

STUDIES OF CHELATING ION EXCHANGE PROPERTIES OF NOVEL COPOLYMER, DERIVED FROM SALICYLIC ACID, AND SEMICARBAZIDE

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ABSTRACT

The Copolymer (SASF-II) was synthesized by condensation of Salicylic acid and Semicarbazide with formaldehyde in the presence of 2M HCL as a catalyst at 126 ± 2 °C for 5 hrs. with molar proportion of reactants. The copolymer (SASF-II) was characterized by elemental analysis, FT-IR, UV-Visible ¹H-NMR Spectroscopy. The chelating ion-exchange property of this polymer was studied for five metal ions viz. Cu (II), Ni (II), Co (II), Zn (II), and Pb (II) ions. The chelating ion-exchange study was carried out over a wide range of pH, shaking time and in media of various ionic strengths. Thermal study of the resins was carried out to determine their mode of decomposition and relative thermal stabilities by elemental analysis, FT-IR, UV-Visible ¹H-NMR Spectroscopy. The thermal decomposition behavior of copolymer was studied by using TGA in static nitrogen atmosphere at a heating rate of 100C/min. Freeman Carroll and Sharp-Wentworth methods were used to calculate the thermal activation energy (E_a), the order of reaction (n), entropy Change (ΔS), free energy change (ΔF), apperent entropy change (ΔS), and frequency factor (Z). The thermal activation energy determined with the help of these method was in good agreement with each other. The antimicrobial activity for certain bacteria such as S. subtilis, , E.coli, S. typhi . A. niger, S. aureus and C. albicans were studied.

Keywords: Synthesis, condensation, antimicrobial screening, thermogravimetric analysis; decomposition, resins.

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INTRODUCTION

Chelating ion-exchange properties of the resin involving poly [(2, 4- dihydroxybenzophenone) butylene] and its polychelates with transition metals are reported [1]. Salicylic acid and melamine with formaldehyde copolymer found to have higher selectivity for Fe^{3+} , Cu^{2+} and Ni^{2+} ions rather than Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions [2]. Resins synthesized by condensation of mixtures of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported [3]. The metal ion uptake capacity increases with increasing mole proportions of the copolymer synthesized from substituted benzoic acid [4].

The study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Thermogravimetric analysis has been widely used to investigate the decomposition characteristics of polymeric matter . Copolymers can be used as high energy material, ion-exchanger, semiconductors, antioxidants, fire proofing agent, optical storage data, binders, molding materials *etc.* Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Copolymer resins are derived from 2,4-dihydroxypropiophenone, biuret and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation [5].

The non-isothermal kinetic studies of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Terpolymers of salicylic acid, thiourea with trioxane and *p*-hydroxybenzoic acid, thiourea with trioxane have been reported in the literature [6].

There is a noteworthy demand to synthesize eco-friendly polymers having some biological activities like antifungal and antibacterial The invasion of polymers by fungi, bacteria and other organism is manifested by loss of mechanical properties, surface degradation, discoloration, staining and other deteriorations [7-10]. Polymers are used as biocidal agents in recent times. By incorporating biologically active organic moieties into the polymer backbone, the activities can be introduced. In terms of their biological activity, these polymers are more effective than their monomers. Such polymers are known for their biocidal activity against some bacterial, fungal and viral strains.

The present paper deals with the synthesis, characterization, ion-exchange properties and non-isothermal thermogravimetric analysis studies and relative antibacterial activity against bacteria of copolymer derived from of Salicylic acid (SA), Semicarbazide (S), with formaldehyde (F). However, the literature studies have revealed that no copolymer has been synthesized by using the said monomers. Sample is subjected to thermal degradation data with Sharp-Wentworth (S-W) and Freeman-Carroll (F-C) methods, activation energy and kinetic parameters such as ΔS , Z , S^* and n (order of reaction) have been evaluated [11-14].

MATERIALS AND METHODS

Materials:

The entire chemical used in the synthesis of various new copolymer resins were procured from the market and were analar or Fluka or chemically pure grade. Whenever required they were further purified by standard methods like thin layer chromatography, reprecipitation and crystallization which are generally used for the analytical purification purpose.

Methods:

Synthesis of SASF-II Copolymer resins:

The new copolymer resin SASF-II was synthesized by condensing Salicylic acid (0.1 mol) and Semicarbazide (0.1 mol) with formaldehyde (0.2 mol) in a mol ratio of 2:1:3 in the presence of 2 M 200 ml HCl as a catalyst at $126 \pm 2^\circ \text{C}$ for 5h, in an oil bath with occasional shaking, to ensure thorough mixing. The separated copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove salicylic acid- semicarbazide formaldehyde copolymer which might be present along with SASF-II copolymer. The yellow color resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of SASF-II is shown in Fig. 1

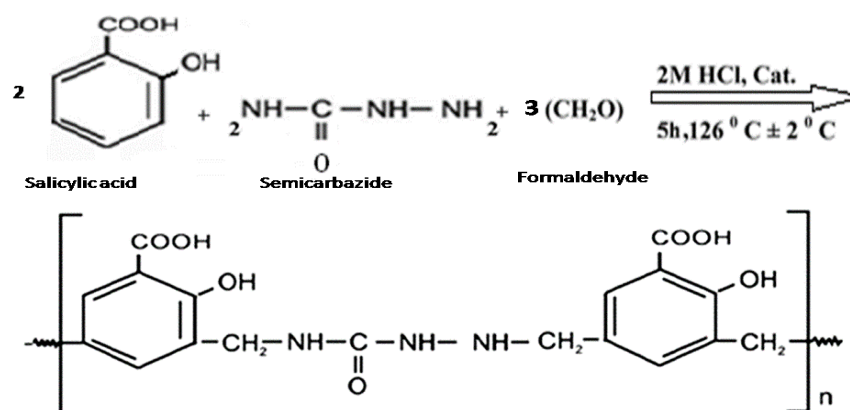


Fig.1: Synthesis of SASF-II copolymer resin.

RESULTS AND DISCUSSION

The newly synthesized purified SASF-II copolymer resin was found to be yellow in color. The copolymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents.

Ion-exchange property

The ion-exchange property of the SASF-II copolymer resin was determined at three different variations given below.

a) Determination of metal uptake in the presence of two different electrolytes and their different concentrations

The copolymer sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. The pH of the suspension was adjusted to the required value using either 0.1 M HNO₃ or 0.1 M NaOH. The suspension was stirred for 24 h at 30°C. To this suspension 2 ml of 0.1 M solution of the metal ion was added and pH was adjusted to the required value. The mixture was again stirred at 30°C for 24 h. The polymer was then filtered off and washed with distilled water. The filtrate and the washing were collected and then the amount of metal ion was estimated by titrating against standard EDTA (ethylenediamine tetraacetic acid) at the same pH (experimental reading). The same titration has been carried out without polymer (blank reading). The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The

experiment was repeated in the presence of several electrolytes. Metal ion, its pH range, buffer and indicator used and colour change are given in Table 1.

Table:1 Summarised Procedure for EDTA Titration

Summarised Procedure for EDTA Titration of cation under investigation					
Metal Ion	Type of Titration	pH range	Buffer used	Indicator used	Colour Change
Cu ²⁺	Direct	9-10	Dil. HNO ₃ /Dil. NaOH*	Fast Sulphone Black-F	Purple to green
Ni ²⁺	Direct	7-10	Aq. NH ₃ /NH ₄ CL	Mureoxide	Yellow to Violet
CO ²⁺	Direct	6	Hexamine	Xylenol orange	Red to Yellow
Zn ²⁺	Direct	10	Aq. NH ₃ /NH ₄ CL	Eriochrome Black-T	Wine red to blue
Pb ²⁺	Direct	6	Hexamine	Xylenol orange	Red to Yellow

Note: *No buffer used therefore pH was adjusted by using either dil. HNO₃ or dil. NaOH

The metal ion uptake can be determined as:

$$\text{Metal ion adsorbed(uptake by resin)} = (X - Y) Z \text{ millimols / gm}$$

Where Z (ml) is the difference between actual experimental reading and blank reading; X (mg) is metal ion in 2 ml (0.1 M metal nitrate solution) before uptake; and Y (mg) is metal ion in 2 ml (0.1 M metal nitrate solution) after uptake. By using this equation the uptake of various metal ions by resin can be calculated and expressed in terms of millimols per gram of the copolymer.

b) Estimation of rate of metal ion uptake as a function of time

In order to estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described above were carried out, in which the metal ion taken up by the chelating resins was determined from time to time at 30°C (in the presence of 25 ml of 1 M NaNO₃ solution). It was assumed that, under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as percentage amount of metal ions taken up after a certain time related to that at the state of equilibrium and it can be defined by the following relationship:

$$\text{Metal ion taken up at different times (\%)} = \frac{\text{Metal ion adsorbed}}{\text{Metal ion adsorbed at equilibrium}} \times 100$$

The percent amount of metal ions taken up at different times is defined as:

$$\text{Percentage of metal ion adsorbed after 1 h} = \frac{100 X}{Y}$$

Where X is mg of metal ion adsorbed after 1 h and Y is mg of metal ion adsorbed after 25 h. Then, by using this expression, the amount of metal adsorbed by polymer after specific time intervals was calculated and expressed in terms of percentage metal ion adsorbed.

c) Evaluation of the distribution of metal ions at different pH

The distribution of each of the five metal ions i.e., Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Pb^{2+} ions between the polymer phase and the aqueous phase was determined at 30°C and in the presence of 1 M NaNO_3 solution. The experiments were carried out as described above at different pH values. The distribution ratio, D, is defined by the following relationship.

$$D = \frac{\text{Amount of metal ion in solution}}{\text{Amount of metal ion on resin}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (gm)}}$$

$$\text{Metal ion adsorbed (uptake) by the resin} = \frac{ZX}{Y} \times \frac{2}{0.025}$$

FT-IR Spectra : A broad band appeared in the region $3000\text{-}3400\text{cm}^{-1}$ may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding . The sharp band displayed at $1600\text{-}1680\text{ cm}^{-1}$ may be due to the stretching vibrations of carbonyl group (C=O) . The presence of -NH in semicarbazide moiety may be assigned due to sharp band at $2800\text{-}3000\text{ cm}^{-1}$. A strong sharp peak at $1625\text{-}1612\text{ cm}^{-1}$ may be ascribed to aromatic skeletal ring . The bands obtained at $1400 - 1200\text{ cm}^{-1}$ suggest the presence of methylene bridges in the polymer chain. The weak band appearing at $800 - 719\text{ cm}^{-1}$ is assigned to C – OH bond. Substitution of

aromatic ring is recognized from the bands appearing between $1201-1276\text{ cm}^{-1}$ respectively [12,15-16].

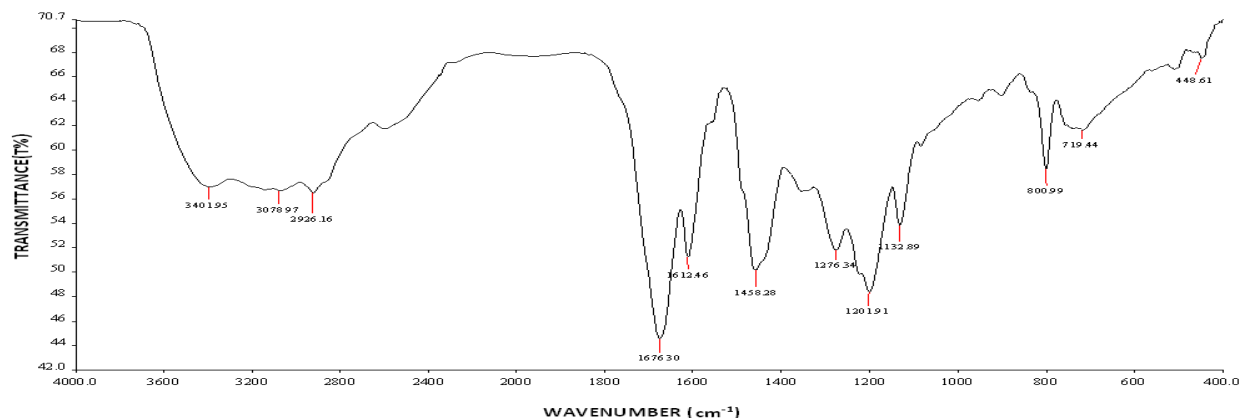


Fig.2: FT-IR Spectra of SASF-II copolymer

NMR Spectra:

Weak signal in the range of 7.00 to 8.0 (δ) ppm is attributed to phenolic -OH proton. The NMR spectra of SASF-II copolymer resins show a weak multiplet signal (unsymmetrical pattern) in the region 6.8 to 7.0 (δ) ppm which is due aromatic protons. A sharp singlet peak appeared at 3.5 – 4.0 (δ) ppm may be assigned to methyl protons of Ar-CH₂-NH group. Intense signal appeared in the region 2 – 3 (δ) ppm may be due to Ar-CH₂-NH. A broad signal appeared in the region 3.42 – 4.84 (δ) ppm can be assigned to amido proton of -CH₂-NH-CO- linkage [12,15-16].

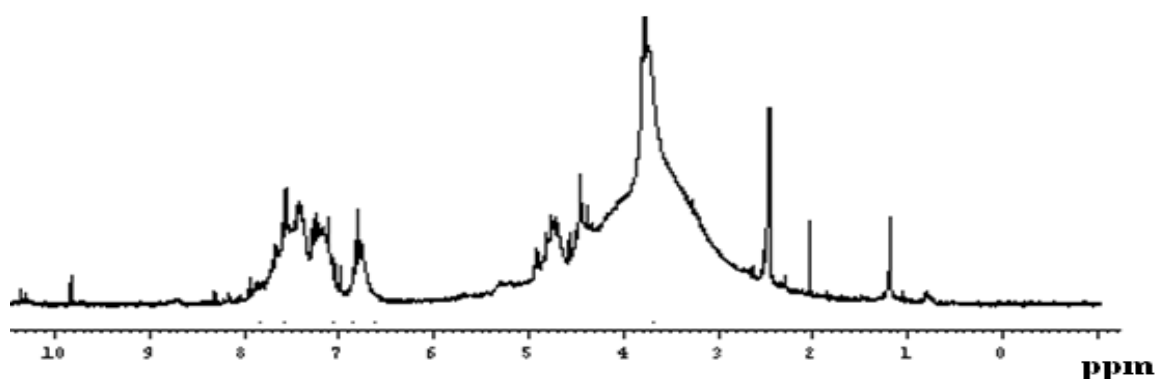


Fig.3: NMR Spectra of SASF-II copolymer

Ion-exchange properties

Batch equilibrium technique developed by De Geiso et al. [17] was used to study ion-exchange properties of SASF-II polymer resin. The results of the batch equilibrium study carried out with the polymer SASF-II are presented in Tables 1, 2 and 3. Five metal ions Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , and Pb^{2+} in the form of aqueous metal nitrate solution were used. The ion-exchange study was carried out using three experimental variables such as a) electrolyte and its ionic strength b) uptake time and c) pH of the aqueous medium. Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake of the polymer similar to the earlier co-workers [18-19] .

Effect of electrolyte and its ionic strength on metal uptake

We examine the influence of chloride, nitrate, chlorate at various concentrations on the equilibrium of metal – resin interaction . The amount of metal ions taken up by a given amount of copolymer depends on the nature and concentrations of the electrolyte present in the solution. The results incorporated in Table. 2 shows that in the presence of nitrate ions, the uptake of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , and Pb^{2+} ions increases with increasing concentrations of the electrolyte. Where as the uptake of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} ions decreases with increasing concentration of the chloride . This may be explained on the basis of the stability constants of the complexes with those metal ions. This may be due to the chloride, ion forming strong chelates with metal ions, while the other anions i.e nitrate form weak chelates. The position of the metal chelate equilibrium is less influenced in the presence of nitrate ions than that of chloride ions.

Table 2: Evaluation of the influence of different electrolytes on the uptake of several metal ions ^a.

Metal Ion	Electrolyte Conc. (mole/lit)	Weight of metal ion (mg)taken up in presence of ^b	
		NaNO_3	NaCl
Cu^{2+}	0.01	0.25	0.69
	0.05	0.28	0.48
	0.10	0.39	0.33
	0.50	0.43	0.24
	1.00	0.50	0.20

Ni²⁺	0.01	0.20	0.53
	0.05	0.23	0.42
	0.10	0.40	0.31
	0.50	0.45	0.22
	1.00	0.54	0.22
Co²⁺	0.01	0.28	0.66
	0.05	0.31	0.57
	0.10	0.42	0.44
	0.50	0.53	0.40
	1.00	0.69	0.29
Zn²⁺	0.01	0.24	0.68
	0.05	0.30	0.58
	0.10	0.32	0.44
	0.50	0.39	0.35
	1.00	0.53	0.30
Pb²⁺	0.01	0.80	1.66
	0.05	0.98	1.24
	0.10	1.19	1.08
	0.50	1.46	0.94
	1.00	1.69	0.72

The amount of uptake of Co²⁺, Zn²⁺ and Pb²⁺ ions by the copolymer under the influence of nitrate is higher than that of the other metal ions. This may be due to the Co²⁺, Zn²⁺ and Pb²⁺ ions form weak chelates with the anions of the nitrate electrolytes [18].

The amount of uptake of Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺ and Pb²⁺ ions by the copolymer under the influence of chloride, ions is lower for all the metal ions. This may be due to the Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺ and Pb²⁺ ions form strong chelates with the anions of the chloride, ions electrolytes. In addition, the copolymer has more porosity in its structure they can accommodate metal ions of specific size, easily into its cavities and acts as a better cation-exchanger [19].

Estimation of the rate of metal ion uptake as a function of time

To determine the time required to reach the equilibrium, the rates of ion absorption by SASF-II copolymer resin samples were measured for Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺ and Pb²⁺ ions. The term refers to the change with time when they were in contact with the copolymer sample the

experiment results, which are shown in table 3. These results indicate that the time taken for the uptake of the different metal ion at a given stage depended on the nature of the metal ions under the given conditions.

The experimental data, which are shown in Table.3 shows that, Cu^{2+} , Ni^{2+} ions required 6 h for the establishment of equilibrium [5-6] whereas Co^{2+} , Zn^{2+} and Pb^{2+} ions required 5 h for the establishment of equilibrium. The experimental results revealed that the rate of metal-ion uptake followed the order of $\text{Pb}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$.

Table 3: Percentage of metal ion uptake ^b at different time (h)

Metal ion	Percentage of metal ion uptake ^b at different time (h)					
	1	2	3	4	5	6
Cu^{2+}	44	35	54	60	84	92.5
Ni^{2+}	11	22	30	38.5	50	92
Co^{2+}	28	34	55	69	92.5	-
Zn^{2+}	29	42	50	70	92	-
Pb^{2+}	29	44	50	75	91	-

Distribution ratios of metal ions at different pH

The effect of pH on the amount of metal ion distributed between the two phases is given in Table 4 which reveals that the amount of uptake of metal ions by the resin at equilibrium increases with increasing pH. The study was carried out up to a definite pH value for the particular metal ion to prevent hydrolysis of metal ion at higher pH.

The SASF-II copolymer resin takes up Co^{2+} and Pb^{2+} ions are more selectively than the other ions under study at all pH values. Among the other ions taken up for the study, Cu^{2+} ions shows selective uptake under moderate pH values. Further, Ni^{2+} , Zn^{2+} ions have lower distribution over the pH range from 2.5 to 6.5. This can be explained as the weak stabilization energy of the metal chelates [19] formed from Ni^{2+} , Zn^{2+} ions. In the present investigation it is observed that the order of the distribution of the metal ions are $\text{Pb}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$

Table 4 : Distribution ratio D^a of Different Metal Ions as a Function of pH^b

Metal ion	Distribution ratio of metal ion at different pH						
	2.5	3	3.5	4	5	6	6.5
Cu²⁺	10.43	18.21	22.22	59.26	72.73	108.64	154.64
NI²⁺	10.67	24.25	33.06	43.36	68.63	104.65	171.88
Co²⁺	11.11	29.04	64.76	200	520.83	1352	1267
Zn²⁺	19.36	34.86	49.78	105.56	196	297	378
Pb²⁺	37.04	64.20	109	254	518	1283	1423

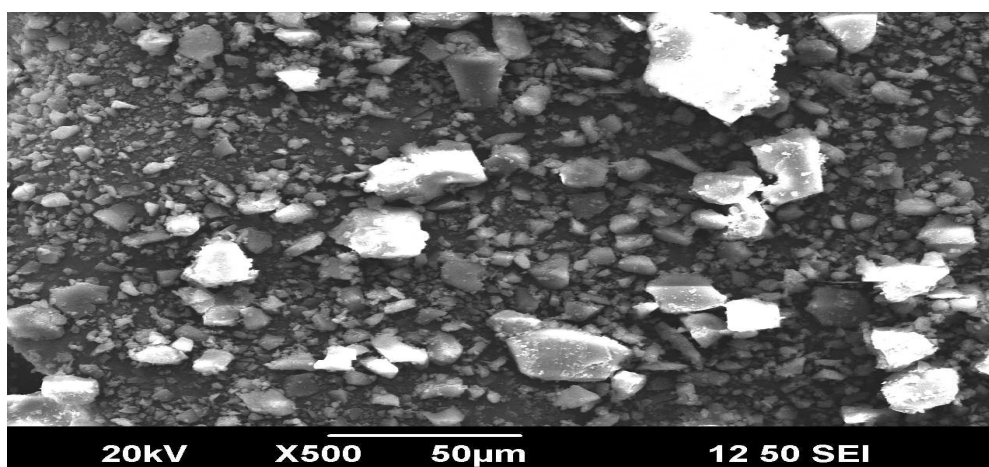


Fig.4: SEM of SASF-II copolymer

SEM micrographs of SASF-II copolymer is shown in Fig.4. The morphology of pure sample shows spherulites with deep pits. This is the transition of crystalline and amorphous layered morphology which is the characteristic of polymer. The monomers have crystalline structures at the beginning of the reaction but during course of condensation polymerization the crystalline structures of monomers lost into amorphous nature in copolymer resin .

CONCLUSION:

- A polymer SASF-II based on the condensation reaction of salicylic acid and semicarbazide with formaldehyde in the presence of acid catalyst was prepared.

- The SASF-II resin is a selective chelating cation exchange polymer resin for certain metals.
- The uptake capacities of metal ions by the polymer resin were pH dependent.

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