Biosorption of anionic metal complexes

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Anionic metal complexes, are very effectively bound by biomass types containing an abundance of amine groups. Readily available chitinous materials such as crab shells sorbed well anionic gold cyanide ($AuCN_2^-$), selenate (SeO_4^{2-}), chromate (CrO_4^{2-}), and vanadate (VO_4^{3-}) at low pH. Equilibrium biosorption uptakes by acid-washed crab shells were up to 0.17 mmol Au /g (pH 3.5), 0.15 mmol Se/g (pH 3.0), 0.56 mmol Cr/g biomass (pH 2.0), 0.79 mmol V/g (pH 2.5). An increased ionic strength (IS as NaCl) suppressed the primary anion uptake as chloride ions competed for biosorbent protonated sites and higher IS reduced the activity of ions in solution.

1. INTRODUCTION

Major industrial activities such as mining, electroplating and power generation have problems with their effluents containing toxic heavy metals, often in anionic complex forms such as anionic chromate (CrO_4^{2-}), vanadate (VO_4^{3-}), selenate (SeO_4^{2-}), and gold cyanide ($AuCN_2^-$)[1,2] conventionally recovered by precipitation, ion-exchange or activated carbon sorption.[1,2,3] However, low recovery efficiencies and high costs of the above methods call for new high-efficiency, low-cost sorbents.

Chitin-containing biomaterials have been recognized as effective biosorbents for metals.[4,5,6,7,8] Chitin is a natural polysaccharide consisting of (1,4) 2-acetamide-2-deoxy-D-glucose units, some of which are deacetylated (chitosan).[9] The ability of chitin/chitosan to form complexes with metal ions, particularly transition and post-transition metal ions, is well documented.[4] The study of the uptake of dyes by chitin through combining $-SO_3^-$ on the dye with fully-protonated amide groups on chitin[10] showed the potential of chitin for anion adsorption. Chitin can be obtained from fungi, insect, lobster, shrimp and krill, but the most important commercial sources are the exoskeletons of crabs obtained as waste from sea-food processing.[11] Crab shells consist of $CaCO_3$ and chitin, usually cross-linked with some protein, and a proportion of lipids.[12] While some estimates report 5,000 – 8,000 tons of industrial crab-shell material disposed of by the seafood industry annually,[13] the figure of millions of tons/year appeared recently.[14] Preliminary experimental results established the potential of acid-washed crab shells for effectively sequestering gold cyanide ($AuCN_2^-$).[8] The uptake of Au by crab shells is higher than that by *Bacillus*, *Penicillium* and *Sargassum*,[15] for the same Au concentration range.

This work focuses on biosorption of anionic metal complexes such as gold cyanide ($AuCN_2^-$), selenate (SeO_4^{2-}), chromate (CrO_4^{2-}), as well as vanadate (VO_4^{3-}) by waste crab shells.

2. MATERIALS AND METHODS

2.1. Biosorbent and solution preparation

Raw crab shells: Waste crab-shells (*Ucides cordatus cordatus*) were obtained sundried from Paraiba, Piaui, Brazil. They were crushed and sieved (6-16 mesh) giving 1-3.35 mm particles.

Acid-washed shells: Raw crab-shell material was washed with 0.2 N HCl for 6 hrs to remove $CaCO_3$ and then rinsed with distilled water until the final pH stabilized at pH 3. The residual material was air-dried and represented approximately 52% of dry raw crab shells. It mainly contained chitin complexed with small amounts of protein, and pigments.[11]

Solutions of anionic metal complexes Au, Se, Cr, and V were prepared by respectively dissolving solid $NaAuCN_2$, $NaSeO_4$, CrO_3, and Na_3VO_4 in distilled water. Ionic strength of solutions was adjusted by NaCl. 0.1M HCl and NaOH was used for pH adjustment. All reagents were ACS reagent grade quality.

2.3. Equilibrium sorption experiments

Approximately 40 mg of dry crab-shell material was added into 20 ml of metal solution in 150 ml Erlenmeyer flasks. The solution was gently mixed and equilibrated for 24 hrs. Uptakes of metal were determined from the difference of metal concentrations in the initial and final solutions. The pH of the solutions before and during the sorption experiments was adjusted with 0.1M NaOH or HCl. The total final equilibrium metal concentration of liquid samples was determined by the ICP-AES (Thermo Jarrell Ash, Trace Scan).

3. RESULTS AND DISCUSSION

3.1. Effect of pH on anionic metal biosorption

All of the examined metal uptakes were strongly affected by the solution pH.

Au adsorption isotherms from $AuCN_2^-$ solution by acid-washed crab shells at an equilibrium pH of 2.5 to 4.5 are presented in Figure 1. The Au uptake increased with pH decreased from 4.5 to 3.5. Au uptake occurred at pH 3.5 with 0.17 mmol/g sorbed at an Au equilibrium concentration of 2.2 $mmol.dm^{-3}$. However, at lower pH of 2.5 the Au uptake was lower .

Raw crab shells mainly consist of $CaCO_3$ and chitin-protein complex.[12] After $CaCO_3$ was removed by acid-washing, the remaining shell material contained mainly the chitin. The pK for fully protonated chitin amide group with positive charge is below 3.5.[16] When the pH was lowered from pH 4.5 to 3.5, the number of positively charged fully protonated sites increased. The gold cyanide complex is a stable anionic species in solution [15, 17] which could be bonded onto the positively charged amide group. However, the lower the pH, the higher the concentration of Cl^- brought into the solution through the HCl addition and that, in turn, could compete with the $AuCN_2^-$ complex for the binding sites. As a result, in the present Au concentration range (0 – 3.3 $mmol.dm^{-3}$), pH 3.5 appears to be the optimum with the maximum binding sites available for $AuCN_2^-$ uptake without excessive Cl^- interference.

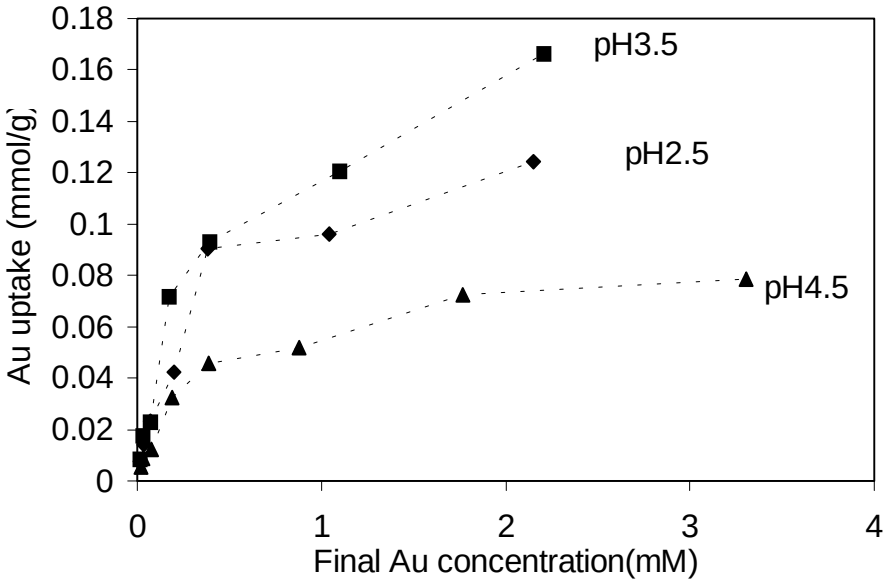

Figure 1: Effect of pH on Au uptake: 0.04 g biomass, 20 ml solution, 24hrs, room temperature.

The effect of pH on Se biosorption from selenate (SeO_4^{2-}) – containing solution is presented in Figure 2 showing Se adsorption isotherms at an equilibrium pH of 1.5 to 3.5. Selenium uptake was affected by different equilibrium pH. All four isotherms reached the maximum uptake at a final metal concentration of 4 mmol/L indicating that all the binding sites were filled under these conditions. The optimum pH for Se uptake was determined to be at approximately pH 3.0, whereby the uptake of Se reached 0.15 mmol/g equilibrated with the Se concentration of 6.2mmol/l. The solution chemistry of selenate indicated the main form of selenate in solution at pH 3.0 is the divalent SeO_4^{2-} with some $HSeO_4^-$ present.[18] As the divalent selenate (SeO_4^{2-}) ions bonded onto the mono-valent positively charged protonated amide group in chitin, another proton in solution may be required to neutralize the extra-negative charge of the bonded selenate (SeO_4^{2-}). This is responsible for the optimum pH for selenate uptake being a little lower than that observed for the uptake of monovalent anion $AuCN^-$. When pH<3, chloride ions start strongly competing for active sites with selenate ions, lowering thus the Se uptake.

Cr adsorption isotherms obtained with chromate (CrO_4^{2-}) solution at pH of 1.5 to 3.5 are in Figure 3. As pH decreased from 3.5 to 2.0, the Cr uptake increased up to 0.56 mmol/g at the Cr equilibrium concentration of 7.7mmol/l. The Cr uptake obtained at pH 1.5 was a lower than at pH 2.0. The solution chemistry of chromate shows the main forms of chromate in solution at pH 1.5 – 3.5 being $HCrO_4^-$ and $Cr_2O_7^{2-}$.[18] One mole of $Cr_2O_7^{2-}$ bound corresponds to 2 moles of Cr - this may account for higher Cr uptake when compared with Se and Au uptakes.

Vanadium uptake isotherms from the solution initially-containing vanadate (VO_4^{3-}) at pH of 1.5 to 3.5 are illustrated in Figure 4. The results show that pH 1.5 gave the lowest V uptake, while at pH3.5 it was slightly higher than at pH 4.5. The V isotherm at pH 2.5 starts off lower than that for pH 3.5, then it rises dramatically, showing the maximum uptake of about 0.79 mmol/g.

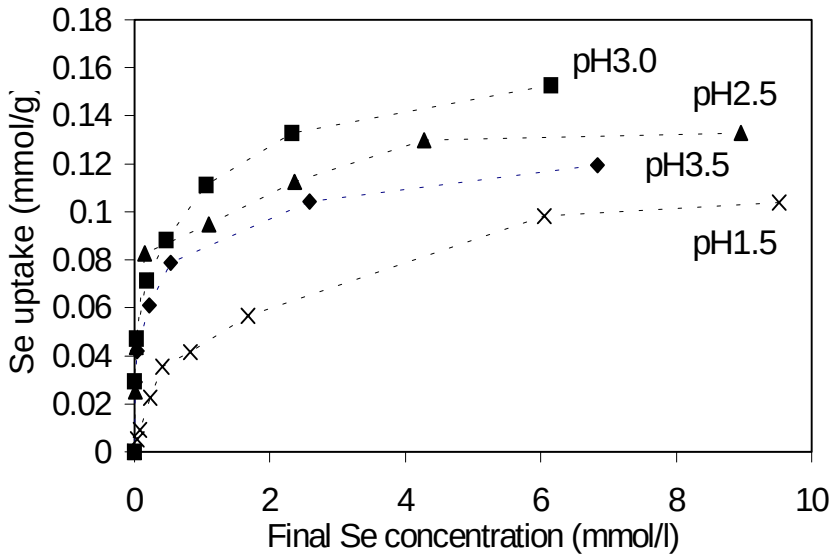

Figure 2: Effect of pH on Se uptake: 0.04 g biomass, 20 ml solution, 24h, room T

The solution chemistry of vanadate (VO_4^{3-}) revealed that at pH 1.5, the predominant form of vanadium is vanadyl ion (VO_2^+),[19] a cation not be attracted to a positively-charged amide group under this condition as the binding constant of fully charged proton on amide is lower than 3.5.[10] Instead, vanadyl ion (VO_2^+) can successfully compete with proton for the nitrogen of the amide group. However its competition is very weak under strongly acidic conditions when the concentration of proton in the solution is high (pH 1.5).

At pH 3.5-4.5, vanadium is in the form of the polyvanadates ($V_{10}O_{28}^{4-}$ and other anionic forms).[19] Consequently, V adsorption under these conditions follows the anion adsorption mechanism of crab shells and the V uptake at pH 3.5 is higher than that at pH 4.5. At pH 2.5, the vanadium is in the form of vanadium pentoxide (V_2O_5), a neutral molecule which is known to form colloidal solutions.[19] A colloid can develop erratic localized charges all over its surface from interactions with other ions in the solution.[20]

Correspondingly, it is possible that two major factors account for the high uptake of vanadium at pH 2.5. Firstly, the colloids can develop charges on their surfaces that might attract such complexes to the binding site in the same manner as the anions at pH 3.5 and 4.5. However, when a polyvanadate anion is sorbed only around 10 vanadium atoms are removed from the solution, when a colloidal particle is sorbed, many orders of magnitude more of vanadium atoms are removed from solution. Secondly, the colloidal particles are much larger than anions, and it is possible that the diameter of the particle could be larger than some of the pores in the crab shells that the particle would encounter while travelling through the polymer matrix of the shells. The shells can then act as a filter as well as a sorbent, removing thus colloidal particles from the solution by trapping them inside its porous structure.

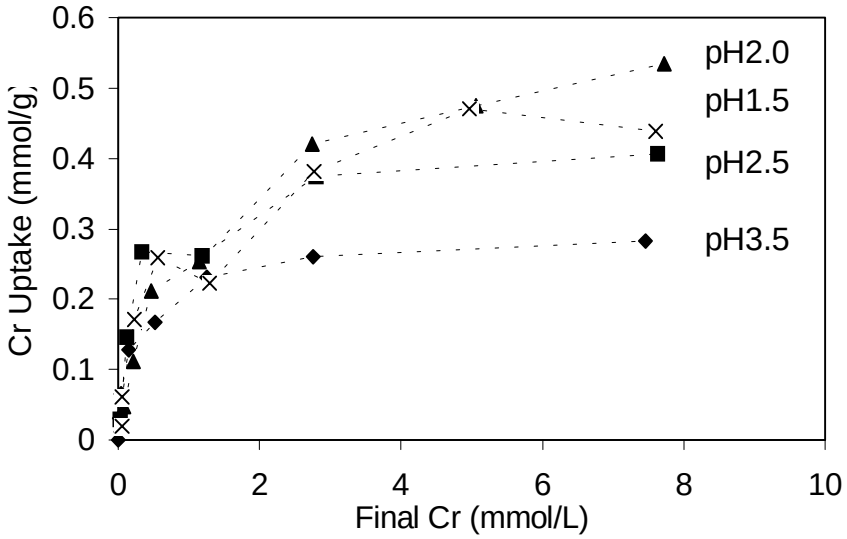

Figure 3: Effect of pH on Cr uptake: 0.04 g biomass, 20 ml solution, 24h, room temperature

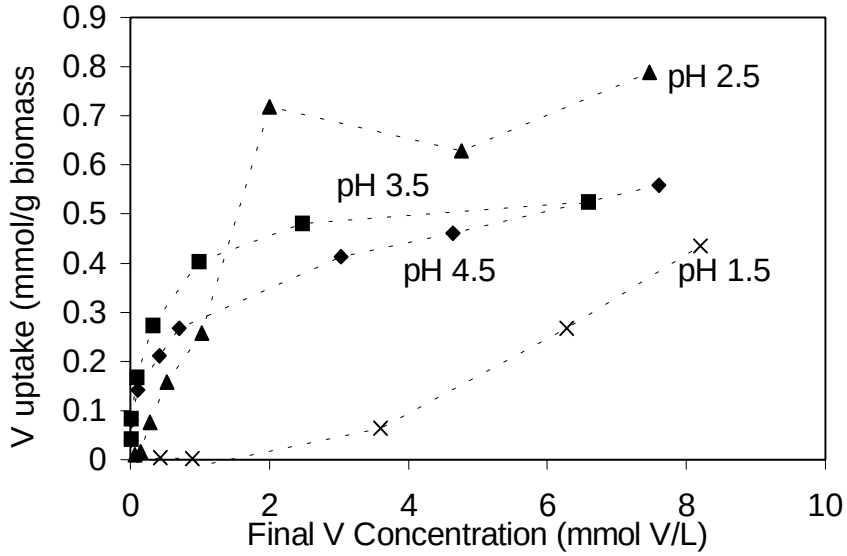

Figure 4: Effect of pH on V uptake: 0.04 g biomass, 20 ml solution, 24h, room temperature

The above results revealed that the optimum pH for anionic metal complex biosorption does not only depend on the dissociation constant of fully charged protons on chitin of crab shells but also on the solution chemistry of the metal complexes.

3.2. Effect of ionic strength

The effect of ionic strength on the biosorption of metal complexes was studied by adjusting the IS using 0.01 M – 0.1 M NaCl to the solution. The results showed that the uptakes of all the anionic metal complexes studied were reduced with increasing the NaCl concentration.[15, 21] Figure 5 illustrated the ionic strength effect on Au biosorption. As the concentration of added NaCl increased to 0.01M, maximum Au uptake in the studied concentration range was reduced to 0.14 mmol/g which is 82% of that obtained without the NaCl, and dropped to 2.4% at 0.1M NaCl. The ionic strength effect on Se uptake is seen in Figure 6. Se uptake did not change significantly at 0.01 M NaCl, however, the maximum Se uptake was reduced to 0.055mmol/g, 37% of the control. Again, in Figure 7 Cr uptake was reduced to 0.43 mmol/g at 0.01 M NaCl, 77% of the control, and to 39% at 0.1M NaCl. Compared with the above metal biosorption behavior, V uptake was not suppressed so seriously at the presence of NaCl. At 0.01M and 0.1M NaCl, V uptake was reduced to 92% and 84% of the control, respectively. This observation may be related to colloid V_2O_5 binding instead of anion adsorption.

Ions such as metal cations and inorganic anion species present in aqueous solution (either in free or complex forms) often display the tendency toward preferential adsorption on ionizable function groups[22]. Changing ionic strength (i.e. the background electrolyte concentration) influences adsorption in at least two ways:

(a) by affecting the interfacial potential and therefore the activity of electrolyte ions;

(b) by affecting the competition of the electrolyte ions and adsorbing anions for sorption sites.

Yun[23] used a Langmuir-based model to describe the effect of ionic strength on chromate and vanadium biosorption at specific pH values. Further work is necessary on modeling anioic biosorption with the consideration of solution pH, the effect of polyion charge on small ions as well as of the electrostatic charge between small ions in the solution.

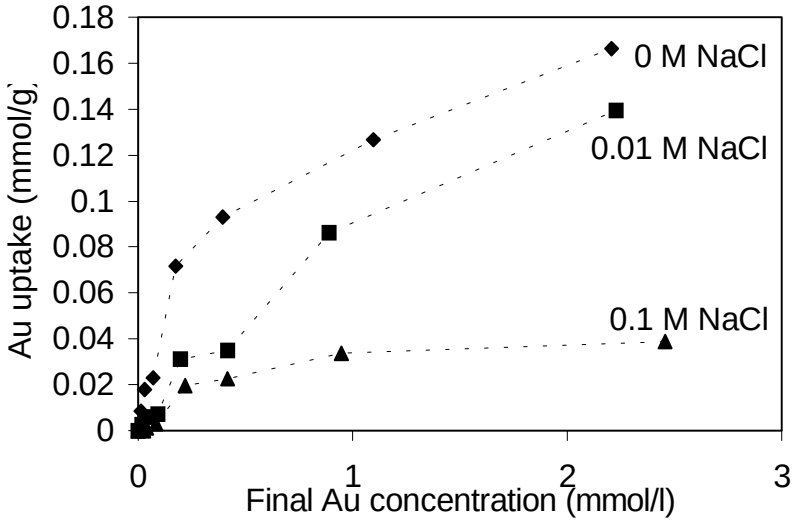

Figure 5: Effect of NaCl on Au uptake**:** 0.04g biomass, 20 ml solution, pH 3.5, 24h, room temperature

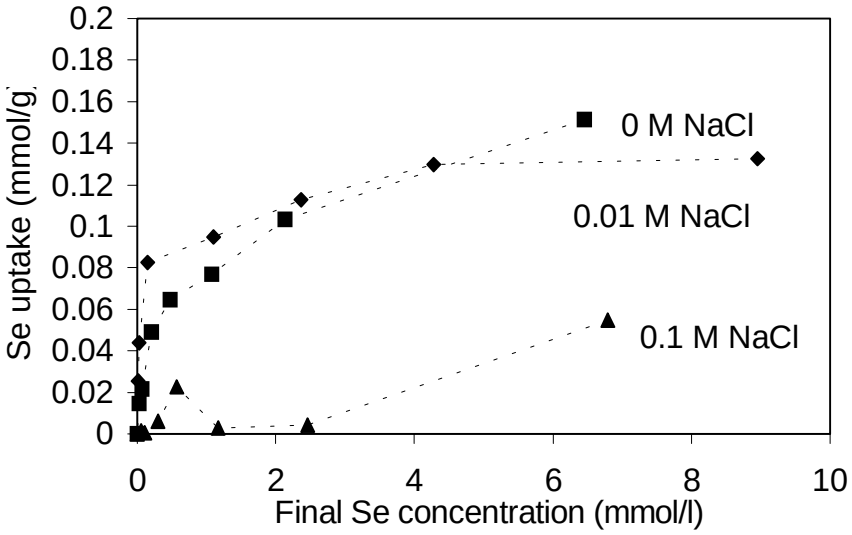

Figure 6: Effect of NaCl on Se uptake**:** 0.04g biomass, 20 ml solution, pH 3.0, 24h, room temperature

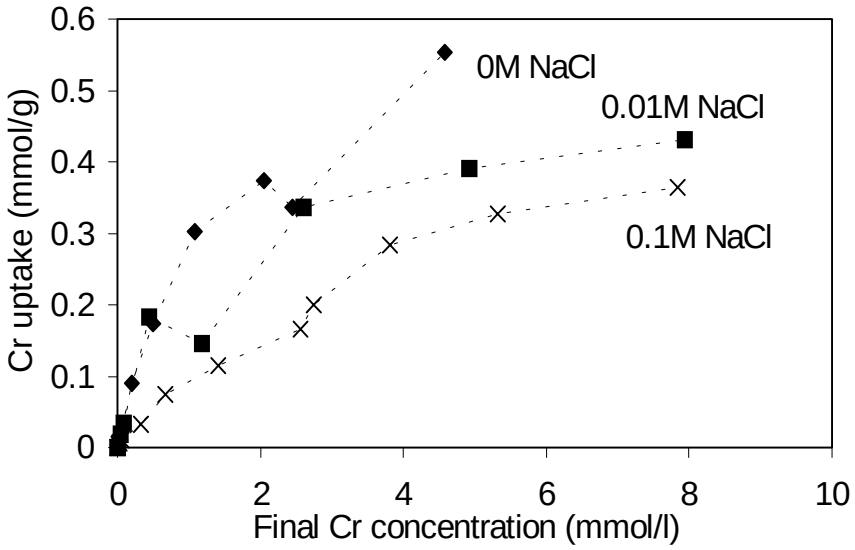

Figure 7: Effect of NaCl on Cr uptake: 0.04g biomass, 20 ml solution, pH 2.0, 24h, room temperature

ACKNOWLEDGEMENT

Special thanks to Michael Sinclair, Andrew Low, Sebastian Chabot, and Elisa Navarro-Florez for their invaluable contribution in the experimental work, and to Dr. R.H.S.F. Vieira for the crab-shell material.

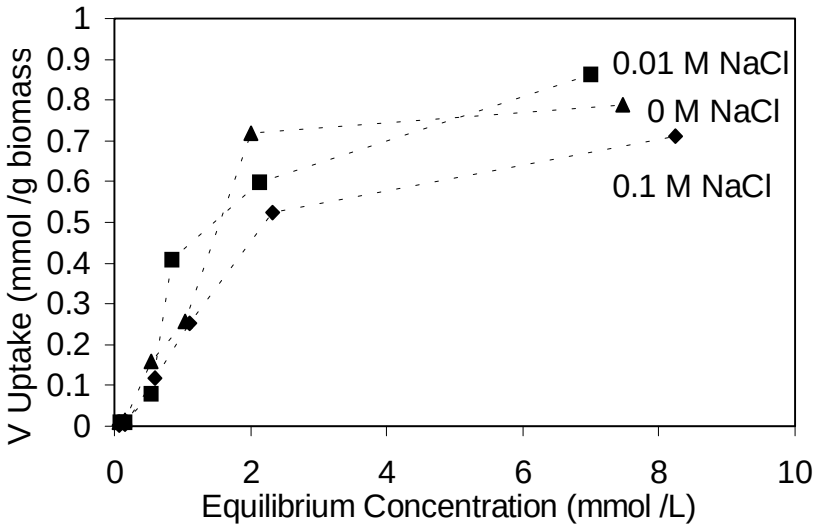

Figure 8: Effect of NaCl on vanadium uptake: 0.04g biomass, 20 ml solution, pH 2.5, 24h, room T.

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