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Selective Sorption of Metal Oxoanions from Dilute Solution by Bead Cellulose Sorbent

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Abstract: Bead sorbent Perloza MT 50 was used for selective removal of metal W, Mo, V, Ge, and Sb oxoanions. All experiments were carried out by dynamic column sorption. Sorption of tungstate and molybdate anions was successful. The sorption capacity decreased with increasing concentration of accompanying anions (chlorides, sulphates) and with increasing pH (3.5–5.5). Sorption of vanadate anion was possible but the sorption capacity was very low. Sorption of Ge(IV) and Sb(III) oxoanion was negligible.

Keywords: Cellulose, tungsten, molybdenum vanadium, antimony, germanium, sorption

INTRODUCTION

Of the many metals that may be present as contaminants in natural waters and wastewater, a few (specifically arsenic, molybdenum, tungsten, vanadium, antimony, and selenium) occur as oxoanions.

Many different methods for the removal of metal-oxoanions from the water solution exist.

1. Liquid-liquid extraction (1–3) it is a selective method, but extraction agent is not completely insoluble in the water. Therefore, this method is not suitable for treatment of drinking water resources.
2. Ion-exchange by standard strong or weak base anion resin (4, 5, 6, 7) —this method is usually not selective enough for metal-oxoanions. A serious

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problem is the desorption, some of the metal-oxoanions (Mo, V, Cr) are difficult (6) to be desorbed and the sorption capacity in the subsequent sorption run decreases considerably.

3. Ion-exchange by chelating resin (8–13) it is the most suitable process for the removal of metal-oxoanions from diluted solutions.
4. Flocculation by Fe^{3+} salts (14,15) —it is a widely used method for the removal of arsenic from aqueous solutions. Its disadvantage is the irreproducibility in achieving As-concentrations lower than 0.01 mg/L.
5. Nanofiltration and ultra filtration (16,17) —these methods are very effective and selective. Polyvalent ions are removed easily by nanofiltration and more spacious ions or molecules are removed by ultra filtration.

It is known (18–21) that low molecular weight substances containing diol-groupings in an appropriate steric conformation can form complexes with metal-oxoanions. These hydroxycompounds can form two kinds of the coordination diol- or polyol- complexes with metal-oxoanions:

1. mono-nuclear complexes (Ge, B, As);
2. bi (*or poly*)-nuclear complexes (V, W, Mo).

The complexation reactions between oxoanions and diol-compounds (diol-ligands) are pH-sensitive. Optimum pH-range for particular oxoanions to form diol (polyol) complexes was determined (22).

The formation of these diol- or polyol- complexes can be utilized for the selective uptake of oxoanions from the water streams, if a solid matrix containing diol- ligands with appropriate sterical configuration of OH-groups will be used as a selective sorbent.

Cellulose (Fig. 1) is the most abundant naturally occurring organic substance, being found as the principal component of cell walls in higher plants where it provides the main structural feature. Cotton is almost pure cellulose at 98%, flax is 80%, and wood is 40–50% with the other 50% made up from other complex polysaccharides.

Bead cellulose (23, 24) is a pure regenerated cellulose which is prepared by a modified viscose procedure. It is characterized by a regular spherical shape of individual particles, controlled porosity, accessibility for high molecular weight substances, high deformation stability, and adequate chemical reactivity. Bead cellulose, which is distributed under the trade mark PERLOZA® (25), is a hydrophilic matrix (26) with the polymer structure stabilized by hydrogen bonds only—there are no covalent cross-linkings.

Different applications of this material are described, for instance physical supports (27), chromatographic materials (23), various derivatives with different functions like ion exchangers (28), metal chelating adsorbents (29), chemisorbents (30), affinity adsorbents (31), and immobilized enzymes carriers (32). Bead cellulose can also be coupled with various active substances giving composite systems.

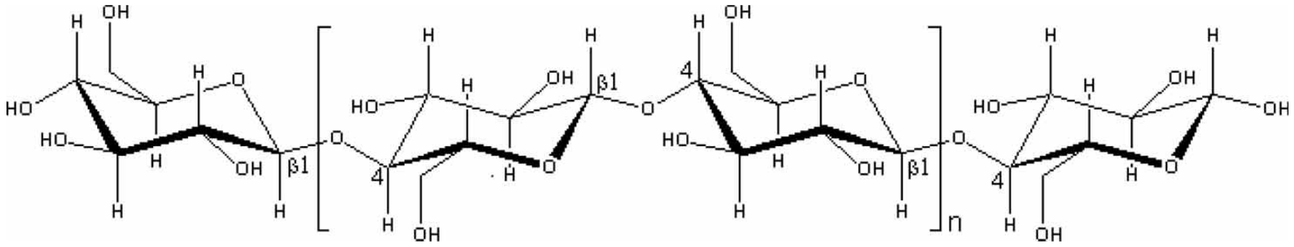

Figure 1. Structure of cellulose.

Previously it was pointed out by ^{11}B NMR studies (33), that crosslinked polysaccharides (Dextran, Sephadex) are able to form polyol-complexes between OH-groups of saccharides and borate oxoanions. The main goal of this study is to determine, whether the steric configurations of OH-groups in the molecule of crosslinked cellulose will guarantee the fast enough reaction rate to form stable enough coordination complexes on dynamic column operation, that this polymeric material can be considered as a selective sorbent for metal-oxoanions.

EXPERIMENTAL

All experiments were carried out in dynamic column sorption mode. The loading solution passed through the column (inner diameter 10 mm) containing 10 ml of sorbent Perloza MT 50 (particles size 30–250 nm, stability within pH range 1–14) at the specific flow rate of 3 BV/h. Fractions of filtrate were collected and metal concentrations were analyzed with ICP-OES technique.

For the preparation of test solutions, $Na_2WO_4 \cdot 2H_2O$, NH_4VO_3, $Na_2MoO_4 \cdot 2H_2O$, GeO_2, and Sb_2O_3 of analytical purity were used. The solutions were freshly prepared before the use, the initial concentration of metal was 0.5 mg/L and the concentration of accompanying anions (Cl^-, SO_4^{2-}) was 100 or 500 mg/L. The experimental pH values ranged from 3.5 to 10. The Perloza MT 50 sorbent was regenerated with 1 mol/L NaOH solution after sorption of oxoanions W(VI), Mo(VI), and V(V), or with 1 mol/L HCl solution after sorption of Ge(IV) and Sb(III). Before every sorption run of W(VI), Mo(VI), and V(V) the sorbent was conditioned by 1 mol/L HCl solution, to keep all OH-groups and also carboxylic groups (34) (which are produced by partial oxidation of -CH_2OH groups during the purification of raw material) in hydrogen form.

For the sorption run the limiting breakthrough concentration of metal was 0.1 mg/L. The sorption capacities of the sorbent were calculated according to the equation:

Sorption capacity = (volume at the breakthrough point × mass concentration)/volume of the sorbent [mg Me/L of sorbent], resp. [mmol-Me/L of sorbent].

RESULTS AND DISCUSSION

Tungstate Oxoanion

The influence of pH on the tungstate oxoanion sorption is shown in the Fig. 2. The concentration of W(VI) in the feed solution was 0.5 mg/L and the concentration of the accompanying anions (Cl^-, SO_4^{2-}) was 100 mg/L. The sorption of W(VI) anion was successful at the pH of 3.5 when the

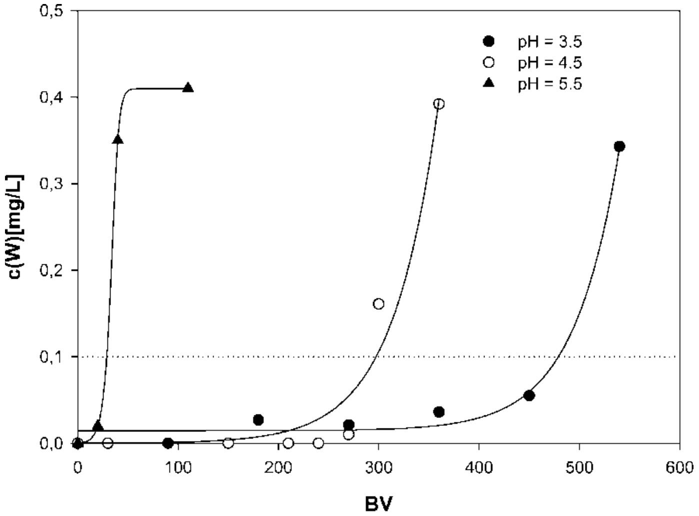

Figure 2. The history of W-sorption—Effect of pH.

sorption capacity was 250 mg/L (1.4 mmol/L), at the pH of 4.5 the breakthrough capacity decreased to 130 mg/L (0.7 mmol/L) and at pH of 5.5 the capacity was only 13 mg/L (0.07 mmol/L).

The capacity of the sorbent decreased very rapidly (Fig. 3). These results come up to the expectation that the tungsten's coordination complexes are more stable in the acid pH range of pH, where W is present in the form of isopolyanions (35) $W_{12}O_{41}^{10-}$ or $H_2W_{12}O_{40}^{6-}$. In these polyanions there are more

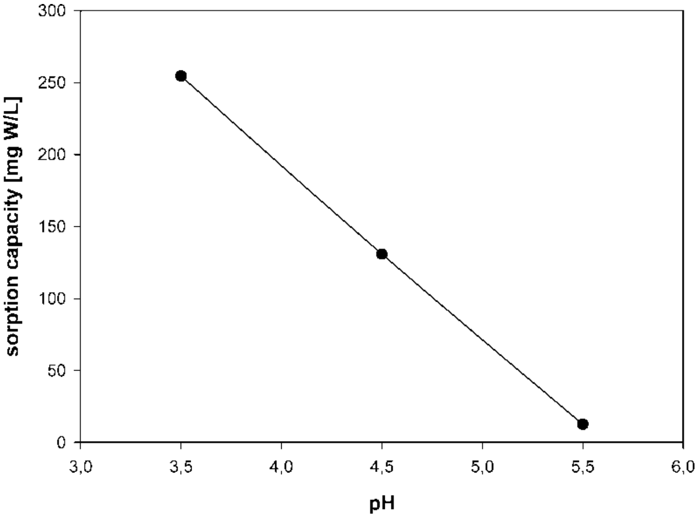

Figure 3. The history of W-sorption—Effect of pH on sorption capacity.

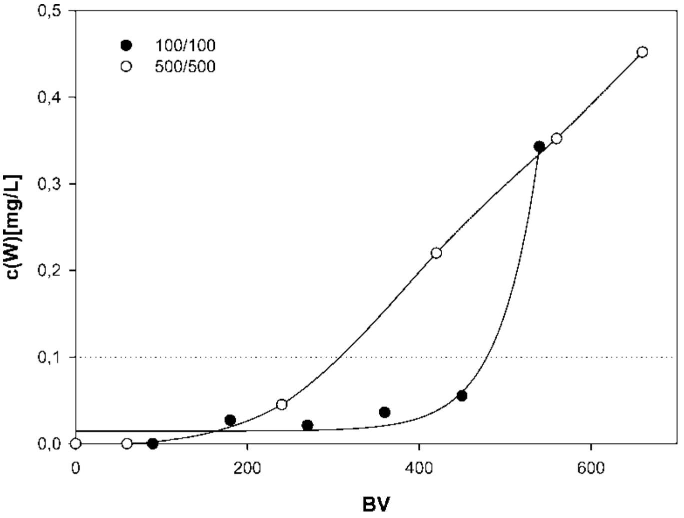

Figure 4. The history of W-sorption—Effect of accompanying anions.

reactive sites (W-O bonds) to form polyolcomplexes with saccharide OH-groups, compared to simple WO_4^{2-} anion, which is present in the neutral and alkaline environment.

When the concentration of sulfates and chlorides in the feed solution was increased from 100 mg/L to 500 mg/L at pH = 3.5 the sorption capacity decreased from 254.5 mg/L (1.384 mmol/L) to 180 mg/L (0.98 mmol/L) (Fig. 4).

Under the presence of increased concentration of accompanying anions in the feed solution the heteropolyanions are formed (36) whose complexing ability is much smaller compared to that of isopolyanions and, consequently, the W-breakthrough capacity is decreased.

The elution of tungsten by 1 M NaOH is shown in Figs. 5, 6–7 BV are sufficient for tungstate displacement, the recovery ratio of tungstate was higher than 90%, tungsten was completely striped within 10 BV of regeneration solution. This result is very important for subsequent sorption run.

Molybdate Oxoanion

The influence of pH (Fig. 6) on the sorption was very similar to the case of tungstate sorption. At the concentration of Mo(VI) in the feed solution 0.5 mg/L and concentration of accompanying anions (Cl^-, SO_4^{2-}) 100 mg/L the breakthrough capacity was 95 mg/L (0.99 mmol/L) at pH of 3.5, at pH of 4.5 the capacity decreased down to 18 mg/L (0.19 mmol/L) and at pH of 5.5 capacity was only 10 mg/L (0.11 mmol/L). In this case the

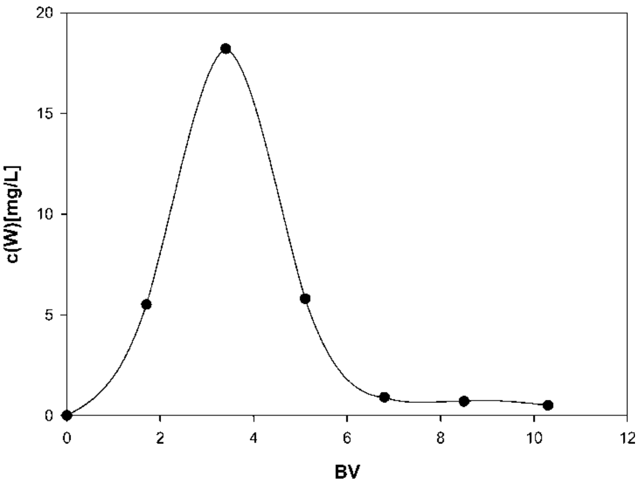

Figure 5. Desorption of tungsten by NaOH solution.

sorption capacity decreased more rapidly than in the case of the sorption of tungstate. This fact is very typical for the sorption of molybdate because the chelate of Mo-oxoanion is less stable than the W-chelate (17) and it is much more sensitive to change of pH.

The effect of pH on the sorption of molybdate oxoanions can be seen in Fig. 7, too. This relation shows that the optimum pH value was 3.5, when the sorption capacity is the highest, while the pH values 4.5 and 5.5 were not suitable for the sorption of molybdate oxoanions by the sorbent Perloza MT 50.

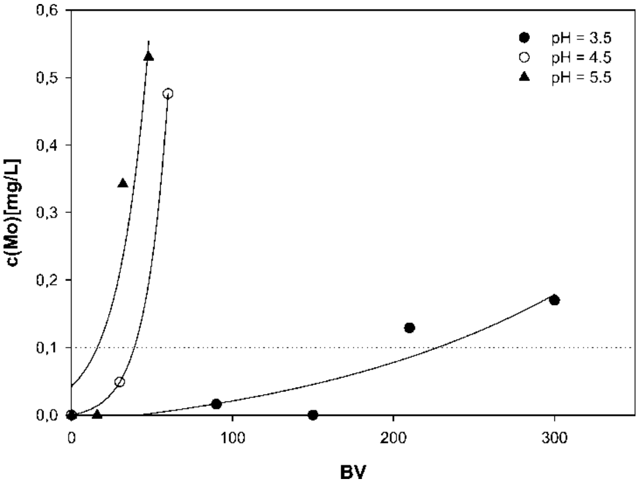

Figure 6. The history of Mo-sorption—Effect of pH.

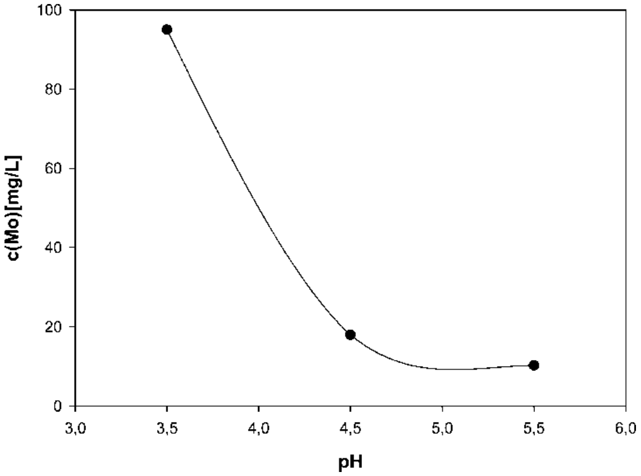

Figure 7. The history of Mo-sorption—Effect of pH on sorption capacity.

The sorption capacity of molybdate oxoanion decreased, when the concentration of sulfates and chlorides increased from 100 mg/L to 500 mg/L (Fig. 8). The sorption capacity in the presence 500 mg/L of accompanying anions was 50 mg/L (0.52 mmol/L). This negative effect of accompanying anions, which is observed also for the sorption of W(VI) anions, is limiting the use of this sorbent in the case when high concentration of accompanying anions is present in the feed solution.

The recovery of molybdate oxoanion provided good yields, when 6 BV of 1 M solution of NaOH (Fig. 9) was used for regeneration, the recovery ratio of

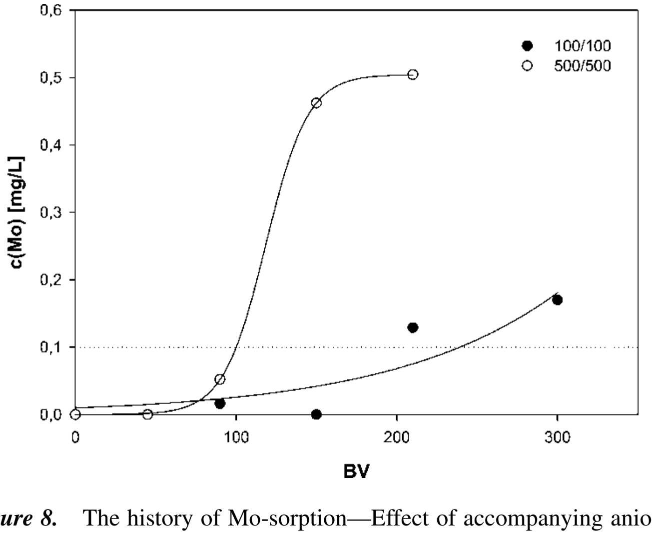

Figure 8. The history of Mo-sorption—Effect of accompanying anions.

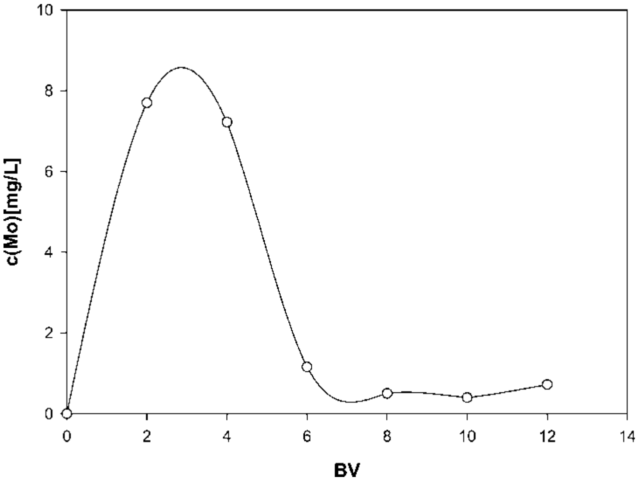

Figure 9. Desorption of molybdenum by NaOH solution.

molybdate within 6 BV was higher than 80%, Mo was completely striped within 10 BV of the regeneration solution. This high desorption efficiency enables the reuse of the sorbent Perloza MT 50.

Vanadate Oxoanion

Sorption of vanadate oxoanion was not very successful. However, a certain sorption capacity exists (Fig. 10) for vanadium at pH of 5.5 it was treated 30 bed volumes of loading solution [i.e. the capacity is 15 mg/L (0.3 mmol/L)] and at pH of 7.5 were processed 18 BV [i.e. 10 mg/L (0.2 mmol/L)] before the breakthrough concentrations were achieved.

A very strong influence of pH on the vanadate sorption capacity (Fig. 11) is determined. Optimum pH values for the sorption were found to be around 5.5 (weakly acidic range of pH). A very low sorption capacity around pH value 4.0 is probably the consequence of the vanadate oxoanion transformate to cationic form of vanadium as VO_2^+, VO^{2+} and these species cannot form the complex with OH-groups of the sorbent.

Antimonate(III) and Germanate Oxanions

In this case, oxoanions of Sb(III) and Ge(IV) breakthrough within the first fractions of the outlet solution. All sorptions were unsuccessful under all selected conditions.

This result is probably caused by the form of Ge and Sb mono-nuclear complexes. For the formation of these types of complexes an optimum

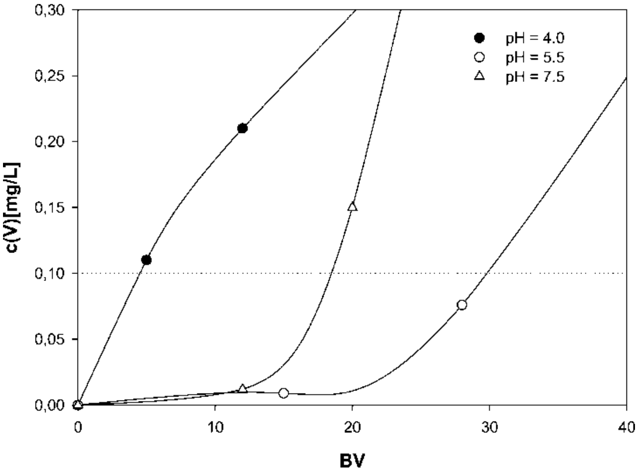

Figure 10. The history of V-sorption—Effect of pH.

steric configuration and number of OH-groups in the molecule is very necessary. But the OH-groups in a *cis*-position are not located at the adjacent C-atoms, and therefore they are not close enough even after cross-linking to form a mononuclear diol complex such as Ge-cellulose type.

The comparison of breakthrough capacities for W-, Mo-, and V-oxoanion is given in Table 1.

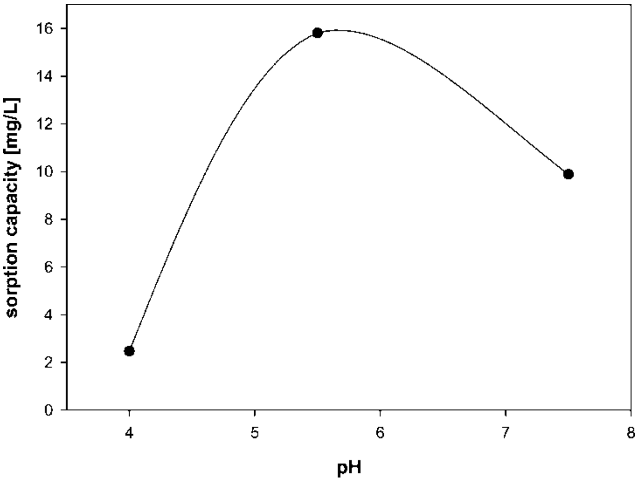

Figure 11. The history of V-sorption—Effect of pH on sorption capacity.

Table 1. The comparison of breakthrough capacities for W-, Mo-, V-oxoanions

	Sorption capacity [mmol/L]		
c (Me)/c(Cl^-)/c(SO_4^{2-})/pH	W(VI)	Mo(VI)	V(V)
0.5/100/100/3.5	1.40	0.99	0.05
0.5/500/500/3.5	0.98	0.52	—
0.5/100/100/4.5	0.71	0.19	0.07
0.5/100/100/5.5	0.07	0.11	0.30
0.5/100/100/7.5	—	—	0.20

CONCLUSIONS

The sorbent Perloza MT 50 having in the structure OH-groups is suitable to separate tungstate, molybdate, and vanadate oxoanions from water. It is the advantage of this material, that the crosslinking process will bring OH-groups close together and binuclear complexes with W, Mo, and V oxoanions can be formed, without any additional and costly functionalization of the polymeric matrix, which is required for other chelating resins.

The best results of sorption of tungstate and molybdate are obtained when the feed solution contains only low concentration (100 mg/L) of accompanying anions (sulfates and chlorides). The sorption capacity was higher at pH 3.5 of the feed solution, when the sorption capacity is 1.40 mmol/L and 0.99 mmol/L, respectively. The sorption of vanadate anion is possible but the sorption capacity is very low (maximum is 0.30 mmol/L–pH of feed solution is 5.5). Sorption of Ge(IV) and Sb(III) oxoanion was not successful under the studied conditions.

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