Electro-oxidation of Saline Wastewater from Tannery and Reuse of Recovered Salt

by

P. Vijayalakshmi[1], G. Rajeswari, S. Sundarapandiyan, R. Chandrasekar, and P. Saravanan*

[1] *Tamilnadu Pollution Control Board*

Guindy, Chennai, India 600 025

Central Leather Research Institute (Council of Scientific Industrial Research, New Delhi)

Adyar, Chennai, India 600 020

Abstract

The objective of this work is to treat the saline wastewater from tanneries to recover salt and to study the reuse of the recovered salt. Soak liquor from the tannery was treated electrochemically using graphite electrodes. The reduction in TKN, protein and COD was 78.52%, 83.02% and 79.35% respectively and complete disinfection was also achieved. The treated soak liquor was evaporated by solar evaporation and the salt recovered used for curing of skins. Curing efficacy was assessed for a period of 32 days. The preservation efficacy of the recovered salt, in terms of moisture and bacterial population of the hides, was found to be on par with that of the hides preserved using fresh salt. Soaking wastewater of volume 1 m^3 was also treated on a commercial scale. Three batches of treatment were carried out. The salt recovered was reused for preservation of raw hides. The quality of the preserved hides and the wet blue leathers were also assessed. Results of the commercial scale experiments were similar to the results of the laboratory scale experiments. Cost of treatment was about 0.68 US $ per m^3. Electrochemical treatment of soak liquor was found to be effective in pollution attenuation.

Resumen

El objetivo de este trabajo es tratar los desperdicios salinos líquidos de curtiembres para recobrar la sal y estudiar la reutilización de la sal así recuperada. El licor resultante del remojo antes de curtir se trato electro-químicamente por medio de electrodos de grafito. La reducción del TKN [nitrógeno total por micro-Kjeldhal], proteína y DQO [demanda química de oxígeno] fue 78,52%, 83.02% y 79.35% respectivamente acompañados de completa desinfección. El baño de remojo se evaporo por medio solar y la sal recuperada se uso para preservar pieles. Eficacia de preservación se revisó durante un período de 32 días. La eficacia de preservación por sal recuperada, en términos humedad y número de colonias de bacterias en las pieles, se encontró ser comparable con pieles preservadas usando sal normal. Agua remanente del remojo de un volumen de 1 m^3 fue también tratado a nivel de escala comercial. Tres lotes de tratamiento se efectuaron. La sal recuperada fue reutilizada en la preservación de pieles verdes. La calidad de las pieles preservadas y los cueros wet-blue fueron evaluados. Los resultados de experimentos a escala comercial fueron similares a los resultados obtenidos de experimentos a escala de laboratorio. Costo de tratamiento fue de aproximadamente US $ 0.68 por m^3. Tratamiento electrolítico del baño de remojo se encontró ser efectivo en la atenuación de la contaminación

*Corresponding author e-mail: dermagroup@yahoo.co.in, telephone and fax: 91 44 24915730
Manuscript received January 20, 2009, accepted for publication July 14, 2009

INTRODUCTION

Leather manufacturing is one of the industrial activities that generate substantial pollution load. Sodium chloride is one of the serious pollutants released during leather manufacturing process. Common salt is used for preservation of skins and pickling. About 15% to 40% (on the weight of the raw hides and skins) is used for preservation. Salted hides and skins are washed and soaked using water. Salt used for preservation is released into the soaking wastewater is associated with significant environmental impacts. Per ton of raw skin or hide about $7m^3$ to $9m^3$ of wastewater is released during soaking[1]. The emission load of soak liquor with respect to chloride, BOD and COD are 85kg/t to 113kg/t, 7kg/t to 11kg/t and 22kg/t to 33kg/t respectively[1]. Discharge of saline wastewater renders the ground water brackish and increases the salinity of the soil. Saline wastewater reduces the soil fertility and is harmed for aquatic life if discharged into water bodies. Overcoming the problems associated with salinity assumes higher priority in many countries. Presently in India, the combined waste stream of soaking and pickling is evaporated in open solar pans and the salt is recovered. During evaporation of soak liquor, the organic contaminants undergo partial degradation and objectionable odour is emanated. The recovered salt is not suitable for reuse as it is contaminated with organic matter and halophilic bacteria. There is no safe disposal technique for the recovered salt. As the soaking waste stream contains very high level of sodium chloride, biological treatment is seldom feasible. Treatment of soak liquor demands initial removal of organic matter chiefly protein and then separation of salt from the wastewater. Treatment of highly saline water using sequencing batch reactor (SBR) has been studied.[2] Treatment of soak liquor in SBR for the removal of organic load was reported. Reduction in COD and TKN by 95% and 96% respectively has been achieved in 5 days retention time in the sequencing batch reactor. Five days hydraulic retention time and the organisms responsible for nitrogen removal being highly sensitive are the disadvantages of SBR process.[3] Anaerobic treatment of soak liquor has been studied using UASB (Upflow Anaerobic Sludge Blanket). Reduction of COD by 78% was attained with 0.5 COD $m^{-3}d^{-1}$ of organic loading rate.[4] Possible generation of methane and odour and need for appropriate post treatment for pathogen removal are the disadvantages of UASB. Advanced methods such as ultrafilteration,[5] reverse osmosis[6] and electro-dialysis[7] have been reported as the options for the treatment of waste streams with high TDS and salinity. Techniques such as ultrafilteration and reverse osmosis demand pre-treatment of wastewater to attain near-total removal of organic load.

Electrochemical techniques have not been widely practiced for the treatment of industrial wastewater.[8] Detoxification of composite wastewater from tannery through electrolysis had been studied where Ti/Pt anode and SS 304 cathode were used.[9] Electrochemical experiments on phenol containing saline wastewater were conducted and the parameters of the process such as conductivity (or salinity), pH, current density, temperature and initial phenol concentration were studied. Salinity facilitated the reduction of COD and addition of small amount of H_2O_2 also found to facilitate COD reduction.[10] Secondary clarified tannery wastewater was treated by electro-oxidation technique using Ti/Pt, Ti/MnO_2 anodes and Ti cathode.[11] Electrochemical treatment is one of the viable techniques for disinfection of water and wastewater. The effect of disinfection of Germinated Brown Rice (GBR) water by electrochemical methods had been studied. At a pulse voltage of 1 kV, the aerobic plate count decreased significantly. At this voltage the *Legionella* bacteria were also disinfected effectively.[12] Electrochemical disinfection of drinking water using TiN electrode has been reported.[13] Disinfection of bacteria *E. coli* and *P. aeruginosa* and bacteriophages MS2 and PRD1 at a population of $1X10^6$ CFU / ml or PFU / ml was reported. The current applied was ranging from 25 to 350 mA in 5s pulses.[14] Pickling wastewater has been treated electrochemically and reused for seven batches.[15]

Soak liquor is contaminated with blood, dirt, dung and globular proteins apart from significant level of sodium chloride. Presence of organic contaminants in soak liquor harbours bacterial growth particularly halophilic bacteria. Removal of organic pollutants and disinfection of soaking wastewater is essential to recover salt suitable for reuse. In this present study electro-oxidation was carried out aiming reduction of organic load and disinfection. It is the aim of this work to study the efficacy of electro-oxidation with respect to pollution reduction (removal of organic pollutants). It is also the aim to study the reuse of the recovered salt for the preservation of hides and skins.

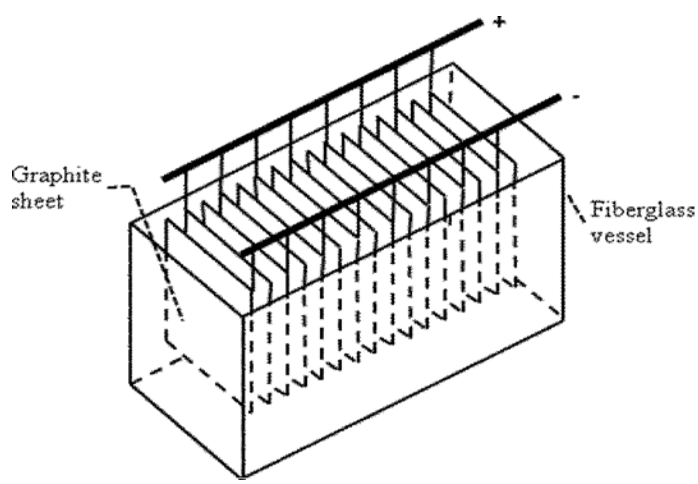


Figure 1. – Schematic Diagram of Commercial Scale Electro-oxidation cell.

TABLE I
Leather Process

Unit Process	Chemical	Input (% w/w)	Time (hour)	Other process details
Soaking I	Water	300	0.5	Soaking was carried out in pits
Soaking II	Water	300	6.0	
Paste liming	Water Lime Sodium sulphide	15.0 10.0 2.5	6.0	Paste applied on the flesh side and kept in pile
Unhairing				Pelts were unhaired
Reliming	Water Lime	300 5	48.0	Liming was carried out in paddle which was run intermittently for 5 minutes for every hour
Fleshing				Pelts were then fleshed in machine
Washing	Water	200	0.5	Washing carried out in drums at 5 rpm
Deliming	Water Ammonium chloride	150 1	0.75	
Washing	Water	200	0.5	Washing carried out in drums at 5 rpm
Pickling	Water Common salt	100 10		Drum run for 10 minutes
	Hydrochloric acid Water	1 10		Acid was given in three instalments at 15 minutes interval and after final feed, the drum was run for 30 minutes. Pelts were checked for pH.
Chrome Tanning	Pickle liquor	50		
	BCS	8	0.75	
	Water	50	0.75	
	Sodium formate	1	0.25	
	Sodium bicarbonate Water	1 10		Alkali was given in three instalments at 15 minutes interval and after final feed, the drum was run for 30 minutes. Leathers were checked for pH.

TABLE II
Pollution Reduction

Parameter	Time (Minutes)				
	0	30	60	90	120
COD (ppm)	24700	23680	19400	14000	5100
COD reduction (%)	0	4.13	21.46	43.33	79.35
TKN (ppm)	824	765	636	459	177
TKN reduction (%)	0	7.16	22.82	44.30	78.52
Protein (ppm)	2120	1600	1100	680	361
Protein reduction (%)	0	24.53	48.11	67.93	83.02
Microbial population (CFU/ml)	39×10^9	52×10^2	0	0	0
Reduction in microbial population (%)	---	99.99	100	100	100

MATERIALS AND METHODS

Electro-oxidation

Electro-oxidation process has been carried out in a cell of an effective capacity of 7 l. Graphite sheets have been used both as anodes and cathodes. The electrodes were of 19 cm length, of 15 cm breath and 0.3 cm thick. The electrical power supply has been provided using laboratory D.C power source of maximum output of 60 A and equipped with current – voltage monitoring.

Commercial scale electro-oxidation treatment was carried out using a cell of working volume of 1 m^3 (Fig. 1). Graphite sheets were used both as anodes and cathodes. The total surface area of anodes was 12.8 m^2. The electrical power supply has been provided with maximum output of 1500 A and 20 V equipped with current – voltage monitoring. The commercial scale electro-oxidation cell had been fabricated by National Metallurgical Laboratory (NML), Chennai.

Chemicals

The chemicals including common salt that were used for leather manufacturing process were of commercial grade.

Total Kjeldahl Nitrogen

TKN was also estimated following the standard procedure as reported by American public health association.[16]

Protein content

Protein content of soak liquor was estimated following Lowry's method.[17]

Chemical Oxygen Demand

COD was estimated as per the procedure reported by American public health association.[16] Open reflux method as given in the standard procedure was followed. The chloride interference in this method was overcome using mercuric sulphate.

Bacterial count

Bacterial population was enumerated both in soak liquor and in cured skins by viable-plate count procedure.[18] In the case of enumerating bacterial population in skins, extract was prepared by shaking 1 mg of skin in 100 ml of sterile distilled water. This skins extract was serially diluted and used for bacterial count. Final results were expressed in terms of CFU per mg of skin.

Purity of salt

Chloride was estimated following the procedure as reported by American public health association.[16]

Hide preservation and leather manufacturing process

Freshly flayed Indian goat skins were taken as the substrate for the laboratory scale experiment and freshly flayed Indian cow hides were taken for the commercial scale experiments. In the case of experiment, 40% w/w of recovered salt was used and for control 40% w/w of fresh salt was used. Salt was applied both on the flesh side and grain side. After 32 days of preservation, the skins were desalted and processed further. The process followed for the experiments pertaining to the reuse of recovered salt is given as Table 1.

Shrinkage temperature

Sampling for physical testing of leather was done as per standard procedures as reported by the society of leather technologists and chemists.[18] Wetblue leathers were tested for shrinkage temperature following the procedure IUP 16.[19]

TABLE III

Preservation efficacy

Period	Moisture content of skin* (% w/w)		Microbial population* (CFU/mg of skin)	
	Control	Experiment	Control	Experiment
0 hrs	66.4	68.3	42×10^3	62×10^3
2 hrs	53.2	52.4	36×10^5	55×10^5
1 day	48.8	49.8	51×10^3	48×10^4
2 days	42.4	41.4	49×10^2	66×10^2
4 days	39.8	38.8	42×10^2	49×10^2
8 days	38.7	37.4	32×10^1	44×10^1
16 days	38.2	37.4	52×10^1	59×10^1
32 days	38.0	37.0	34×10^1	41×10^1

* Values are the average of four values of four skins

TABLE IV

Pollution Reduction – commercial scale experiments

Experiment	Characteristics								
	TKN (mg/l)			COD (mg/l)			Bacterial Population (CFU/ml)		
	Before treatment	After treatment	Reduction (%)	Before treatment	After treatment	Reduction (%)	Before treatment	After treatment	Reduction (%)
Batch 1	930	177	81	26300	5786	78	22×10^{10}	0	100
Batch 2	970	194	80	28200	7050	75	18×10^{10}	0	100
Batch 3	900	153	83	27700	6648	76	20×10^{10}	0	100

TABLE VI

Preservation efficacy – commercial scale experiments

Period	Moisture content of skin (% w/w)				Microbial population (CFU/mg of skin)			
	Control	Exp 1	Exp 2	Exp 3	Control	Exp 1	Exp 2	Exp 3
0 hrs	70.2	68.5	69.3	68.4	50×10^3	48×10^3	45×10^3	53×10^3
After 10 days	51.5	55.3	52.1	50.7	38×10^2	39×10^2	34×10^2	32×10^2
After 20 days	40.7	41.2	42.6	41.7	28×10^2	11×10^2	21×10^2	17×10^2
After 30 days	37.4	36.5	34.8	36.2	22×10^1	21×10^1	19×10^1	12×10^1

TABLE V

Characteristics of recovered salt – Commercial scale

Experiment	Characteristics		
	Moisture (%)	Purity (% w/w of Nacl)	Salt recovered (kg)
Batch 1	2.7	95.7	10
Batch 2	3.9	94.9	11
Batch 3	2.9	96.3	10

Chromium content

Samples were cut from butt portion as per the official procedure IUC 2 and the chrome content was analyzed as per IUC 8 of IULTCS methods. For assessing layer wise chromium distribution, samples were taken from the butt portion and then the samples were split into three layers. Chromium content of these layers was estimated. For the assessment of area wise distribution of chromium, samples were cut as per IUC 2 from different areas.[19]

RESULTS

Electro-oxidation at laboratory scale of soak liquor was carried out at pH 7.0 with current density of 0.012 A/cm^2 for 2 hours. The voltage and ampereage applied were 2.8 V and 7.5 A respectively. Soak liquor prior to electro-oxidation was analyzed for TKN, Protein content and COD. Samples during electro-oxidation were collected at 30 minutes interval for 2 hours and were analyzed for TKN, Protein content and COD. In two hours of electro-oxidation protein content, TKN and COD of the soak liquor were reduced by 83.02%, 78.52% and 79.35% respectively (Table II). Protein content, TKN and COD of the treated soak liquor were found to be 361 ppm, 177 ppm and 5100 ppm respectively. Electrochemical oxidation could bring about total disinfection simultaneously. The bacterial population of soak liquor that had a initial bacterial count of $39X10^9$, was reduced by 99.99% in 30 minutes. The electrical energy consumed for electro-oxidation was 0.042 kwh for 7 litre.

The treated soak liquor was evaporated naturally under the sun similar to the open solar evaporation system followed in India. About 10 gm of salt was recovered from 1 litre of soak liquor. The recovered salt was analysed for moisture content and purity. It was found that the moisture content of the salt was 3.2% and the purity (on moisture free basis) was 93.8%.

Four Indian goatskins weighing approximately 1 kg were taken for the study. In the case of experiment the recovered salt was used. For control fresh salt was used. Right halves of the skins were taken for control and the left halves were taken for experiment. Preservation was carried out using 40% salt on the weight of the skins. After preservation, the skins were kept in pile and monitored for 32 days under ambient conditions.

The skin samples were collected intermittently (after 12 hrs, 1 day, 2 days, 4 days, 8 days, 16 days and 32 days) and analyzed for moisture content and bacterial population (Table III). Salt during preservation brings down the moisture content of the hides. In hypertonic solutions bacteria may shrink and become desiccated. Moisture content of the skin is reduced by the salt so that bacterial action is curtailed and salt being a bacteriostatic agent, hampers the growth of bacteria. Therefore the efficacy of salt for preservation can be assessed by estimating the moisture content of the hide and bacterial population. Moisture content of the skins was reduced to 38% from 66.4% in the case of control. The effective reduction in moisture was found to be 42.77%. Experimental case was also found to render similar dehydration effect, where the moisture content was reduced to 37% from 68.3%. The overall moisture reduction in the case of experiment was found to be 45.8%. The bacterial population of control skins was reduced from $42X10^3$ CFU/mg of skin (Colony Forming Units per milligram of skin) to $34X10^1$ CFU/mg of skin in 32 days. Similarly in the case of experiment, the bacterial population was reduced from $62X10^3$ CFU/mg of skin to $41X10^1$ CFU/mg of skin. The experimental trend in the reduction of bacterial population was also similar to that of the control (Table III).

After 32 days of preservation, the skins were processed into wetblue leathers. Shrinkage temperature and chromium content of the wetblue were tested. Chromin contents of control and experimental wetblue were 3.6% w/w and 3.5% w/w of Cr_2O_3 (on moisture free basis). Shrinkage temperature of both control and experimental wetblue was found to be 102°C. There was no much variation in chromium content and shrinkage temperate in experimental wetblue comparing the control.

Experiments of electro-oxidation of soaking wastewater and recovery of salt were carried out at commercial scale. Three experiments were carried out with 1 m^3 of soaking wastewater in each experiment. Electro-oxidation was carried out for 2 hours with a current density of 0.012 A/cm^2 maintaining 3.2 V and 1000 A. Soaking wastewater was characterised before and after the electro-oxidation (Table V). The average salt of the soaking wastewater was found to be 11,600 mg/l of NaCl. Electro-oxidation of soak liquor was resulted in TKN and COD reduction similar to the results obtained in laboratory scale experiments. Average reduction in TKN and COD was found to be 81.3% and 76.3% respectively. Treated wastewater was evaporated to recover salt. The salt recovered from each experiment was analysed (Table V). Results indicate that the salt was adequately pure and suitable for preservation.

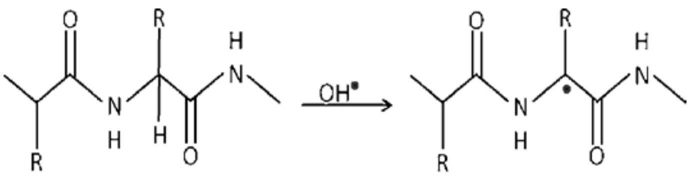
Three experiments of reuse of recovered salt were carried out. A control study was also done using fresh salt. Freshly flayed Indian cowhides were taken for the experiment. Salt recovered from the first batch (i.e 10 kg) was used for the preservation of 25 kg of cowhide. Similarly the salt recovered from second and third batches i.e 11.2 kg and 10 kg were also used for preservation of 28 kg of cowhide and 25 kg of cow hide respectively. Fresh salt weighing 10 kg was used for preserving 25 kg of cowhide. Salt offer was maintained at 40% w/w on the weight of the hide. Preservation efficacy was assessed after 10 days, 20 days and 30 days in terms of moisture reduction and bacterial population (Table VI). Average moisture reduction in the case of experiment was 47.86% against 46.72% of moisture reduction in the case of control. The average reduction in bacterial population of the hide in the case of experiment was 99.64% against 99.56% of reduction in bacterial population in the case of control. From the results it is evident that the preservation efficacy of the recovered salt was similar to that of the fresh salt.

The hides were then processed into wetblue and the chromium-tanned leathers were assessed for chromium content and shrinkage temperature. Average chromium uptake and shrinkage temperature of experiment were 3.17% of Cr_2O_3 and 101.3°C respectively. Chromium uptake and shrinkage temperature in the case of control were 3.2% Cr_2O_3 and 101°C. Results indicate that the preservation by recovered salt did not have significant impact on chromium uptake and shrinkage temperature.

For the electrochemical oxidation of 3 m^3 of soak liquor 19.2 kWh of electrical energy was spent. The total energy cost is about US \$0.68 per m^3 of wastewater. In other words, the energy cost associated with the recovery of 1 ton of salt is US \$67.85.

DISCUSSION

The electrochemical reactions during electrolysis of brine solution are complicated and not unravelled completely. Some of the important products of electrolysis are Cl_2, ClO_2, O_3, $OH^\cdot$, $O^\cdot$, $ClOH^\cdot$, H_2O_2, O_2, H_2 and CO_2. The radicals $OH^\cdot$, $O^\cdot$ and $ClOH^\cdot$ are short lived due to their high oxidation potential. They may undergo decomposition to produce other oxidants or oxidize the organic compounds and the process is called as direct oxidation. The primary (Cl_2 and O_2) and secondary (ClO_2, O_3 and H_2O_2) oxidants have quite long life. They are diffused into the areas away from the electrodes and continue to oxidise the pollutants[9]. In the oxidation of proteins, as the first step organic radicals may be formed by hydrogen abstraction. In the second step, dioxygen may react with organic radical.



$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$
$$ROO^{\bullet} + R'H \longrightarrow ROOH + R'^{\bullet}$$

Further abstraction of a hydrogen atom leads to the formation of organic hydroperoxide (ROOH) and another organic radical. The organic hydroperoxides are relatively unstable and undergo decomposition to cause molecular breakdown.[20] In the present experiment, the protein present in the soak liquor might have undergone oxidation to produce peptides initially and amino acids later. Further, electro-oxidation may lead to the production of H_2O, CO_2 and N_2. This would result in the reduction of COD and TKN. During electro-oxidation there was no increase in temperature of the wastewater. The mass of floating mass was very much insignificant. Moreover as the electro-oxidation progresses, the floating mass became absent. It was reported that chlorine is formed from chloride during electro-oxidation of saline wastewater and the chlorine then gets converted into chloride.[9] This suggests that there is no significant release of chlorine during electro-oxidation. In the present case also, chlorine and hypochlorite might have been formed and have brought about the oxidation of organic matter. Electro-oxidation conditions such as pH 7.0, current density of 0.012 A/cm^2 for 2 hours using graphite electrodes could bring about substantial reduction in organic load. Reduction in protein load almost follows a perfect linearity. Reduction trends in COD and TKN are similar to each other. About 79% reduction in COD and TKN was attained in two hours. Electro-oxidation also brought about disinfection of the soaking wastewater. Because of the oxidation of organic matter and elimination of bacteria, the bad odour from soak liquor is absolutely arrested. No odour measurement has been carried out to substantiate this. However it was evident that the treated soak liquor was free from objectionable odor.

Therefore the treatment of soaking wastewater following electro-oxidation was found to be efficient. The recovered salt was found to be of good quality and suitable for reuse for preservation of hides.

The capital cost for the commercial scale electro-oxidation cell (1 m^3) including the rectifier is about US $ 10620. Even by not considering the environmental benefits of safe management of saline waste stream, recovered salt alone brings about encouraging economical benefits. The cost of commercial common salt is about US $ 106 per ton. The cost of recovered salt is US $ 70. This clearly indicates that the present system of treatment of soak liquor and reuse of the recovered salt for preservation is economically viable.

Conclusions

Electro-oxidation of soak liquor could bring about substantial reduction in pollution load and elimination of bacterial population. The recovered salt was found to be very much suitable for preservation. This process provides a comprehensive and cost effective solution to the environmental problems associated with soaking wastewater. Moreover this technique does not generate any solid waste. Commercial scale experiments proved that the system is practically feasible.

Acknowledgement

It is acknowledged herewith that this project has been carried out under the network project (SMM 10) of Council of Scientific Industrial Research, India. The authors are also thankful to M/s S A Abdul Azeez & Co, Erode, India for having consented to conduct the commercial scale experiments in their tannery.

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