BIOSORPTION OF CATIONIC DYES FROM AQUEOUS SOLUTION BY WATER HYACINTH ROOTS

Ö. SALTABAŞ[1*]
M. TEKER[2]
Z. KONUK[2]

[1]Department of Jewelry Engineering
Istanbul Commerce University
34840 Istanbul, Turkey
[2]Department of Chemistry, Sakarya University
54100 Sakarya, Turkey

*to whom all correspondence should be addressed:
e-mail: osaltabas@iticu.edu.tr

ABSTRACT

Water hyacinth *Eichhornia crassipes* was found to have biosorption capacity for cationic dyes, malachite green and methylene blue from aqueous solutions. To evaluate the biosorption capacity and characteristics, the effect of solution pH, initial dye concentration, temperature, dose of biosorbent loading, contact time and shaking rate were investigated in a batch mode. Biosorption was increased with the increasing temperature for both studied dyes. The Langmuir and Freundlich adsorption models were used for mathematical description of the sorption equilibrium. Equilibrium data was fitted well to the Langmuir model in the studied concentrations (1-200 mg L^{-1}) at 293 and 313 K. Based on the Langmuir isotherm plots the maximum biosorption capacity values were calculated to be 44.64 mg g^{-1} for malachite green and 42.55 mg g^{-1} for methylene blue at 313 K. Various thermodynamic parameters such as ΔG^o, ΔH^o, and ΔS^o were evaluated with results indicating that this system was an endothermic spontaneous reaction and kinetically suited to pseudo-second-order model.

KEYWORDS: dye, malachite green, methylene blue, decolorisation, biosorption, adsorption isotherms, Water hyacinth roots.

1. INTRODUCTION

Synthetic dye stuffs are used extensively in industries such as textiles, leather, paper, plastic, etc. to color their final product. The extensive use of dye often poses pollution problems in the form of colored wastewater discharged into water bodies. However, colored dye effluents are known to be very toxic to aquatic life. They reduce the photosynthetic activity and primary production.

Physico-chemical processes such as electro-coagulation, ozonation, photocatalysis, membrane filtration and adsorption have been employed for the treatment of dye containing wastewater (Capar *et al.*, 2006; Shu, 2006; Silva *et al.,* 2006; Alinsafi *et al.,* 2005). Among these technologies, adsorption process is considered to be a promising technology which involves phase transfer of dye molecules onto adsorbent leaving behind the clear effluent. Activated carbon is the most popular and widely used adsorbent for the removal of color from textile effluents but it is not used on a large scale due to its high cost, problems in regeneration or disposal of the used carbon. Recently, there has been a considerable amount of research to find cheaper alternatives to activated carbon. Recent progress in dye treatment technology has led to the development of new approaches utilizing low-cost, renewable, locally available biological or agricultural materials. Some of the adsorbent materials have already been used in dye sorption. These were activated clay (Özdemir *et al.,* 2006; Weng and Pan, 2007), wheat bran (Sulak *et al.*, 2007), fungal biomass (Aksu and Çağatay, 2006; Iqbal and Saeed, 2007), granular kohlrobi peel (Gong *et al.,* 2007), macro alga (Marungrueng and Pavasant, 2006), brown seaweed (Vijayaraghavan and Yun, 2008), rice husk (Ponnusami *et al.,*

2007), fermentation wastes (Vijayaraghavan and Yun, 2007; Won and Yun, 2008) and yeast (Kumari and Abraham, 2007).

Water hyacinth has been used for removal of nutrients, heavy metals, organic compounds or pathogens from water. It is demonstrated that Water hyacinth roots have the high metal binding capacity (Saltabaş *et al.*, 2001). Water hyacinth roots were used in basic dye biosorption (Low *et al.*, 1995). However research on biosorption capacity of this biomass to remove dye from effluent is relatively limited.

In this study, biosorption of malachite green (MG) and methylene blue (MB), commonly used in textile industry for coloring clothes, onto dried *Eichhornia crassipess* roots biomass was investigated.

2. MATERIALS AND METHODS

2.1. Preparation of the biosorbent

Water hyacinth was collected from the Botanic garden of Istanbul University. The roots of collected Water hyacinth were separated and washed thoroughly with tap water for several times to remove earthy matter and all the particles. It was finally washed with distilled water three times and dried in an oven at a temperature of 80 °C for 48 hours. Dry biomass was crushed into granules, sieved to different particle sizes and then preserved in a desiccator for subsequent uses. The particles less than 300 µm were used in the experiments.

2.2. Preparation of cationic dye solutions

All chemicals used in this study were analytical grade. Malachite green (molecular weight: 329.46 g mol^{-1}, λ_{max}: 617.3) and methylene blue (molecular weight: 319.85 g mol^{-1}, λ_{max}: 664.8) were obtained from Merck AG and used without purifications. The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 1000 mg L^{-1}. The experimental solutions were obtained by diluting the dye stock solutions in different concentrations.

2.3. Experimental procedure

Biosorption studies were carried out by the batch technique to obtain equilibrium data. The initial pH values of the solutions were adjusted with solutions of 0.1 M HNO$_3$ or 0.1 M NaOH before mixing the biomass suspension. The biosorption capacity of Water hyacinth roots was determined by contacting 100 mL of dye solutions of known concentration with certain amount of biosorbent in 250 mL flasks. The biosorbent in dye solution was shaken on an orbital shaker and removed from dye solution by centrifugation at 4500 rpm for 5 minutes. The concentration of unadsorbed cationic dyes in the biosorption medium was measured colourimetrically using a spectrophotometer (UV-2410PC, Shimadsu, Kyoto, Japan). Blanks containing dye but no biosorbent were used for each series of experiments. The sorption experiments were carried out at 20 and 40 °C to determine the effect of temperature and to evaluate the thermodynamic parameters. All the experiments were carried out in duplicate and the results reported are the mean values from two separate measurements.

2.4. Adsorption model

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid and solid phase when the adsorption process reaches an equilibrium state. The Langmuir and Freundlich isotherm equations are usually employed for the liquid-solid systems.
The Langmuir theory assumes that sorption takes places at specific sites within the adsorbent. This means that once a molecule occupies a site, no further adsorption can take place at that site. Therefore, at equilibrium, a saturation point is reached beyond which no further adsorption can occur. The Freundlich model assumes that the sorption takes place on heterogeneous surfaces and adsorption capacity depends on the concentration of molecules at equilibrium.
The equilibrium data obtained for biosorption of MG and MB onto Water hyacinth roots biomass was analyzed using linearized Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) isotherms (Eqs. (1) and (2), respectively).

$$C_e/q_e = 1/Q_m b + C_e/Q_m \tag{1}$$

$$\ln (q_e) = \ln k_F + 1/n (C_e) \tag{2}$$

where C_e (mg L^{-1}) is the concentration of dye solution at equilibrium, q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, Q_m (mg g^{-1}) is the maximum biosorption capacity. It represents a practical limiting adsorption capacity when the sorbent surface is fully covered with monolayer sorbate ions and b (l mg^{-1}) is the adsorption constant related to the free energy of adsorption. The Q_m and b values were calculated from the slopes ($1/Q_m$) and intercepts ($1/bQ_m$) of linear plots of C_e/q_e versus C_e. 1/n and k_F (mg g^{-1}) are empirical Freundlich constants and indicate adsorption capacity and intensity, respectively. Their values were obtained from the intercepts ($\ln k_F$) and slopes (1/n) of linear plots of $\ln q_e$ versus $\ln C_e$.

2.5. Kinetic modeling

In order to investigate the controlling mechanism of biosorption process such as mass transport and chemical reaction processes, the pseudo-first order and pseudo-second order kinetic models are expressed as (Lagergren, 1898):

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where k_1 is the pseudo first order rate constant (min^{-1}) of adsorption and q_e and q_t (mg g^{-1}) are the amounts of dye molecules adsorbed at equilibrium and time t (min.), respectively. The pseudo-first-order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites. A straight line of $\ln (q_e - q_t)$ versus t indicates the application of the first-order kinetics model. In a true first-order process $\ln q_e$ should be equal to the intercept of a plot of $\ln (q_e - q_t)$ against t.

In addition, a pseudo-second-order equation (Ho and Mckay, 1998) based on adsorption equilibrium capacity may be expressed in the form:

$$t/q_t = 1/[k_2(q_e)^2] + (1/q_e) t \tag{4}$$

where k_2 (g mg^{-1} min^{-1}) is the second-order reaction rate equilibrium constant. A plot of t/q_t against t should give a linear relationship for the applicability of the second-order kinetic.

2.6. Thermodynamic parameters of biosorption

In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change, ΔG^o, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG^o is a negative quantity. The Langmuir coefficient b (l mg^{-1}) was used to calculate the Standard Gibbs free energy change (ΔG^o) according to the following equation:

$$\Delta G^o = - RT \ln b \tag{5}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), b, the Langmuir constant and T is the absolute temperature (K). Change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) for the adsorption process were calculated using the Eqs. (3)-(5) (Rajgopal *et al.*, 2006).

$$\ln (b_2/b_1) = - \Delta H^o/R (1/T_2 - 1/T_1) \tag{6}$$
$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

where, b_1 and b_2 are Langmuir constants at temperatures T_1 and T_2, respectively.

3. RESULTS AND DISCUSSIONS

3.1. Effect of pH on dye uptake

The pH of the aqueous solution is one of the important controlling parameters in the biosorption process. The variations in the biosorption of MB and MG dye were studied within the pH range 1-12. The results for this range are given in Figure 1.
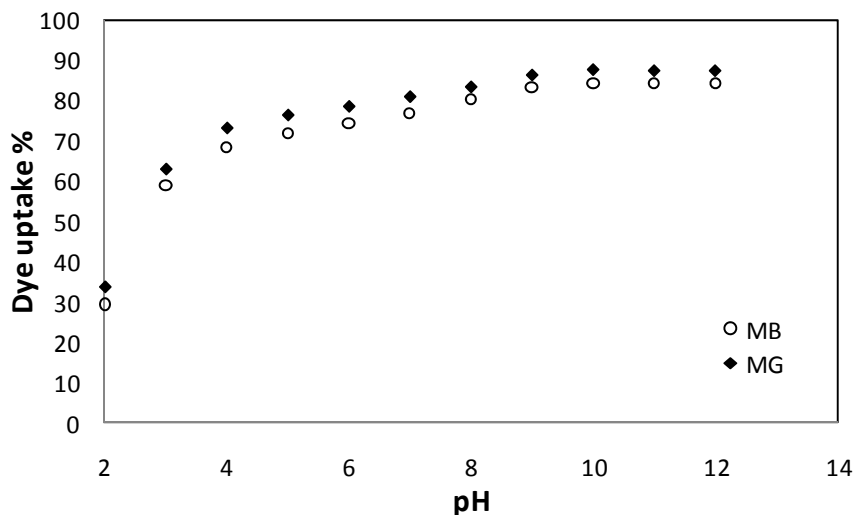
Figure 1. Effect of pH on the biosorption capacities of water hyacinth roots
(weight of biosorbent: 100 mg of biosorbent per 100 mL, initial dye concentration: 3 mg L^{-1},
contact time: 60 min., temperature: 20 ^{o}C, shaking rate: 150 rpm)

As seen in the Fig. 1, the uptake of MG and MB exhibits the maximum value at pH 9.5. Therefore, pH 9.5 was used in the subsequent experiments for both MG and MB.

3.2. Effect of contact time on dye uptake

Fig. 2 indicates the MG and MB dye uptake as a function of contact time at temperature of 20 ^{o}C. Figure 2 shows that the rate of dye uptake by water hyacinth roots is quite rapid. Maximum uptake occurred in the first 10 minute amounting to over 94.92 % for MG and 91.75 % for MB. This rapid rate of cationic dye uptake by Water hyacinth roots has a significant importance for applications in small reactor volumes. Thus it gives economical and effective advantages.
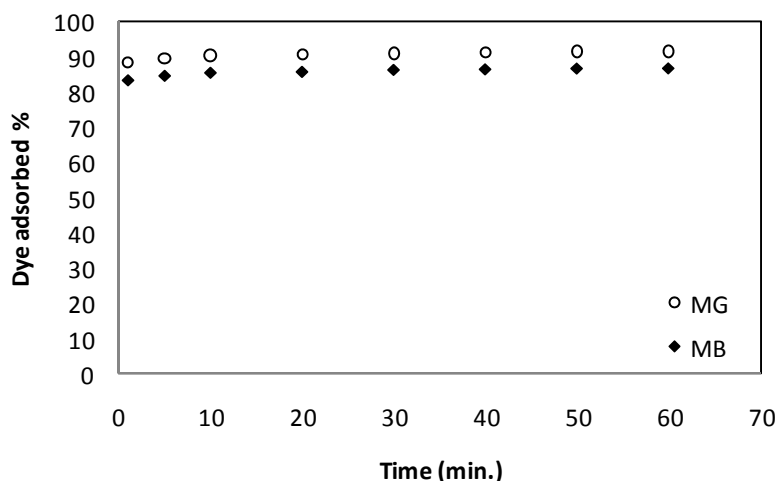

Figure 2. Effect of contact time on dye uptake (weight of biosorbent: 100 mg of per 100 mL, initial dye concentration: 2 mg L^{-1}, pH: 9.5, temperature: 20 ^{o}C, shaking rate: 150 rpm)

3.3. Adsorption kinetics modeling

In order to analyze the adsorption kinetics of metals, the pseudo-first-order and pseudo-second-order kinetic models were applied to data. The pseudo-second-order model was perfectly fitted to the experimental data. The comparison of experimental biosorption capacities and the theoretical values estimated from the above two models are presented in Table 1. The theoretical q$_e$ values estimated from the first-order kinetic model gave significantly different values than those of the experimental values, and the correlation coefficients were also found to be lower. These results

indicate that the first-order kinetic model does not describe adsorption of MG and MB by Water hyacinth roots. The correlation coefficients for the linear plots of t/q_t against t for the second-order equation are 1 for both dyes for contact time of 60 min. The theoretical q_e values of MG and MB were very close to the experimental q_e values in the case of second-order kinetics.

Table 1. Theoretically determined constants of pseudo-first and second-order reaction kinetics based on biosorption of MG and MB from 5 mg L^{-1} dye solutions by 100 mg biosorbent per 100 mL at pH 9.5 for 60 min

Dye	Experimental q_e (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
MG	22.549	0.0859	0.713	0.9187	1.68	4.59	1
MB	22.469	0.0814	0.703	0.9595	1.50	4.35	1

3.4. Effect of biosorbent dosage on dye uptake

Dye removal percentage versus the adsorbent dosage at 293 K is shown in Figure 3. The dye uptake percent increased as the adsorbent quantity increased. However the biosorbed dye concentration was decreased from 18.97 to 0.27 mg g^{-1} biomass for MG and from 18.00 to 0.26 mg g^{-1} biomass for MB with increasing in biosorbent concentration, from 0.01 to 1.0 g/100 mL. The decrease in biosorption capacity with increasing biosorbent concentration could be explained by not only unsaturation of biosorption sites through the adsorption reaction but also the particle interaction such as aggregation occurring at high biosorbent concentration and leading to decrease in total surface area.
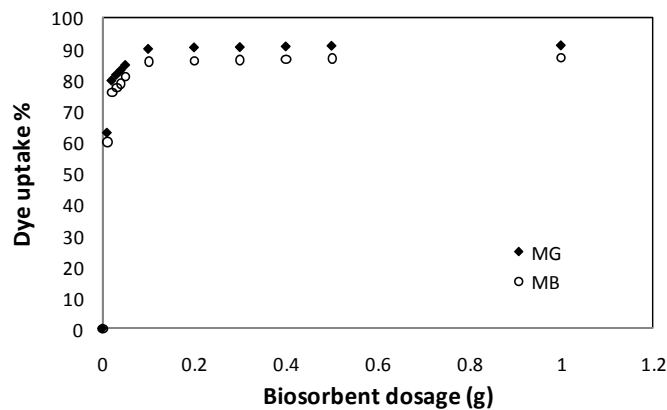

Figure 3. Effect of biosorbent dosage on dye uptake uptake (initial dye concentration: 3 mg L^{-1}, pH: 9.5, temperature: 20 $^{\circ}$C, contact time: 60 min., shaking rate: 150 rpm)
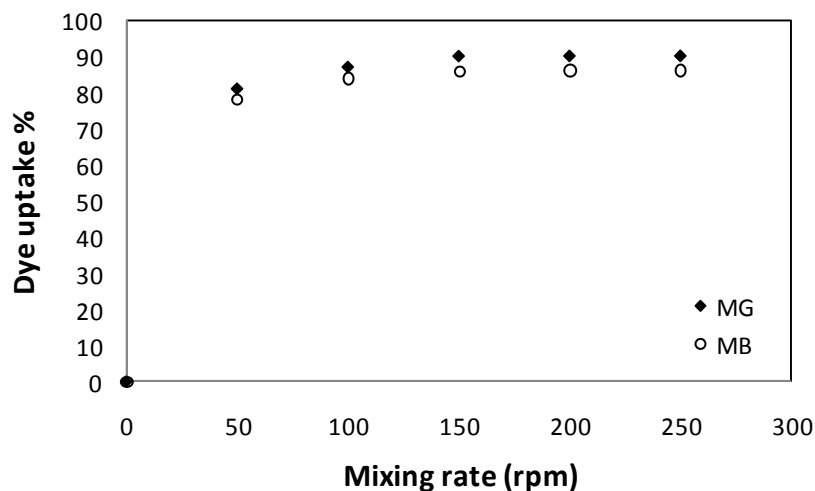

Figure 4. Effect of mixing rate on dye uptake (initial dye concentration: 3 mg L^{-1}, pH: 9.5, weight of biosorbent: 100 mg of biosorbent per 100 mL, temperature: 20 $^{\circ}$C, contact time: 60 min.)

3.5. Effect of mixing rate on dye uptake

As shown in Figure 4, the dye uptake was found to increase with an increase in mixing rate. It is because the increase of mixing rate improves the diffusion of dye molecules to the surface of the adsorbent. It is found that 150 rpm mixing rates were sufficient to assure the surface binding for both dye uptakes.

3.6. Effect of initial dye concentration and temperature on dye uptake

The equilibrium sorption capacity of the biomass increased as the initial MG and MB dye concentration increased, while the adsorption yield of dye showed the opposite trend. The temperature also influenced remarkably the equilibrium dye uptake. With the change in temperature from 293 to 313 K, the uptake capacity increased from 23.80 to 43.96 mg g^{-1} and from 22.02 to 41.56 mg g^{-1} at 200 mg L^{-1} initial MG and MB dye concentrations.
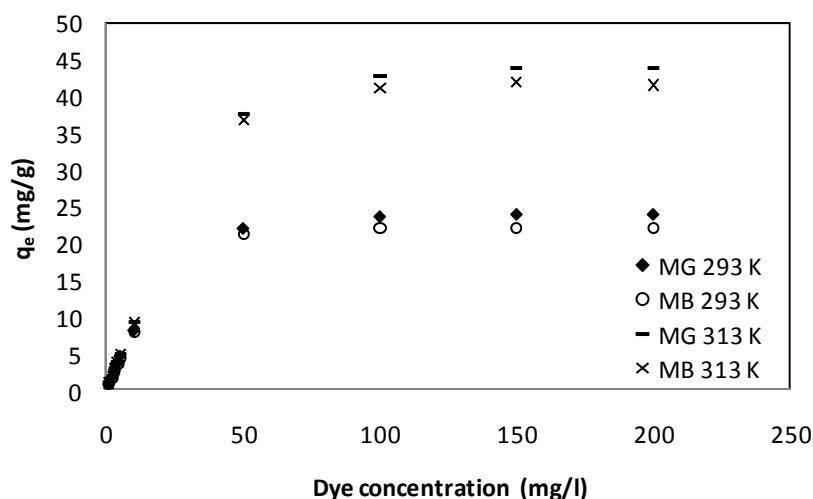

Figure 5. Effect of initial dye concentration on dye uptake at 293 and 313 K (pH: 9.5, weight of biosorbent: 100 mg of biosorbent per 100 mL, shaking rate: 150 rpm, contact time: 60 min.)

3.7. Adsorption isotherm

With the data in Figure 5, the Langmuir and Freundlich equations were employed to study the sorption isotherms of dyes. The maximum adsorption capacity (Q_m) and Langmuir constant (b) were calculated from the plot between C_e and C_e/q_e, the results were summarized in Table 2.

Table 2. Langmuir and Freundlich isotherm constants for the biosorption of MG and MB dye onto Water hyacinth roots at varying temperatures

Dye	Biosorption temperature (K)	Langmuir constants			Freundlich constants		
		Q_m (mg g^{-1})	b x 10^{-3} (l mg^{-1})	R^2	k_F	1/n	R^2
Malachite green	293	24.27	0.34	0.9998	4.05	0.4042	0.8864
	313	44.64	0.43	0.9998	6.92	0.4416	0.9028
Metylene blue	293	22.57	0.30	0.9997	4.66	0.4028	0.8742
	313	42.55	0.42	0.9997	5.73	0.5133	0.9266

Table 3. Thermodynamic parameters for the biosorption of MG and MB dye onto Water hyacinth roots as a function of temperature

Biosorption temperature (K)	Malachite green			Methylene blue		
	ΔH^o (kJ mol^{-1})	ΔG^o (kJ mol^{-1})	ΔS^o (J mol^{-1}K^{-1})	ΔH^o (kJ mol^{-1})	ΔG^o (kJ mol^{-1})	ΔS^o (J mol^{-1}K^{-1})
293	9.35	-28.32	128.57	12.57	-27.93	138.25
313		-30.89	128.57		-30.70	138.25

In view of the values of linear regression coefficients in the Table 2, the Langmuir model exhibited better fit to the biosorption data of dye than the Freundlich model in the studied concentration and temperature ranges. The isotherm constants Q_m were increased with increasing temperature.

As shown in Table 3, negative values of ΔG^o indicated that the biosorption process was favorable and spontaneous in nature for both MG and MB. It may be noted that with the increase in temperature from 20 to 40 ^{o}C, the value of ΔG^o decreased from -28.32 kJ mol^{-1} to -30.89 kJ mol^{-1} for MG and from -27.93 kJ mol^{-1} to -30.70 kJ mol^{-1} for MB. Thus biosorption of MG and MB dyes onto Water hyacinth roots biomass was enhanced at higher temperature. High temperatures increased the kinetic energy of the dye and, hence, enhanced the mobility of the dye ions. This led to a higher chance of the dye being adsorbed onto the adsorbent and an increase in its adsorption capacity. The positive value of enthalpy chance (ΔH^o) confirmed the endothermic nature of the biosorption process. Positive values ΔS^o suggested good affinity of the dye towards the adsorbent. The same trend was reported by Patel and Suresh (2008).

4. CONCLUSIONS

This study confirmed that the biosorbent prepared from Water hyacinth roots, a low cost, easily available and environmentally problematic plant, could effectively remove MG and MB dye from an aqueous solution. The results would be useful for the design wastewater treatment plants for removal of dye. The equilibrium data fitted well to the Langmuir model in the studied concentration range at all the temperatures studied. According to Langmuir model, the maximum biosorption capacity was found to be 45.05 mg g^{-1} for MG and 52.08 mg g^{-1} for MB dye under optimum conditions. The batch experiments showed the importance of solution pH and temperature in the biosorption of MG and MB. The biosorption capacity is strongly dependent on the temperature and increases significantly with increase in the temperature from 20 to 40°C. Thermodynamic parameters showed that the biosorption of the MG and MB dyes was endothermic in nature. Negative values of ΔG^o indicated that the biosorption process was favorable and spontaneous in nature. Positive values ΔS^o suggested good affinity of the dye towards the adsorbent. The biosorption processes followed the pseudo-second-order rate kinetics.

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