Inhibitory effects of *marigold* leaves extract on the mild steel corrosion in 0.5 M sulphuric acid solution

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Abstract
The corrosion inhibition function of extract of *marigold* leaves on mild steel in 0.5 M H_2SO_4 was investigated using weight loss measurements, UV-Visible and scanning electron microscope (SEM) surface analysis as well. The adsorption mechanism follows Langmuir's adsorption isotherm. The inhibition efficiency was found to be 90.51% at optimum concentration of inhibitor at 298 K in 0.5 M H_2SO_4. The values of the free energy of adsorption strongly supported physisorption mechanism of inhibitor components on the mild steel surface. SEM analysis shows a significant improvement on the mild steel surface morphology in the presence of inhibitor.
Keywords: Adsorption; Corrosion; *marigold leaves*; SEM

Introduction

Mild steel is one of the most frequently used constructional material in various industries due to its low cost, good ductile strength, and accessibility [1]. In the industrial environments mild steel is severely corroded by using acid solutions like sulphuric acid, and hydrochloric acid for various industrial process (acid pickling, chemical cleaning, oil well acidification) [2]. For these reasons inhibitors are employed as one of the most practical methods for corrosion protection [3]. Most of the well-known organic corrosion inhibitors are compounds containing nitrogen, oxygen, sulphur and multiple bonds. Nowadays the uses of many organic corrosion inhibitors have been limited because they are expensive, and hazardous for environment as well as human beings [10, 12]. Presently various plant extracts, containing mixture of compounds having oxygen, sulphur and nitrogen elements, are employed as green corrosion inhibitors for acidic solution. In the sense plant extracts are non-hazardous, friendly, cheap, readily available and renewable sources [10].The extracts of *Artemisia pallens* [11], *henna* [14], *Uncaria gambir* [15], and *Murraya koenigii* [16] were studied for their corrosion inhibition of mild steel in acidic media. Plant extracts usually contain terpenoids, davanone, linalool [11], Lawsone, Gallic acid, a-D-Glucose and Tannic acid [14], catechin [15], β caryophyllene, β gurjunene, β trans-ocimene, β hujene, β bisabolene [16], and other organic nitrogen bases, alkaloids as well as carbohydrates products [10-16]. In the present study extract of *marigold* leaves was selected for the mild steel corrosion inhibitor. The aim of this study is to evaluate the inhibitive effect of extract of *marigold* leaves on the corrosion of mild steel in 0.5 M sulphuric acid solution. The evaluation of the corrosion behaviour was studied using weight loss measurement, and the morphology of inhibited mild steel surface was examined by scanning electron microscope (SEM). Thermodynamic data was obtained from adsorption isotherms.

Experimental

Materials preparation

The chemical composition wt. % of mild steel used for all experiments was as follow:

C	O	Si	P	S	Cr	Ni	Fe
0.23	1.99	0.58	0.02	0.01	0.03	0.03	balance

Mild steel coupons were cut into 5 x 2 x 0.1 cm sizes from steel sheet and polished sequentially using different grades of emery papers. Next, it were degreased with acetone and washed with double distilled and dried in desiccator before use. AR grade of sulphuric acid (Merck) used for all the experiments.

Inhibitor preparation

Marigold leaves were collected from the campus of the National Institute of Technology, Raipur, India. For corrosion study, the *marigold* leaves were washed in running tap water for few minutes then thoroughly washed with double distilled water, than ultimately dried in a hot air oven and grounded well. Powdered *marigold* leaves refluxed for 3 h in the 0.5 M sulphuric acid solution (1000 mL) and left overnight. The acidic solution was filtered and make up to 1000 mL by using the same acidic solution. This solution was used to prepare solutions of different concentrations by dilution method for all the experiments.

Gravimetric analysis

The weight loss measurement is probably the most extensively used method for mild steel corrosion inhibition assessment. Weight loss measurements were conducted under total immersion of mild steel specimens using 100 mL capacity beakers at 298-328 K maintained in a thermo stated water bath. Experiments were performed at different concentrations of *marigold* leaves extract for 24 h of immersion time. Specimens in uninhibited and inhibited solutions were weighed using metteler Toledo AL204 electronic balance, Accuracy in weighing up to 0.0001 g. The corrosion rate (ρ) in mg cm $^{-2}$ h^{-1} was calculated from the equation given below [23]:

$$\rho = \frac{\Delta W}{At} \quad (1)$$

Where ΔW is the weight loss (mg), A is the total area of metal specimen (cm^2), and t is the immersion time (24 h). Inhibition efficiency (*%I*) was calculated by using the following equation [23]:

$$\%I = \left(\frac{\rho^1 - \rho^2}{\rho^1}\right) \times 100 \quad (2)$$

Where ρ^1 and ρ^2 are the corrosion rates of the mild steel coupons in the absence and presence of inhibitor, respectively. The surface coverage (θ) was calculated as given:

$$\theta = \frac{\%I}{100} \quad (3)$$

UV-Visible spectroscopy

Important support for the complex formation between metal ions with inhibitor components is often obtained by UV-visible spectroscopic analysis. Furthermore, it has been observed that change in position of the absorbance maximum and change in the value of absorbance show the formation of a complex between metal ions and inhibitor components in solution. Absorption spectra of UV–visible measured for 0.M H_2SO_4 solution without and with mild steel immersion in optimum concentration of CRRE at room temperature for 48 h. All the spectral measurements were carried out using a SHIMADZU UV- Visible 1800 spectrophotometer.

Surface morphological studies

The surface morphologies of the mild steel in 0.5 M sulphuric acid solution was investigated by scanning electron microscope (SEM). For SEM analysis mild steel specimen were dipped in 0.5 M H_2SO_4 solution in the absence and presence of optimum concentration of inhibitor for 24 h. The surface morphology of mild steel specimens was examined by using scanning electron microscope ZEISS EVO SEM 18 model oxford.

Results and discussion

Weight loss measurements

Values of mild steel corrosion rates ρ (mg cm^{-2} h^{-1})) and inhibition efficiency (%*I*) obtained with pre-corroded mild steel specimens after 24 h of immersion time in test solutions at temperature ranging from 298-328 K (Table 1). Fig.1 revealed the relationship between surface coverage (θ) and temperature for inhibitor at different concentration in 0.5 M H_2SO_4, indicated that degree of surface coverage decreases as temperature decreased. The data obtained for the weight loss (g cm^{-2}) versus temperature (K) measurements for mild steel in 0.5 M H_2SO_4 of inhibitor presented in Fig. 2. It is seen from the plot that the amount of material lost (g cm^{-2}) increases linearly and significantly as temperature increased. Table 1 shows the variation of inhibition efficiency (% *I*) with increase in inhibitor concentrations. It was observed that extract of *marigold* leaves inhibits the corrosion of mild steel in 0.5 M H_2SO_4 solution, at all studied concentrations 1-4 g l^{-1}. Maximum inhibition efficiency (90.51%) obtained at the 4g L^{-1} concentration of the inhibitor in 0.5M H_2SO_4 at 298 K temperature. Table 1 also reveals the corresponding trend of corrosion rate for various concentrations of *marigold* leaves extract and as calculated, corrosion rate increased gradually with inhibitor concentration in 0.5 M H_2SO_4 solution. Also, the inhibition efficiency decreases with increase in temperature both in absence and presence of inhibitor. These results indicated that *marigold* leaves extract acts as an effective inhibitor in the temperature range 298-328 K.

Table 1. Corrosion parameters obtained from weight loss results of mild steel in 0.5 M H_2SO_4 at various temperatures for 24 h immersion time in the presence and absence of different concentrations of *marigold* leave extract.

Concentration (*g L* $^{-1}$)	**Corrosion Rate,** ρ, **(mg cm^{-2} h^{-1})**				**Inhibition Efficiency (%*I*)**			
	298K	308K	318K	328K	298K	308K	318K	328K
0	3.27	3.85	4.18	4.78	-	-	-	-
1	0.90	0.96	1.39	1.99	72.47	75.06	66.74	58.36
2	0.77	0.80	1.05	1.32	76.45	79.22	74.88	72.38
3	0.55	0.63	0.98	0.91	83.18	83.63	76.55	80.96
4	0.31	0.46	0.83	0.87	**90.51**	88.05	80.14	81.79

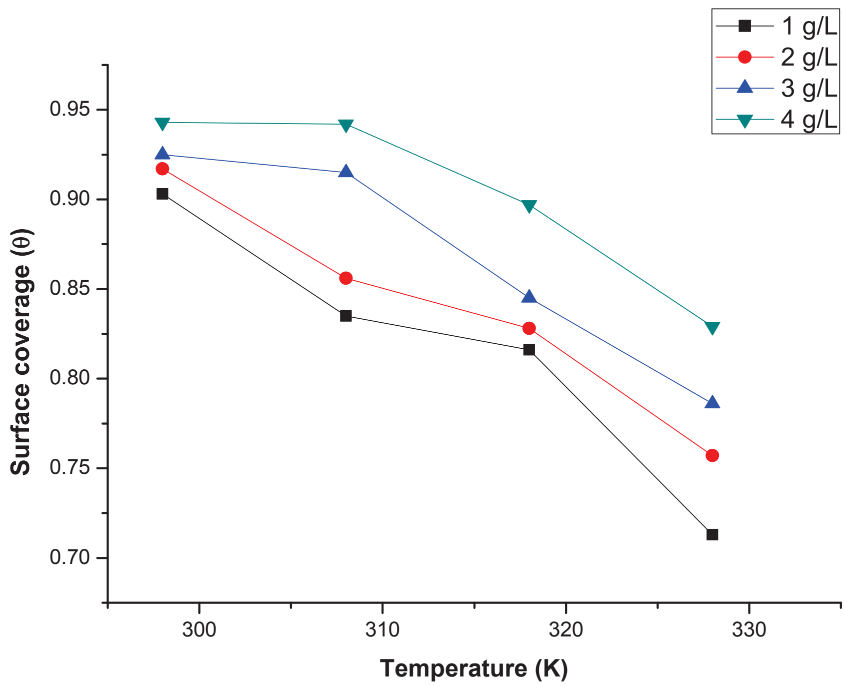


Fig.1 The relationship between θ and temperature for *marigold* leaves extract at different concentration in 0.5 M H_2SO_4.

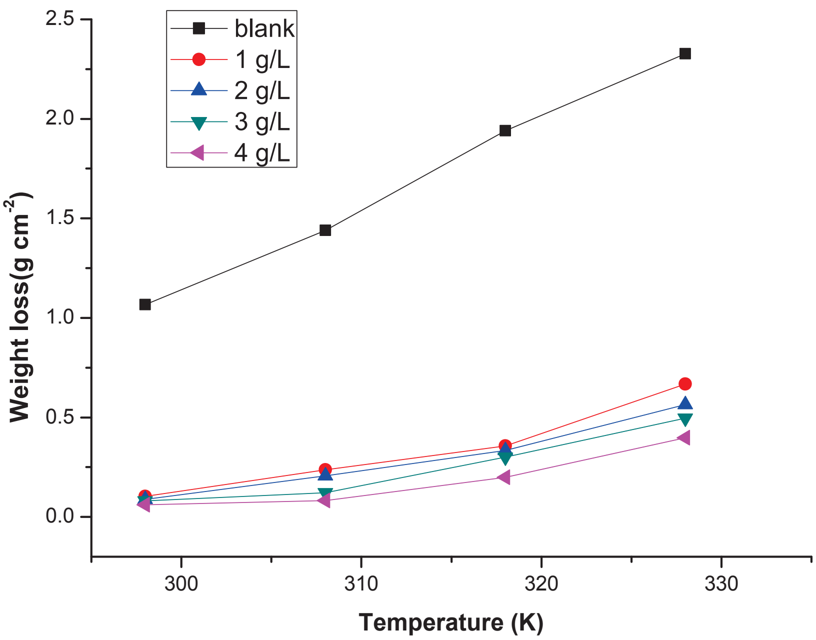


Fig.2 Variation of weight loss against temperature for mild steel corrosion inhibition in 0.5M H_2SO_4 in the presence of different concentration of extract of *marigold* leaves.

Adsorption and thermodynamic consideration

Adsorption isotherms provide information about the interaction with the metal electrode surface with inhibitor components. For the studied inhibitor extract of *marigold* leaves, it was found that the parameters obtained from weight loss measurements fitted Langmuir's adsorption isotherm, which is given by [5]:

$$\frac{C}{\theta} = \frac{1}{Kads} + C \quad (4)$$

Where θ is the surface coverage, K_{ads} is adsorptive equilibrium constant, and C is the equilibrium inhibitor concentration. Fig.3 represents the Langmuir adsorption isotherm plot between C versus C/θ for the studied inhibitor at different temperatures. K_{ads} values can be obtained from the intercept of the straight lines, and related to the free energy of adsorption, ΔG_{ads} by the given equation [7]:

$$\Delta G_{ads} = -RT \ln (55.5K_{ads}) \quad (5)$$

Where R is gas constant, T is temperature, and K is the binding constant. Generally speaking, negative values of ΔG_{ads} values indicate the stable interactions between the inhibitor molecules and the mild steel surface and involve the spontaneous process [2]. ΔG_{ads} for inhibitor was approximated from the slope of the graph under the experimental conditions and presented in Table 2. Generally, an exothermic process signifies either chemisorption or physisorption while endothermic process is attributable to the chemisorption process between inhibitor molecules and metal surface [5]. Generally, values more than ΔG_{ads} -40 kJ/mol are associated with chemisorption as a result of sharing of electrons from the inhibitor components to the metal surface whereas values lower than ΔG_{ads} -20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal known as physisorption [18]. In this paper, the calculated ΔG_{ads} values are less negative than −20 kJ/mol indicating that the adsorption of inhibitor molecules on the metal surface involves the physisorption process.

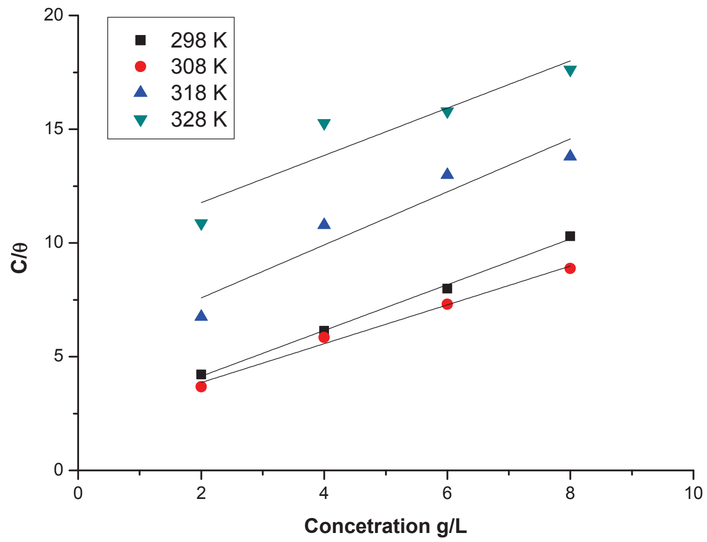


Fig.3 Linear fitting of *marigold* leaves extract to Langmuir adsorption isotherm at different temperature.

Table 2. Thermodynamic parameters for the adsorption of *marigold* leaves extract in 0.5 M H_2SO_4 on the mild steel surface after 24 h immersion time at different temperature.

T (K)	R^2	K_{ads} (L mol $^{-1}$)	ΔG_{ads} (kJ mol $^{-1}$)
298	0.996	0.885	-9.648
308	0.987	0.463	-8.312
318	0.869	0.190	-6.227
328	0.817	0.103	-4.754

UV-Visible spectroscopy

UV–Visible absorption spectrophotometric detection is the most suitable technique for identification of complex ions. Change in the value of absorbance and change in position of the absorbance maximum show the formation of a complex between two species in solution [8]. Fig. 4 shows absorption spectra of UV–visible measured for 0.5 M H_2SO_4 solution without and with mild steel immersion in 4.0 g L^{-1} extract at room temperature for 48 h immersion. The absorption spectrum of the solution resulting from mild steel immersion in 0.5 M H_2SO_4 containing inhibitor is different from the spectra containing inhibitor and Fe^{2+}. Solution containing inhibitor extract shows a high intensity band with an absorption maximum near at 250 nm, while the spectrum for inhibitor and Fe^{2+} in 0.5 M H_2SO_4 shows low intensity absorption band near at 250 nm indicates the formation of new products in the solution. In both case, UV-visible absorption spectra reveals that chemical structures of the components in *marigold* leaves extract are stable in 0.5 M H_2SO_4 solution. These experimental results give strong evidence for the possibility of the complex formation between Fe^{2+} cation and inhibitor in 0.5 M H_2SO_4 on mild steel surface.

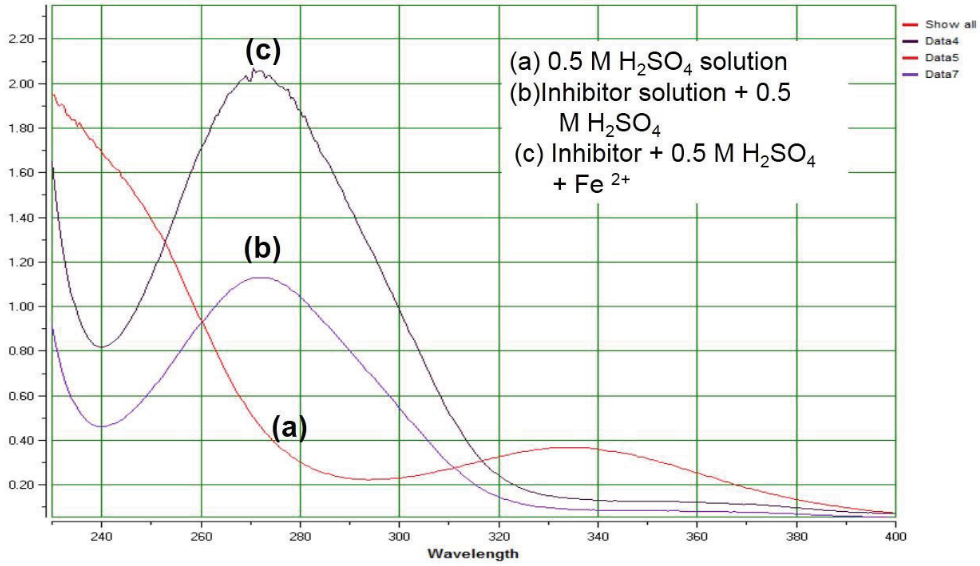
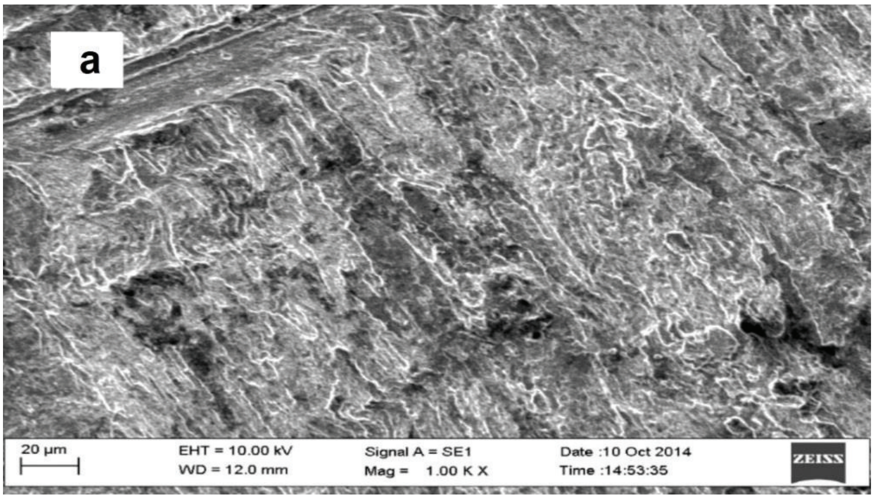


Fig. 4 UV–visible spectra of the formation of Fe (II) CRRE complex at 298 K (a) 1M HCl + Fe^{2+} and (b) 1M HCl + Fe^{2+} + 3g L^{-1} CRRE.

SEM analysis

SEM analysis was recorded for the mild steel surface immersed in the acidic solution in the absence and presence of the inhibitor to prove the changes in surface morphology of mild steel surface. Fig 5a and b shows the surface of mild steel that was immersed in the 0.5 M H_2SO_4 solution in the absence and presence of inhibitor for 24 h, respectively. According to the figure 5a, the mild steel surface severely corroded in the absence of the inhibitor. On the other hand, no corrosion could be observed in the case of mild steel sample immersed in the inhibited solution at optimum concentration of inhibitor (fig 5b). In general, less damage to the surface can be seen in the presence of *marigold* leaves extract, indicated that the inhibitor compounds are stable in 0.5 M H_2SO_4 solution and able to provide an effective corrosion inhibition of mild steel surface [3].



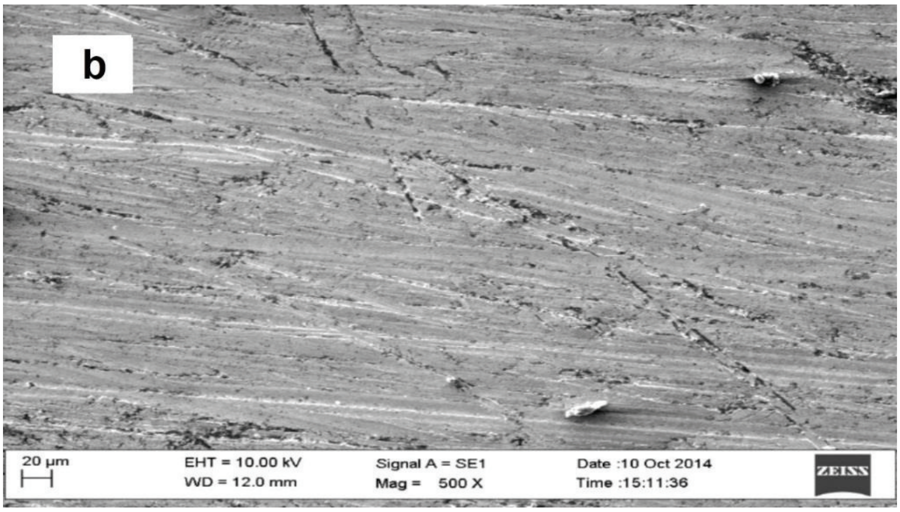


Fig. 5 SEM images of (a) mild steel in 0.5 M H_2SO_4, and (b) mild steel in the presence of inhibitor for 24 h.

Mechanism of inhibition

As follows from weight loss measurements, UV-Visible and SEM analysis mild steel corrosion in 0.5 M H_2SO_4 is inhibited in the presence of different concentrations of the *marigold* leaves extract. The results clearly showed that the inhibition mechanism involves blocking of mild steel surface by inhibitor molecules via adsorption. The values of thermodynamic parameters for the adsorption of inhibitors on mild steel can provide important information about corrosion inhibition mechanism. In this work the average value of free energy of adsorption, Δ*G*ads (-07.23 kJ mol-1) has been measured less negative value inside the range of physical adsorption mechanism. The majority of well know corrosion inhibitors are compounds containing heteroatoms, such as O, N, P, or S and aromatic rings which allow an adsorption on the mild steel surface from acidic solutions. These inhibitor components create a barrier to corroding attack on the metal surface by the adsorption mechanism [10]. It has been found that the adsorption of inhibitor components on the mild steel surface depends on the physico-chemical properties of the electron density at the donor atom and functional groups. The adsorption process occurs due to the interaction between the lone pair and/ or p-orbitals of inhibitor with d-orbitals of the mild steel surface. These interactions suggests a greater adsorption of the inhibitor components on the mild steel surface, leading to the formation of protection film against corrosion [8]. Adsorption of inhibitor components on mild steel surface may be occur by the following mechanisms: (1) electrostatic interaction of protonated inhibitor molecules with already adsorbed sulphate ions, and (2) adsorption of π-electrons of an aromatic ring of inhibitor constituents onto the mild steel surface in acidic solution [22].

Conclusion

Results of gravimetric analysis shows that extract of *marigold* leaves acts as a good mild steel corrosion inhibitor in 0.5M H_2S0_4. The inhibition efficiency increases with the increase in inhibitor concentration but decreases as temperature increases. The maximum inhibition efficiency value of 90.51% was obtained for 4 g l^{-1} inhibitor concentration at 298 K. The adsorption isotherm of *marigold* leaves extract follows the Langmuir adsorption. Values of free energy of adsorption indicates that the adsorption of *marigold* leaves extract on the mild steel surface involves the physisorption process and the average value was found to be -07.23 kJ mol^{-1}. SEM micrographs show that protective layer formed over the metal surface from the inhibitor molecules and prevent from the further corrosion.

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