# SUMMARY

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The aim of this thesis is to study the interaction of some metal ions, of nuclear and environmental importance, with the most widely distributed materials on the earth's surface; humic materials.

The metal ions investigated are $Cs^+$, $Pb^{2+}$,$Co^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Th^{4+}$and $La^{3+}$, in addition to the radionuclides $^{60}Co$, $^{(152-154)}Eu$ and $^{137}Cs$. The study involved separation, purification as well as characterization of humic fractions, (humic acid, fulvic acid and humin) and the determination of the parametrs that govern the interaction of these ligands with the metal ions. The fulvic acid sample used in these studies is separated from organic soil (peat), a sample of humin (Hn) and soil humic acid (SHA) are separated from agricultural soil and a sample of humic acid (ICHA) was separated from the bottom sediments of Ismailia canal.

The characterization methods include elemental analysis. potentiometric titration, infrared and UV-visible spectroscopies. The thesis is classified into three chapters.

<u>Chapter one:</u> The introduction, contains some aspects of the radionuclides (natural and artificial) in the environmental, the essential properties of the investigated elements and the properties of humic substances with a special emphasis on their: occurrence, formation, fractions, extraction and characterization, with a reference to the elemental content, the reactive functional groups, the spectroscopic characteristics and the potentiometric titration. This part is ended with some information about the molecular weight of humic substances, their structure, properties, uses and a survey for peat humic substances, with reference to ion selective electrode.

**Chapter two**: the experimental, includes: The source of samples and the methods of separation, purification and characterization of humic materials. This chapter includes also the preparation of the investigated radioactive tracers; the different chemicals used, the instrumental procedures applied for the preparation of the organic and aqueous solutions for the ion selective electrode and radiometrical investigations, and the working procedures used.

**Chapter three:** the results and discussion, includes the experimental results and their explanation as follows:

### 1-Characterization of humic materials:

#### a) Elemental analysis:

The elemental analysis of the humic materials indicates that the humic compounds have nearly identical elemental composition. The O/C ratios of humic acid samples were found around 0.6 while for fulvic acid it found of higher ratio (0.7) and for humin it was of lower ratio (~ 0.5). The H/C ratios are clustered around 1.0 for humic and fulvic acid samples. The ratio in case of humin is higher (1.3), which indicates a lower degree of unsaturation and a higher aliphatic character in both humic and fulvic acids.

#### b) The $pK_a$ values and the carboxylate capacities

The investigated humic compounds were titrated potentiometrically to evaluate the total carboxylate capacities which were calculated from the second maxima of the first derivative to be 6.00, 6.60, 7.75, 12.96, 7.75 and 5.81 meq OH /g for PFA, ICHA, BHA, GHA, SHA and humin, respectively. The $pK_a$ at 50% ionization ($\alpha = 0.5$) were found 2.94, 4.625, 4.25, 3.81, 4.56 and 5.99 for PFA, ICHA, BHA, GHA, SHA and humin, respectively.

### c) The IR spectroscopy:

The infrared analysis of the investigated humic materials were found to have more or less similar spectra with a variety of bands that are in good agreement with the results of the titration; indicating the major constituents of the humic materials (aliphatic, aromatic, carboxylic,.....) and the purity of these samples.

### d) Ultraviolet and visible spectroscopy

UV-visible spectroscopy is useful in the estimation of the degree of humification using the $E_4/E_6$ ratio by measuring the absorbancies of dilute aqueous fulvic and humic acid solutions at 465 and 665 nm. The values of the $E_4/E_6$ ratio were found 4.07, 4.03, 5.79 and 6.00 for ICHA, BHA, SHA and PFA, respectively.

The data obtained indicates that PFA and SHA have higher $E_4/E_6$ ratio than the other fractions. This means that it has a low aromatic condensation and smaller molecule which contains less carbon, more oxygen and – COOH groups. The results of $E_4/E_6$ ratio, elemental composition, potentiometric titration and IR spectra of the investigated humic materials indicate that they are in good agreement with each other.

### d) Functional group analysis

The determination of functional groups of humic acid is based on the acidic properties of the group involved. The values of oxygen-containing functional groups in ICHA was found 856, 495, 360, 676.5, 316 and 793 for total acidity, COOH, phenolic OH, total OH, Alcoholic OH and carbonyl C=O, respectively. The data obtained were found in agreement with that obtained prevuiosly.

## 2- Interaction of humic materials with metal ions

### A) Cs –humate complexation

### I) Radioactive investigations

#### a) Effect of shaking time

The formation of Cs-humate complex was studied radiometrically using $^{137}Cs$. The process was carried out by shaking the system at different periods of time, as a preliminary test, to know the suitable time of equilibration. The formation of complex increases with time and becomes constant at 60 minutes, which was taken as the minimum time needed for the reaction.

#### b) Effect of metal ion concentration

The Cs-humate precipitate was found to increase with increasing the metal ion concentration and the pH. A concentration of $10^{-3}$ g/l humic acid was completely precipitated by $10^{-3}$ M of $Cs^+$ ion at pH 5.8.

#### c) Effect of pH

The precipitation of $Cs^+$ by humic acid was found to increase by increasing the pH. This behaviour is discussed in the light of exchange properties of the hydrogen ions and their competitive effect for the available exchange sites. Increasing the pH of the solution results in an additional ionization of the acidic groups of the humic acid. This can enhance the attraction of the $Cs^+$ cations to the humic acid, with subsequent formation of Cs-humate complex.

#### d) Effect of humic acid concentration

The formation of Cs-humate complex was found to increase by increasing humic acid concentration where $10^{-3}$ M of $Cs^+$ precipitated $10^{-3}$ g/l of humic acid.

## II) Ion-selective electrode investigation

### A) Cs-humate complexation

The formation of Cs-humate complex was studied using ISE after calibration of the sensor by $Cs^+$. The effect of shaking time, metal ion concentration, and humic acid concentration were studied. It was noted that the behaviour is almost similar to that obtained radiometrically where the time needed for equilibration was found 60 minutes.

### B) Cs-fulvate complex

The complexation of $Cs^+$ with fulvic acid was studied by ISE. The effect of metal ion concentration and fulvic acid concentration were investigated and found that fulvic acid has no ability to complex with $Cs^+$.

### C) Sorption of $Cs^+$ by humin

The sorption of $Cs^+$ by humin was studied by the batch technique using ISE and the percentage of uptake values were calculated.

#### a) Rate of uptake

The rate of sorption of the investigated element showed a sharp increase in % uptake with increasing the time then attains a constant value after equilibration at 60 minutes.

#### b) Humin weight

The results indicated that the percentage of uptake increases sharply with increasing the humin weight then becomes constant after saturation at 0.01 g of humin.

### b) Effect of metal ion concentration

The percentage of uptake of $Cs^+$ by humin was found to decrease by increasing the metal ion concentration. This behavior is attributed to the saturation of humin by the metal ion and the consumption of the exchangeable protons of the acidic groups in the humin molecule.

### B) Lead-humate complex

The formation of Pb-humate complex was studied using ISE after calibration for the sensor by $Pb^{2+}$. The effect of shaking time, metal ion concentration, and humic acid concentration was evaluated using the sensor. The time required for equilibration was found 20 minutes.

### C) Lead-fulvate complex

The complexation of $Pb^{2+}$ with fulvic acid was investigated by ISE. The effect of shaking time, metal ion concentration and fulvic acid concentration was evaluated. The free metal concentration was found to decrease gradually with the time, showing an increase in the formation of lead-fulvate complex.

### D) Sorption of $Pb^{2+}$ by humin

The sorption of $Pb^{2+}$ by humin was studied by the batch technique using ISE and the percentage of uptake values were calculated.

### a) Rate of uptake

The rate of sorption of the investigated element showed a sharp increase in % uptake with increasing the time then attains a constant value and the equilibration time was 30 minutes.

### b) Humin weight

The results obtained indicated that the percentage of uptake increases sharply with increasing the humin weight then it becomes constant after saturation at 0.15g of humin.

### c) Effect of metal ion concentration

The percentage of uptake of lead by humin was found to decrease by increasing the metal ion concentration. This behavior is attributed to the saturation of humin by the metal ion and the consumption of the exchangeable protons of the acidic groups in the humin molecule.

### d) Effect of competing cations on lead-humate complex

The lead-humate complex was prepared and investigated using ISE. The competition effect of the investigated cations on the formation of lead-humate complex was studied using radioactive isotopes of $^{137}Cs$, $^{60}Co$ and $^{(152\text{-}154)}Eu$. The results indicated that $Pb^{2+}$ forms a stable lead-humate complex.

### F) Disposal of radioactive waste by humic materials

The decontamination of radioactive waste solution of the radioelements $^{137}Cs$, $^{60}Co$ and $^{(152\text{-}154)}Eu$ depends on the interaction of these metal ions with humic acid or humin.