CHARACTERIZATION OF Cd(II) BINDING BY TWO HUMIC ACIDS THROUGH POTENTIOMETRIC AND IR STUDIES

Badr M. H*[1], El-Halafawi M. H[2] and Abd El-al Zeid E. R[3]

[1]Asst. Professor of Chemistry Department, Faculty of Science, Al-Azhar University (Girls) [2] Professor of Water and Soil, Faculty of Agriculture, Alexandria University, [3]Research student.

ABSTRACT

This work is a comparative investigation on the complexation of Cd(II) with humic acids extracted from the composts of sewage sludge (HAss)and Nile water hyacinth (HA_{NWH}). The analysis was realized at different ionic strength using the pH-titration technique of Calvin–Bjerrum as adopted by Irving and Rossotti and IR spectroscopy on the solid complexes. The results show that both HA_{SS} and HA_{NWH} has ability to form strong complexes with Cd (II) at low ionic strength, at the pH range of 5-8.5 The rise in pH lead to hydrolysis of the formed complexes. The increase of the salt content of solution decreases the ability to bind Cd^{2+} ions. The results showed noticeable higher stability constants of HA_{NWH}-Cd complex. According to the IR spectra Cd^{2+} ions are bound preferentially to two COOH or a COOH and an OH group in case of HAss. The IR spectra of HA_{NWH} - Cd complex shows, participatition of nitrogen atoms in binding of Cd^{2+} ions by HA_{NWH}, and formation of stronger chelate complex. Accordingly, the use of HA_{NWH} may be more effective in removing Cd^{2+} ions from aqueous solutions.

Corresponding author: Dr Mogeda Badr / e. mail, drbadrmh @yahoo.com

INTRODUCTION

Cadmium is one of the heavy metals, which is highly toxic to human, plants and animals. Cadmium toxicity contributes to a large number such as heart disease, cancer and diabetes. Cadmium concentrates in the kidney, liver and various other organs and is considered more toxic than either lead or mercury. It is toxic at levels one tenth that of lead, mercury, aluminum, or nickel **(Nag et al., 2012)** .Also most aquatic organisms have the capability of concentrating the metals by feeding and metabolic processes, which can lead to accumulation of high concentrations in their tissues **(Osman et al., 2009)**.

The main anthropogenic pathway through which cadmium enters environment is via wastes from industrial processes such as electroplating, smelting, alloy manufacturing, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining (Rao et al., 2010) **.**The reduction of cadmium as well as any toxic elements in environment is needed by any acceptable method.

Humic substances(HSs) -which include humic acids(HA), fluvic acids, and humine-are naturally occurring organic substances. They occur in environment as a final degradation products of plant and animal residues. They are highly functionalized carbon-rich biopolymers with a great capacity to bind metal cations, They affect the mobility and transport of heavy metal ions in the environment. Humic acids present heterogeneous compositions that depend on the chemistry of how they were generated. Thus it is difficult to identify their structures. However it is known that within these geopolymers the main chelating groups are catechol, salicylate and phthalate derivatives which are distributed through the humic acid structure. **(Merce et al., 1999)**. Also they are considered complex macromolecules having various functional groups and are very effective in the binding and removal of different pollutants including heavy metals. **(Paul & Jayakumar, 2010)**.

In recent years, ,it was reported on the importance to promote the use of these environmentally-safe humic acids (HA) in the remediation of heavily contaminated environments **(Chang et al., 2007)**. In field of soil remediation, the addition of HA to soils reduces the bioavailability of Cd **(Shuman, 1998).** Composite adsorbent materials containing humic

acids was used to remove Cd from industrial waste- Water (**Dogan, 2012**).The treatment of the fish pond water by humic acid significantly reversed the effects of the cadmium toxicity(**Osman et al., 2009**).

Humic acids were introduced as a novel material for preparation of cross linked ion-exchange (HUMASORB) having properties to remove heavy metal and organic contamination from polluted water (**Sanjay et al., 1996**).

Among the numerous sources of humic acids are composts such as water hayacimth compost (**Badr et al., 2007; Marthinna, 2012**) and sewage sludge (**Amir et al., 2004**). These two composts were used in this study as sources of humic acids

Many methods were used to study the binding of metal ions by humic acids. These include: potentiometric titration with a cadmium ion selective electrode (**Jelkovic et al., 2006; Kaschl et al., 2002 and Evangelou and Marsi, 2002**).Titration and Spectrophotometry (**janot et al., 2010**). Differential pulse anodic stripping Voltammetry (**Waldemartal, 2000; Marc et al., 2002**).

The present paper investigates and compare between of the stability constants of complexes of Cd(II) at different ionic strengths with the two extracted humic acids. The method of (**Calvin and Wilson, 1945; Bjerrum, 1941**) as adopted (**Irving and Rossotti,1954**) was used . The chemical characterization of the two extracted humic acids, and their dissociation constants were previously evaluated (**Badr et al., 2012**).

MATERIALS AND METHODS

Sample collection

Nile water hyacinth plants were mechanically collected from the water surface of Nile River. *Sewage Sludge* samples are obtained from the drain station institute present in the area 9N of Alexandria city /Egypt. The samples were prepared for humic acids extraction as given elsewhere (**Badr et al., 2012**).

Humic acids extraction, purification and analysis

Extraction and purification of Nile water hyacinth humic acids (HA_{NWH}) and sewage sludge humic acids (HAss), were carried out at 6hrs in absence of air according to IHSS (International Humic

Substances Society (**Swift, 1996**). Drying, elemental analysis, moisture content, ash contents, determination of total acidity (carboxylic, and phenolic OH groups) by potentiometric analysis, and E_4/E_6 (the ratio of absorbance at 400nm to absorbance at 600nm of sodium humate solution) were conducted as given in details in (**Badr et al., 2012**).

Preparation of solid Cd Humate Complexes

The solid cadmium humate complexes were prepared by dissolving 0.1 g of humic acid in 50 ml distilled water with the assistance of 0.1 N NaOH. Cadmium chloride solution 0.1M was titrated carefully to each HA solution till first coagulation. The resulting complex precipitates were collected by centrifugation (1000rev/min) and then washed with distilled water to a negative chloride test. Finally, the precipitates were air dried and kept in closed bottles (**Khalili, 1990).**

FT-IR Spectra:-

The FT-IR spectra of the two humic acids samples and their metal complexes with Cd^{2+} were recorded over a wave number range 400 – 4000 cm^{-1} on a Jasco FTIR 460 plus spectrometer. The samples were prepared by grinding the solid compound with anhydrous potassium bromide, and then pressed into the form of a disc for convenient sampling.

Binding of Cd^{2+} ions with humic acids at different ionic strengths

According to (**Stevenson, 1982; Senkyr et al., 1999 and Choppin, 1999**), it is possible to use the acidity values corresponding to – COOH, and phenolic –OH groups, which are determined by standard methods for expressing humic acids concentration. 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. Based on this idea the metal: ligand ratio used was equivalent: equivalent. The following mixtures were prepared:-

i) Each of the two suspensions of d HA_{NWH} was prepared by dissolving 0.03 g. HA in a minimum volume of 0.05 M NaOH solution in absence of air and precipitated by adding suitable excess of 0.1M HCl. The suspensions transferred into a 50 ml volumetric flask with appropriate

volumes of 1.0M NaCl to adjust the ionic strength at 0.01., 0.1, 0.2, and 0.4. The volume bringing up to the mark with distilled water.

ii) The above mixtures are prepared again as above, but Cd^{2+} ions solution was added to attain 1:2 metal: ligand ratio.

iii) Blank mixtures were prepared contain no metal nor humic acids

       The whole volumes were transferred into titration vessels. Potentiometric measurements were made by using pH-meter (precision of 0.1 mV or 0.01 units of pH) using combination glass electrode (51935–00). Throughout the titrations N_2 atmosphere was maintained by slightly bubbling through the solution, at room temperature. The titrations were performed against standardized NaOH solution. The pH was recorded after addition of equal increments (0.1ml. titrant) after constant time intervals of 30 sec.

RESULTS AND DISCUSSION

       According to Calvin–Bjerrum, Irving and Rossotti, the average number of the protons associated with the reagent molecule, $\bar{n}_A$, was determined at different pH values by applying the following equation

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^o + E^o)}{(V^o - V_1)TC_L^o}$$

where Y is the number of available protons (Y = 2) and V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, V_o is the initial volume (50 cm^3) of the mixture, T_{CL} is the total concentration of the ligand, N is the concentration of sodium hydroxide solution, and E is the initial concentration of the free acid. The average number of the reagent molecules attached per metal ion, $\bar{n}$, and free ligand exponent, pL, can be calculated using the equations.

$$\bar{n} = \frac{(V_3 - V_2)(N^o + E^o)}{(V^o - V_3)\bar{n}_A TC_M^o}$$

and

$$pL = \log_{10} \frac{\sum_{n-o}^{n-J} \beta_n^H \left(\frac{1}{antilog\ pH} \right)^n}{TC_L^o - \bar{n}TC_M^o} \cdot \frac{V^o + V_3}{V^o}$$

Where $T_{C\ L}^{\circ}$, $T_{C\ M}^{\circ}$ is the total concentration of the ligand and metal ions present in the solution, $\beta^H{}_n$ is the overall proton—reagent stability constant. V_1, V_2, and V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, humic acid, and complex, respectively. The metal–ligand stability constants log K_1 and log K_2 values were obtained by point wise calculation method using the following equations:

$$log\ K_1 = pL - log\ (1\text{-}\overline{n}\,)/\overline{n}$$
$$log\ K_2 = pL - log\ (2\text{-}\overline{n}\,)/\,(\overline{n}\text{-}1).$$

Where log K_1 and log K_2 (stability constant of ML_1 and ML_2 complexes respectively)equal to the intercepts, on the y- axis, of the straight lines resulted the from plotting each of log $\overline{n}$ /1-$\overline{n}$ and log($\overline{n}$ -1) / (2-$\overline{n}$) against pL.

Chemical characteristics of HAss and HA$_{NWH}$

Table (1) shows the basic characteristics of the two humic acids extracts. The percent of carbon, hydrogen and nitrogen are in agreement with literature. **(Stevenson, 1982; Rice and MacCarth, 1991)**. HA$_{SS}$ has higher percent of nitrogen which may be due to pertinacious structures **(Deiana1990)**. As E$_4$/E$_6$ was taken as indication of humic acids molecular weights where as it decrease with increasing of molecular weight. HAss expected to have molecular weights lower than HA$_{NWH}$. HA$_{NWH}$ has lower acidity than HAss, but characterized by higher COOH content than HA$_{ss}$ in which phenolic OH groups predominates.

Table (1) : Chemical characteristics of HAss and HA$_{NWH}$
(C,H,N% on dry ash free base).

Properties	HA$_{NWH}$	HAss
C%	50.32	50.15
H%	05.84	4.26
N%	04.29	9.05
O%	39.55	36.54
E$_4$/E$_6$	4.301	4.92
T.A meq/g	2.92	6.56
COOH meq/g	1.40	4.47
OH meq/g	1.52	2.09

The dissociation constant values of COOH and phenolic OH acidic groups, pKa1 and pKa2 of each of the two acids were determined potentiometrically under the different ionic strength using Henderson-Hasselbach equation. The details are given in **(Badr et al., 2012)**. Table (2) summerizes the final results.

Table (2): PKa'S of HA_{SS} and HA_{NW} at different ionic strengths and Room temperature (26°C).

μ	Dissociation constants							
	HA_{SS}				HA_{NWH}			
	pKa_1	pKa_2	p Ka	β	pKa_1	pKa_2	p Ka	β
0.01	6.45	9.74	16.19	6.46×10^{-17}	6.75	10.10	16.85	14.22×10^{-16}
0.1	5.25	9.55	14.80	1.59×10^{-15}	6.50	10.30	16.80	16.03×10^{-16}
0.2	5.34	8.72	14.06	8.73×10^{-15}	6.90	9.20	16.10	4.60×10^{-16}
0.4	5.15	8.58	13.73	1.86×10^{-14}	6.70	9.80	16.50	32.0×10^{-16}

Binding constants of HAs - Cd $^{2+}$ complexes under different ionic strengths

The titration curves of: HCl, HCl +HA, HCl + HA + Cd ions for HA_{NWH} and HAss are given in Figure (1). The following remarks and observations can be pointed out:

-The cadmium ions solution used in the present study was dilute, according to **(Sanyal & Sengupta, 1990)** there was no possibility of formation of polynuclear complexes

- A deep brown precipitate of Cd-humate, was observed in the titration vessel which confirm the complex formation and indicating that the possibility of formation of metal hydroxide is excluded.

- The cadmium titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand.

- The pH at which the titration curve separation observed is affected strongly by the ionic strength of the solution. Higher ionic strength ($\mu=0.2$ and 0.4) leads to very low separation. This may due to reduction of metal ability to form strongly bound metal-organic compounds under the influence of complexing effect of chloride on metal ions.

- At higher pH, for all ionic strength studied, there are clear inflections points with more decrease in the in pH of the metal titration curves relative to ligand titration curves. This can be attributed to the hydrolysis of the metal ions species. (**Baker & Khalili, 2007**). In the formation of a hydroxo-complex, the substrate reacts with water, splitting a water molecule into hydroxide and hydrogen ions which result in pH decrease. Table (3) shows The pHs of hydrolysis inflection points for HAss and HA_{NWH} under different ionic strength . At $\mu = 0.01$,Cd- HAss complex hydrolyze at pH higher than Cd - HA_{NWH} complex.

Bjerrum, Irving and Rosstti functions $\bar{n}A$, $\bar{n}$ and PL of Cd^{2+} ions complexation by HA_{NWH} and HA_{ss} at the studied conditions were calculated. The graphical representation of log $\bar{n}/1-\bar{n}$ against pL of HA_{NWH} and HAss- Cd chelate at $\mu= 0.01$, 0.1, 0.2, and0.4 for ML complexes and are given in fig (2).

At $\mu = 0.01$, maximum values of $\bar{n}$ were in the range $0 - 2$, indicating the formation of ML and ML_2 in case of HAss and HA_{NWH}. At $\mu = 0.4$ the values of $\bar{n}$ were very small, indicating very week complex formation.

Table (3): The pHs of hydrolysis inflection points for HAss and HA_{NWH} titration curves under different ionic strength (μ) and room temperature.

	pH	
μ	**HAss**	**HA_{NWH}**
0.01	10.0	8.5
0.1	9.0	9.0
0.2	9.0	9.0
0.4	9.0	9.2

Table (4) shows the binding constants values at different ionic strength and the pH range at which the complexation occur for HAss and HA$_{NWH}$. These results show that the increase of the salt content of solution decrease the ability of HAss and HA$_{NWH}$ to bind Cd^{+2} ions. This results is in agreement with literaures **(Schnitzer and Hansen,1970; Reddad et al., 2002; Chen and wang, 2007 and Mercer et al., 2008)**.

The decrease in the ability to bind Cd^{2+} ions with increase of the ionic strength may be due to the conformational changes which may occur in these humic acids with the change in the suspension salt content **(Badr et al., 2012)**.

Accordingly, HA$_{SS}$ and HA$_{NWH}$ have strong ability to form complexes with Cd ions at low ionic strength and the pH range of 5-8. Also it can be concluded that the ability of humic acids extracted from Nile water hyacinth is stronger than humic acids extracted from sewage sludge.

Generally, ion exchange or outer-sphere surface complexation is influenced by ionic strength, whereas inner-sphere surface compexation is affected by pH values a **(Zhang et al., 2011) and (Chen and Wang, 2007).** Based on the above theory, one can deduce that ion exchange or outer-sphere surface complexation mainly contribute to Cd(II) binding on HA at pH 5- 8.5.In the outer sphere surface complexes, no covalent bonds formed. Thus, other interactions such as electrostatic attraction, hydrogen bonding, or hydrophobic attraction are responsible for the reaction

Infrared Study of Humic Acids Complexed by Cd^{2+} ions

In humic acids, the complexation ability has been attributed particularly to carboxylic groups and phenolic OH groups, but amine groups may also be involved **(Erdogan *et al.*, 2007)**. Fig. (3) Shows the FTIR spectra of HAss (a) and HA$_{NWH}$ (a$^-$). Both acids exhibit, generally similar spectra with the typical major peaks reported for humic acids. But HA$_{NWH}$ show more peaks than HAss, Which means that HA$_{NWH}$ has more functional groups. The similarity of the two spectra generally point to similar basic structures.

According to **(Iheoma et al., 2007; Erdogan et al., 2007; Jlkovic e t al., 2006 and Giovanela et al.,2004)** the major infrared absorption bands (in cm^{-1}) for HAss and HA$_{NWH}$ are assigned as follows :-
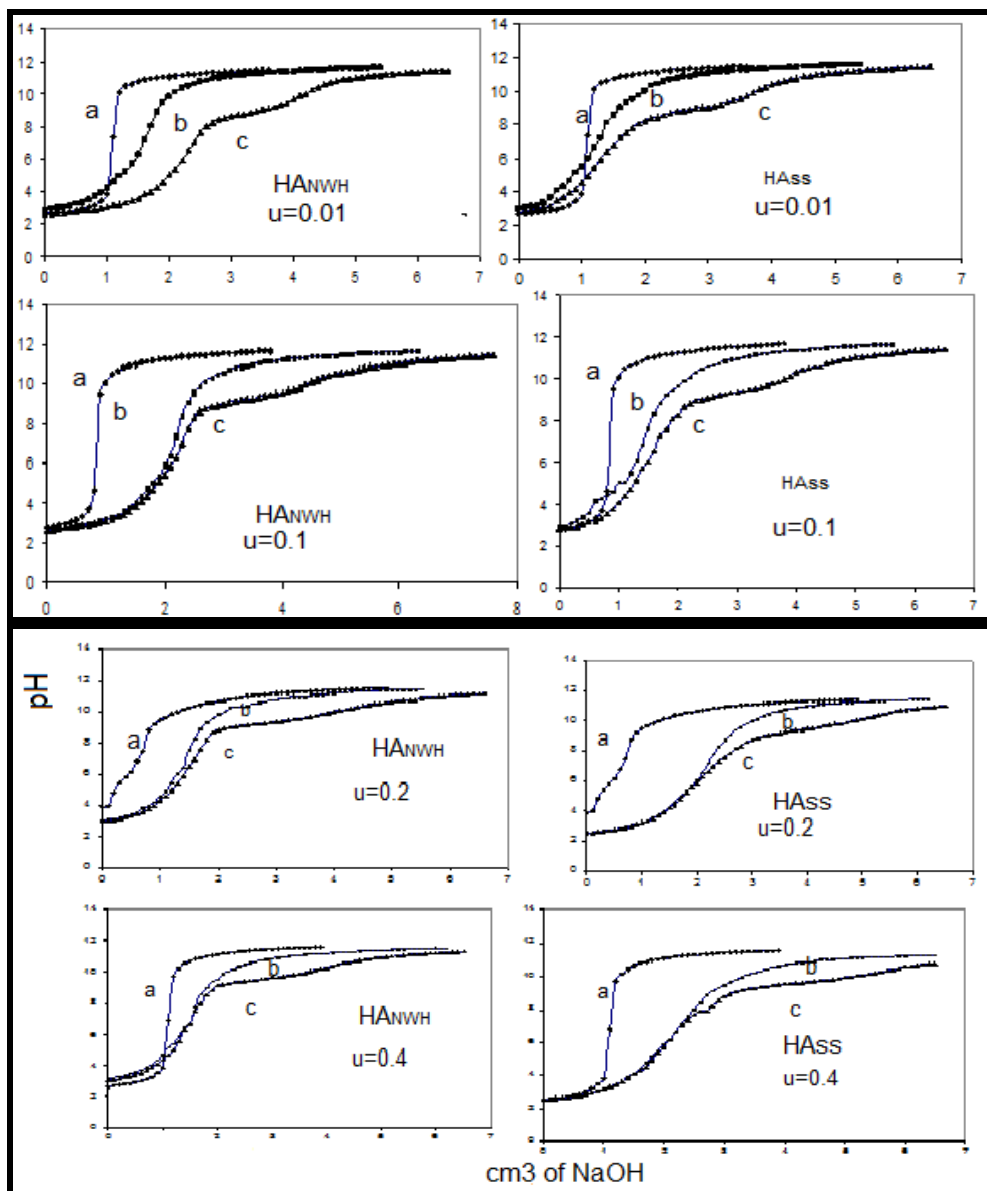
Fig (1): Titration curves of humic acids at different ionic strength,
t=26°C,(HCl blank)a,(HCl + HA)b, (HCl + HA + Cd + ions) c.
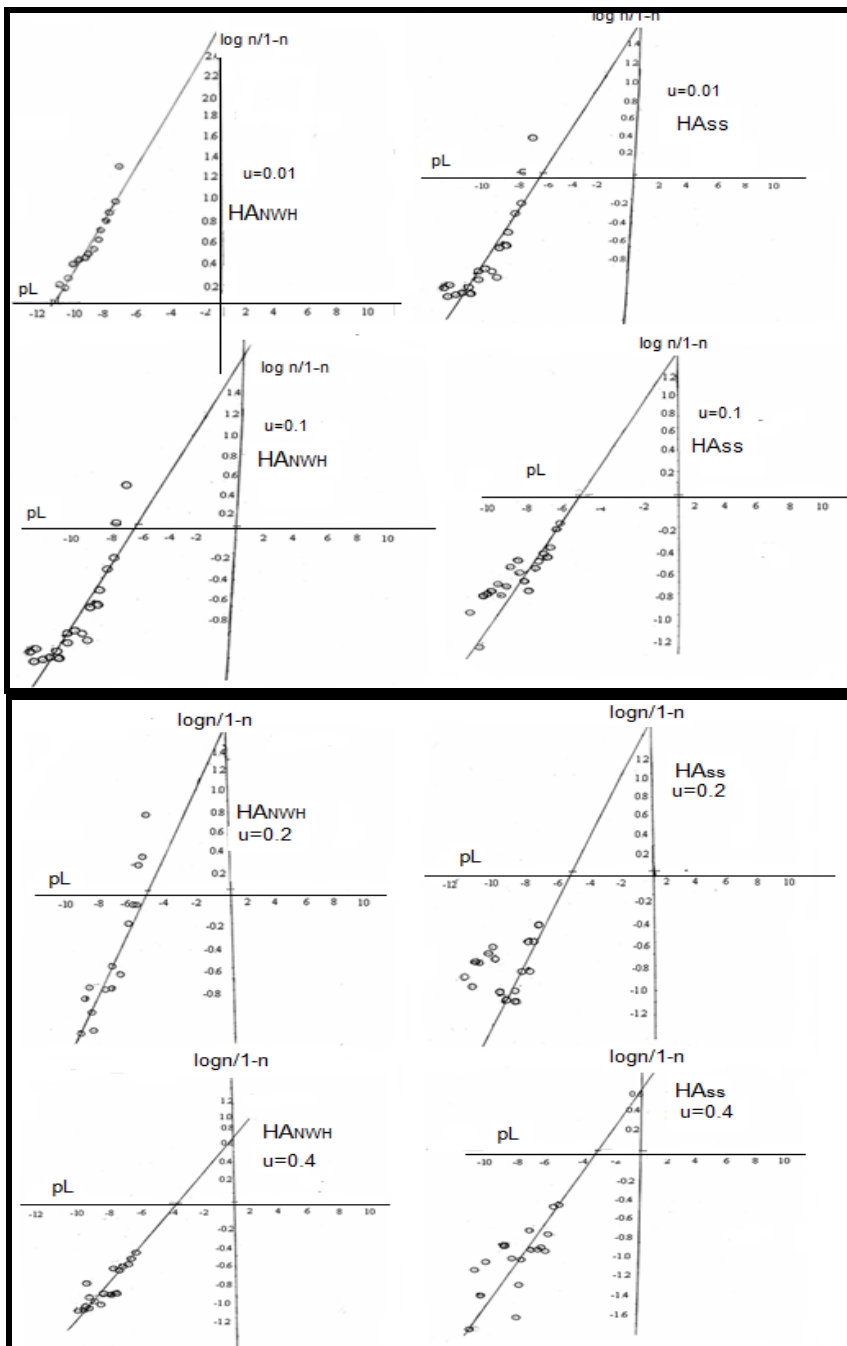
Fig(2): Linear formation plots of HAss-Cd and HA$_{NWH}$-Cd chelates at different ionic strength

Table (4): Binding constants of HAss and HA$_{NWH}$ with Cd^{2+} ions at different ionic strength and the pH range at which the complexation occur

-The peaks at region 3360 cm^{-1}, are assigned to OH stretching vibration and possibly NH stretching vibration, for intermolecular hydrogen bonding and /or (H-bonded OH groups) attributed to phenolic group

– Double band at region 2920 cm^{-1}, this band attributed to aliphatic C-H bands for which deformation appears at 1450 cm^{-1}.
1650 cm^{-1} region is attributed to C=C band, C=O and COO$^-$ groups, or to C=N amide I stretching.

- The band at region 1540 cm^{-1} corresponds to the amide II of protein - like substances, which is clearer for HAss.

-The band at region 1230cm^{-1} assigned to C=O stretching and OH deformation of COOH.

- The two bands at 1166 cm^{-1} and 1125 cm^{-1} are attributed C-O stretching of polysaccharide or polysaccharide like substances.

 -The band at region 1033 cm^{-1} due to ortho substitution, C-C-O of primary alcohol.

 - and the bands below 1000 cm^{-1} (915 cm^{-1} and 687 cm^{-1}) suggest the presence of substituted aromatics
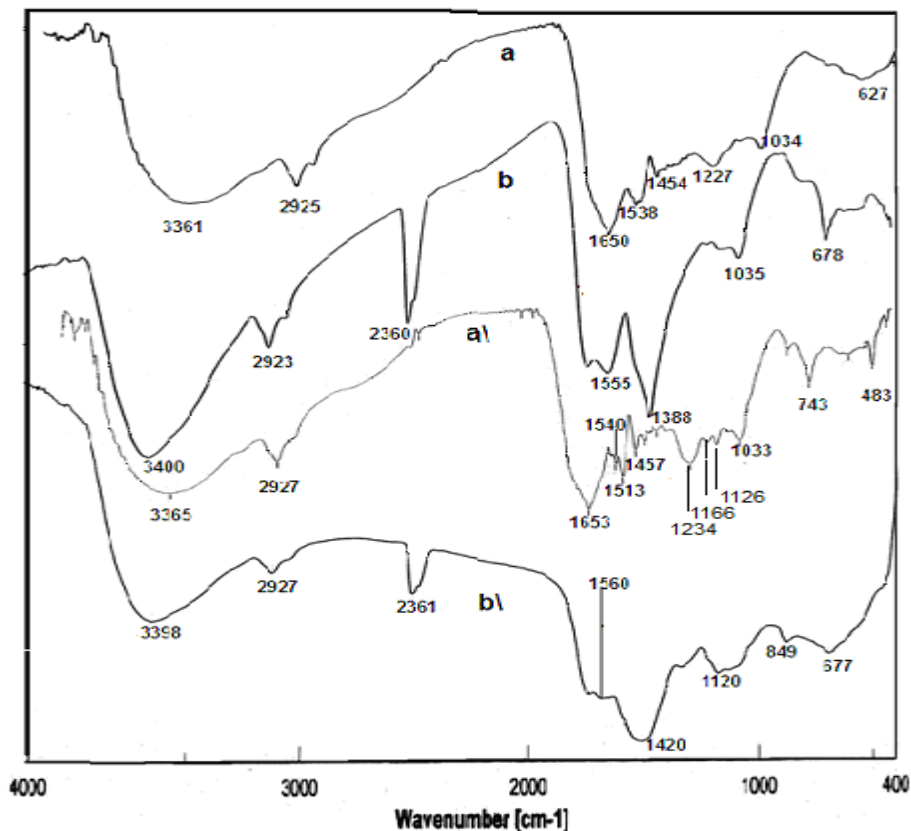
Fig. (3): Complexation of HAss and HA$_{NWH}$ by Cd^{2+} ions as revealed by FTIR spectra, (a,a$^{\backslash}$) FTIR spectra of HAss and HA$_{NWH}$, (b,b$^{\backslash}$) for their Cd - complexes respectively

IR spectra of the metal complexes are shown in Fig. (3-b, b$^{\backslash}$).The spectra affirm the binding of Cd^{2+} ions by the two acids. They show the potential sites which participate in complexation in case of HAss are different from those used within HA$_{NWH}$. For HAss there is:

- Sharpening of IR band at about 3360cm^{-1} (OH peak) and hypsochromic shift (blue shift) of the band to higher frequencies ($\Delta \upsilon^{-}$ = 39 cm^{-1}.) This owing to the influence of a change in environment which may be due to increased hydrogen bonding results from the occurrence of hydration water.

- Sharpening of IR band at 1650cm^{-1} and the disappearance of the band at 1220 cm^{-1} for the free acid, which is assigned to C=O stretching and

OH deformation of COOH, and the appearance of a new bands at the region 1380 cm^{-1}(antisymmetric COO$^-$ stretching **(Khalili,1990)** suggest the conversion of COOH groups to the COO$^-$ form.

-The appearance of the band at the region 1540 cm^{-1} in case of HAss and HAss-Cd complex indicate that nitrogen atom doesn't participate in binding of Cd^{+2} by HAss.

-Sharpening and strengthens of IR band at 627 cm^{-1}, indicate the participation of aromatic substitution.

-The binding of Cd by both humic acids lead to development of narrow sharp peaks at 2330 – 2360 cm^{-1}. This peak does not present in the spectra of both free humic acids. It can be assigned to Cd—O bond formed after complexation.

According to the above difference between the ir spectra of HAss and HAss- Cd,-complex, HAss binds of Cd^{2+} through two COOH groups or one COOH and one phenolic OH side groups aromatic substitution. The mode of binding and the hydrolysis of the formed complexes are in agreement with that proposed by **(Stevenson, 1976)** for binding of metal ions with humic acids. Accordingly the Cd^{2+} binding and the hydrolysis of the formed complex can be represented as given in Fig (4).

Cd^{2+}binding by HA$_{NWH}$

The IR spectra of HA$_{NWH}$ –Cd complex show disappearance of the active sites bands at 1653cm^{-1}, at1540 cm^{-1} region and at 1234 cm^{-1} which indicate the participation of COOH and nitrogen in amide I and amide II moieties. The appearance and strengthen of the bands at 1420 cm^{-1} (antisymmetric COO$^-$ stretching) support the occurrence
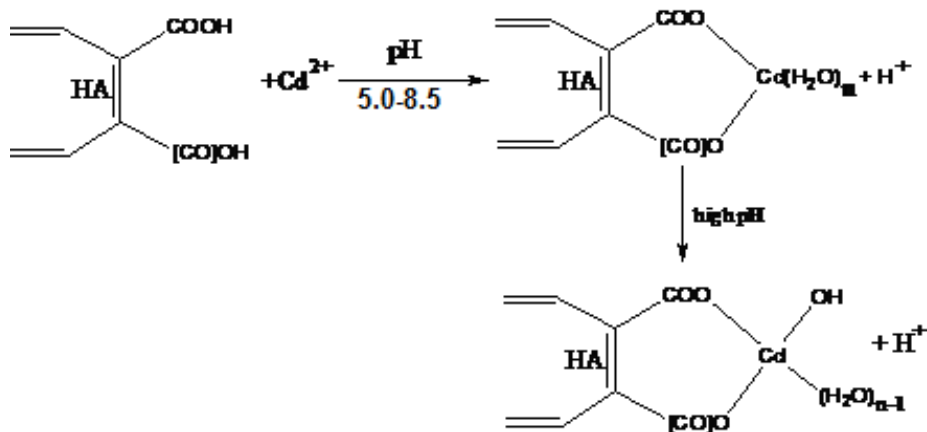
Fig (4): Proposed structure for Cd binding by two COOH sites or one COOH and one OH group in case of HAss and the hydrolysis of the formed complexes at higher pH.

of the binding reaction. The observed great difference between the free HA_{NWH} and HA_{NWH} –Cd complex spectra indicate the formation of strong chelate compound.

CONCLUSION

Both HA_{SS} and HA_{NWH} have ability to form complexes with Cd^{2+} ions at low ionic strength and at pH range of 5-8.5. The rise in pH leads to hydrolysis of the formed complexes. Also it was found that the increase of the salt content of solution decrease the ability to bind Cd^{2+} ions. The results showed noticeable higher stability constants of HA_{NWH}-Cd complex than HA_{ss}-Cd complex. According to the IR spectra Cd^{2+} ions are bound preferentially to two COOH or COOH and OH groups in case of HAss. The IR spectra of HA_{NWH} –Cd humate shows the participation of nitrogen atoms and COOH groups in binding of Cd $^{2+}$ ions by HA_{NWH}, which lead to formation of stronger chelate complex. Accordingly, the use of HA_{NWH} may be more effective in removing Cd^{2+} ions from aqueous solutions.

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المقارنـة بين ترابط نوعين من أحماض الهيوميك مع ايونات الكادميوم (II)
بواسطة دراسات المعايرة الجهدية وطيف الأشعة تحت الحمراء

مجدة حسين ابراهيم ¹ ، محمد الحلفاوي حسن ² ، ابتهار عبد العال زيد ³

¹ استاذ مساعد بقسم الكيمياء، كلية العلوم جامعة الأزهر (بنات)، ² أستاذ المياه و التربة بكلية الزراعة، جامعة الإسكندرية ، ³ طالبة بحث بكلية العلوم، جامعة الأزهر (بنات) .

تم إستخلاص أحماض الهيوميك من حمأة مياه الصرف المعالجـة HA$_{SS}$ ومن ورد النيل المتحلل HA$_{NWH}$ ودراسة خواصهما الكيميائية والطيفية ،وقد تم إجراء تفاعلات التراكب بين ايونـات الكـادميوم والاحمـاض بالنسـب المبينـة في البحـث، تحت ظروف مختلفـة مـن قوة الايـون بإسـتخدام كلوريـد الصـوديوم . وقد استخدمت تقنيـة المعـايرة الجهدية لـ Calvin–Bjerrum والمعتمدة من Irving and Rossotti في حساب ثابت التكوين، و قد تم تحضير المتراكبات الصلبة ودراسة طيف الاشعة تحت الحمراء لها.

أظهرت النتائج أن كلا HA$_{SS}$ و HA$_{NWH}$ لديه القدرة على تكوين متراكبات قوية مـع الكـادميوم (II) في حالة انخفاض القوة الأيونيـة ، في نطـاق الأس الهيدروجيني من ٥–٨،٥ وأن ارتفاع الرقم الهيدروجيني يؤدي إلى تميه المتراكبات المتكونة. كما تؤدى الزيادة في محتوى المحلول من الملح إلى ضعف ثبات المتراكب.

أظهرت النتائج زيـادة ملحوظـة في ثوابت الاستقرار لمتراكب HA$_{NWH}$ مـع أيونـات الكادميوم بالمقارنة مع HA$_{SS}$ ، وبناء على أطياف الأشعة تحت الحمراء فإن HA$_{SS}$ يرتبط بأيونات الكادميوم بواسطة مجموعات الكربوكسيل و مجموعات الهيدروكسيل ، أمـا فى حالـة HA$_{NWH}$ فإن ذرات النتروجين الموجودة فى مجموعات الاميد الفعالة تشارك فى التفاعل مما يؤدى تكوين متراكبات كلابية قوية. وبناء على هذة الدراسة فإن استعمال احماض الهيوميك المستخلصة من ورد النيل تكون أكثر تاثيرا فى إزالة ايونات الكادميو م من المحاليل المائية.