.95	-1.52	0.11	0.12	0.0045
SS/H_3PO_4/10	0.57	-2.31	0.02	0.01	0.0045
SS/H_3PO_4/15	0.34	500	0.02	0.05	0.0134
SS/$ZnCl_2$/5	0.80	-1.99	0.09	0.08	0.0045
SS/$ZnCl_2$/10	0.23	1.96	0.03	0.14	0.0492
SS/$ZnCl_2$/15	0.47	-1.91	0.01	0.01	0.0000

SS/H_3PO_4/5 = shea nut shell catalyzed with H_3PO_4, activated for 5 minutes.
SS/H_3PO_4/15 = Shea nut shell catalyzed with $ZnCl_2$, activated at 15 minutes.

The correlation coefficient (R^2) had the highest value to be 0.95 for data generated using second order model. The best fit generally follows the trend: SS/H_3PO_4/5 > SS/$ZnCl_2$/5 >SS/H_3PO_4/10 > SS/$ZnCl_2$/15 > SS/H_3PO_4/15 > SS/$ZnCl_2$/10. In terms of nearness of calculated and experimental q_e, $q_{e\ (cal)}$ values were closer to the experimental $q_{e\ (exp)}$ values therefore the best fit generally follows the trend: SS/$ZnCl_2$/15> SS/H_3PO_4/5>SS/$ZnCl_2$/5 > SS/H_3PO_4/10 >SS/ SS/H_3PO_4/15 > SS/$ZnCl_2$/10. It was thus, concluded that the pseudo-second-order kinetic model provided a good correlation for the adsorption of BOD on the adsorbent compared to the pseudo-first –order model. This is in agreement with the work by Hameed (2008), who reported pseudo-second-order kinetics for adsorption of methylene blue on papaya seeds activated carbon.
Besides the values of R^2, the applicability of both kinetic models was verified through the statistical sum of error (SSE %). Sample with least percentage statistical sum of error (SSE %) was accepted for a given kinetic model. Comparing tables 9 and 10, the percentage statistical sum of error on table 10 was low compared to that of table 9. It was also found that the adsorption of BOD on activated carbon could best be described by the second-order-kinetic model. The general trend for best fit in terms of % SSE is as follows: SS/$ZnCl_2$/15 > SS/H_3PO_4/5, SS/H_3PO_4/10, SS/$ZnCl_2$/5 > SS/H_3PO_4/15 > SS/$ZnCl_2$/10 in Table 10.

CONCLUSION

The present research showed that shea nut shell can be effectively used as a raw material for the preparation of activated carbon for the adsorption of biochemical oxygen demand from industrial effluent. The adsorption kinetics can best, be described by pseudo-second-order kinetic. Considering, the R^2, this parameter fits well for SS/H_3PO_4/5 than it does for the SS/$ZnCl_2$/10 biosorbent. In terms of nearness of $q_{e\ (cal)}$ to $q_{e\ (exp)}$, the parameter is better for SS/$ZnCl_2$/15 than SS/$ZnCl_2$/10. For percentage statistical sum of error (% SSE), SS/$ZnCl_2$/15 is better than SS/$ZnCl_2$/10. The role of the activation dwell time, contact time and nature of activating agent cannot be over emphasized. The results of the present research revealed that shea nut shell; a low-cost adsorbent could be employed as an alternative to commercial activated carbon for the removal of biochemical oxygen demand from industrial effluent.

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