Thermodynamic parameters of zinc sorption in some calcareous soils

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Abstract: Sorption is one of the most chemical important process, in which determine micronutrients availability in soil. Sorption isotherms provide useful information about sorption capacity of soils. Sorption data can be used to determined sorption thermodynamic parameters. To evaluate the sorption of zinc (Zn) onto some soils, an experiment was conducted with ten calcareous soils of Hamadan province in the west of Iran. Half g soil samples were equilibrated at 25 ± 1 and $45\pm1°C$ with 25 ml of 0.01M $CaCl_2$ containing 0 to 30 mg L^{-1} Zn as $ZnSO_4$. Suspensions were centrifuged, filtered and concentration of Zn in the clear extract solution was determined using atomic absorption spectrophotometer. Amount of Zn sorbed by the soil was calculated from difference between initial and final concentration of Zn in the equilibrium solution. Sorption of Zn was evaluated using adsorption isotherms. The thermodynamic parameters viz. K , G , H and S were determined using sorption data and concentration of Zn in equilibrium solution at two different temperatures.The results showed that Zn Sorption was described by linear, Feeundlich, Temkin and D-R models. The values of K^o increased with rise in temperature from 25 to 45 °C in all the soils. The G^o values at 25 °C and 45 °C were negative and ranged from -7.00 to -16.64 and -13.24 to -41.93 kJ mol^{-1}, respectively. The values of H^o and S^o were positive and ranged from 357.47 to 74.02 kJ mol^{-1} and 1255.97 to 281.79 J mol^{-1} K^{-1}**,** respectively. Evaluation of thermodynamic parameters provide an insight into mechanism of Zn sorption in the soils. The values of G^o were found negative indicating Zn sorption was spontaneous and the values of H^o were positive indicating Zn sorption was endothermic. Thermodynamic parameters revealed Zn sorption increased as the value of K^o, G^o, H^o and S^o increased with temperature. Also the results showed that calcareous soils can sorb high amounts of Zn and that thermodynamic parameters are useful in describing Zn sorption. we suggest that such research be done in contaminated soils. Also we suggest that effect of thermodynamic sorption parameters on Zn uptake by plant be done using the pot experiment. [Journal of American Science 2010;6(7):298-304]. (ISSN: 1545-1003).

1.Introduction

Adsorption is one of the most important chemical processes in soils. It determines the quantity of plant nutrients, metals, radionuclides, pesticides and other organic chemicals that are retained on soil surfaces and, therefore, it is one of the primary processes that affect transport of nutrients and contaminants in soils. Sorption also affects the electrostatic properties of suspended particles and colloids. The electrostatic properties affect coagulation and settling (Sparks 1995). Sorption reactions on soil mineral surfaces potentially attenuate toxic soil solution . Sorption isotherm analysis is a useful technique to study the retention of metals in soils. Sorption isotherms provide useful information about the soil retention capacity and the strength by which the sorbate is held onto the soil. Zinc sorption capacity correlates with soil contents of aluminosilicate clays, metal oxides, and carbonates (Kalbasi et al. 1978). Aluminosilicate clays affect Zn sorption mainly through their effects on soil cation exchange capacity (CEC) (McBride 1989). Soil pH, solution ionic strength, and solution ionic composition also affect Zn sorption. Increasing soil pH increases the total number of negative sites of clay minerals and organic matter (OM), and therefore increases the capacity for Zn sorption (Harter 1983; McBride 1989). For proper evaluation of the environmental threat posed by Zn, or its availability, it is necessary to supplement the individual sorption characteristics (Arias et al. 2006).

Zinc deficiency is common in calcareous soils. It is believed that this is a consequence reaction taking place between soluble Zn and soil solid phase leading to Zn reduced plant availability. Adsorption and or precipitation on surfaces of soil solids decrease the concentration of Zn in solution phase (Lindsay 1972).

Isothermal sorption batch experiments are very important in soil science research. Theoretically, maximum monolayer sorption, empirical adsorption constants, and other important adsorption parameters can be determined by this method. Cation exchange capacity of soils and soil components can also be quantified. Copper and Zinc are individually more soluble in acid soils than in calcareous soils, and their marked sorption hysteresis is most marked in the case of sorption by organic soil components (Wu et al. 1999).

Adsorption increase with increasing temperature due to the increase in number of active sites (Yavuz et al. 2003; Bouberka et al. 2005). To gain further insight into sorption process and

mechanisms, thermodynamic approach may be used to predict the final state of metal in the soil system from an initial non-equilibrium state (Jurinak and Bauer 1956; Sposito 1984). Evaluation of the free energy change corresponding to the transfer of element from bulk solution into the appropriate site of the double layer or clay mineral lattice are helpful to express the sorption process. Similarly, an understanding of change in enthalpy and entropy helps in determining the free energy change and disorders occurring during sorption process (Adhikari and Singh 2003). Adhikari and Singh (2003) showed that the high values of G° both for Pb and Cd indicated that both reactions are spontaneous. The values of H° were found to be negative for Cd and positive for Pb, indicating that Cd sorption reaction was exothermic while Pb sorption was endothermic reaction in all the soils. (Adhikari and Singh 2003). The values of S were found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process (Unlu and Ersoz 2006). Information about Zn sorption characteristics and sorption thermodynamic parameters (STP) are limited for the soils of Iran. The objectives of this research were to study the Zn sorption characteristics and determination of STP in ten surface soils of Hamadan province in the west of Iran.

2.Materials and Methods

We collected bulk samples of topsoils (0-30cm depth) from ten calcareous soils from Hamadan province in the west of Iran. All samples were air dried, crushed and sieved through a 2-mm sieve prior to soil analysis and sorption studies. Characteristics of the soils such as particle size distribution, pH, EC, CEC, organic C, and calcium carbonate equivalent were determined using standard analytical methods (Gee and Bauder 1986; Rhodes 1996; Summer and miller 1996; Nelson and Sommers 1996; Nelson, 1982). Concentration of available Zn in the soil samples was determined using DTPA method (Lindsay and Norvell 1978).

To study the sorption of Zn by soils, 0.5 g soil subsample from each soil was placed in a 100 ml plastic bottle and equilibrated with 25 ml of 0.01 M $CaCl_2$ solution containing levels of Zn, i.e. 0, 2, 5, 10, 15, 30 mg l^{-1} Zn as $ZnSO_4$ solution. Solutions were prepared in 0.01 M $CaCl_2$ to keep the ionic strength constant. Each sorption set, for Zn, was replicated three times. The soil suspensions were shaken for 30 min and equilibrated for 24 h at 25 ± 1 and 45 ± 1°C in an incubator. Based on preliminary studies, an equilibrium period of 24 h and soil/solution ratio of 1:50 were found optimum beyond which no significant change in metal content of equilibrium solution was recorded. After equilibration time, the suspension was filtered, and concentration of Zn in the clear extract solution was determined using Varian Atomic Absorption Spectrophotometry. Amount of Zn sorbed by soils was calculated from the difference between the initial and final concentration of Zn in the equilibrium solution.

For studying the sorption relationship, the data were fitted to the following equations:

$C_e/q = 1/Kb + C_e/b$ Conventional Langmuir

$\log q = \log K_f + n \log C_e$ Freundlich equation

Where C_e is the Zn concentration in the equilibrium solution (mg/l), q is the amount of Zn sorbed by the soil (mg kg^{-1}), b is the sorption maxima (mg kg^{-1}), and K is the bonding energy coefficient (L mg^{-1}), K_f is the Freundlich distribution coefficient, and n is an empirical constant.

Langmuir and Freundlich isotherms don't give any idea about sorption mechanism but Dubinin-Radushkevich (D-R) isotherm describes sorption on a single type of uniform pores. In this respect, the D-R isotherm is analogus of Langmuir type but it is more general, because it does not assume a homogeneous surface or constant sorption potential (Unlu and Ersoz, 2006). In order to understand the adsorption type, D-R isotherms were determined. The D-R isotherm has the form:

$\ln q = \ln q_m - k \varepsilon^2$

and

$\varepsilon = [RT \ln (1 + (1/C_e))]$

where ε is Polanyi potential, q is the amount of Zn sorbed by the soil (mol g^{-1}), k is a constant related to the adsorption energy (mol² kJ^{-2}) and q_m is the adsorption capacity (mol g^{-1}). The mean free energy of adsorption (E) was calculated from the k values using the equation:

$E = (-2k)^{-0.5}$

The magnitude of E is useful for estimating the type of adsorption process. If this value is between 8 and 16 kJ mol^{-1}, adsorption process can be explained by ion exchange (Unlu and Ersoz 2006).

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant, K°, computed by following the procedure outlined by Biggar and Cheung (1973). The value of K° for adsorption reaction can be defined as:

$K° = a_s/a_e = \gamma_s C_s / \gamma_e C_e$

where a_s denotes activity of adsorbed metals, a_e is activity of metals in equilibrium solution, C_s is milligrams of metals adsorbed per litre of solution in contact with the adsorbent surface, C_e is milligrams of solute per litre of solution in equilibrium solution, γ_s is the activity coefficient of the sorbed metals and γ_e represents the activity coefficient of metals in equilibrium solution. Since at lower concentration activity coefficient approaches unity, Eq. 6 was reduced to:

$K° = C_s/C_e$

The values of K° were obtained by plotting ln (C_s/C_e) vs. C_s and extrapolating to zero C_s. The

standard free energy (G°) was calculated as follows:

G° = -RT ln K°

The standard enthalpy (H°) was obtained from integrated form of the Vant Hoff equation:

$\ln K°_2/K°_1 = - H°/R[1/T_2 - 1/T_1]$

The standard entropy (S°) was calculated as

S° = (H° - G°) /T

3.Results and Discussion

Selected chemical and physical characteristics of the soils are presented in Table 1. The texture of the soil samples are clay loam to sandy clay loam. The calcium carbonate equivalent ranged from 5 to 53.8%. Organic matter content ranged from 0.68% to 2.40%. The pH of the soils varied from 7.44 to 8.20 which indicated that all of the soils were alkaline. The CEC ranged from 10 to 25.1 $cmol_c$ kg^{-1}. The DTPA extractable Zn ranged from 0.49 to 4.15 mg kg^{-1}.

Table 1. Physicochemical properties of the experimental soils

Soil. No.	pH (1:2.5)	CEC cmol(+)kg^{-1}	EC ds.m^{-1}	O.M	Clay	Silt	CaCO3	Zn- DTPA (mg kg^{-1})
					%			
1	7.80	10.9	0.23	0.90	27.0	7.5	11.0	1.09
2	8.10	11.5	0.30	1.03	33.2	15.0	14.1	4.15
3	7.96	14.2	0.19	0.83	34.2	19.1	33.5	1.49
4	7.45	23.5	0.13	0.68	38.3	10.3	5.0	0.66
5	8.20	16.0	0.34	2.40	22.0	15.0	53.8	0.49
6	8.00	15.5	0.20	0.80	20.8	25.3	17.1	0.56
7	7.44	20.9	0.19	1.06	27.0	27.8	22.1	0.63
8	7.90	25.1	0.20	1.10	36.4	25.9	27.4	0.65
9	7.90	14.5	0.26	0.80	38.1	17.6	39.4	1.15
10	7.85	10.0	0.30	1.40	27.6	9.5	6.1	2.56

For proper evaluation of the environmental threat posed by Zn or its availability, it is necessary evaluate the Zn individual sorption characteristics. Langmuir, Freundlich and D-R equations were fitted to sorption data to predict the behaviour of Zn sorption by the soils (Tables 2). The Freundlich and D-R equations irrespective of the level of Zn added, gave better fit (R^2 = 0.92–0.99** and 0.88*- 0.99** respectively) than Langmuir equation (R^2 = 0.81*– 0.99**). Elzinga et al. (1999) also evaluated batch sorption data and established general purpose Freundlich isotherms for various heavy metals in soils.

The values of the Langmuir constants b and k are presented in Table 2. The values of sorption maxima (b) ranged from 625 to 1250 mg kg^{-1} soil (Table 2). The sorption maxima were related to the calcium carbonate equivalent (CCE) (r=0.927**), and other physicochemical properties such as OM, CEC and clay content did not significantly improve the relationship (Table 3). Reyhanitabar et al. (2007) studying Zn retention of 20 calcareous soils of central Iran, reported a significant relationship between Langmuir b with percentage of clay and CEC, but not CCE.

Trehan and Sekhon (1977) reported correlation between CCE and adsorption maxima, which is similar to our findings. Udo et al. (1970) reported the effect of soil clay on adsorption maxima (b). The effect of pH on b has also shown by other researchers (Karimian and Moafpourian 1999) but in our study this was not seen, perhaps due to the narrow range of pH of the studied soils (Table 1). Therefore CCE was the principle factor contributing to correlation with the Zn sorption

maxima. The correlation of the sorption maxima with the CCE suggest that the soil carbonates sorbed the added Zn. The lack of relation between the zinc sorption maxima and CEC indicates that Zn^{2+} was sorbed through electrostatic as well as non-electrostatic processes. The cations competing with Zn^{2+} for adsorption were primarily calcium from the cation exchange complex and the dissolution of soil carbonates. The lack of correlation between the zinc sorption maxima with organic matter and clay content suggest that these two soil components were not responsible for the retention of native zinc in these calcareous soils. The affinity of metal bonding varied with soil types and metal concentration. All soils showed high affinity for Zn sorption. The bonding energy (k) ranged from 11.432 to 0.941 L mg^{-1} (Table 2). Bonding energy showed a highly significant (p<0.01) relationship with percentage of O.M and significant (p<0.05) relationship with CCE. Reyhanitabar et. al. (2007) studying Zn retention of 20 calcareous soils of central Iran, reported a significant relationship between Langmuir k, percentage of clay and CCE which is in agreement with others reports (Karimian and Moafpourian 1999) and in case of CCE is similar to our findings. This could be used to partially explain the widespread Zn deficiency in plants grown on calcareous soils.

The applicability of the Freundlich sorption isotherm was also analyzed by plotting log q versus log C. Table 3 shows the Freundlich sorption isotherm constants and the correlation coefficients. Freundlich distribution coefficient (K_f) ranged from 225.5 to 1121.5 l kg^{-1}. Distribution coefficient

represents the sorption affinity of the metal cations in solution for the soil solid phase and can be used

to characterize the mobility and retention of Zn in a soil system.

Table 2.   Langmiur, Freundlich and D-R[a] constants of Zn sorption in experimental soils

Soil No.	Langmiur costants				Freundlich constants		
	b (mg kg^{-1})	k_L (l mg^{-1})	$K_d = M$	R^2	k_f (l kg^{-1})	n	R^2
1	769.23	1.30	1000.0	0.99**	292.89	2.23	0.97**
2	833.33	1.71	1428.6	0.99**	372.82	2.63	0.99**
3	1000.00	1.67	1666.7	0.98**	436.51	2.17	0.98**
4	769.23	1.86	1428.6	0.99**	357.03	2.49	0.97**
5	1250.00	11.43	14285.7	0.94**	1121.5	2.74	0.98**
6	769.23	1.08	833.3	0.98**	285.10	2.02	0.95**
7	1000.00	1.11	1111.1	0.81*	382.38	2.65	0.97**
8	1111.11	4.50	5000.0	0.85**	632.85	3.98	0.92**
9	1111.11	1.29	1428.6	0.95**	461.42	1.96	0.99**
10	625.00	0.94	588.2	0.98**	225.53	2.30	0.97**

Table 2.Continued

Soil No.	D-R constants			
	k (mol^{2}kJ^{-2})	q_m (mmolg^{-1})	E (kJmol^{-1})	R^2
1	-0.0033	-2.8824	12.3091	0.98**
2	-0.0026	-3.1530	13.867	0.99**
3	-0.0032	-2.5503	12.5000	0.99**
4	-0.0028	-3.0325	13.3631	0.98**
5	-0.0019	-2.7855	16.2221	0.95**
6	-0.0037	-2.5965	11.6248	0.97**
7	-0.0025	-3.1936	14.1421	0.95**
8	-0.0013	-3.6758	19.6116	0.88*
9	-0.0035	-2.3007	11.9523	0.98**
10	-0.0032	-3.1785	12.5000	0.98**

Table 3.Correlation coefficients between soil characteristics and D-R, Langmuir and Freundlich parameters of sorption for Zn

soil characteristics	Freundlich		Langmuir				D-R			
	n	K_f	q_m	K_a	$K_d = M$	S	K	q_m	E	
CCE	0.12	0.84**	0.93**	0.71*	0.74*	0.93**	0.33	0.38	0.34	
Clay	0.22	0.12	0.11	-0.30	-0.31	0.44	0.27	-0.13	0.35	
Silt	0.35	-0.16	0.44	-0.004	0.02	0.11	0.13	-0.11	0.14	
O.M	0.27	0.80**	0.45	0.88**	0.88**	0.45	0.50	-0.12	0.43	
EC	-0.05	0.43	0.19	0.48	0.50	0.20	0.11	0.09	0.07	
CEC	0.64*	0.26	0.38	0.19	0.18	0.38	0.60	-0.44	0.63	

 * Significant at the 0.05 probability level
** Significant at the 0.01 probability level

A distribution coefficient can be related to both plant uptake and environmental pollution. Low distribution coefficients indicate that most of the metals present in the system remain in the solution and are available for transport, chemical processes and plant uptake (Jalali and Moharami 2007).Whereas high values indicate lower mobility and higher retention of metal in the soil. So that Zn in soil no 5 had the lowest mobility and in soil no 10 had the highest mobility.

The order of sorption for Zn is similar to those found in case of Langmuir sorption equation. Freundlich K_f for Zn showed a highly significant (p<0.01) relationship with percentage of O.M and CCE. Reyhanitabar et. al. (2007) studying Zn retention of 20 calcareous soils of central Iran, reported a significant relationship between Freundlich K_f with percentage of clay, CEC and CCE but not with OM. Karimian and Moafpourian (1999) reported that in calcareous soils of the southern part of Iran Freundlich K_f showed a highly

significant relationship with soil pH and Clay but not with CEC, CCE and OM. Freundlich constant n which indicates adsorption intensity varied from 1.96 to 3.98. Freundlich n showed a significant (p<0.05) relationship with CEC. Reyhanitabar et al. (2007) reported a significant relationship between Freundlich n with percentage of clay. Elrashidi and O Connor (1982) reported a significant relationship between Freundlich coefficients and percentage of clay, CEC and pH, but not with OM.

The values of q_m constant (D-R isotherm) which is the adsorption capacity (mol g^{-1}) ranged from -2.3007 to -3.6758 (Table 2). The values of k (D-R isotherm) which is a constant related to the adsorption energy (mol^2 kJ^{-2}) ranged from -0.0013 to -0.0037. This finding is similar to the results obtained from 1/n freundlich parameter. The magnitude of E which is calculated from D-R isotherm is useful for estimating the type of adsorption process. In this study, E values ranged from 11.62 to 19.61 kJ mol^{-1} (Table 2). Therefore it is possible to say that adsorption mechanism of Zn ions onto soils can be explained with an ion-exchange process.

Because the Langmuir adsorption isotherm was found to fit the Zn adsorption data of our soils (Table 2), its k and b values were used to calculate the distribution coefficient K_d as used by Bolt and Bruggenwert (1976), or to calculate maximum buffering capacity MBC, as used by Iengar and Raja (1983), Karimian and Moafpourian (1999) and Reyhanitabar et al. (2007):

$K_d = MBC = Kb$

The calculated K_d of soils (Table 2) ranged from 588.2 to 14258.7 L kg^{-1}. Karimian and Moafpourian (1999) and Reyhanitabar et al. (2007) reported a range of maximum buffering capacity,

309 to 3509 for the calcareous soils of southern Iran and 212.7 to 625.0 for the calcareous soils of central Iran. K_f were significantly correlated with OM and CCE. Reyhanitabar et al. (2007) studying Zn retention of 20 calcareous soils of central Iran, reported a significant relationship between K_f with percentage of clay, CEC and CCE.

Evaluation of thermodynamic parameters viz. K°, G°, H°, S° provide an insight into mechanism of Zn sorption in the soils. The data in Table 4 indicate that value of K° increased with the rise in temperature from 25 to 45 ºC in all the soils. The G° values for Zn were negative in all the soils (Tables 4). These negative values indicate that the sorption process is spontaneous. The G° at 25 ºC and 45 ºC ranged from -7.00 to -16.64 and -13.24 to -41.93 kJ mol^{-1}, respectively. In all the soils, the free energy (G°) of the Zn sorption was more negative at higher temperature which suggested that the spontaneity of the process increased with rise in temperature (Jurinak and Bauer 1956).

The values of isoteric heat (enthalpy) of Zn sorption (H°) were positive and ranged from 74.02 to 357.47 kJmol^{-1} (Table 4). This indicates that sorption reaction was endothermic. Similar findings were also reported by Biggar and Chung (1973), Adhikari and Singh (2003), Dali-youcef et al. (2006) and Unlu and Ersoz (2006).

Values of H° for heavy metals within the range of the enthalpy change of adsorption for ion exchange (i.e. 8.4 to12.6 kJ mol^{-1}) suggest that adsorption process is an ion exchange in nature (Helfferich 1962). The values of H° in this study were greater than 12.6 kJ mol^{-1} suggesting the presence of other mechanism for the sorption of Zn in addition to ion exchange mechanism.

Table 4.Sorption thermodynamic parameters of Zn in soil studied

soil No.	K°		G° (KJ mol^{-1})		H° (KJ mol^{-1})	S° (J mol^{-1})	
	25ºC	45ºC	25ºC	45ºC		25ºC	45ºC
1	26.80	1199.42	-8.06	-18.74	149.74	529.555	529.830
2	74.64	9542.58	-10.58	-24.22	191.09	676.737	677.098
3	50.58	2057.81	-9.62	-20.17	145.98	522.172	522.500
4	55.47	363.18	-9.85	-15.58	74.02	281.454	281.790
5	4384.80	3094076.39	-20.56	-39.51	258.38	936.083	936.785
6	48.05	149.83	-9.49	-13.24	44.79	182.187	182.511
7	47.98	19789.37	-9.49	-26.15	237.23	827.935	828.259
8	883.24	7709778.37	-16.64	-41.93	357.47	1255.400	1255.967
9	37.79	18508.771	-8.91	-25.97	244.00	848.693	848.997
10	17.38	249.56	-7.00	-14.59	104.96	357.714	375.953

The values of S° for Zn sorption were positive and ranged from 281.79 to 1255.97 J mol^{-1} K^{-1} (The values of S° at 25 and 45 ˚C were similar). The positive values of S° indicates an increased randomness at solid-solution interface during the adsorption of Zn. The decrease in the degree of randomness leads to an increase in the

adsorption capacity of the ion on the sorbent (Abou-Mesalam 2003).

The thermodynamic equilibrium constant (K°) at 25°C significantly correlated with CCE and OM (Table 5). While K° at 45°C did not correlate with soil physicochemical properties. Standard free energy (G°) at 25°C significantly (p<0.05)

correlated with CCE and OM, but ΔG^o at 45°C correlated (p<0.05) only with CCE. Standard entropy (ΔS^o) significantly correlated with CCE but

standard enthalpy (ΔH^o) did not significantly correlated with soil physicochemical properties (Table 5).

Table 5.Correlation coefficients between soil characteristics and thermodynamic parameter

soil characteristics	K^o (25)	K^o (45)	G^o (25)	G^o (25)	H^o (25)	S^o (25)	S^o (45)
CCE	0.71*	0.36	0.68*	0.70*	0.60	0.62*	0.62*
Clay	-0.37	0.13	-0.35	-0.09	0.25	0.24	0.24
Silt	-0.03	0.36	0.24	0.34	0.39	0.39	0.39
O.M	0.91**	0.35	0.73*	0.57	0.37	0.39	0.39
EC	0.54	0.04	0.32	0.31	0.25	0.27	0.27
CEC	0.10	0.57	0.41	0.43	0.37	0.38	0.38
pH	0.50	0.24	0.45	0.32	0.18	0.20	0.20

* Significant at the 0.05 probability level
** Significant at the 0.01 probability level

4. Conclusion

In this study the experimental data were better described by D-R and Freundlich isotherms than were by Langmuir isotherm. The most influential soil characteristics on Zn sorption in the studied soils are OM, CCE and CEC.

Thermodynamic studies revealed that Zn sorption reaction in all the soils were spontaneous and endothermic. This suggests that the sorption capacity of these soils enhanced with an increase in temperature. Therefore, in addition to soil properties and nature of pollutant, soil environment of factors particularly soil temperature needs to be considered when developing suitable strategies for proper management of heavy metal pollution.

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