



EFFECTS OF pH AND TEMPERATURE ON THE INTERACTION OF Pb(II) WITH AZRAQ HUMIC ACID STUDIED WITH SCHUBERT'S ION EXCHANGE METHOD

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ABSTRACT

The binding of Pb(II) to humic acid extracted from the Azraq Oasis was studied. The influence of temperature and pH was investigated at a constant ionic strength of 0.1. This analysis was done using Schubert's ion-exchange equilibrium method and its modified version. The data showed temperature and pH dependence. The derived conditional stability constants ($\log \beta_n$) for 1:1 and 1:2 lead-humate complexes were determined. It was noticed that the conditional stability constant ($\log \beta_1$) increased with increasing pH and temperature. The derived constants and their temperature dependences were used to calculate the corresponding thermodynamic parameters ΔG , ΔH and ΔS . The results indicate that the stability of these complexes derives from a very favorable entropy increase.

Keywords: Humic acid; Schubert's method; lead; stability constant; thermodynamic parameters

1. INTRODUCTION

Organic matter in soil, sediment and natural water can be divided into two classes of compounds: nonhumic material (e.g. proteins, polysaccharides, nucleic acids and small molecules such as sugars, and amino acids), and humic substances [1].

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Humic substances are heterogeneous colloidal macromolecules that are poorly understood. They are a major fraction (60-70%) of soil organic matter and 30-50% of surface organic matter, and possibly the most abundant naturally occurring macromolecules on the earth. They have a yellow to black appearance and are formed from plant and animal residues by microbial decay. The process of humification occurs in soils, sediments and natural waters and, according to the origin of humic substances, they can be classified as aquagenic material (aquatic source) or pedogenic humic material (terrestrial source) [2-8].

Humic acid is a typical humic substance with high molecular weight reported to range from several hundred to several hundred thousand Daltons. It is not possible to define a detailed molecular structure for humic acid as it consists of a non-uniform distribution of functional groups joined by a variety of aliphatic and aromatic units. It consists of 40-60% carbon, 30-50% oxygen, 1-3% nitrogen and 0.1-2% sulfur combined in aliphatic and aromatic ring structures associated with carbonyls, alcoholic and phenolic hydroxyl, carboxylates, amines, amides, and other functional groups. All of these features make humic acid hydrophilic and hydrophobic.

Fulvic and humic acids are recognized to play an important role in the aquatic environmental system [9-11]. The strongest acid group was classified as carboxylates ortho to a phenolic group. Clustering of these carboxyl groups results in strong acid characteristics by electrostatic field effects and also results in strong metal binding by polydentate mechanisms. All the other carboxylates fall in the second weaker group in addition to the hydroxyl-phenolic group. These carboxylic groups (strong and weak) and hydroxyl groups (aromatic and aliphatic) are capable of complexing metal ions [12-15].

Humic substances must be studied because they have acid-base properties with a wide range of pK_a values and are mixtures of cross-linked polymers of different molecular weight and charge densities. They have high affinities for surfaces, both organic and inorganic. In addition, they are very representative of complex environmental chemical systems that pose an experimental and conceptual challenge to environmental chemists [16].

1.1. Metal Ion Interactions

For metal complexation studies in aquatic media, most of the interpretations in the literature are based on theories developed for simple systems, e.g. containing one metal and one (or a few) low molecular weight ligands with well-defined structures. This situation very rarely occurs in natural aquatic systems, where

particulate, colloidal or macromolecular complexants such as humic acids play a much larger role compared with simple "ligand" (e.g. acetate, EDTA) [17, 18]. It was reported that there are four possibilities of binding of humic acid with metal ions [14, 19].

1. by chelation between carboxyl and phenolic hydroxyl groups.
2. by chelation between two carboxyl groups.
3. by complexation with one carboxyl group.
4. by phenols and phenolic ethers.

In order to investigate the strength of metal-humate complexation, the conditional stability constant is estimated. The total ligand concentration is necessary for that determination, but it is difficult to obtain this value experimentally because of the heterogeneity of humic acid groups. As a first approximation, it is possible to use the total acidity value corresponding to $-COOH$, phenolic and enolic $-OH$ groups, which is determined by standard methods. [1, 20].

The concentrations of ionized carboxylate and hydroxy phenolic groups binding sites in an aqueous sample of humic acid are used in the equilibrium expression to calculate the conditional stability constant. Thus, the free humic acid concentration is expressed in terms of equivalents/Liter of these ionized binding sites, thereby avoiding the problem of distribution in molecular weights. In addition, metal ions may directly associate with donor groups or associate more generally with an ionic macromolecule [9].

The main driving forces for metal ion complexation with ligands [21, 22] are identified to be (1) dehydration of the complexing metal ion; and (2) relaxation of the double layer, especially release of water molecules. The electrostatic attractions cannot be the only contribution to binding, since it depends only upon the magnitude of the charge of the binding cation. The chemical contribution will have two components; enthalpic and entropic [3].

This paper describes the complexation of Azraq humic acid with heavy metal ions. The determination of the stability constants for Cd-humate and Zn-humate complexes by applying Schubert's ion exchange method and its modified form was done, and its temperature dependence, from which the ΔG , ΔH , and ΔS of the complexation reaction were determined. This work was carried out at pH 4 and 5 to avoid hydrolysis of metal ions and carbonate formation. The water and soil pH of Azraq falls between 6.5-7.5.

1.1.1 Ion Exchange Equilibrium Method

The uptake of metals by humics has been studied by a

variety of methods. Whatever the analytical method, the general procedure involves producing a mixture of dissolved humic acid, a metal salt and a background electrolyte such that the total amount of each component in the system is known.

The ion exchange equilibrium method [23, 24] is the most interesting one because its theory is based on what happens in nature. In the environment, there is competition between dissolved humic complexes and solid phases. A known weight of a well-defined ion exchange resin is added to a solution containing a mixture of a humic acid and a metal. The resin and humic acid will compete for the metal and a certain proportion will bind to each. This distribution of a metal ion between a solution and a solid phase is measured in the absence and presence of a dissolved ligand. Since the binding strength of the resin is known, both the free metal concentration and the amount bound to humic acid can be calculated, and hence the binding strength can be determined. Any metal may be treated by this method.

Using this ion exchange equilibrium method one can derive the conditional stability constant by two different approaches:

1. Schubert's method, where the metal ion concentration remains fixed.
 2. The modified Schubert's method, where the metal ion concentration is changing.
- Ardakani and Stevenson [25] proposed this modified approach.

Schubert's Ion Exchange Method and its Modified Form. In this method, the metal is regarded as the central group. This is only true when the concentration of metal ions is much smaller than that of the ligand. This complexation can be expressed by the reaction



where j is the number of metal ions combined per complex molecule, and i is the number of ligands, L , (or binding sites) per complexed molecule.

For proper application of the method [26, 27], a large excess of bulk electrolyte maintains a constant ionic strength with constant pH, the total concentration of the metal cations is negligible compared to the concentration of the complexing ligand and the cation exchange resin must be previously saturated with the cation component of the bulk electrolyte. In addition, neither the complexing ligand nor the metal-ligand complex should bind to the resin; the ratio of free metal ion concentration to resin sites must be maintained at those observed on the linear portion of the metal resin ion-exchange isotherm by having a small metal concentration

compared to resin-exchange sites and ligand concentration. Moreover, the equilibrium temperature of the system must be constant.

If all the above conditions are met then the distribution coefficient between the resin and solution phases for metal ion M^{n+} , in the absence of a humic acid (D_o) and the presence of humic acid are given by these equilibrium ratios:

$$D_o = [M_r] / [M] \quad (2)$$

and

$$D = [M_r] / [M] + [M_c] \quad (3)$$

where $[M]$ is the free metal concentration in solution; $[M_r]$ is the concentration of metal bound to the resin; and $[M_c]$ is the concentration of complexed metal ion in solution. The slope of the plot of $[M_r]$ versus $[M]$ at different loadings of M^{n+} will give D_o . Combining equations (2) and (3) gives:

$$(D_o/D) - 1 = [M_c] / [M] = j[M_iL_i] / [M] \quad (4)$$

where j is the number of metal ions combined per complex molecule, and i is the number of ligands, L , (or binding sites) per complexed molecule. By measuring the quantity $[M] + [M_c]$, for the equilibrium determination of D , $[M_r]$ is calculated by difference.

When the central metal atom ($j = 1$) is present, equation (4) simplifies to

$$\log (D_o/D) - 1 = \log \beta_i + i \log [L] \quad (5)$$

Equation (5) is the basic equation used to determine conditional stability constants if the complexes are mononuclear. Therefore, $\log \beta_i$ can be determined from a plot of $\log ((D_o / D) - 1)$, where D_o and D are determined experimentally, versus $\log [L]$, which is commonly called a Schubert's plot. Parameters i and $\log \beta_i$ can be obtained from the slope and intercept of the straight line [28].

Recently, possible problems with Schubert's method have been raised. Because of dissolution of resin, the value of $j \neq 1$ and the assumption that D_o is constant for the range of metal ion concentrations used is not valid. A modified method of data treatment and analysis was proposed to eliminate the sources of these errors in the ion exchange method [29-31] and this led to the following equation

$$\log [M_c] = \log j + \log \beta_{ji} + j \log [M] + i \log [L] \quad (6)$$

In the two different approaches, the enthalpy change for the complexation of metal and humic acid can be obtained from the temperature dependence of the stability constant by the equation:

$$-\Delta H/R = \partial \ln \beta_{ji} / \partial (1/T) \quad (7)$$

A plot of $\log \beta_{ji}$ vs. $1/T$ should be linear with a slope equal to $-\Delta H/(2.303 R)$ and with intercept equal to $\Delta S/2.303 R$ [32]. These quantities are related via

$$-RT \ln \beta_{ji} = \Delta G = \Delta H - T \Delta S \quad (8)$$

2. EXPERIMENTAL

2.1. Chemicals and Reagents

A stock solution (1000 mg/L) of Pb(II) (BDH, Analar) was prepared by dissolving an appropriate quantity of lead(II) nitrate in 0.1 M $HClO_4$ (BDH, Analar). The metal ion solution was adjusted to the desired pH by adding 0.1 M NaOH (GCC) and/or 0.1 M $HClO_4$ solution. The pH was chosen in the range where no precipitation of metal hydroxide takes place. Dowex 50wX8 (20-50 mesh, Na-form) was from Fluka. This cation exchange resin was equilibrated with a stock solution of 0.1 M $NaClO_4$ for several hours, and then washed several times with distilled deionized water. After washing, the resin was air dried and stored in an airtight glass bottle.

2.2. Humic Acid Sample and the Preparation of Humic Acid Solutions

Humic acid was isolated from the O horizon of a soil from the Azraq Oasis, which is located in the eastern desert of Jordan. A detailed description of the method of isolation and purification is given by Khalili [33].

Humic acid was obtained by extraction with 0.5 M NaOH under N_2 followed by coagulation, centrifugation, washing with 0.5% HF and 0.5% HCl, and finally by passing through a cation exchange resin column (Dowex). Then it was washed with distilled deionized water and freeze-dried. Carboxylic acid groups and total acidity per gram of humic acid were determined by treatment with calcium acetate and barium hydroxide methods and phenolic groups were calculated by difference [34] as shown in Table 1. The humic acid solutions were prepared as described in our previous work [12]. The concentration of stock solution of humic acid is based on the total acidity in equivalent/liter.

2.3. Instrumentation

Dissolved metal ion was determined by atomic absorption spectrophotometry with a Varian Spectra AA-250 Plus and an air-acetylene flame. The absorbance of metal-humate and pure humic acid was determined with a Cary Varian 1 E double beam UV-VIS spectrophotometer. All the samples were shaken in a Memmert model WB 22 water bath. An Orion model 525 pH-meter and a Shimadzo model AW 120 analytical balance were used.

Table 1 Some characteristic features of Azraq humic acid (HA)

Characteristics	
E_4/E_6	5.34
Total acidity	10.8 meq/g
Total carboxylate	2.3 meq/g
pK_{a1}	3.82
pK_{a2}	9.74
Elemental analysis	
% C	55.7
% H	5.1
% N	2.9

2.4. Batch Ion Exchange Experiment

2.4.1 Time of Equilibration

The time of equilibration was investigated at 25°C, 35°C, 45°C, 55°C, and 65°C \pm 0.1°C for Pb(II) complexation by taking an accurate amount of Na-saturated cation exchange resin and adding it to 25.0 ml of metal ion solution. The samples were shaken for different times; the period to attain equilibrium was determined to be less than 5 hours by measuring the concentration of the supernatant. This procedure was repeated at every desired pH value.

2.4.2 Establishing the Metal-Ion Exchange Isotherm in the Absence of Humic Acid (D_0)

Two different ion-exchange isotherms were done for Pb(II) complexation by resin, one at pH 4 and the other at pH 5. For each measurement, different volumes of metal stock solutions were added to a 25.0 mL volumetric flask along with 0.1 M NaClO₄. The pH was adjusted to the required value by addition of 0.1 M NaOH and/or 0.1 M HClO₄ solution. After pH adjustment the volumes were brought to 25.0 mL with 0.1 M NaClO₄. 50.0 mg of the cleaned, Na-saturated cation exchange resin was added to 25.0 ml of the prepared metal solutions and shaken in a constant-temperature water bath at the desired temperature for

at least 24 hr, which was sufficient to ensure equilibration.

The distribution experiments were carried out at 25°C, 35°C, 45°C, 55°C, and 65°C. After the equilibrium period, the samples were removed from the shaker and the exchange resin was removed by filtration. The supernatant was taken and analyzed for Pb by atomic absorption spectrophotometry. This procedure was done at different pH and metal ion concentrations to attain the required suitable conditions for every experiment. Each experimental datum represents the average of two or more measured values.

2.4.3 Determination of Conditional Stability Constants of Metal-Ligand Complexes

The ion exchange procedure was used to determine the distribution coefficient (D) in order to estimate the stability constants for ligand and divalent cations was similar to the previous procedure in section (2.4.2) that was used to establish the distribution coefficient (D_0) between the metal cation and resin. However, the difference here is the presence of humic acid as a complexing ligand. Different concentrations of humic acid were chosen for metal ion binding at the desired pH so the saturation of humic acid with metal ion did not occur. The concentration range for metal ion was taken in which the distribution coefficient (D_0) does not vary with the metal loading of the ion exchange resin over a particular free metal ion concentration range.

2.4.4 Determination of Conditional Stability Constants of Pb(II)-Ligand Complexes

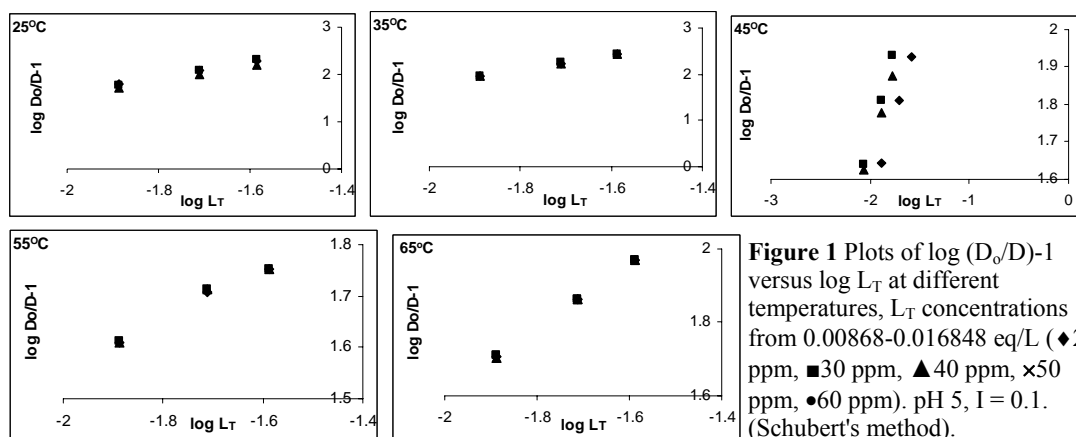
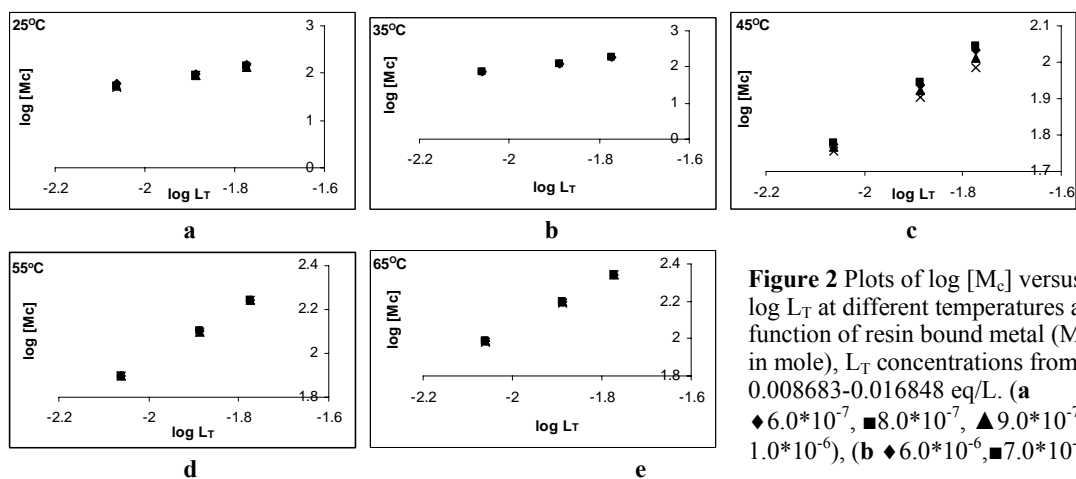
Two different ion-exchange equilibrium experiments in the presence of humic acid were done. At pH = 4, the concentrations of Pb(II) at which the linear range is established are 5, 10, 15, and 20 ppm. Three different concentrations of humic acid were used, 0.02592, 0.01944, and 0.01296 equivalent/L. At pH = 5 the concentrations of Pb(II) at which the linear range is established are 10, 20, 30, 40, 50 and 60 ppm. Three different concentrations of humic acid were used, 0.01685, 0.01296, and 0.008683 equivalent/L.

2.4.5 Investigation of Adsorption by the Resin Surface

The absorbance of the supernatant of each experiment described in section 2.4.4, and of humic acid was measured at 465 nm before and after equilibration with the resin [1]. We found that no humic acid or metal-humate was adsorbed at the resin surface.

Table 2 Conditional stability constants, $\log\beta_n$, for Pb(II)-humate complex derived at different temperatures at pH 4 and 5 and ionic strength of $I = 0.1$.

Temperature °C	Schubert's Method				Modified Schubert's Method			
	pH = 4							
	i	log β	logβ ₁	logβ ₂	i	log β	logβ ₁	logβ ₂
25	1.57±0.02	4.78 ±0.01	3.41±1.92	5.32±3.62	1.40±0.10	4.47±0.18	3.54±2.72	5.11±4.41
35	1.61±0.03	4.99±0.06	3.52±2.39	5.45±4.14	1.57±0.06	4.94±0.11	3.60±2.91	5.43±4.61
45	0.94±0.01	3.52±0.02	3.55±0.24	----	0.76±0.09	3.10±0.16	3.66±1.20	----
55	0.48±0.07	2.52±0.12	3.61±1.39	----	0.47±0.07	2.51±0.12	3.68±2.75	----
65	0.88±0.01	3.36±0.01	3.62±1.04	----	0.84±0.003	3.31±0.01	3.67±2.49	----
pH=5								
25	1.62±0.03	5.01±0.05	3.37±1.98	5.52±3.86	1.42±0.11	4.66±0.21	3.59±2.80	5.40
35	1.47±0.01	4.88±0.03	3.70±0.30	5.56±0.30	1.40±0.05	4.73±0.09	3.74±0.62	5.47±0.83
45	0.77±0.02	3.34±0.04	3.85±0.03	----	0.87±0.03	3.56±0.06	3.87±0.20	----
55	1.23±0.02	4.43±0.03	3.88±0.06	5.27±0.17	1.22±0.02	4.40±0.04	3.88±0.11	5.22±0.40
65	1.25±0.02	4.56±0.03	3.95±0.07	5.19±0.20	1.23±0.02	4.53±0.04	3.96±0.11	5.36±0.34

**Figure 1** Plots of $\log (D_0/D) - 1$ versus $\log L_T$ at different temperatures, L_T concentrations from 0.00868-0.016848 eq/L (♦ 20 ppm, ■ 30 ppm, ▲ 40 ppm, × 50 ppm, ● 60 ppm). pH 5, $I = 0.1$. (Schubert's method).**Figure 2** Plots of $\log [M_c]$ versus $\log L_T$ at different temperatures as a function of resin bound metal (M_r in mole), L_T concentrations from 0.008683-0.016848 eq/L. (a) ♦ 6.0×10^{-7} , ■ 8.0×10^{-7} , ▲ 9.0×10^{-7} , × 1.0×10^{-6} , (b) ♦ 6.0×10^{-6} , ■ 7.0×10^{-6} , ▲ 8.0×10^{-6} , × 9.0×10^{-6} , (c) ♦ 9.0×10^{-7} , ■ 1.0×10^{-6} , ▲ 1.25×10^{-6} , × 1.27×10^{-6} , (d) ♦ 1.3×10^{-6} , ■ 1.4×10^{-6} , ▲ 1.5×10^{-6} , × 1.6×10^{-6} , (e) ♦ 1.4×10^{-6} , ■ 1.5×10^{-6} , ▲ 1.6×10^{-6} , × 1.7×10^{-6} . pH 5, $I = 0.1$.

3. RESULTS AND DISCUSSION

3.1. Establishing the Metal(II)-Ion Exchange Isotherm in the Absence of Humic Acid (D_0)

The isotherm behavior of Pb(II) ion at different temperatures and different pH values was investigated. The linear range was obtained from each isotherm curve to estimate the D_0 in order to choose the appropriate concentrations for both metal ions and humic acid to avoid the effect of metal loading. Increasing the loading of cations onto a polyelectrolyte should result in an increase in the neutralization of the polyelectrolyte charge density and a decrease in the electrostatic repulsion within the polyanion. This will lead to a smaller net negative charge and a more compact (more folded) configuration. Furthermore, a process called "cross-linkage" becomes possible as the polyanion becomes more contracted. This occurs when the polyanion begins to fold around the metal ion to neutralize its negative charge density. As a result, aggregation would occur [35].

3.2. Determination of Conditional Stability Constants of Pb(II) - Ligand Complexes

The values of i obtained for metal ion-humate complex at different pH values and different temperatures are summarized in Table 2. Figs. 1 and 2 illustrated these results for Pb(II) at pH 5 as an example for both Schubert's method and its modified form. It is obvious that all values of i are nearly identical to each other in each approach. Also, it was found that there is no positive correlation between the values of i with increasing temperature and pH. Since the values of i should be an integer, values of $i > 1$ indicate that the complexation of metal ions with humic acid leads to the formation of both 1:1 complex and complexes with a higher ligand to metal ratio. Thus, $i > 1$ at pH 4 and 5 at some temperatures: for Pb(II) ion this means that 1:1 and 1:2 complexes were formed [21]. However, i was noticed to be < 1 at some temperatures at both pH 4 and 5, which may be due to the formation of mixed complexes 1:1 and 2:1.

Table 3 The value of j for Pb(II) in the ion-exchange equilibrium system at different temperatures and pH values (Modified form of Schubert's method)

Temperature °C	j at pH 4	j at pH 5
	Pb-HA	Pb-HA
25	0.80±0.10	0.88±0.10
35	0.95±0.10	0.96±0.10
45	0.79±0.10	0.92±0.10

55	1.00±0.10	1.00±0.10
65	0.93±0.10	1.03±0.10

Table 3 shows the values of j , which is nearly equal to one for Pb(II).

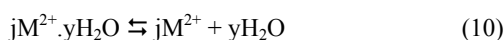
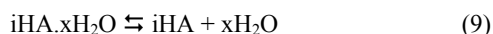
Ligands with such different complexing abilities are not surprising with a large heterogeneous molecule such as humic acid. Furthermore, it is not obvious whether the 1:2 complex is a metal ion binding with two groups of the same humic acid molecule or with groups on different humic acid molecules. Considering the size of the humic acid molecule and the number of binding sites per molecule, the binding of a metal ion to two groups of the same humic acid seems to be more probable.

β_1 and β_2 values were obtained from plots $((D_0/D) - 1) / L_T$ versus L_T (Fig. 3) according to Schubert's method, and from the plot $(M_0/M)/L_T$ versus L_T (Fig. 4) according to Schubert's modified method, both at pH 5. The conditional stability constant $\log \beta_1$ was found to increase with increasing both pH and temperature for Pb(II)-humate complexes, as summarized in Table 2.

It is assumed that humic acid shows a rod-like structure of a helical strand [36]. At higher pH, greater deprotonation of humate polyanions results in a larger negative charge and a more extended configuration. A change in molecular shape, such as unfolding and uncoiling will take place because of the electrostatic repulsion between the negative charges on humic acid. The more open configuration at high pH allows faster diffusion of cations and thus rapid chelation to a larger number of negative binding sites.

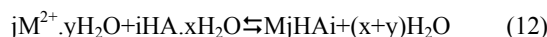
On one hand, there are more deprotonated carboxylic acid and phenol groups available for specific binding site at higher pH, so that the formation of strongly bound metal-humate complex is facilitated. On the other hand, there will be more surface binding. By decreasing the pH, the positive charge will increase, so there will be a competition between hydrogen ions and metal ions for anionic binding sites of humic acid. Due to neutralization of the active functional groups, a change in configuration will take place by coiling and folding of the rod-like humic acid. With increasing temperature and pH there is an increase of $\log \beta_1$ for Pb(II)-humate complexes.

It was assumed that there are three elementary reactions for complexation of metal ion with humic acid as shown below:



The complexation reaction between these metal ions and humic acid can be explained by these equa-

tions. Equation (9) involves dehydration of the humic acid double layer, while equation (10) shows the dehydration of the metal ions and equation (11) represents the binding of the dehydrated M^{2+} ions with dehydrated HA ligands. Dehydration of either M^{2+} ions or HA ligands may not remove all coordinated water molecules [21]. The sum of these three elementary reactions can be given in the following reaction



The enthalpy and entropy changes of reaction (12) are the sums of enthalpies and entropies of the previous three elementary reactions.

The first two reactions are both endothermic with positive entropy changes, while the interaction between the dehydrated positive ion and the humic acid ligand in equation (11) is exothermic with a negative entropy change. It was found that a spontaneous complexation reaction takes place between Pb(II) and humic acid with a large, favorable entropy and an endothermic overall reaction at both pH values as illustrated in Fig. 5 (a, b) and summarized in Table 4.

The relatively large positive entropy changes of metal-humate complexation indicate the importance

of dehydration of M^{2+} ions and HA ligands prior to metal complexation with humic acid. Positive entropy changes in the dehydration reactions are large enough to compensate for the negative entropy change of reaction (11), and the total entropy of complexation is positive. As a result, the reaction is spontaneous (ΔG is negative) [37].

Pb(II) is a non-transition metal ion that forms stable complexes with the oxygen-carrying donor groups of humic acid [38]. There are many factors that contribute to the stability of metal ion-humate complex that should be considered: the rate constant for water exchange (rate of water loss), hydration energy, polarizability of the metal ion and ligand and the polyelectrolyte effect (electrostatic interactions between the charges on the humic acid and those on the cations). However, Pb(II) is an intermediate Lewis acid with non-polarizable character and hence low in contributing to covalent bonding. This effect increases the bond strength of Pb(II) with a polyanion through a significant electrostatic contribution. Also, Pb(II) has a low hydration energy (-1481 kJ / mol), which means no strong interaction between the metal ion and water molecules which would lead to a low solvation enthalpy.

Table 4 Thermodynamic parameters of Pb-HA complexes at 298 K. pH 4 and 5, and ionic strength of I = 0.1.

Complex	Schubert's Method			Modified Schubert's Method		
	ΔG kJ eq ⁻¹	ΔH kJ eq ⁻¹	ΔS J eq ⁻¹ K ⁻¹	ΔG kJ eq ⁻¹	ΔH kJ eq ⁻¹	ΔS J eq ⁻¹ K ⁻¹
pH = 4						
Pb-HA	-19.4± 0.06	9.1±0.86	96.7±2.68	-20.2±0.07	6.1± 0.99	88.5±3.09
pH = 5						
Pb-HA	-19.2±0.16	26.0± 2.80	154±8.86	-20.5±0.08	17.3± 1.24	127.4±3.90

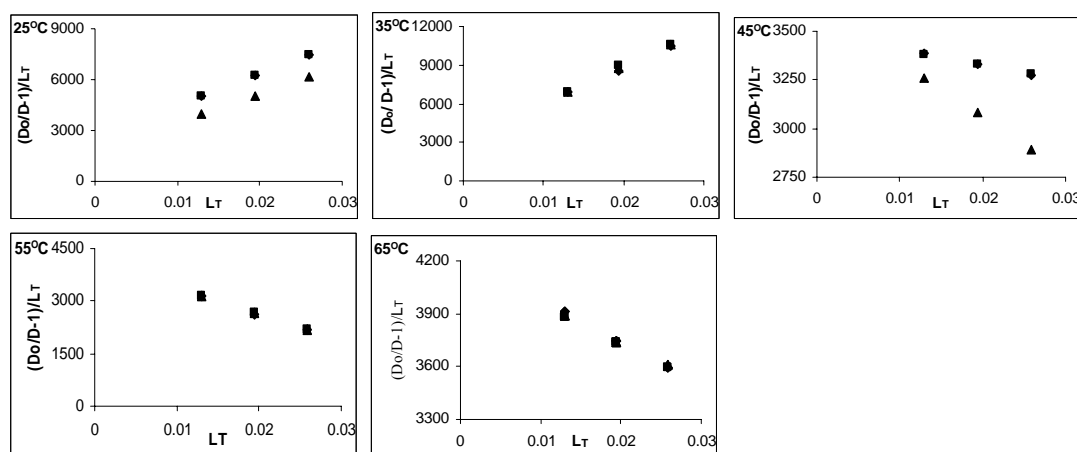


Figure 3 Plots of $((D_0/D)-1)/L_T$ versus L_T at different temperatures, L_T concentrations from 0.00868-0.016848 eq/L (♦ 20 ppm, ■ 30 ppm, ▲ 40 ppm, × 50 ppm, ● 60 ppm). pH 5, I = 0.1. (Schubert's method).

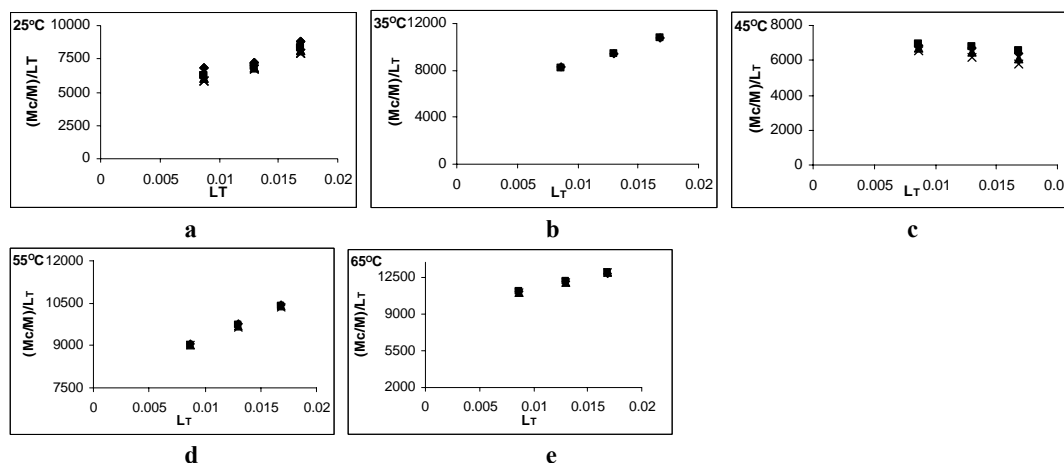


Figure 4 Plots of $(Mc/M)/L_T$ versus L_T at different temperatures as a function of resin bound metal (M_r in mole), L_T concentrations from 0.008683-0.016848 eq/L. (a $\diamond 6.0 \times 10^{-7}$, $\blacksquare 8.0 \times 10^{-7}$, $\blacktriangle 9.0 \times 10^{-7}$, $\times 1.0 \times 10^{-6}$), (b $\diamond 6.0 \times 10^{-6}$, $\blacksquare 7.0 \times 10^{-6}$, $\blacktriangle 8.0 \times 10^{-6}$, $\times 9.0 \times 10^{-6}$), (c $\diamond 9.0 \times 10^{-7}$, $\blacksquare 1.0 \times 10^{-6}$, $\blacktriangle 1.25 \times 10^{-6}$, $\times 1.27 \times 10^{-6}$), (d $\diamond 1.3 \times 10^{-6}$, $\blacksquare 1.4 \times 10^{-6}$, $\blacktriangle 1.5 \times 10^{-6}$, $\times 1.6 \times 10^{-6}$), (e $\diamond 1.4 \times 10^{-6}$, $\blacksquare 1.5 \times 10^{-6}$, $\blacktriangle 1.6 \times 10^{-6}$, $\times 1.7 \times 10^{-6}$). pH 5, $I = 0.1$.

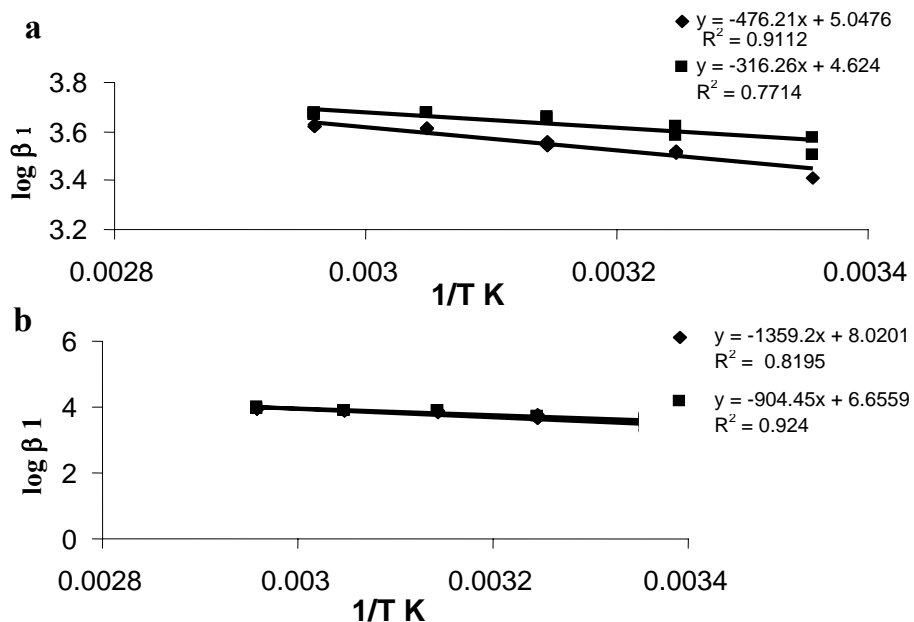
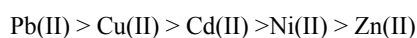


Figure 5 (a, b) Temperature dependence of $\log \beta_1$ a- pH = 4, b- pH = 5. $I = 0.1$ \blacktriangle Schubert's method, \blacksquare Modified form of Schubert's method.

Lead(II) has a high rate constant for water exchange ($\approx 1 \times 10^9 \text{ s}^{-1}$), which means that there will be a high probability to lose water molecules and interact with another ligand. The greater the value of the water-loss rate constant for a metal, the greater affinity of that metal over other metals in binding to form complex with humic acid [39-41].

From our studies of metal ions Cu(II), Cd(II), Ni(II), and Zn(II) complexation with humic acid, it

was found that the conditional stability constant $\log \beta_1$ for all the metal ions at all the desired temperatures and at pH 4 and 5 follows this trend



Of the five divalent metal ions examined, Pb(II) (the only non-transition metal ion) was found to form the most stable complex with the oxygen-carrying donor groups of humic acid. The trend that

Cu(II) > Ni(II) > Zn(II) agrees with the Irving-Williams series [12, 42, 43]

4. CONCLUSIONS

Water pollution is a major environmental problem. It involves the accumulation of chemical, physical and biological contaminants in oceans, lakes, rivers and streams. This adversely affects the environment. Heavy metal ions are common pollutants and must be removed if present at concentrations higher than required by environmental regulations. The environmental significance of this project stems from the ability of humic acid from Azraq to bind with toxic metal ions such as lead. Because of the highly oxygenated nature of Azraq humic acid, it has a high affinity to form stable complexes with this heavy metal ion. This study used Schubert's ion-exchange equilibrium method and its modified form. There is good agreement between the values obtained by Schubert's ion-exchange equilibrium method and those obtained from its modified form. The obtained values of i for this metal ion at different pH values indicate that there are 2:1, 1:1 and 1:2 metal-humate complexes. On the other hand, the obtained values of j indicate that one metal ion interacts with humic acid. The stability constants increased with temperature and pH. The uptake of metal into the exchangeable fraction may be explained in terms of dehydration of the cation and the relaxation of the humic acid double layer. The overall metal ion-humate complexation reaction is endothermic. The values indicate spontaneous change (ΔG negative) with a large favourable entropy change (ΔS positive) at pHs 4 and 5.

5. REFERENCES

- [1] Stevenson FJ. *Humus chemistry: Genesis, composition, reactions*. New York: Wiley, 1982, 285-288.
- [2] Tochiyama O, Yoshino H, Kubota T, Sato M, Tanaka K, Niibori Y, Mitsugashira T. Complex formation of Np(V) with humic acid and polyacrylic acid. *Radiochim. Acta*, 2000, 88: 547-552.
- [3] Bryan ND, Jones D, Griffin D, Regan L, King S, Warwick, P, Carlsen L. Combined mechanistic and transport modeling of metal humate complexes. *Forschungszentrum Karlsruhe Technik und Umwelt*, 1998, 4: 303-337.
- [4] Guthrie JW, Mandal R, Salam MSA, Hassan NM, Murimboh J, Chakrabarty CL, Back MH, Grégoire DC. Kinetic studies of nickel speciation in model solutions of a well-characterized humic acid using the competing ligand exchange method. *Anal. Chim. Acta*, 2003, 480: 157-169.
- [5] Baker H, Halim H. Removal of nickel ions from aqueous solutions by using insolubilized humic acid: Effect of pH and temperature. *Asian J. Chem.*, 2007, 19: 233-245.
- [6] Rozenbaha I, Odham G, Järnberg U, Alsberg T, Klavins M. Characterization of humic acid substances by acid catalyzed transesterification. *Anal. Chim. Acta*, 2002, 452: 105-114.
- [7] Wu FC, Evans RD, Dillon PJ. Fractionation and characterization of fulvic acid by immobilized metal ion affinity chromatography. *Anal. Chim. Acta*, 2002, 452: 85-93.
- [8] Landgraf MD, Silva S, Rezende M. Mechanism of metribuzin herbicide sorption by humic acid samples from peat and vermicompost. *Anal. Chim. Acta*, 1998, 368: 155-164.
- [9] Choppin GR. *Chemical separation technologies and related methods of nuclear waste management*. Netherlands: Kluwer Academic Publishers, 1999, 247-260.
- [10] Shin H, Monsallier JM, Choppin GR. Spectroscopic and chemical characterizations of molecular size fractionated humic acid. *Talanta*, 1999, 50: 641-647.
- [11] Baker H, Khalili F. Analysis of the removal of lead(II) from aqueous solutions by adsorption onto insolubilized humic acid: temperature and pH dependence. *Anal. Chim. Acta*, 2004, 516: 179-186.
- [12] Baker H, Khalili F. Comparative study of binding strengths and thermodynamic aspects of Cu(II) and Ni(II) with humic acid by Schubert's ion exchange method. *Anal. Chim. Acta*, 2003, 497: 235-248.
- [13] Davies G, Fataftah A, Cherkasskiy A, Ghabbour EA, Radwan A, Jansen SA, Kolla S, Paciolla MD, Sein LT, Buermann W, Balasubramanian M, Budnick J, Xing B. Tight metal binding by humic acids and its role in biomineralization. *J. Chem Soc. Dalton Trans.*, 1997, 4047-4060.
- [14] Pandey A, Pandey S, Misra V, Viswanathan PN. Formation of soluble complexes of metals with humic acid and its environmental significance. *Chem. Ecol.*, 1999, 16: 269-282.
- [15] Filella M, Buffle J. Effects of physico-chemical heterogeneity of natural complexants. Part I. Voltammetry of labile metal-fluvic complexes. *Anal. Chim. Acta*, 1990, 232: 209-223.
- [16] Buffle J. The analytical challenge posed by fulvic and humic compounds. *Anal. Chim. Acta*, 1990, 232: 1.
- [17] Milne CJ, Kinniburgh DG, Wit JCDE, Van Riemsdijk WH, Koopal LK. *Geochim. Cosmochim. Acta*, 1995, 59: 1101-1112.
- [18] Bargar JR, Persson P, Brown GE, Jr. Outer-sphere adsorption of Pd(II)EDTA on goethite.

- Geochim. Cosmochim. Acta*, 1999, 63: 2957-2969.
- [19] Sahu S, Banerjee DK. Complexation of copper(II), cadmium(II) and lead(II) with humic and fulvic acids of Yamuna river sediments. In: Pawlowski et al., eds. *Chemistry of the Protection of the Environment*. New York: Plenum Press. 1996, 375-387.
- [20] Senkyr J, Rocakova A, Fetsch D, Havel J. The acidobasic and complexation properties of humic acid. III. Study of humic acids complexation with cadmium(II) and lead(II) by pulse anodic stripping voltammetry. *Toxicol. Environ. Chem.*, 1999, 68: 377-391.
- [21] Samadfam M, Niitsu Y, Sato S, Ohashi H. Complexation thermodynamics of Sr(II) and humic Acid. *Radiochim. Acta*, 1996, 73: 211-216.
- [22] Buckau G. Effect of humic substances on the migration of radionuclides: Complexation and transport of actinides. *Forschungszentrum Karlsruhe Technik und Umwelt*. 2000, 1-69.
- [23] Schubert J. The use of ion exchangers for the determination of physicochemical properties of substances, particularly radiotracers in solution: I. *Theoretical. J. Phys. Colloid Chem.*, 1947, 52: 340-350.
- [24] Schubert J, Richter JW. The use of ion exchangers for the determination of physico-chemical properties of substances, particularly radiotracers in solution: II. *Theoretical. J. Phys. Colloid Chem.*, 1947, 52: 350-357.
- [25] Ardakani M, Stevenson FJ. A modified ion-exchange technique for the determination of stability constants of metal-soil organic matter complexes. *Soil Sci. Soc. Amer. Proc.*, 1972, 36: 884-890.
- [26] King SJ, Warwick P, Bryan N. A study of metal complexation with humic and fulvic acid: The effect of temperature on association and dissociation. *Forschungszentrum Karlsruhe Technik und Umwelt*. 1998: 217-244.
- [27] Brown GK, MacCarthy P, Leenheer JA. Simultaneous determination of Ca, Cu, Ni, Zn, and Cd binding strengths with fulvic acid fractions by Schubert's method. *Anal. Chim. Acta*, 1999, 402: 169-181.
- [28] Kurk DN, Choppin GR. Determination of Co(II) and Ni(II)-humate stability constants at high ionic strength NaCl solution. *Radiochim. Acta*, 2000, 88: 583-586.
- [29] Ibarra J, Orduna P. Variation of the metal complexing ability of humic acids with coal rank. *Fuel*, 1986, 65: 1012-1016.
- [30] Adhikari M, Ray JN. Stability constant of humic acid and their phosphorylated derivatives with Cu^{2+} and Al^{3+} . *J. Ind. Chem. Soc.*, 1976, 53: 238-241.
- [31] Lenhart JJ, Cabaniss SE, MacCarthy P, Honeyman BD. Uranium(VI) complexation with citric, humic and fulvic acids. *Radiochim. Acta*, 2000, 88: 345-353.
- [32] Khairy AH, Davies G., Ibrahim HZ, Ghabbour EA. Adsorption of aqueous nucleobases, nucleosides, and nucleotides on compost-derived humic acid. *J. Phys. Chem.*, 1996, 101: 2410-2416.
- [33] Khalili FI. The nature of the Azraq Oasis humic acid. *J. Iraqi Chem. Soc.*, 1988, 13: 71-85.
- [34] Khalili F. Preparation and characterization of selected metal-humate complexes. *Soil Sci.*, 1990, 150: 565-570.
- [35] Rao L, Choppin GR, Clark SB. A study of metal-humate interactions using cation exchange. *Radiochim. Acta*, 1994, 66/67: 141-147.
- [36] Davies G, Ghabbour EA, Khairy AH, Ibrahim HZ. A "site creation" model for specific adsorption of aqueous nucleobases, nucleosides, and nucleotides on compost-derived humic acid. *J. Phys. Chem.*, 1997, 100: 2410-2416.
- [37] Nash LK, Choppin GR. Interaction of humic and fulvic acids with Th(IV). *J. Inorg. Nucl. Chem.*, 1980, 42: 1045-1050.
- [38] Millward GE. Processes affecting trace element speciation in estuaries. *Analyst*, 1995, 120: 609-614.
- [39] Huheey J. *Inorganic chemistry, principles of structure and reactivity*, 4th edn. New York: Harper-Collins, 1993, 449-453.
- [40] Pearson RG. Hard and soft acids and bases. *J. Am. Chem. Soc.*, 1963, 84: 3533-3539.
- [41] Cotton FA, Wilkinson G. *Advanced inorganic chemistry*, 3rd edn. New York: Wiley, 1972: 644-645.
- [42] Chakrabarty CL, Lam MT, Murimboh J, Sekaly A, Mandal LR, Hassan N, Gregoire DC, Lu JY, Schroeder WH. *A novel scheme for chemical speciation of potentially toxic metals and metalloids in aqueous environmental samples*. Conference on chemical measurement and monitoring of the environment, Ottawa, 1998, 569-580.
- [43] Baker H, Khalili F. A study of complexation thermodynamics of humic acid with cadmium(II) and zinc(II) by Schubert's ion-exchange method. *Anal. Chim. Acta*, 2005, 542: 240-248.

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