Comparative Adsorption Behavior of Malachite Green Dye onto Charred and Aminated Sal (*Shorea robusta*) Sawdust from Aqueous Solution

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ABSTRACT

Chemically treated Sal sawdust was used to study the adsorption of Malachite Green (MG) dye from an aqueous solution. Raw Sal sawdust (RSSD) was charred and aminated. The surface functional groups of raw and modified adsorbents were determined by Fourier Transform Infrared (FTIR) Spectra. The influence of pH on batch experiments, concentration and contact time for charred Sal sawdust (CSSD) and aminated Sal sawdust (ASSD) were investigated. The dye uptake was highest at a pH of 4, and adsorption was found to be 62.63 % and 92.15% for CSSD and ASSD, respectively, at an adsorbent dose of 0.025 g and agitation speed of 190 rotations per minute (rpm). The pertinency of Langmuir isotherm was tested, and the kinetic data was found best fitted for pseudo-second-order. The adsorption capacity of MG dye onto ASSD and CSSD was found to be 91.9 mg/g and 64 mg/g, correspondingly. This showed that ASSD is a more efficient adsorbent than CSSD for excluding MG dye from an aqueous solution.

Keywords: Adsorption-isotherms, Aminated Sal sawdust, Charred Sal sawdust, Malachite green

1. INTRODUCTION

A dye is a natural or artificially synthesized coloured substance that capacitates to be attached to a substance. Dyes comprise chromophore groups such as –N=N–, >C=O, $–NO_2$, etc. which impart colour by absorbing light in the visible region (Khattri & Singh 2009). The presence of auxochrome groups such as $–NH_2$, –OH, $–SO_3H$, –COOH, etc., increases the colour intensity. Malachite green (MG) is a commonly used dye in industries as a colouring material, and its adsorptive removal uses commercially available low-cost carbon materials like chemically modified charred and xanthated wheat bran great significance (Dhami & Homagai 2020). Commercially, MG may be marketed in the form of its oxalate salt. It is a toxic compound that can cause carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity. Therefore, it is a major pollutant in industrial effluents. In this context, removing this dye from the effluent of chemical industries seems essential before its disposal (Hameed & Khaiary 2008). Many researchers have attempted to make chemically modified adsorbents from agricultural wastes such as banana peels, tea leaves, sawdust, wheat bran, coffee grounds, coconut husk, and rice husks for these applications (Sharma *et al.* 2009). Locally available biomaterials and their remnant wastes can be used as bio-adsorbent as a low-cost, eco-friendly, renewable, with profound dye-removing capacity. Abbas developed activated carbon from apricot stones and applied it for the removal of malachite green. Malachite green removal was increased until equilibrium and spontaneity of the process were predicted based on negative free energy value.

(–ΔG) and positive enthalpy (ΔH) (Abbas 2020). Low-cost adsorbents could be suitable materials for removing the dye from an economic point of view (Gupta & Suhas 2009). Sartape *et al.* (2017) used *Limonia acidissima* to create a low-cost adsorbent for removing malachite green dye from an aqueous solution. They looked at the impact of many factors, such as adsorbent dosage, initial dye concentration, contact time, pH, temperature, etc.

Among many available biomass resources, sal sawdust is a commonly available raw material with high carbon content (Chatterjee *et al.* 2010). The major constituents of sal saw dust includes cellulose, hemicellulose, and lignin, with some functional groups such as –COOH, -NH, - CHO, etc. The presence of a particular functional group imparts a corresponding surface charge to the materials (Dawadi *et al.* 2020). Adsorbents with negatively charged functional groups attract positively charged dye ions. Previously reported articles showed that sal sawdust potentiates for adsorptive removal of dyes such as methyl red (Kour *et al.* 2013). To investigate malachite green dye (Singh *et al.* 2017), sal seed activated char was developed. Charring removes hydrogen and oxygen from a substrate upon combustion, leaving behind a mass of carbon, and as produced carbons will be porous with a relatively high surface area. Large surface area imparts higher adsorptive capacity.

Furthermore, the non-polar nature of activated carbon preferentially adsorbs non-polar adsorbent or very low polar adsorbent. Charring and chemical activation can enhance the adsorption capacity. Both carried out the activated carbons' chemical activation by mixing the zinc chloride solution and animal waste precursors (Demiral & Demiral 2008). Besides this, the adsorptive removal of dyes or heavy metal ions is influenced by adsorbent particle size, pore structure and distribution, surface chemical properties, surface free energy, level of unsaturation and adsorbate concentration.

Lesser or greater, activated carbon consists of oxygen and hydrogen in the form of functional moieties such as carbonyl group, phenolic group, ether group, lactone, quinone, etc. Some of such functional groups are inherently present during the activation process, or some of the functional groups are introduced to enhance the adsorptive removal performance. The introduction of amino groups onto the surface of activated carbon is amination. The nitrogen atom of the amine group could serve as a chelating group or lone pair donor in complex formation. In this context, the amination of activated carbon seems to be a promising technique to increase the efficacy of dye adsorption (Amina *et al.* 2003 & Andersen *et al.* 2006).

This work prepared sal saw dust by treating raw sal sawdust with acid, followed by an amination process. Finally, the adsorption capacity of CSSD and ASSD was compared using Malachite Green (MG) dye. Then adsorption isotherms and kinetics were studied.

2. MATERIALS AND METHODS

2.1 Materials

Pyridine, thionyl chloride, acetone, dimethyl sulphoxide (DMSO), sodium carbonate, ethylene diamine, and HCl were bought from the chemical suppliers, Kathmandu. All the chemicals utilized were of analytical quality (Thermo-Fischer Scientific, India) and were used without further purification.

2.2 Methods

2.2.1 Preparation of Adsorbent from Raw Sal Sawdust (RSSD)

Raw Sal sawdust was obtained from a nearby sawmill in Gwarko, Lalitpur. The sawdust was then sun-dried for 2-3 days to remove moisture.

2.2.2 Preparation of Charred Sal Sawdust (CSSD)

Conc. H_2SO_4 was poured into 200 g of raw Sal sawdust in a bucket with a 5-litre capacity and stirred with a wooden spatula until the dust turned completely black. Then it was left for 24 h, resulting in the ring-opening of cellulose (Homagai *et al.* 2011). The charcoal was washed with distilled water, neutralized completely to pH 7, and dried. The dried charcoal powdered was sieved to a fineness of 250 microns and labelled as CSSD.

2.2.3 Preparation of Aminated Sal Sawdust (ASSD)

Thionyl chloride ($SOCl_2$) was added drop by drop in three-necked flasks placed in an ice bath at 0°C, where CSSD was soaked with pyridine. The suspension was agitated for 10 minutes,kept in a fume hood, and then heated for $_{2.5}$ h. The unreacted thionyl chloride was washed multiple times with water and then washed with acetone. It was dried at 70 °C in an oven, and the dried powder was processed for 48 h at 70 °C with dimethyl sulphoxide (DMSO), sodium carbonate, and ethylene diamine (Kour *et al.* 2013). Finally, the sample was labelled as ASSD and was stored in an airtight bottle. The alcoholic and phenolic –OH groups in lignin, cellulose, and hemicelluloses were thought to be replaced by amino groups during amination (Khatri & Singh 2009; Abbas 2020).

2.2.4 Physicochemical Characterization

The surface functional moieties were studied using Fourier-transform infrared spectroscopy (FT-IR; Perkin Elmer, USA), and the surface morphology of as-synthesized AC was studied using field emission scanning electron microscopy (FE-SEM, Hitachi, SUB8230, Tokyo, Japan) at an accelerating voltage of 5.0 kV. X-ray diffraction patterns of the samples were obtained using an X-ray diffractometer with Cu-Kα (XRD, Japan, $\lambda = 1.544426$ Å). The X-ray source is operating at 30 kV/10mA. These characterizations were carried out at the center for university-wide research facilties (CURF), Jeonbuk National University (JBNU), the Republic of Korea.

2.2.4 Batch Adsorption Experiment

A double-beam UV-spectrophotometer (Labtronics, LT-2802) was used for the measurement of the UV absorbance of the solution. A digital pH meter (Labtronics-11) was used to measure the pH of the test solution. On a mechanical shaker, 25 mL of MG dye solution of known concentration (25-800 mg/L) was shaken for 24 hours at a stable agitation speed of 190 rpm with a constant adsorbent dose of 25 mg. 1 M HCl and 1 M NaOH solution were used to alter the pH of the solution. The equilibrium concentrations (Ce) were measured after equilibrium, and the amount of MG dye adsorbed (q) in mg/g at equilibrium was calculated using the following equation.

$$q = \frac{(Ci - C_e)}{W} \times V \qquad (1)$$

Where the initial and equilibrium concentrations of MG dye in mg/L are Ci and Ce, respectively. W is the weight of the adsorbent in grams, and V is the volume of MG dye solution in litres. All experiments were performed in triplicate, and average values were reported. The percentage of dye adsorption (A) was estimated using the following formula:

$$A\,(\%) = \frac{(CiCe)}{Ce} \times 100 \qquad (2)$$

3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy

Fig. 1 depicts the combined Fourier Transformation Infrared Spectrum (FTIR). The 3200-3600 cm^{-1} broadband is caused by vibrations in the -OH groups of alcohols, phenols, and carboxylic acids. In raw, this band is very strong; however, it weakens in processed samples. This signifies that following chemical treatment, the moisture level was found to be significantly lower. Medium adsorption near 3400 cm^{-1} peak represents the presence of –NH. Peaks around 1034.48 cm^{-1} (RSSD), 1211.63 cm^{-1} (CSSD), 1108.65 cm^{-1} (CSSD ads.), 1208 cm^{-1} (ASSD) and, 1107.70 cm^{-1} (ASSD ads.) are the features of C-O group of the primary hydroxyl group.

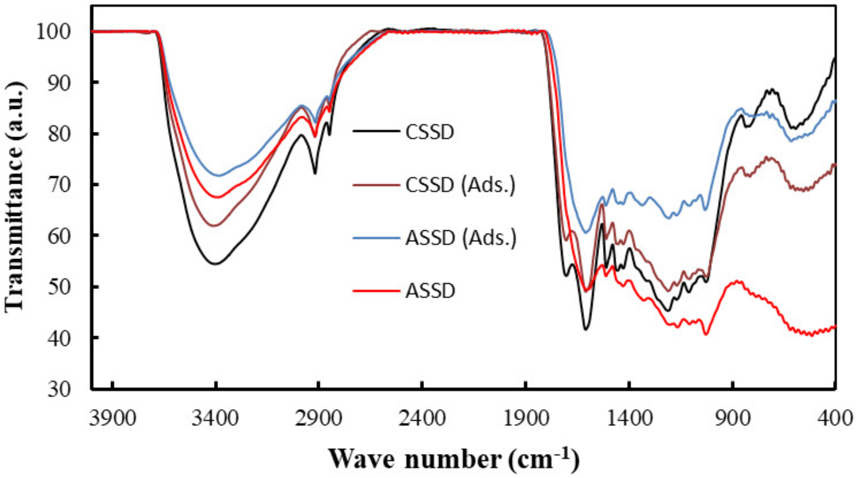

Fig. 1. FTIR images for the surface morphologies of CSSD and ASSD before and after adsorption

The –CHO group generated during the charring process before the alteration of CSSD could be responsible for the band seen at 1704 cm^{-1}. After converting CSSD to ASSD, this peak vanishes, leaving intense broadband at 1610.7 cm^{-1}. Thus, the primary amine can be observed in the 3100-3500 cm^{-1} and, as a result, the band 3406.28 cm^{-1} at ASSD has been modified from 3384.35 cm^{-1} indicating that the amine group has been placed onto CSSD. Fig. 1 demonstrates that ASSD, which contains a nitrogen group, was more effective as a bio adsorbent for removing MG dye than CsSD

3.2 Field Emission Scanning Electron Microscope (FE-SEM) Analysis

The surface morphology of RSSD, CSSD, CSSD (ads), ASSD and ASSD (ads) was characterized by SEM images, as shown in Fig. 2a-2e. RSSD's surface was discovered to be smooth. CSSD's fibre surface, on the other hand, was found to be relatively rough and non-uniform. This could be owing to a powerful sulphuric acid-induced hydrolysis process on the surface of sal sawdust. The rough surface could provide a high surface area for the entrapment of dyes. This justified the charring process's efficacy for increasing the sal sawdust's higher surface area.

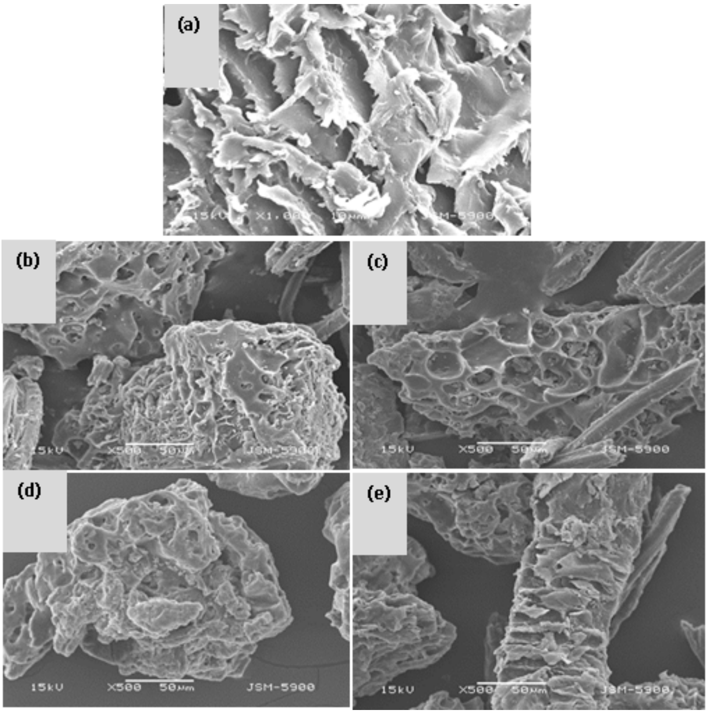

Fig. 2. Fig. Scanning electron microscopy image of (a) RSSD, (b) CSSD, (c) CSSD (ads), (d) ASSD, (e) ASSD (ads). The scale bar is 50 µm on each case.

3.3 X-ray Diffraction (XRD) Analysis of Adsorbents

Fig. 3 depicts the RSSD, CSSD, and ASSD X-ray diffraction (XRD) patterns. Both types of pyrolysis (treating with conc. S and heating in an inert atmosphere) change the structure of CSSD and ASSD (Fig.3), which can be noticed by the appearance of sharp peaks (Gupta and Suhas 2010). The peak at 21.90° of ASSD is associated with the graphite plane due to the presence of a few parts of lignin. Moreover, the broad hump type of shape is noticed in RSSD at 2Θ = 22°, indicating the amorphous state, but this type is not seen in modified samples which proved CSSD and ASSD are more crystalline due to the presence of few parts of lignin.

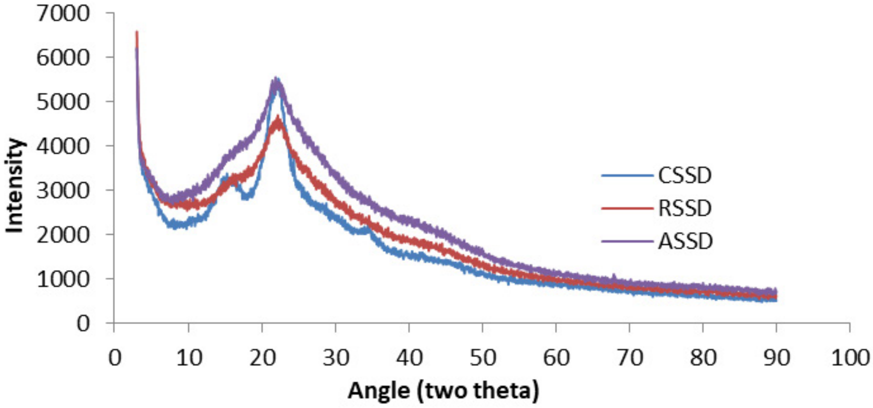

Fig. 3. XRD patterns of RSSD, CSSD (Ads.) and ASSD (Ads.)

3.4 Effect of pH

Activated carbon exhibits a higher adsorption rate in an acidic solution than in its alkaline solution. In this context, it is worthwhile to study the influence of pH. Effect of pH on adsorption of MG dye onto CSSD and ASSD at an initial concentration of 50 ppm at room temperature, as shown in Figure 4. According to the pH studies, the ideal pH for both CSSD and ASSD is 4.0. The percentage elimination of MG dyes in ASSD is found to be more effective than in CSSD, i.e., 92.15% and 62.63%, respectively, as found in Fig 4. As known, pH value influences the state and solubility of adsorbate in aqueous media and influences adsorption efficacy. The amino group's N-atom has been discovered to be a more effective chelating group, with a higher inclination to donate a lone pair of electrons for sharing with dye ions in the formation of complexes. It was corroborated by observing a rapid increase in the final pH of the solution at the ideal pH for maximum dye adsorption.

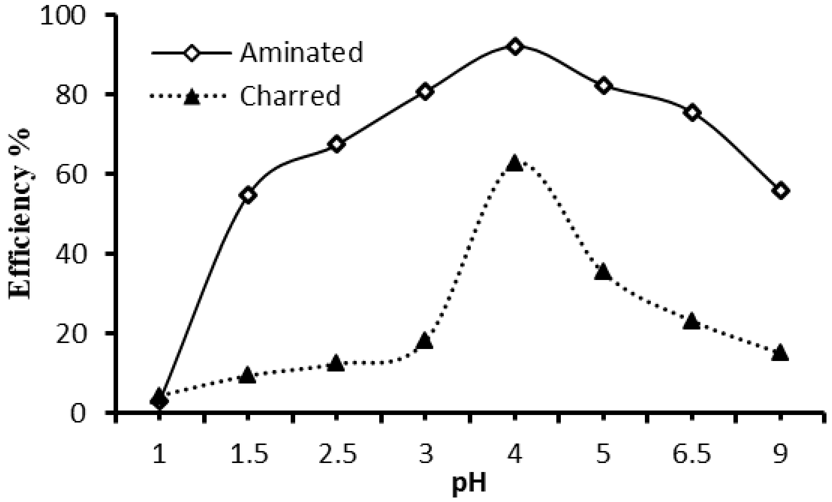

Fig.4. Effect of pH for adsorption of MG dye onto CSSD and ASSD

3.5 Kinetic Studies of Adsorption of MG Dye

Kinetic studies reveal optimum conditions, sorption mechanisms, and potential rate-controlling steps in the batch adsorption process. At an initial dye concentration of 25 ppm, kinetics investigations of the adsorption of MG dye onto CSSD and ASSD were displayed as a function of time. For this purpose, a linear and nonlinear form of pseudo-first- and pseudo-second-order kinetics are applied to adsorption data. The pseudo-first-order equation is given as:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (3)$$

For dye adsorption, plotting t/q_t against t yields a straight line, from which the value can be derived using the slope and intercept, respectively. The pseudo-second-order model looks like this:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

The adsorption of MG dye onto CSSD and ASSD concurrently was plotted as a pseudo-second-order kinetics plot of (t/qt) vs t, yielding a perfectly straight line, suggesting that the adsorption reaction can be monitored using the pseudo-order kinetic model. Figure 5 shows the correlation coefficient of 0.991 and 0.995, i.e., near unity for charred and aminated adsorbents, respectively. Therefore, the R^2 value indicated that the pseudo-second-order kinetic model could be useful for the adsorption of MG dye onto CSSD and ASSD and also confirmed the chemisorption of dye.

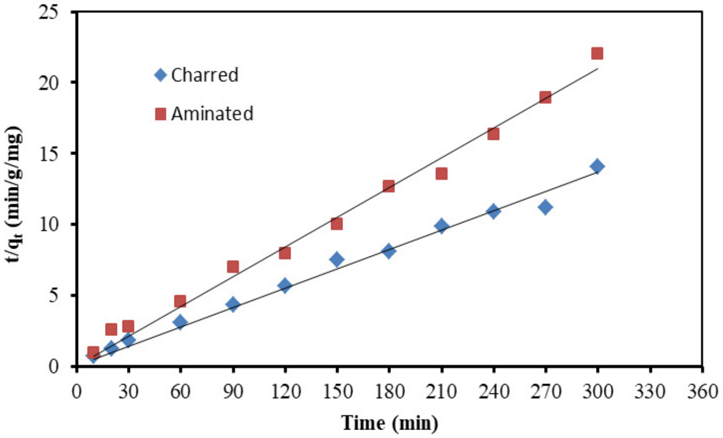

Fig. 5. Pseudo-second order for adsorption of MG dye onto ASSD and CSSD.

3.6 Adsorption Isotherm Studies

Various amounts of adsorbents were placed in reagent glass bottles to conduct an adsorption isotherm experiment. Each case of dye solution prepared in the lab received a different number of adsorbents. The absorbance of the supernatant clear liquid is measured spectrophotometrically at the dye's maximum wavelength after a four-hour equilibration interval. A graph was used to calculate the amount of dye adsorbed. The correlation coefficient values for Freundlich and Langmuir isotherms were used to determine the applicability of the isotherms. The Langmuir equation can be stated in linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (5)$$

Where (mg/L) is the concentration of adsorbate at equilibrium, (mg g^{-1}) is the amount of adsorbate adsorbed by an adsorbent at a time ''t', is the maximum adsorption capacity (mg g^{-1}). The Langmuir constant, b, is connected to binding energy and can be correlated with variations in the adsorbent's appropriate area and porosity, implying that a larger surface area and pore volume would result in a higher adsorption capacity. The Langmuir plot for MG dye adsorption onto CSSD and ASSD is shown in Fig. 6. The Langmuir correlation coefficient '''R^2' found near unity confirmed that the Langmuir isotherm model is best fitted.

Table 1. Langmuir adsorption isotherm model parameters

Dye (MG)	q_m (mg/g)	b (L/mg)	R^2
MG onto ASSD	91.9	0.005	0.995
MG onto CSSD	64	0.01	0.993

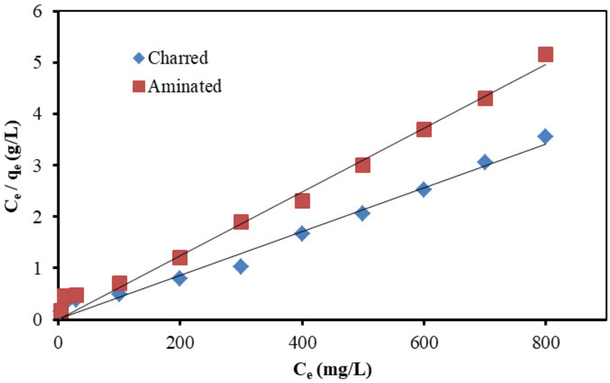

Fig. 6. Langmuir plot for adsorption of MG dye onto CSSD and ASSD

3.6 Comparison of Adsorption Capacities

The MG uptake capacities of CSSD and ASSD were comparable with the different modified and / or unmodified biosorbents given in the literature (Table 2). From these results, it can be concluded that the developed bio-adsorbent CSSD and ASSD would be potential adsorbents for removing MG from wastewater.

Table 2: Comparison of adsorption capacities with previously reported results

Adsorbents	MG adsorption(mg/g)	References
Charred Sal sawdust	64	Present study
Aminated Sal sawdust	91.9	Present study
Charred wheat bran	69	Dawadi *et al.* (2020)
Xanthated wheat bran	112.9	Dawadi *et al.* (2020)
Activated carbon (eucalyptus seed)	451.8	Renita *et al.* (2021)

4. CONCLUSION

For the removal of MG dye from an aqueous solution, the adsorption capability of chemically produced ASSD and CSSD were evaluated. The pH of the solution, the dye content, and the contact time all influence adsorption. With an adsorbent dosage of 0.025g and an agitation speed of 190 rpm, the removal percentage was determined to be 92.15 percent on ASSD and 62.63 percent on CSSD. The results were in good accord with Pseudo-second-order kinetics and the Langmuir isotherm. The maximum uptake of MG dye from adsorption isotherm was to be 91.9 mg/g and 64 mg/g onto ASSD and CSSD, respectively. As a consequence of the comparison, it can be stated that ASSD is a more effective adsorbent than CSSD for removing MG dye from aqueous solutions.

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