

Sorptive Behavior of Silica and its Enhancement with Phosphate Treatment

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ABSTRACT

Silica with and without phosphate treatment was used as a model sorbent to develop a simple method to modify the sorbent surface for immobilization, reduction and/or attenuation of heavy metals in aquatic environments. Results showed that pH is an important factor influencing sorption of Pb and Zn on silica as illustrated in isotherm plots and adsorption edges. The sorption affinity as depicted by Freundlich constant, K_f increases not only with pH but also with the concentration of phosphate used during treatment. The values of Freundlich constant K_f for the sorption of Pb were 1.51, 2.40 and 3.10 at pH 6.0 for the control, and the silica treated with 0.1M and 0.3M phosphate respectively. The sorption enhancement is attributed to the formation of newly created chelating groups at the surface.

INTRODUCTION

Activities such as sewage sludge disposal, landfilling of solid wastes, or the application of pesticides and fertilizers can lead to increasing concentrations of heavy metals in soils. The transport of metals through the soil profile into ground water is a prime environmental concern. The remediation of contaminated soils and groundwater has proven to be extremely challenging. Proper management of these activities requires an understanding of heavy metal mobility. The mobility of heavy metals in aquatic environments is often characterized by sorption parameters such as affinity constant (Freundlich constant, K_f in this study). High values of K_f indicate that the metal is essentially retained by the solid through sorption reactions, while low values indicate that most of the metal remains in solution where it is available for transport and biological or geochemical reactions.

In the case of chemical behavior of heavy metals in aqueous system, the most important environmental parameters are: the type of heavy metal and its concentration, the types of the sorbents and the available surface area, pH, and the types and concentrations of organic and inorganic ligands present. In aquatic environments, solids (the sorbents) generally occur as complex mixtures of sand (which is an accumulation of mineral matter, largely silica), clays, organic matter, and metal oxides. The solution composition also affects metal distribution through complexation, cation competition, and ionic strength effects. Christensen (1985) found that Cd distribution coefficients determined in waste leachates were lower by almost two orders of magnitude than those determined in unpolluted soil solutions. Which of these components influence metal distribution determines the sorptive behavior and the choice of remediation methods for the system.

The purpose of the present study was (1) to examine the distribution of heavy metals such as Pb and Zn in aqueous system in terms of K_f at various pH conditions using silica as a model sorbent, and (2) to develop a method which would modify and thus enhance the sorptive behavior of the solid surface for heavy metals. Numerous field

studies have demonstrated that sorption processes recognized as an effective retardation for the migration of pollutants are important in natural environments. Silica was chosen as a model sorbent solid in this study, because it is the most abundant oxide in nature, and the most important interface in natural water systems. In addition, its surface properties are reasonably well understood and adsorption energies are available for many metals.

MATERIALS AND METHODS

Silica (Oklahoma 5 micro) was obtained from Pennsylvania Glass Sand Corporation and was used without further purification. Phosphate solutions were prepared from reagent grade KH_2PO_4 obtained from Fisher Scientific. The metal standards used in this study were prepared from dilution of appropriate volumes taken from 1000 mg/L stock solutions which were purchased from Fisher Scientific. All other chemicals used were reagent grade.

A. Solution of Lead and Zinc on Silica at Various pH

(1) Sorption Isotherm

Batch equilibrium sorption were conducted in 250 mL polycarbonate Erlenmeyer flasks. A known mass of silica (0.1 g) was added to each Erlenmeyer flask that contained 100 mL of the sorbate lead or zinc, the concentration of which ranged from 1.0 to 8.0 mg/L for lead and 0.1 to 1.6 mg/L for zinc. pH of the suspension was adjusted to the value required. Samples were sealed under nitrogen and shaken overnight in a shaker at 150 revolutions per minute and 25°C . After this period samples were removed from the shaker, pH readjusted and the aqueous phase was then filtered through a polycarbonate filter. The filtrate was retained for metal analysis using SpectrAA-20 - a Varian atomic absorption spectrophotometer (AAS). The difference between the initial concentration and the equilibrium concentration was used to compute the amount of metal removed from the solution as a result of sorption. Preliminary studies indicated no sorption of the test metal to the filter assembly. The effect of pH on sorption of lead and zinc on silica was studied at the range of pH 5 - 8.

(2) Adsorption Edge

To further study the effect of pH on the sorption of metal ions on silica, adsorption edges for the sorption of lead and zinc on silica were determined. To the suspension of silica, the appropriate sorbate (lead or zinc) was introduced. The initial concentration of lead or zinc used was 5 mg/L in a 0.5 g/L suspension of silica. The suspension of silica at pH 2 where no sorption was anticipated was equilibrated under nitrogen for 1 hour. After this time a 50 mL aliquot was drawn and retained. The pH of the suspension was now adjusted upward in step to pH 10, and 50 mL aliquots were drawn at each pH. Samples were sealed under nitrogen and then shaken overnight in a shaker at 150 revolutions per minute and 25°C . After this period pH of the samples were readjusted, equilibrated and then filtered. The concentration of lead and zinc in the filtrate was analyzed by AAS. The difference between the initial and final concentration was taken as the amount sorbed.

B. Effect of Sorbed Phosphate on Sorption of Lead

Silica that had been treated with 0.1 M and 0.3 M phosphate solution for 48 hours, filtered, washed, dried and then sieved using a 125 μm sieve was used. 0.1 g of this silica was weighed into 250 mL polycarbonate Erlenmeyer flasks containing 1.0 - 8.0

TABLE 1. Freundlich Isotherm Constants for the Sorption of Pb and Zn on silica at pH 5-8 and 25°C

Adsorbate	Constant	pH			
		5.0	6.0	7.0	8.0
Lead	K_f	0.46	1.47	5.49	8.32
	$1/n$	0.35	0.61	0.67	0.61
Zinc	K_f	0.23	0.44	0.88	4.34
	$1/n$	0.90	0.83	0.90	0.90

mg/L of lead. pH was adjusted to 6.0 and samples shaken overnight in a shaker at 150 revolutions per minute and 25°C. After this period the pH was readjusted and samples filtered using a polycarbonate filter. The filtrate was analyzed for lead. The difference between the initial and final concentration was taken as the amount sorbed.

C. Calculation

The sorption isotherms for the heavy metals in our studies were best described by the Freundlich equation:

$$\Gamma = K_f C^{1/n} \quad (1)$$

where Γ is equal to the equilibrium concentration of the test metal in the solid phase (milligrams per gram dry weight), C is equal to the equilibrium concentration of the test metal in solution (milligram per liter). $1/n$ is an empirical constant, and K_f is the Freundlich constant, a measure of the strength of sorption. These sorption partition constants, K_f at various pH were obtained by fitting the mean of the duplicate values measured for each set of eight concentrations of Pb or Zn to the linear form of Equation 1:

$$\log \Gamma = \log K_f + 1/n \log C \quad (2)$$

Values for K_f and $1/n$ were obtained by linear regression analysis. The K_f values provide a quantitative estimate of the relative affinity of silica for the heavy metals, while $1/n$ is used as an indication of whether sorption remains constant ($1/n = 1$) or decreases with increasing sorbate concentrations ($1/n < 1$).

RESULTS

Sorption Isotherms and pH Effect

The equilibrium solid- vs. liquid-phase concentrations of the metals were plotted at various pH from 5 to 8, and the results are shown in Figures 1 and 2 for Pb and Zn respectively. Results from the sorption isotherms indicated that both Pb and Zn were readily sorbed to silica and the amount sorbed increased with the pH increased.

From the linear form of Freundlich equation (Equation 2), plots of $\log \Gamma$ versus $\log C$ were plotted and are shown in Figures 3 and 4 for lead and zinc respectively. Values of Freundlich isotherm constants, K_f and $1/n$ for the sorption of lead and zinc on silica were evaluated from the plots and are summarized in Table 1.

Note that K_f increases with pH, and $1/n$ less than unity remains nearly the same for each metal.

Adsorption Edge

The pH effect on the sorption of Pb and Zn on silica is further illustrated by the adsorption edges shown in Figures 5, where the percentage of lead or zinc sorbed is plotted against the pH. From Figure 5, sorption of lead increased from about zero at pH 3.0 to nearly 100% at pH 9.0. A major change in sorption occurred between pH 6 and 8, the pH of maximum sorption being pH 9.0. At approximately pH 7.1 the sorption of lead on silica was 50%. Sorption of zinc increased from nearly zero at pH 4.0 to nearly 100% at pH 10.0. A major change in sorption also occurred between pH 6 and 8. At approximately pH 7.3 the sorption of zinc on silica was 50%. Both results show the bulk of the sorption occurring over a pH range of 2 units in good agreement with literature (Lion et al., 1982).

Sorption of Lead on Silica treated with Phosphate

The effect of sorbed phosphate on the sorption of lead on silica was investigated using silica treated with deionized water (the control), 0.1M and 0.3M phosphate solution. Sorption experiments were carried out at pH 6.0 and 25°C. The results are presented in Figure 6 and indicate that the sorption of silica for Pb was enhanced with phosphate treatment.

The Freundlich constant, K_f values obtained by linear regression analysis (Equation 2) for the sorption of Pb, were 1.51, 2.40, and 3.10 at pH 6.0 for the control and the silica treated with 0.1M and 0.3M phosphate respectively. It can be seen that sorption of lead as illustrated in Figure 6 and the values of K_f , increased further as concentration of phosphate used in silica treatment increased from 0.1M to 0.3M. The results are similar to the recent findings in this laboratory in the study of the effect of phosphate in solution on the sorption of lead and zinc on aluminum oxide (Kimaro, 1997). Lead and zinc sorptions on oxides were found to increase with the increase of the concentration of phosphate in aqueous phase. Since it has been known that phosphate is readily sorbed by oxide (Kimaro, 1997; Samba, 1989; Eshete, 1995; Stumm et al., 1980), the similarity between these two studies can be attributed to the common effect of sorbed phosphate as discussed below.

DISCUSSION

The isotherm plots can be analyzed to determine the performance of silica at various pH and to compare the sorptive behavior of the treated and untreated silica.

Effect of pH

The sorptions of Pb and Zn on silica as illustrated in Figure 1 and 2 respectively were both increased with pH from 5 to 8. Our data were found to fit to the linear form of Freundlich equation (Equation 2) as shown in Figure 3 and 4 for lead and zinc respectively. The sorption parameters given in Table 1 show that the sorption affinity (given by Freundlich constant, K_f) of silica for Pb and Zn were increased with pH, while the values of $1/n$ remain essentially the same within a narrow range except somewhat lower value of $1/n$ for Pb at pH 5, which could be caused by the frustration of the very low end concentration data. Obviously pH is one of the most important factors influencing sorption, resulting in higher sorptions of Pb and Zn on silica at higher pH values. This could be accounted for the nature of the surface charge coupled with surface complexation. The surface chemistry of silica consists of a network of oxygen bridge between the silicon atoms. The oxygen atoms at the surface are free to react with water forming Si-OH groups. The majority of these active sites become more

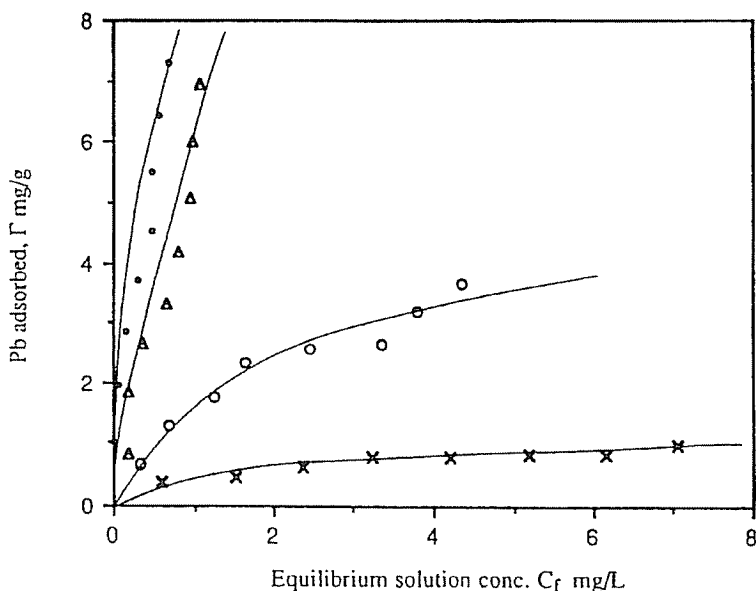
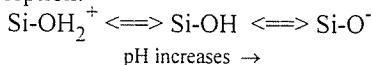
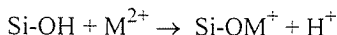


FIGURE 1. Plot of Γ versus C_f for the adsorption of Pb on silica at pH 5 (x), pH 6 (o), pH 7 (Δ), and pH 8 (\bullet) at 25°C.

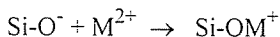
negatively charged at the higher pH values. This situation creates a more favorable condition for metal ion sorption.



In addition to electrostatic effect, the metal sorption on oxides can be explained in terms of surface complexation, a coordination reaction between the metal ion in solution and the hydroxyl functional groups of the oxide particle (Niven et al., 1993)



or



where M^{2+} is either Pb^{2+} or Zn^{2+} .

As also illustrated in the adsorption edge (Figure 5), sorptions of Pb and Zn increase from nearly zero to near 100% as pH increases through a critical range of 2 units wide which are in good agreement with literature (Lion et al., 1982). This means that a small shift in pH in the system, as may occurs in waters, causes a sharp increase or decrease in dissolved metal levels.

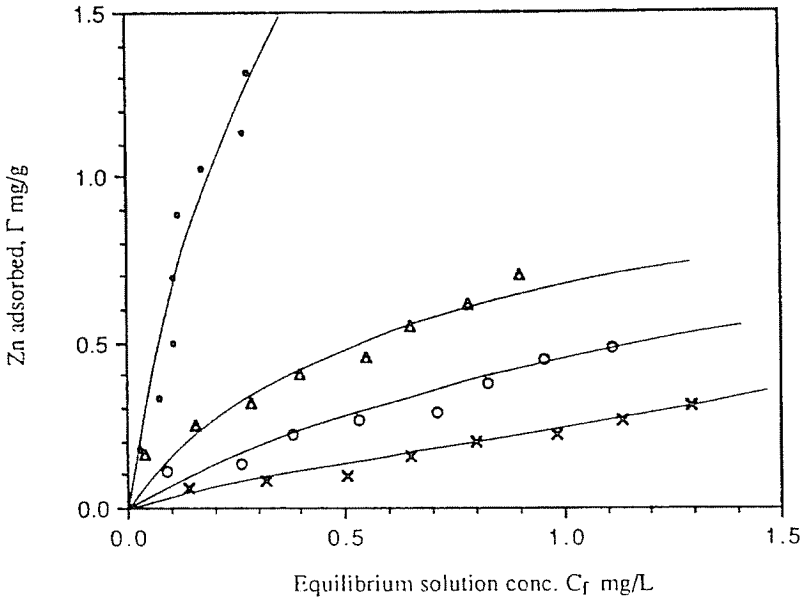


FIGURE 2. Plot of Γ versus C_f for the adsorption of Zn on silica at pH 5 (x), pH 6 (o), pH 7 (Δ) and pH 8 (\bullet) at 25°C.

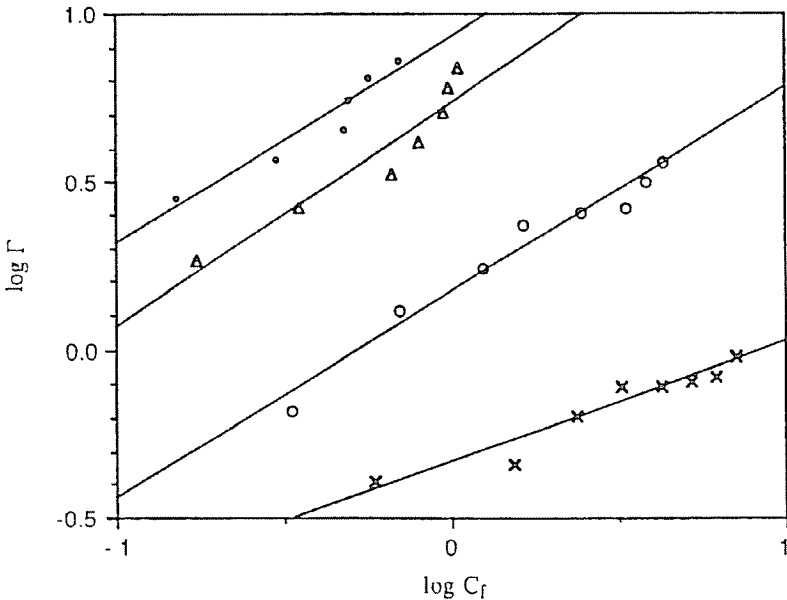


FIGURE 3. Plot of $\log \Gamma$ versus $\log C_f$ for the adsorption of Pb on silica at pH 5 (x), pH 6(o), pH 7 (Δ) and pH 8 (\bullet) at 25°C.

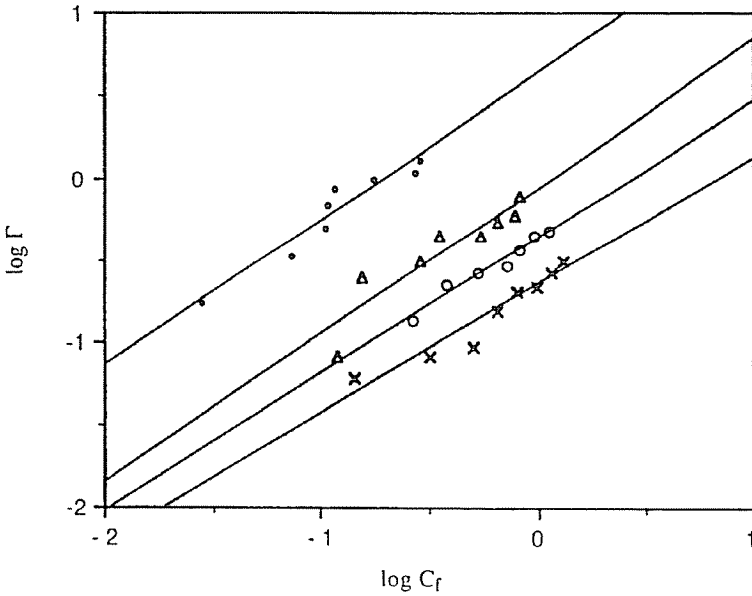


FIGURE 4. Plot of $\log \Gamma$ versus $\log C_f$ for the adsorption of Zn on silica at pH 5 (x), pH 6 (o), pH 7 (Δ), and pH 8 (\bullet) at 25°C.

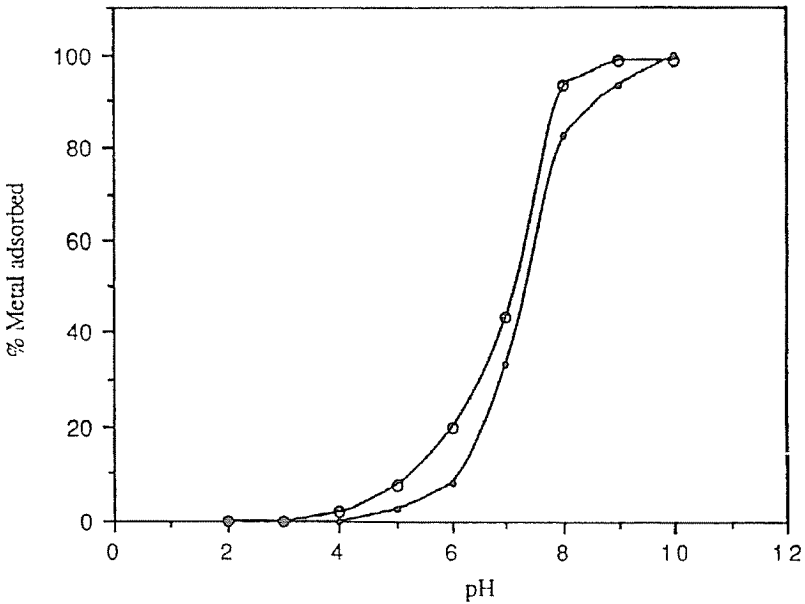


FIGURE 5. Plot of % metal adsorbed versus pH for the adsorption of Pb (o) and Zn (\bullet) on silica at 25°C. The initial concentration of Pb or Zn was 5 mg/L.

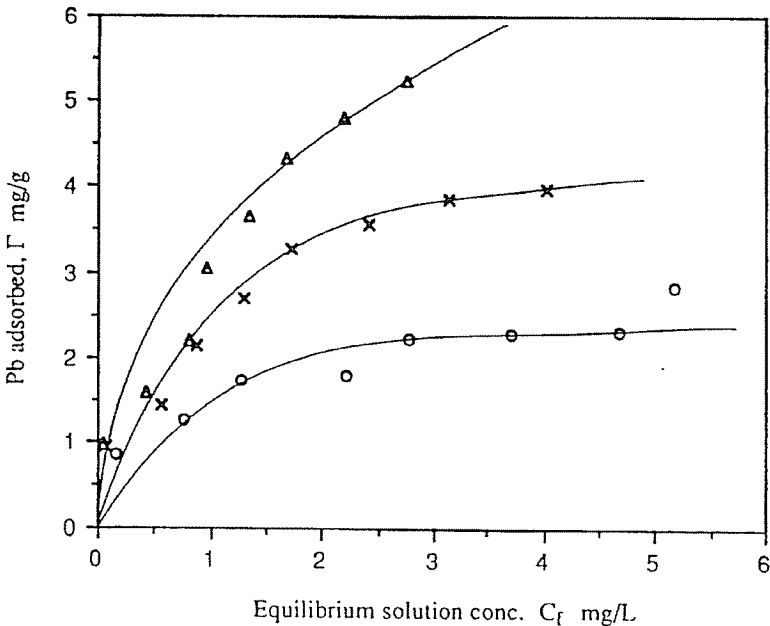
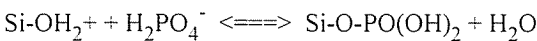
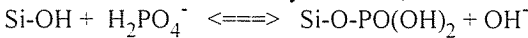


FIGURE 6. Plot of Γ versus C_f for the adsorption of Pb on silica untreated (o) and treated with 0.1 (x) and 0.3 (Δ) M phosphate at pH 6 and 25°C.

Effect of Sorbed Phosphate

The comparison of the sorption of Pb in Figure 6 shows higher sorption on the silica treated with phosphate. With this simple modification, the sorptive capability of silica for Pb was greatly enhanced. It has been known that phosphate is readily sorbed by oxides (Kimaro, 1997; Samba, 1989; Eshete, 1995; Stumm et al., 1980; Hawke et al., 1989) and soil (Barrow, 1983). The sorption of phosphate on oxides may be interpreted as complex formation of inorganic base with surface metal or silicon atoms. This is consistent with a mechanism (Huang, 1975) involving ligand exchange of anionic group with OH and H₂O of surface Si-OH and Si-OH₂⁺ groups, respectively. On the assumption that complex formations between phosphate ion and surface hydroxyls of oxides in aqueous environment are essentially the same, thus in this study



where H₂PO₄⁻ and HPO₄²⁻ are the predominant dissolved species of orthophosphate over the pH range 5 to 9.

In this way, the association with phosphate is expected to have a great influence on subsequent sorption of heavy metals. The primary mechanism postulated here is that sorbed phosphate covers mineral surfaces through the ligand exchange with hydroxyls,

and this in turns provides newly created functional groups for further complexation reactions with metal ions from solution. Since only one or two phosphate chelating groups involved in the ligand exchange interactions on sorption, the excess phosphate chelating groups are still available for further complexation, thus new functional groups being provided for subsequent complexation reactions with metal ions, and so affecting the fate of metal ions in solution. Binding of phosphate to the surface also change the effective surface charge on the solid (Stumm et al., 1981), further increasing metal ion sorption. The enhancement of sorption capability for Pb can be attributed to the presence of newly created chelating groups at the surface. Complexation of Pb with the newly created groups of sorbed phosphate is stronger than complexation with uncovered surface hydroxyls. This investigation provides useful information on how the surface can be modified to possibly immobilize heavy metals, and this information would be used to meet the need in waste remediation by the retention and/or attenuation of heavy metals in waste sites. However, further studies are needed to extend this investigation on other heavy metals and also to test this postulate for the immobilization of other contaminants.

Our results of the sorptive behavior of silica treated with phosphate (retained in the solid phase) agree with the findings presented by Ma et al. (1995) who found that phosphate rocks were very effective in immobilizing lead from aqueous solutions with a lead removal of 39.9 - 100%. In their study, the effectiveness of phosphate rocks in removing lead was increased significantly by increasing the amount of phosphate rocks added at the same initial lead concentration.

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