Nanofiltration Membranes via Layer-by-layer Assembly and Cross-linking of Polyethyleneimine/Sodium Lignosulfonate for Heavy Metal Removal

Meng-Yun Xie, Jiang Wang, and Qing-Yun Wu

Abstract

Layer-by-layer (LbL) assembly technology is a facile method for constructing thin film composite membrane. Herein, a novel nanofiltration (NF) membrane was prepared by LbL assembly of polyethyleneimine (PEI) and sodium lignosulfonate (LS) followed by cross-linking. The surface composition, morphology, and property of PEI/LS bilayer were detailedly investigated by FTIR/ATR, XPS, SEM, AFM, and water contact angle test. The PEI/LS bilayer full of amino and hydroxyl groups presents increased roughness and improved hydrophilicity. Moreover, the NF performance of PEI/LS LbL assembly membranes can be modulated by bilayer number, polyelectrolyte concentration, and salt content. The water flux reduced while the salt rejection greatly improved as increasing the bilayer numbers, PEI concentration, or NaCl content. More than 95% MgSO$_4$ and MgCl$_2$, as well as 80% NaCl can be rejected by a NF membrane prepared by 6 PEI/LS bilayers, 1 wt% PEI, 0.5 wt% LS, and 1 mol/L NaCl. Furthermore, this NF membrane can be used to remove more than 95% heavy metal ions (Cd$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$). This work proposed a promising NF membrane by using PEI/LS as low cost polyelectrolytes and facile LbL assembly method, which should receive much attention in water purification.

Keywords Desalination; Nanofiltration; Sodium lignosulfonate; Layer-by-layer; Heavy metal

INTRODUCTION

Nanofiltration (NF) technology attracts more and more attention due to its low operation pressure, low energy consumption, and high separation efficiency.$^{[1−5]}$ As the key of NF technology, NF membranes are generally required to be with a molecular weight cut-off (MWCO) of 200−1000 and pore size of 1−2 nm.$^{[3−5]}$ Besides, a charged surface endows NF membrane with a charge repulsion effect to effectively remove heavy metal ions or dyes, which are popular in water purification application.$^{[5−8]}$ Thus, several processes are developed to prepare novel NF membranes with improved performance, such as phase inversion,$^{[9]}$ surface coating,$^{[10]}$ interfacial polymerization,$^{[11,12]}$ surface modification,$^{[13]}$ etc. Hu et al.$^{[14]}$ obtained a thermostable NF membrane by interfacial polymerization, showing a Na$_2$SO$_4$ rejection as high as 98.4%. Shen et al.$^{[15]}$ developed a polyamide film nanofiber composite NF membrane by a reverse phase interfacial polymerization, whose water flux was as high as 135.6 (L/m$^2$·h) (LMH) at 0.5 MPa. Nevertheless, these fabrication processes for NF membranes are still complicated, time-consuming, and highly costly.

Layer-by-layer (LbL) assembly technology is known to be a facile method for fabricating thin film composite NF membranes.$^{[16−19]}$ A thin film can be constructed on a substrate by alternately immersing the substrate in a polycation solution and a polyanion solution. For example, Guo et al.$^{[20]}$ prepared a NF membrane by LbL assembly technology using plant polyphenol tannic acid and hydrophilic Jeffamine, which showed good rejection performance for dyes with molecular weights of 269−1017 g/mol. On the other hand, the thickness, morphology, and property of polycation/polyanion thin films can be modulated by changing polyelectrolyte types, solution concentrations, dipping time, bilayer numbers, and additives.$^{[18,19,21]}$ Among others, the selected polyelectrolytes play an important role in the surface composition and surface charges, finally determining the membrane performance.$^{[5−8,22]}$ Several kinds of polyelectrolytes have been applied to fabricate NF membranes via LbL assembly, including poly(acrylic acid),$^{[16]}$ polydopamine,$^{[23]}$ polystyrene sulfonic acid sodium salt,$^{[24]}$ and poly(allylamine hydrochloride).$^{[25]}$ However, the complicated and high cost synthesis of most polyelectrolytes offset the facile of LbL assembly method to some extent. In contrast, sodium lignosulfonate (LS) as a lignin derivative has advantages of widespread sources, simple preparation, and low price. Moreover, LS molecules
have excellent hydrophilicity and good water solubility due to the large amount of hydroxyl and carboxyl groups \cite{26,27}. More importantly, LS has a good adsorption capacity for heavy metal ions in water or organic matters such as anions, dyes, and alcohols.\cite{26–29} Therefore, it should be meaningful to construct NF membranes by using LS as a polyanion.

Herein, LS and polyethyleneimine (PEI) were chosen as the polyanion and polycation, respectively, to form a thin film on polysulfone (PSf) ultrafiltration membrane by layer-by-layer assembly and cross-linking. The surface composition, morphology, and property of the PEI/LS films were investigated in detail. Moreover, their NF performances including water flux and salt rejection were carefully studied as a function of bilayer number, polyelectrolyte concentration, and salt content. The NF membrane with PEI/LS LbL thin film showed excellent heavy metal ions removal performance. This work proposed a novel, cheap, and effective NF membranes.

**EXPERIMENTAL**

**Materials**

Polysulfone (PSf) ultrafiltration membranes were provided by Hangzhou Water Treatment Technology Development Center Co., Ltd. Polyethyleneimine (PEI, $M_w = 7.0 \times 10^4$, 50 vol% in water) and glutaraldehyde (GA, 50 vol% in water) were purchased from Aladdin Industrial Co., Shanghai, China. Sodium lignosulfonates (LS) was supplied by Tokyo Chemical Industry Co., Ltd. Sodium chloride (NaCl), magnesium sulfate ($MgSO_4$), magnesium chloride ($MgCl_2$), cadmium chloride ($CdCl_2$), zinc chloride ($ZnCl_2$), nickel chloride ($NiCl_2$), manganese sulfate ($MnSO_4$), chromium chloride ($CrCl_3$), and copper chloride ($CuCl_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd.

**Preparation of Nanofiltration Membrane**

Nanofiltration (NF) membrane was prepared by layer-by-layer (LbL) assembly process combined with cross-linking, as shown in Fig. 1. Firstly, PSf membrane was immersed in PEI aqueous solution (0.5 wt%–2.0 wt%, pH = 5) containing 0–2.0 mol/L NaCl for 15 min. Secondly, the PSf membrane was taken out and rinsed with deionized (DI) water, following by immersed in DI water for 15 min to thoroughly remove the surplus PEI molecules on the membrane surface. Thirdly, the membrane was transferred to LS aqueous solution (1.0 wt%, pH = 8) containing 0–2.0 mol/L NaCl for 15 min. Fourthly, the membrane was cleaned by the same cleaning step as mentioned above in order to completely remove the excess LS aqueous solution on the membrane surface. As a result, the PSf membrane was covered with a PEI/LS bilayer. Different bilayer numbers can be constructed by repeating the above four steps. At last, a cross-linking step was conducted to stabilize the LbL layer, during which the LbL membrane was immersed in 1.0 wt% GA aqueous solution at 60 °C for 60 min and then cleaned by DI water. The obtained NF membrane was named as $x$PEI$_{y}$/LS$_{z}$PEI$_{x}$, where $x$ represents the bilayer numbers, and $y$ and $z$ indicate the NaCl molar concentration in PEI solution and LS solution, respectively. Unless otherwise specified, the concentrations of PEI and LS solutions were 0.5 wt% and 1.0 wt%, respectively.

**Characterization**

Attenuated total reflection Fourier transform infrared spectroscopy (FTIR/ATR, Cary660, Agilent (China) Technologies Co., Ltd.) was conducted to collect spectra from 400 cm$^{-1}$ to 4000 cm$^{-1}$ by cumulating 64 scans at a resolution of 2 cm$^{-1}$. X-ray photoelectron spectra (XPS) were recorded by a ESCALAB 250Xi spectrometer (Thermo Fisher Scientific (China) Co., Ltd.) using Al Kα excitation radiation (1486.6 eV). The water contact angle of membrane was measured by a DSA109 optical contact angle measurement system (KRUSS GmbH, German). Atomic force microscopy (AFM, BRUKER Dimension Edge, US) was performed to observe the surface roughness of membrane by tapping mode with a scan area of 5 μm × 5 μm. A field emission scanning electron microscope (FESEM, S4800, Hitachi) was used to observe the surface and cross-section morphologies of membranes.

**Membrane Performance Test**

The water flux and salt rejection of NF membranes were measured by a cross-flow filtration setup at 25 °C under 0.5 MPa. A NF membrane with an effective membrane area of 4.5 cm$^2$ was first installed in the permeation cell and pre-compacted under 0.6 MPa for 30 min. The feed solution (NaCl, MgCl$_2$, or $MgSO_4$ aqueous solution at 200 ppm) was flowed at a rate of 3.0 L/min. Then, the filtrate was collected when the pressure was lowered and stabilized under 0.5 MPa. The flux ($J$, LMH) and salt rejection ($R$, %) were calculated by the following equations:

$$J = \frac{V}{A \cdot t} \quad (1)$$

$$R = (1 - \frac{C_p}{C_f}) \times 100\% \quad (2)$$

![Fig. 1 Schematic image of preparation process of PEI/LS membrane.](https://doi.org/10.1007/s10118-020-2422-x)
where $V$ is the filtrate volume, $A$ is the effective membrane area, $t$ is the measuring time required to collect the filtrate, and $C_p$ and $C_f$ are the salt concentrations of the filtrate and the feed solution, respectively. The salt concentration was determined by the conductivity of the solution using a conductivity meter (DDSJ-308A, INESA Scientific Instrument Co., Ltd, Shanghai, China).

Similar measurement was conducted to evaluate the rejection of NF membrane against different heavy metal ions including $\text{Cr}^{2+}$, $\text{Cd}^{2+}$, $\text{Zn}^{2+}$, $\text{Ni}^{2+}$, $\text{Mn}^{2+}$, and $\text{Cu}^{2+}$. The concentration of the feed solution was fixed at 200 ppm. The concentration of heavy metal ions of the filtrate was determined by an inductively coupled plasma emission spectrometer (ICP-OES, PerkinElmer 8300, PerkinElmer Inc., US).

RESULTS AND DISCUSSION

Surface Composition of PEI/LS Membranes

Fig. 2 shows the FTIR/ATR spectra of PSf and 6-PEI$_{1.0Na}$/LS$_{1.0Na}$ membranes, which reflect the surface composition of membranes. Compared with the nascent PSf membrane, a broad band around 3100–3600 cm$^{-1}$ obviously exposes on the FTIR/ATR spectrum of 6-PEI$_{1.0Na}$/LS$_{1.0Na}$ membrane, assigned for the stretched vibration of $\text{O}―\text{H}$ and $\text{N}―\text{H}$ groups (Fig. 2a). Moreover, a new band appearing at 1038 cm$^{-1}$ corresponds to the symmetric stretching vibration of sulfonate from LS molecules (Fig. 2b). These results suggest that both PEI and LS are deposited on the PSf membrane after LbL assembly of PEI/LS. On the other hand, a new shoulder peak at 1660 cm$^{-1}$ results from the formation of $\text{C}≡\text{N}$ bonds between PEI and GA by cross-linking as shown in Fig. 2(e). The surface composition of membrane was further revealed by XPS spectroscopy. As shown in Fig. 2(c), the nascent PSf membrane only shows peaks of O 1s, C 1s, and S 2p, while new peaks of N 1s, Na Auger, and Cl 1s arise after deposition with PEI/LS multilayers. A further peak-differentiation of N 1s reveals the formation of $\text{C}≡\text{N}$ bonds between PEI and GA. In addition, the S/O ratio decreases from 0.22 for PSf membrane to 0.05 for 6-PEI$_{1.0Na}$/LS$_{1.0Na}$ membrane.
which suggests the coverage of PEI/LS multilayer on PSf membrane.

To investigate the effect of salt on the deposition contents of PEI and LS, we compared the FTIR/ATR spectra of four kinds of modified PSf membranes with different NaCl contents as shown in Fig. 3. The vibration band at 1645 cm⁻¹ corresponding to the asymmetric C=O–C stretching was chosen as the reference peak. Table 1 lists the relative peak heights of the vibration bands at 3430, 1660, and 1038 cm⁻¹, which correspond to the relative contents of PEI, cross-linking, and LS, respectively. Obviously, the deposition of PEI and LS can be enhanced by adding moderate amount of salt. NaCl in the polyelectrolyte solution increases the ionic strength and changes the electrostatic interaction between polyelectrolytes. The molecular chain of the polyelectrolyte becomes curled and the effective charge density decreases. Thus, the formation of the bilayer requires more polyelectrolyte, which promotes the deposition of polyelectrolyte.

However, the relative peak height of the vibration bands decreases to some extent when NaCl concentration is more than 1 mol/L. This result may be due to the desorption of polyelectrolyte and a swelling of the adsorbed layer, resulting in a decrease in the amount of polyelectrolyte adsorption.

Surface Morphology and Property of PEI/LS Membranes

SEM and AFM were applied to characterize the surface morphology of PSf and 6-PEI/LS membranes with different NaCl contents. As shown in Fig. 4, the nascent PSf membrane presents smooth surface as well as pores with a diameter of 10–20 nm, which can be confirmed by its corresponding AFM image with a small surface roughness ($R_a = 6.27$ nm). However, the surface pores of 6-PEI/LS membranes cannot be observed by SEM under the same magnification. This result is ascribed to the coverage of PEI/LS multilayers on the substrate surface, which can be further supported by the dense and thick top layer of 6-PEI/LS membranes (Fig. S1 in the electronic supplementary information, ESI). Moreover, the surface of 6-PEI0.0Na/LS0.0Na membrane becomes heterogeneous and full of tiny particles, and thus the surface roughness increases to 11.7 nm. These particles further aggregate into large clusters on the surface of 6-PEI1.0Na/LS1.0Na membrane when 1.0 mol/L NaCl was added into the polyelectrolyte solutions. Correspondingly, the surface roughness of 6-PEI1.0Na/LS1.0Na membrane significantly increases to 38.8 nm. In comparison, the roughness of 6-PEI0.20Na/LS0.20Na membrane (40.8 nm) is close to that of 6-PEI1.0Na/LS1.0Na, but the particles on 6-PEI2.0Na/LS2.0Na membrane become uniform at 2.0 mol/L NaCl. Similar salt-induced roughening has been observed in the poly(sodium 4-styrenesulfonate)/poly(allylamine hydrochloride) and poly(acrylic acid) complexes (PSS/PAH-PAA) LbL assembly system.[33] and some other literatures.[34–36] The addition of salt will vary the ion strength of polyelectrolyte solution, and further change the conformation of polyelectrolyte molecular chain, thus affecting the structure and performance of the membrane.[33–38] PEI or LS molecules in the solution without salt display a relatively extended conformation due to the electrostatic repulsion of charged groups on the polymer chains. The extended PEI and LS molecules are alternately deposited on PSf membrane leading to a relatively smooth PEI/LS multilayer. However, a conformation transition is induced when adding salt into polyelectrolyte solutions, resulting in coiled polymer chains by screening the electrostatic repulse of the charged groups. A rough surface full of particle clusters is formed by coiled PEI and LS polymer chains.

The surface wettability of membranes was detected by water contact angle measurement. Fig. 5 presents the contact angles of a 5 μL water droplet on the surface of membranes. It is clear that the water contact angle of 6-PEI0.0Na/LS0.0Na membrane (65°) is about 30% lower than that of PSf membrane (89°), indicating the enhanced surface hydrophilicity by LbL assembly of PEI/LS system. This result can be attributed to the intrinsic hydrophilicity of PEI and LS molecules. Moreover, the addition of salt plays an important role in the surface hydrophilicity of 6-PEI/LS membranes. The water contact angles of 6-PEI/LS membranes gradually decline from 65° to 30° when the NaCl content in both solutions increases to 2.0 mol/L. The surface hydrophilicity of membranes is highly related to the surface roughness, which can be enhanced by

![Fig. 3 FTIR/ATR spectra of 6-PEI0.0Na/LS0.0Na, 6-PEI0.5Na/LS0.5Na, 6-PEI1.0Na/LS1.0Na, and 6-PEI2.0Na/LS2.0Na membranes.](image)

![Table 1 The relative peak heights of the vibration bands at 3430, 1660, and 1038 cm⁻¹ for PEI/LS membranes.](table)

| Sample                  | 3430 cm⁻¹ | 1660 cm⁻¹ | 1038 cm⁻¹ |
|-------------------------|-----------|-----------|-----------|
| 6-PEI0.0Na/LS0.0Na      | 0.20      | 0.07      | 0.20      |
| 6-PEI0.5Na/LS0.5Na      | 0.16      | 0.07      | 0.12      |
| 6-PEI1.0Na/LS1.0Na      | 0.27      | 0.11      | 0.23      |
| 6-PEI2.0Na/LS2.0Na      | 0.23      | 0.09      | 0.17      |

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adding NaCl in PEI and LS solutions as mentioned above. These results prove that the surface wettability of PEI/LS bilayers can be finely tuned by varying the ion strength in PEI or LS solutions.

**Nanofiltration Performance of PEI/LS Membranes**

The nanofiltration performance of PEI/LS membranes was characterized by testing the water flux and salt rejection of membranes when using three kinds of inorganic salt solutions (NaCl, MgCl$_2$, and MgSO$_4$). PEI/LS membranes with different bilayer numbers were prepared by adding 1.0 mol/L NaCl to both polyelectrolyte solutions. As can be seen in Fig. 6, 2-PEI$_{1.0\, Na}$/LS$_{1.0\, Na}$ membrane shows a water flux as high as 60 LMH but a relatively small salt rejection of 35.6% for NaCl solution. As the bilayer number increases, the water flux for NaCl solution dramatically declines to 12.9 LMH for 4-PEI$_{1.0\, Na}$/LS$_{1.0\, Na}$ membrane and 10.4 LMH for 6-PEI$_{1.0\, Na}$/LS$_{1.0\, Na}$ membrane. On the contrary, the salt rejection for NaCl solution significantly rises to 59.3% and 80.2% for 4-PEI$_{1.0\, Na}$/LS$_{1.0\, Na}$ and 6-PEI$_{1.0\, Na}$/LS$_{1.0\, Na}$ membranes, respectively. These results are due to the thickening of PEI/LS multilayers on PSf membrane as a function of bilayer numbers, which leads to the increasing resistance of PEI/LS multilayers for both water and salt molecules.

Fig. 4  Top view SEM and AFM images of membranes: (a1–a3) PSf, (b1–b3) 6-PEI$_{0.0\, Na}$/LS$_{0.0\, Na}$, (c1–c3) 6-PEI$_{0.5\, Na}$/LS$_{0.5\, Na}$, (d1–d3) 6-PEI$_{1.0\, Na}$/LS$_{1.0\, Na}$, and (e1–e3) 6-PEI$_{2.0\, Na}$/LS$_{2.0\, Na}$ membranes.

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The polyelectrolyte concentration is another important factor affecting the NF performance of PEI/LS membranes. To discuss the effect of NaCl contents in polyelectrolyte solutions on the performance of NF membrane, three kinds of PEI/LS membranes were prepared by varying NaCl contents. As can be seen in Fig. 8, the water flux of PEI/LS membrane decreases and the salt rejection almost increases with the increasing of NaCl concentration. As NaCl reaches 1.0 mol/L, the salt rejection reaches a peak of 80.2% for NaCl, 95.2% for MgCl$_2$, and 94.3% for MgSO$_4$. However, when the salt concentration increases to 2.0 mol/L, the salt rejection is slowly down to 75.5% for NaCl, 90.5% for MgCl$_2$, and 89.8% for MgSO$_4$. As mentioned above, the deposition of polyelectrolytes on the membrane surface can be promoted by adding a certain amount of NaCl in polyelectrolyte solution, which facilitates other literatures.$^{[46,47]}$ This result can be ascribed to an insufficiently effective charge density of the solution as the polyelectrolyte is not enough, which results in an insufficient adsorption of polyelectrolyte and an uncompact polyelectrolyte bilayer.$^{[32]}$ A compact bilayer has a high resistance to water molecules and salt ions, leading to a decreasing water flux and an increasing salt rejection.$^{[48]}$

The polyelectrolyte concentration is another important factor affecting the NF performance of PEI/LS membranes. Fig. 7 shows that the water flux of PEI/LS membrane reduces from 12.8 LMH to 7.8 LMH as PEI concentration increases from 0.25 wt% to 1.0 wt% when filtrating 200 ppm NaCl solution. Similarly, PEI/LS membrane shows a deceasing water flux for MgCl$_2$ solution and MgSO$_4$ solution when PEI concentration increases. On the other hand, the salt rejection increases to 80.2% for NaCl, 95.2% for MgCl$_2$, and 94.3% for MgSO$_4$ as PEI concentration increases to 0.5 wt%. Although the salt rejection slightly reduces as PEI concentration increases to 1.0 wt%, it is still above 76.9% for NaCl and 90% for both MgCl$_2$ and MgSO$_4$. Similar results were reported by many references.$^{[39−41]}$ It should be pointed out that 6-PEI$_{0.5Na}$/LS$_{1.0Na}$ membrane displays the highest salt rejection that reaches about 95% for MgCl$_2$ and MgSO$_4$, and meanwhile a salt rejection for NaCl higher than 80%. This salt rejection performance of 6-PEI$_{0.5Na}$/LS$_{1.0Na}$ membrane is better than the most other NF membranes, especially for NaCl.$^{[46,47]}$

Fig. 5 Water contact angles of membranes.

Fig. 6 The water flux and salt rejection of PEI$_{0.5Na}$/LS$_{1.0Na}$ membranes as a function of bilayer numbers. PEI concentration is 0.5 wt%, LS concentration is 1.0 wt%, and NaCl contents in PEI and LS solutions are 1.0 mol/L.

Fig. 7 The water flux and salt rejection of PEI/LS membranes as a function of PEI concentration. The PEI/LS membranes were constructed by six PEI/LS bilayers, 1.0 wt% LS solution, and 1.0 mol/L NaCl in polyelectrolyte solutions.

Fig. 8 The water flux and salt rejection of PEI/LS membranes as a function of NaCl content in polyelectrolyte solutions. The PEI/LS membranes were constructed by six PEI/LS bilayers, 0.5 wt% PEI solution, and 1.0 wt% LS solution.
to construct compact and perfect bilayers. However, excess salt results in the desorption of polyelectrolyte, and the expansion of bilayers,[32] and thus both the water flux and salt rejection decrease.

**Heavy Metal Removal of PEI/LS Membranes**

According to the membrane performance, 6-PEI$_{1.0}$/LS$_{1.0}$ membrane was chosen as a typical sample to remove six kinds of heavy metal salts (CrCl$_2$, ZnCl$_2$, NiCl$_2$, CuCl$_2$, MnSO$_4$, and CdCl$_2$) from aqueous solutions. Fig. 9 presents that more than 95% heavy metal ions can be removed by 6-PEI$_{1.0}$/LS$_{1.0}$ membrane, and the corresponding water flux is around 8 LMH. Such a high rejection for heavy metal ions profits from not only the compact structure of PEI/LS multilayers as mentioned above but also the LS chains as an adsorbent.[30] The phenol hydroxyl groups in LS chains improve the chelation between lignin molecules and metal ions.[39,44]

**CONCLUSIONS**

Polyethyleneimine (PEI) and sodium lignosulfonate (LS) were deposited on polysulphone (PSf) membrane surface to prepare nanofiltration (NF) membrane by layer-by-layer (LbL) assembly and cross-linking technology. The deposition amounts of polyelectrolytes as well as the surface morphology and roughness of PEI/LS bilayers can be tuned by NaCl content in polyelectrolyte solutions. Based on the intrinsic hydrophilicity and the rough surface, the PEI/LS bilayers display good hydrophilicity, which can be further improved by increasing NaCl content in polyelectrolyte solutions. The obtained PEI/LS membrane can be used for nanofiltration. The water flux reduced while the salt rejection greatly improved as increasing the bilayer numbers, PEI concentration, or NaCl content. More than 95% MgSO$_4$ and MgCl$_2$, as well as 80% NaCl can be rejected by a NF membrane prepared by 6 PEI/LS bilayers, 1 wt% PEI, 0.5 wt% LS, and 1 mol/L NaCl. Furthermore, the PEI/LS membrane can be applied to remove more than 95% heavy metal ions (Cd$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Cr$^{3+}$, Cu$^{2+}$, or Ni$^{2+}$).

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