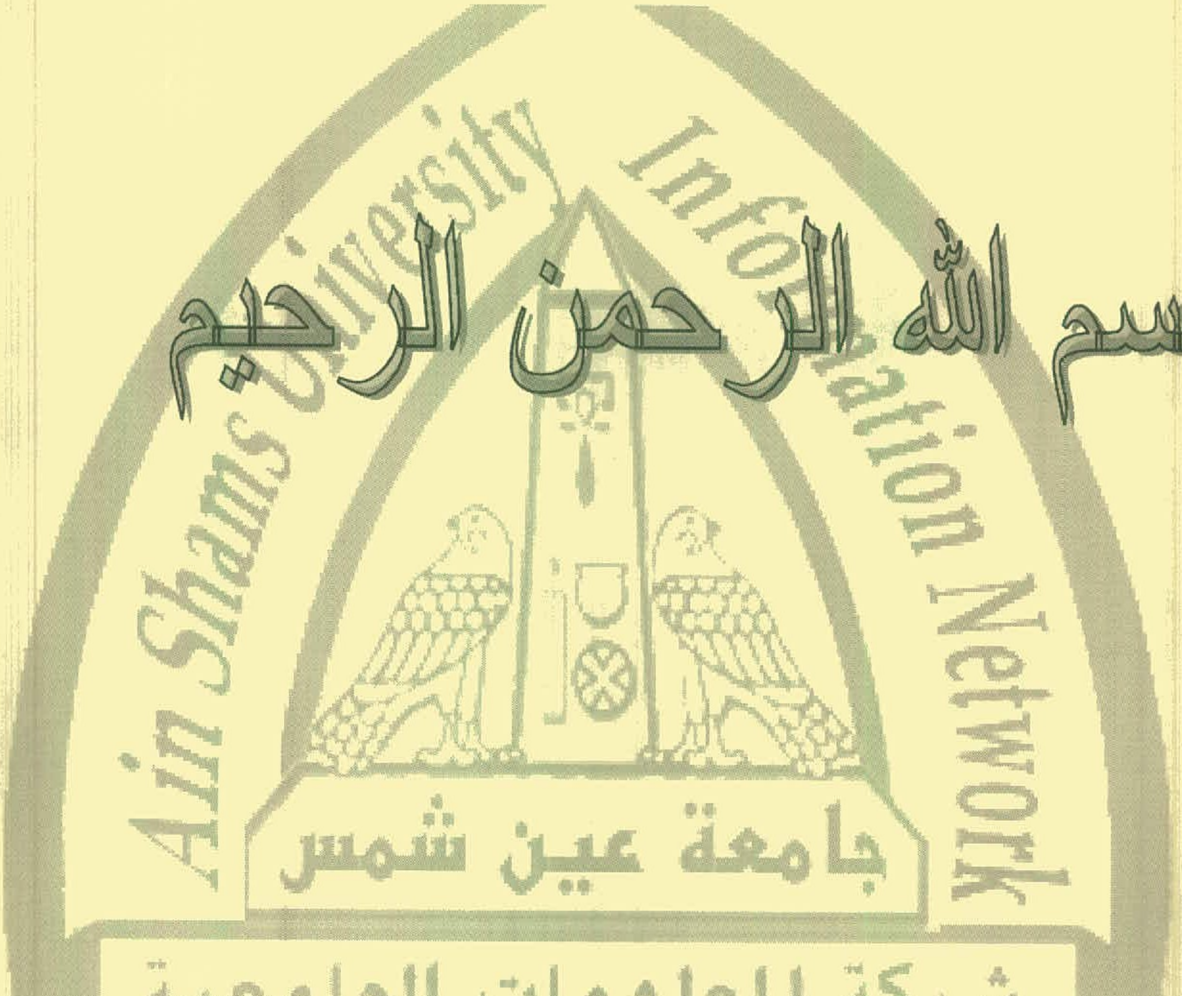
بسم الله الرحمن الرحيم




Ain Shams University
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جامعة عين شمس
شبكة المعلومات الجامعية
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شبكة المعلومات الجامعية

# جامعة عين شمس

التوثيق الالكتروني والميكروفيلم

## قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأفلام قد أعدت دون أية تغيرات

## يجب أن

تحفظ هذه الأفلام بعيدا عن الغبار

في درجة حرارة من ١٥-٢٥ مئوية ورطوبة نسبية من ٢٠-٤٠%

**To be Kept away from Dust in Dry Cool place of**
**15-25- c and relative humidity 20-40%**

# بعض الوثائق الاصلية تالفة

بالرسالة صفحات

لم ترد بالاصل

# CHEMICAL SPECIATION OF SOME METAL IONS IN AQUEOUS SOLUTIONS BY ELECTROCHEMICAL METHODS

**Thesis**

Submitted by

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To
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For the degree of Ph.D. of Science
(Chemistry)

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# Abstract

The geochemistry and bioavailability of trace metals are affected by their chemical speciation. An understanding of metal speciation is essential for predicting the transport, transformation and fate of metals in freshwaters. Metal species can be characterized by speciation parameters, which are related to their bioavailability. The main objective of this thesis was to investigate the applicability of the electrochemical techniques (AdCSV and ASV) in obtaining information on the speciation of nickel and cadmium in various model systems and freshwater samples. In the first part, the competitive ligand exchange method with the adsorptive cathodic stripping voltammetry was used to estimate the dissociation rate constants of the nickel complexes in model solutions of different organic complexants and in polluted freshwaters samples. The dissociation rate constant is one of those speciation parameters which represents how rapidly a metal complex dissociates to form free metal ion (i.e .the metal-aquo complex) and hence is a very important speciation parameter, especially in the case where free metal ion is the bioavailable species. It was found that the co-presence of the other trace metals, copper, cobalt, calcium and magnesium, compete effectively with the nickel in its complexes leading to the fast dissociation of the free nickel ions which reported to be toxic.

Polluted freshwater samples from Sudbury, Canada, had been collected two times, to study the effect of different experimental parameters on the bioavailability of the nickel complexes. Dimethylglyoxime (DMG) and 2,2'-bipyridine (Bipy) were employed as the competing ligands, each ligand in a separate experiment, so that the results obtained with one ligand could be compared with those of the other ligand. The results show that the dissociation rate of the nickel complexes of naturally occurring organic complexants in the above samples of freshwaters was slower than the rate of formation and adsorption of $Ni(DMG)_2$ and $Ni(Bipy)_3$ complexes on the electrode surface. This has allowed the extraction of dissociation rate constants of the nickel organic complexes from the $i_p/i_0 = f(t)$ curves, where $i_p$ and $i_0$ are the current for the nickel complex and the reference current under conditions of no complexation, respectively. It was concluded that, as the time of the UV-irradiation increase, the % of the free nickel ions increases. This is because the UV-irradiation break down the bonds between the nickel ions and its complexes leading to the formation of less stable nickel complexes which dissociate very fast (labile fraction) in the environment. This labile fraction increases gradually as the ratio of total nickel concentration over the Dissolved Organic Carbon (DOC) increases. The results obtained using both the

competing ligands, i.e., DMG and BiPy, are in good agreement with each other.

Stability constant is a speciation parameter that represents thermodynamic stability of a metal complex, and gives a measure of the availability of free metal ions at equilibrium. The effect of the major cations on the stability of the nickel/EDTA complex was studied. There was a good agreement between the kinetic and stability studies, as we found that the presence of the major cations decreased the stability of the nickel/EDTA complex due to the screening effect.

At the other part, we investigated the effects of competing major cations, Ca(II) and Mg(II), and the trace metals, Cu(II), Pb(II), and Zn(II) on the Cd(II) complexation by polyacrylic acid (PAA) and by Lurentian fulvic acid (LFA), using square wave anodic stripping voltammetry, keeping the ionic strength and pH constant. The average conditional stability constant of the Cd(II) complexation was estimated from titration curves obtained by adding complexing agents, PAA and LFA, separately, to a solution containing Cd(II) ions, in the absence and presence of other competing cations. It was found that, the stability constants of the Cd(II)-PAA and the Cd(II)-LFA complex increased with increase in the pH and decrease of the ionic strength of the test solutions. The effects of the competition of the major cations $Ca^{2+}$, and $Mg^{2+}$ were to decrease stability of the Cd(II) complex by competitive binding to binding sites in addition to the polyelectrolyte effect. The effects of the competition of the trace metal ions: $Cu^{2+}$, $Pb^{2+}$, and $Zn^{2+}$ were to decrease stability constant of the Cd(II) complex by competitive binding to binding sites. For the metals, Cu(II), Pb(II), Zn(II) and Cd(II), the effects of the above competition can be interpreted in terms of the complex stability sequence of the metals: $Pb(II) > Cu(II) > Zn(II) \approx Cd(II)$.

The environmental significance of the work was to study kinetics stability and the thermodynamic stability of a metal complex (which is a measure of the availability of free metal ions) which is a very important property for classifying the metal species in the aquatic and the terrestrial environment.

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