

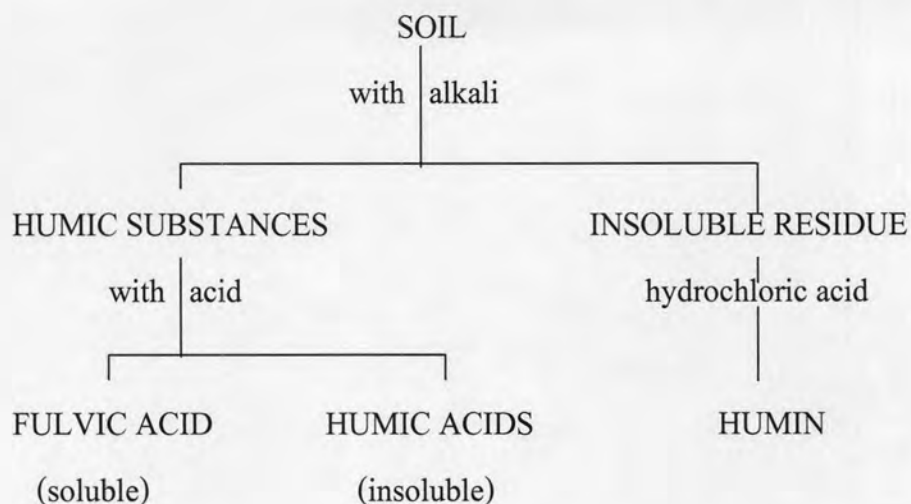
## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Humic acids

##### 2.1.1 Definition [1]

The humic matters are defined as a series of naturally occurring high molecular weight, amorphous, polydispersed substances with yellow to brown-black color. They are hydrophilic and acidic molecules which are the main component of organic matter in soil and natural water. They come from the decomposition of organic matter and the process is called humification. They are usually obtained from soils by extraction, fractionation and isolation procedures with basic and acidic solutions. The humic matters can be classified, according to their solubility characteristics in aqueous media, into three main subclasses (Figure 2.1): humic acids (HAs), the soluble fraction of humic substance at high pH values; fulvic acids (FAs), the soluble fraction of humic substances under all pH conditions and humin, the insoluble fraction of humic matter under all pH condition.

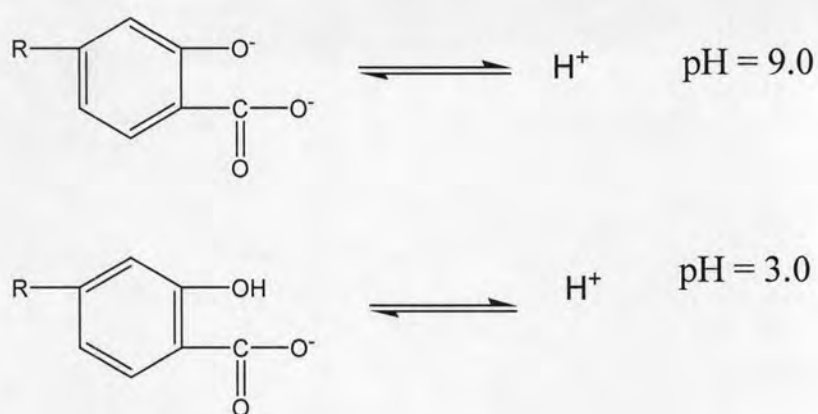


**Figure 2.1** Flow sheet for extraction of humic substances from soils, peat and other terrestrial deposits [1].

Humic acids are large complex molecules with molecular weight about 2,000-400,000 Dalton and their formula are from  $C_{10}H_{12}O_5N$  to  $C_{72}H_{88}O_{38}N_4$ . Humic acids have aromatic rings in their structure with carboxylic ( $-COOH$ ) and hydroxyl ( $-OH$ ) groups. The solubility of humic acids in aqueous solution mostly depends on a number of  $-COOH$  and  $-OH$  groups in their molecule. The increasing in number of these functional groups results in the increasing in the solubility.

### 2.1.2 Functional groups and intrinsic property

**Carboxyl groups** give acidic characteristic to the humic molecule and make humic acids exhibit charge properties, and have the capacity to adsorb and exchange cations. These carboxyl groups will dissociate their hydrogen atoms at pH 3.0 as shown in Figure 2.2 [1].



**Figure 2.2** Development of variable of changes in humic molecule by dissociation of protons from carboxyl groups at pH 3.0, and from phenolic-OH groups at pH 9.0.

**Hydroxyl groups** in humic acids can be classified into three major types: total hydroxyls, phenolic-hydroxyls and alcoholic hydroxyls;

*Total hydroxyls* are the OH groups which associated with all functional groups, such as phenols, alcohols and hydroquinones but refer only to the sum of phenolic and alcoholic OH groups usually measured by acetylation.

*Phenolic hydroxyls* are OH groups attached to aromatic structures.

*Alcoholic hydroxyls* are OH groups associated with nonaromatic carbon.

The hydroxyl groups exhibit the same characteristics as the carboxyl groups. They will dissociate their protons at pH 9.0 as shown in Figure 2.2.

### 2.1.3 Chemical composition and characteristics

#### 2.1.3.1 Carbon and nitrogen content

Some of carbon and nitrogen amount in the humic acid molecule come from the starting organic matters and microbial cells during the humification. It is generally believed that the C/N ratio will also decrease with increased rate or degree of humification, and C/N ratios between 10 to 15 are often considered to be characteristic for well-developed humic acids.

### 2.1.3.2 Atomic percentage

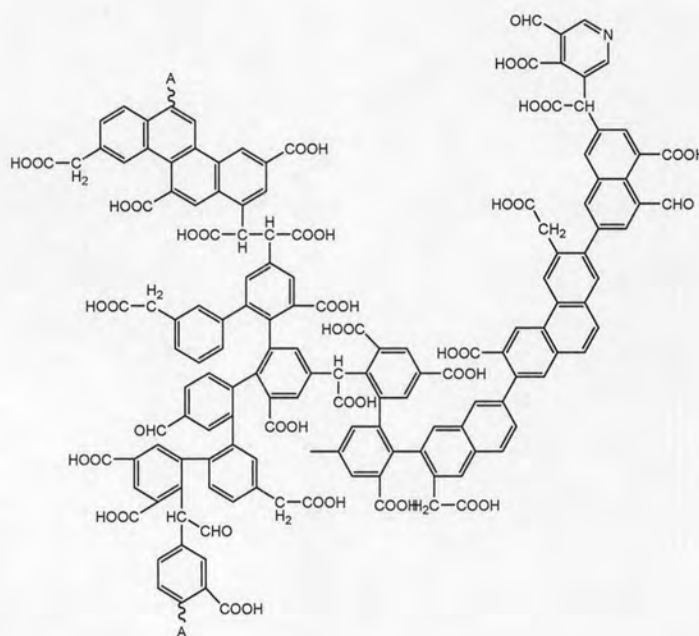
The composition of humic acids contains approximately one atom of oxygen to two atom of carbon and there is at least one hydrogen atom for every carbon atom. The percentages of nitrogen atom are approximately twice larger than in fulvic acids of terrestrial soils.

### 2.1.3.3 Aromaticity

Aromaticity of humic acids is defined as a percentage of aromatic moieties relative to the aliphatic substances. This data is importance for assessing the origin, stability, and chemical behavior of humic acids. The twice higher percentage of aromaticity in humic acids than fulvic acid is a result from the humification process.

### 2.1.3.4 Molecular structures

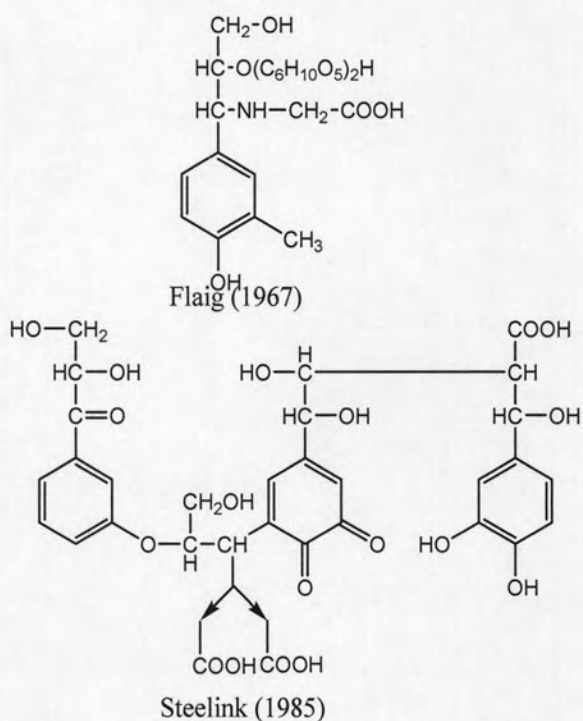
The supramolecular architecture of humic acids illustrated in Figure 2.3.



**Figure 2.3** Supramolecular architecture of humic acid [1].

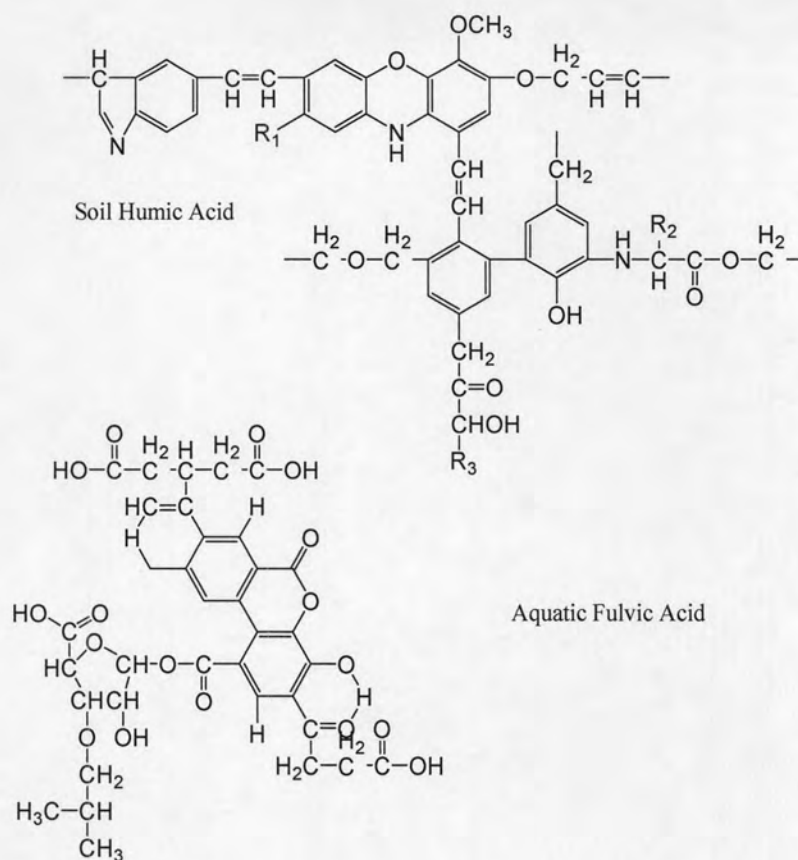
There are some methods and opinions presented in the construction of molecular structures of humic acids [1] which are shown below;

**Structures based on the ligno-protein** designs that humic acids are based on lignin monomer units as shown in Figure 2.4.



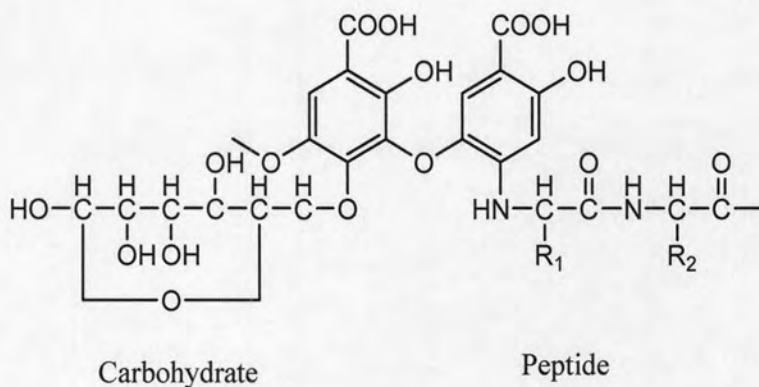
**Figure 2.4** Humic acid structures according to the lingo-protein concept.

**Structures based on the phenol-protein** show complex networks of phenol units linked together by other carbon unit, presented in Figure 2.5.



**Figure 2.5** Structure models according to the phenol-protein theory.

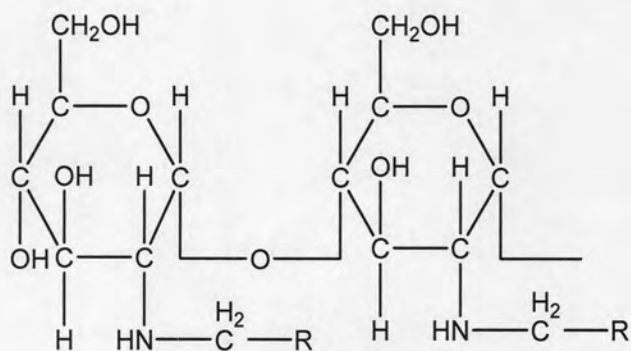
Structures based on the phenol dimer concept of Stevenson show the linkage of two phenol units to which a protein is attached as the basic or smallest unit of a humic molecule (Figure 2.6).



**Figure 2.6** A structure model of humic acid based on the dimer concept of Stevenson [4].

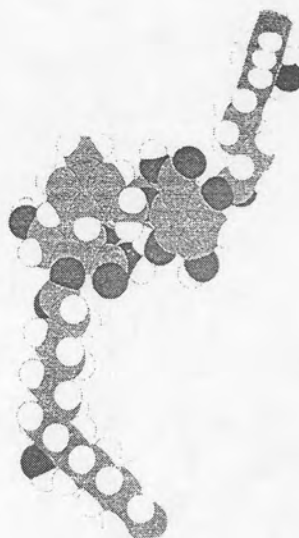


**Structures based on the sugar-amine condensation concept** which show the key components for an aquatic humic structure that are sugar and amine or amino acid, and no lignin derivatives are required. A structural model of such a humic acid is illustrated in Figure 2.7.



**Figure 2.7** A structure design showing the linkage of two glucosamine molecule forming humic acid according to the sugar amine condensation theory.

**Structures based on a computer modeling** have been made to design molecular structures for humic acids (Figure 2.8).



**Figure 2.8** A Black and white three-dimensional computer model of a hypothetical humic acid decamer structure: C = shaded grey, H = white, O = black, and N = not shown [5].

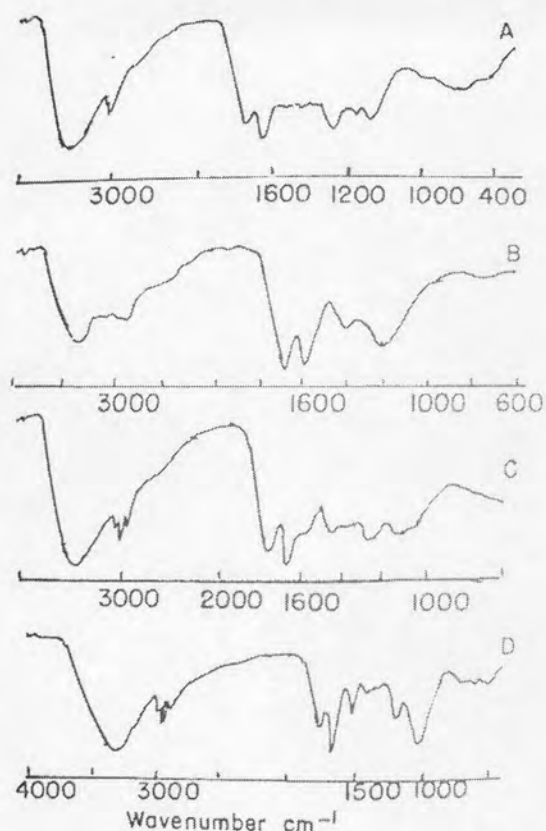
#### 2.1.4 Extraction, Fractionation and Characterization

The International Humic Acid Society (IHSS), Soil Science Society of America has published a general procedure for the fractionation and isolation of humic substances from soil. The method recommended that NaOH was the most effective for the quantitative removal of humic matters [4]. The preparation of pure humic acids and fulvic acids require additional refining steps, such as reprecipitation and HCl / HF treatment for the removal of inorganic impurities.

Several methods have been used to separate and characterize humic acids. The chromatographic technique based on size exclusion appeared to be the most useful. Electrophoresis methods provide the detailed characterization of humic substances. Gas chromatography with mass spectrometric detection was typically used to identify the products of pyrolysis or thermochemolysis of humic substances. Furthermore, chemical modification has enabled NMR spectrometry to become one of the most powerful analytical tools for revealing structural entities [6]. Fong and Mohamed [7] studied the characterization of humic acids by using sized exclusion chromatography, FTIR, UV-Vis, acid-base titration, and elemental and total hydrolysable carbohydrate analyse. Also in the study of Burba and coworkers [8] used membrane filtration to investigated the molecular size of humic substances.

Owing to humic acid structure is very complex, infrared spectroscopy seems to be the most used technique for its characterization. The main features of the IR spectra [9] are (a) a common, intense broad band at about  $3,400\text{ cm}^{-1}$  usually attributed to O-H stretching and secondarily, to the N-H stretching of various functional group; (b) a strong aliphatic C-H absorption band between  $2980$  and  $2920\text{ cm}^{-1}$ , and (c) two strong absorption bands for carbonyls and carboxyls in  $\text{COO}^-$  at  $1720$  and  $1650\text{ cm}^{-1}$ , respectively. In addition, the humic acid spectrum lacks the strong band at  $1000\text{ cm}^{-1}$  (Figure 2.9).





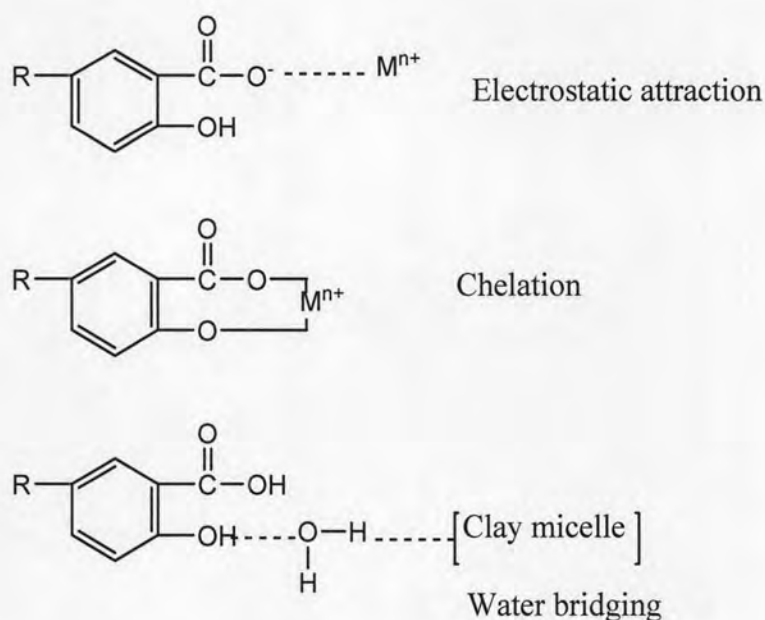
**Figure 2.9** Infrared spectra of humic acids from different sources [4,10].

Moreover, the interesting study of Hernandez and coworker [9] used fluorescence spectroscopy to characterized the contents of humic acids.

### 2.1.5 Metal complexation and chelation of humic acids

Metal ions can form complex with humic acids through electron-pair sharing of the carboxyl and hydroxyl functional groups. The resulting product is called a metal coordination compound, which can be in the form of cations, anions, or neutral molecules. The metal is the electron-pair acceptor, whereas humic acids are the electron-pair donors. The number of ligands bonded to the metal ion in a definite geometry depends on the coordinated number of the metal. The most common metals which can form complex to humic acids are the transition metals.

When a ligand binds the metal ion with two or more donor functional groups to form a ring structure is called chelation. Figure 2.10 shows the differences between adsorption, complexation or chelation between a metal ion and humic acids. Adsorption is an electrostatic attraction of metal ion by the negative charge of the humic acid surface, while complexation is a coordinate covalent bonding through electron pair sharing.



**Figure 2.10** Adsorption or electrostatic attraction by humic acid (top), complex or chelation reaction (middle), and water bridging or coadsorption (bottom).  $M^{n+}$  = cation with charge  $n+$ , and R = remainder of humic acid molecule [1].

More studies show the ability of humic substances to form complex with metal ions, such as cadmium, lead, copper, zinc and thorium [11-14]. The results showed these metal ions can form complex with humic substances at the acidic functional groups. The capacities of complexation may be related to the occurrence of a number of carboxyl and phenolic hydroxyl groups [12].

In addition, a research work suggested that humic acid can reduce the poison of a heavy metal in soil and water by forming a complex with such metal ion [15, 16]. The highest amount of humic substance to be bonded with metal equals to binding capacity of

such type of humic acid [17]. There are competitions between different metal ions, proton and organic matter to bond with humic substance, thus the ligand and pH of wastewater directly affect the efficiency of humic substance in bonding with heavy metals [11, 12].

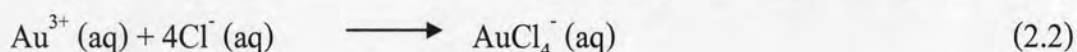
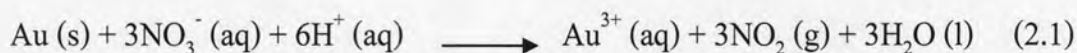
## 2.2 Heavy metals

The background information of the studied metals is summarized as follows.

### 2.2.1 Gold [18]

Gold is very unreactive metal but it can form ions. Gold ions in solution do not normally occur, but solution can be prepared. Gold ion is referred to as  $\text{Au}^{3+}$  or gold(III).

Aqua regia is the most common solution which can dissolve gold. It is the combination of two acids because nitric acid is a powerful oxidizer, which will actually dissolve a virtually undetectable amount of gold, forming gold ions ( $\text{Au}^{3+}$ ) while hydrochloric acid provide ready supply of chloride ions ( $\text{Cl}^-$ ), which reacts with the  $\text{Au}^{3+}$  to produce chloroaurate anions ( $\text{AuCl}_4^-$ ) in solution. The appropriate equations are:

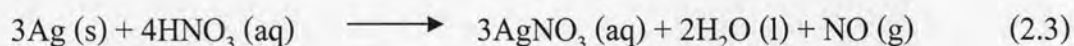


The species  $\text{AuCl}_4^-$  is very stable in all concentration range of HCl, and does not trend to dissociated to  $\text{AuCl}_3$  or positively charged ions.

### 2.2.2 Silver [19]

Silver occurs in four oxidation state in nature: 0, I, II and III and Ag(I) are the most common while II and III species are rare.  $\text{Ag}^+$  is very reactive species and forms stable

complexes with negative binding sites in suspended soils and sediments. Silver nitrate ( $\text{AgNO}_3$ ) is the most important compound of silver, it is used to prepare other silver salts, to silver mirrors, and as a reagent in analysis. Silver nitrate crystals can be produced by dissolving silver metal in a solution of nitric acid and evaporating the solution. The equation is as follows:



Silver nitrate is very soluble in water.  $\text{Ag}^+$  is stable in solution in the pH range of 0-12, in higher pH media, it can form  $\text{Ag(OH)}_2$  and  $\text{Ag}_2\text{O}$ .

Soluble silver salts is very effective against bacteria and other lower life. The bioavailability and toxicity of Ag depended on water hardness, pH, alkalinity,  $\text{Cl}^-$  and dissolved organic carbon.

### 2.2.3 Cadmium [19]

Cadmium is a transition metal in group II-B of the periodic table which almost always divalent in all stable compounds. It is soluble in nitric acid solution. In solution with  $\text{pH} < 4$ , all of dissolved cadmium will exist as the free  $\text{Cd}^{2+}$  while  $\text{CdHCO}_3^+$  and  $\text{CdCO}_3$  are dominant species when pH between 6 and 8.2 and at pH between 8.2 and 10, all of cadmium will exist as a neutral carbonate complex  $\text{CdCO}_3$ . A complexation of Cd with organic matter is weak because there is the competition for binding sites especially with Ca. Cd adsorption is also strongly influenced by the presence of competing cations such as divalent Zn.

Cadmium is an extremely toxic and very hazardous heavy metal. Kidney damage, and at high levels bone damage, are the main effects. Inhalation of vapors can lead to lung damage. Cadmium also is a frequent material in industrial waste discharges and has been introduced into water systems through mining operations.

It has also been employed in metal plating, where it is used as a sacrificial coating to prevent rust on steel.

#### 2.2.4 Chromium [19]

Chromium is in group VI-B of the periodic table. The most stable oxidation state of chromium is III but also occurs in the oxidation 0 and VI. It has two trivalent forms: the  $\text{Cr}^{3+}$  cation and the anion  $\text{CrO}_2^-$ , which forms coordinate readily with ligands containing O and N. The solution pH effect to the distribution of Cr(III) species.  $\text{Cr}^{3+}$  is dominant species when pH below 4 whereas  $\text{CrOH}^{2+}$  is dominant species when pH between 4 and 7 while there are some species of  $\text{Cr(OH)}_2^+$  and  $\text{Cr(OH)}_3$  occur when pH 5 to 11.

Chromium is used in harden steel, manufacture stainless steel, and form many useful alloys. It is mostly used in plating to produce a hard, beautiful surface and to prevent corrosion. Chromium gives glass an emerald green color and is widely used as a catalyst. The refractory industry uses chromite for forming bricks and shapes, as it has a high melting point, moderate thermal expansion, and stability of crystalline structure.

All compounds of chromium are colored. The most important chromate is those of sodium and potassium, the dichromates, and the potassium and ammonium chrome alums. The dichromates are used as oxidizing agents in quantitative analysis, also in tanning leather. Other compounds are of industrial value; lead chromate is chrome yellow, a valued pigment. Chromium compounds are used in the textile industry as mordants, and by the aircraft and other industries for anodizing aluminium. Chromium compounds are toxic and should be handled with proper safeguards.

#### 2.2.5 Nickel [19]

Nickel is in group VIII of the periodic table. It is soluble in dilute nitric acid, slightly soluble in hydrochloric and sulfuric acid but insoluble in water and ammonium hydroxide. The most common species in nature is 0 and II. Ni(II) is stable over a wide



range of pH and redox conditions. It can form complexes with organic ligands better than inorganic ligands.

Nickel is widely distributed in the environment. Nickel concentration in environment is related to the consumption of fossil fuels, emissions from nickel mining and refining, and by the incineration of wastes. Nickel dusts can rapidly damage the respiratory system and can cause occupation cancers, including lung cancer.

### 2.2.6 Lead [19]

Lead is in group IV-A of the periodic table. The common oxidation states are II and IV. The oxidation state in most inorganic compounds is II. The solution pH strongly effect to the species of lead.  $Pb^{2+}$  is important species when pH below 4 while  $Pb(OH)^+$  is important species when pH between 6 and 10 and  $Pb(OH)_2$  is important species when pH above 10.

$Pb(II)$  forms comparatively covalent bonds with some appropriate donor group in complexes, generally favoring sulfur and nitrogen over oxygen donors, and it may own some of its physiological action to replacement of the metals in some enzymes.

Low levels have subtle effects on the nervous system, while higher levels can lead to many symptoms, such as severe effects on the nervous system, including loss of sight and hearing, as well as symptoms of gout, headache, insomnia, anemia, kidney damage, diarrhea, stomach pains, intestinal paralysis and eventually death. Like other heavy metals strongly bound by biological complexing agents, lead is a cumulative poison and can act through long-term ingestion of relatively small quantities, Lead can be retained in the body for long periods, especially in bones, where it can replace some of the calcium.



### 2.2.7 Zinc [19]

Zinc is a nutritionally essential element. It is necessary for growth and is involved in several physiological functions. Some of zinc compounds can be hazardous. These include zinc chloride, zinc sulfate, zinc sulphide, zinc chromate and zinc oxide. Zinc oxide has been identified as the main cause of metal fume fever. Among its symptoms are headache, fever, chills, muscle aches and vomiting. The fume is irritating to the upper respiratory tract. An outdoor exposure to zinc chloride fume may also be encountered from smoke generators and smoke bombs. The ingestion of elemental zinc has been shown to cause lethargy. Eating large amount of zinc can cause stomach cramps, nausea and vomiting.

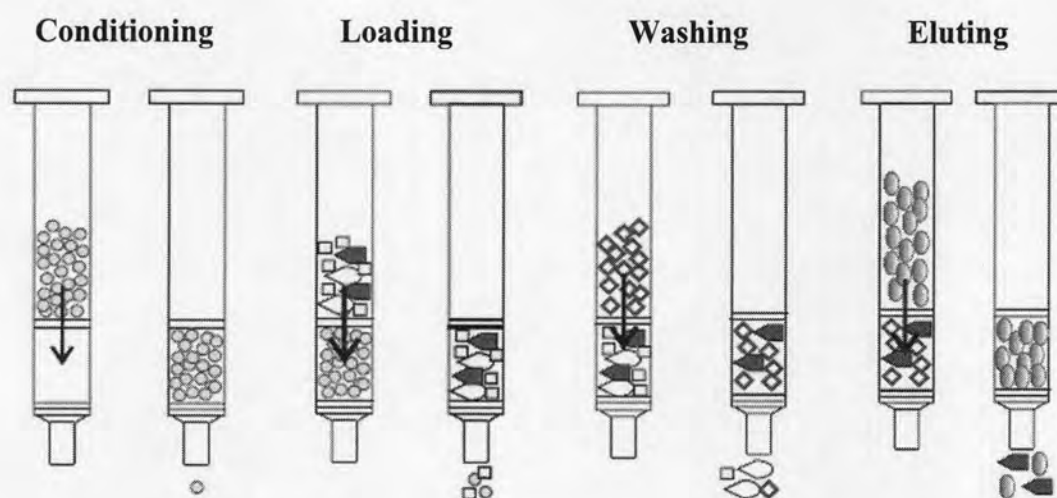
Zinc enters the environment in a number of ways. Some is released through natural process but most come from human activities such as mining, coal burning steel production and burning of waste. The oxidation state of zinc in nature is II. It is in group II-B of periodic table and occurs divalent in every its compounds. Several factors such as solution pH influence the soluble of zinc. In acidic solution, zinc is in the form of  $Zn^{2+}$  ion and its solution is colorless.  $Zn(OH)_2$  precipitates and it form  $Zn(OH)_4^{2-}$  complex.in high pH solution.

## 2.3 Solid-Phase Extraction

The solid-phase extraction (SPE) [20] is an effective method of separation or extraction of heavy metal ions from liquid sample. It is used in both wastewater and analytical purposes. The SPE technique consists of two methods; batch and column. The batch method is operated by mixing a suitable selected solid sorbent and a liquid sample for the desired extraction time, then the solid is separated and the retained species is eluted by an appropriate solvent. While the column method, more frequently used, consists of the

following steps. Firstly, the liquid sample was passed through a column packed with a suitable solid support, then the species retained on the sorbent in the column and finally, the retained species will be recovered by the elution with an appropriated solvent. Many sorbents such as activated carbon, silica gel, Amberlite XAD resin and other sorbents have been used for extraction of heavy metal ions from various matrix, but in this work, the new sorbent would be created by using humic acid immobilized on aminopropyl silica.

The basic principles of SPE column method mostly consists of three to four steps which are illustrated in Figure 2.11.



**Figure 2.11** SPE operation steps [20].

**Conditioning step:** The objective of this step is the remove of air in the column and fills the void volume with solvent. The nature of the conditioning solvent must be similar to the sample to ensure a good wettability of the functional groups of the sorbent. For aqueous samples, the conditioning solvent should have pH and ionic strength similar to the sample.

**Loading step:** Loading step is the percolation of the sample through the sorbent in the column which may be applied by gravity, pumping, aspirated by vacuum or by an

automated system. The sample flow rate should be optimized to ensure the quantitative retention along with minimization of the time required for sample processing. Matrix components may also be retained on the solid sorbent, some of them pass through, thus enabling some purification of the sample. The extractants are concentrated on the sorbent during this step.

**Washing step:** The washing of the solid sorbent with an appropriate solvent which have low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the desired extractants.

**Eluting step:** The retained species will be eluted by an appropriate solvent without removing retained matrix component. The solvent volume and the flow-rate should be correctly adjusted to ensure efficient elution.

### **2.3.1 Mechanisms of the retention of elements on the sorbent**

The mechanisms of retention depend on the nature of the sorbent, which may include simple adsorption, chelation, ion-pairing or ion-exchange.

#### **2.3.1.1 Adsorption**

Trace elements are usually adsorbed on a solid sorbent through van der Waals forces or hydrophobic interaction, which occurs when the solid sorbent is highly non-polar. The most common sorbent is octadecyl-bonded silica. Recently, polymeric reversed sorbent have emerged, especially the styrene-divinylbenzene copolymer that provides additional  $\pi$ - $\pi$  interaction when  $\pi$ -electrons are present in the analyte. However, because most trace element species are ionic, they will not be retained by such sorbents.

There was a study tried to explain the mechanism of the adsorption of metal ions on humic acids. Klucakova and Pekar [2] tried to propose a new adsorption model, which would be more correct from point of view of physical chemistry and surface reaction on

humic particles. Their assumption is that metal ions can form complex at the binding site of carboxylic, phenolic and enolic groups of humic acids. These binding sites are active centers, which only one layer can be formed on.

### 2.3.1.2 Chelation

Trace elements can form chelation with several functional groups. The atoms in the functional group, which will give an idea of selectivity of the ligand toward trace elements, most frequently present in the chelating agent are nitrogen (e.g. N present in amines, azo groups, amides, nitriles), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (e.g. S present in thiols, thiocarbamates, thioethers). From the Hard Soft [Lewis] Acid Base principle, inorganic cations and ligands are classified into three groups:

-group I: Hard cations or hard Lewis acids (e.g.  $H^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Cr^{3+}$  etc.) prefer to form complex with hard Lewis bases (e.g.  $OH^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $CH_3COO^-$ , etc.)

-group II: Borderline cation or borderline Lewis acids (e.g.  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Mn^{2+}$ , etc.) possess affinity for both hard and soft ligands.

-group III: Soft cations or soft Lewis acids (e.g.  $Cd^{2+}$ ,  $Ag^+$ ,  $Au^+$ ,  $Hg^+$ , etc.) possess affinity for intermediated and soft ligands.

Binding of metal ions to the chelate functional group is dependent on several factors: (1) nature, charge and size of the metal ion, (2) nature of the donor atoms present in the ligand, (3) buffering conditions which favor certain metal extraction and binding to active donor or groups, (4) nature of the solid support (e.g. degree of cross-linkage for a polymer).

### 2.3.1.3 Ion-pairing

An ion-pair reagent (such as a long aliphatic hydrocarbon chain) and a polar portion (such as acid or base) can be added to the sorbent when a non-polar sorbent is to be used. The non-polar portion interacts with the reversed-phased non-polar sorbent, while the polar portion forms an ion-pair with the ionic species present in the matrix which could be either free metallic species in solution or complexes.

### 2.3.1.4 Ion-exchange

Ion-exchange sorbents usually contain cationic or anionic functional groups that can exchange the associated counter-ion. Strong and weak sites refer to the fact that strong sites are always present as ion-exchange sites at any pH such as sulfonic acid groups (cation-exchange) and quaternary amines (anion-exchange), while weak sites are only ion-exchange sites at pH values greater or less than their  $pK_a$  such as carboxylic acid groups (cation-exchange) or primary, secondary and tertiary amines (anion-exchange). These groups can be chemically bound to silica gel or polymers (usually a styrene-divinylbenzene copolymer), allowing a wider pH range.

## 2.3.2 Selection of solid sorbent

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to development of SPE methodology. In practice, the main requirements for a solid sorbent are: (1) the possibility to extract a large number of trace elements over a wide pH range (along with selectivity towards major ions), (2) the fast and quantitative sorption and elution, (3) High capacity, (4) regenerability and (5) accessibility.

In particular, sorbents that allow fast reaction rates are preferred to achieve faster extraction as well as higher loading capacity. Hence, sorbents based on hydrophilic



macroporous polymers and cellulose or fibrous materials provide excellent kinetic properties. [21]

The broad variety of sorbents available explains one of the most powerful aspects of SPE, which is selectivity. Sorbents can be mainly categorized into inorganic based ones (silica gel  $\text{SiO}_2$ , alumina  $\text{Al}_2\text{O}_3$ , magnesia  $\text{MgO}$  and other oxide species) and organic based ones (natural polymers, as well as synthetic polymers), as given in Table 2.1.



**Table 2.1** Type of based sorbent and their advantages, disadvantages

Type of based sorbent	Remarks
<b>Inorganic based sorbents</b>	
Silica gel	present the advantages of mechanical, thermal and chemical stability under various conditions, high selectivity towards a given metal ion but suffer from different chemical limitations, namely the presence of residual surface silanol groups and a narrow pH stability range.
Other inorganic oxides	may be influenced by the presence of salts in the matrix. In particular, high concentrations of phosphates and sulfates may decrease trace element retention on titanium dioxide (TiO <sub>2</sub> ). On the opposite, major cations (Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> and Mg <sup>2+</sup> ) are weakly adsorbed on TiO <sub>2</sub> .
Polystyrene-divinylbenzene based sorbents (PS-DVB)	Amberlite XAD series: highly hydrophobic character and no ion-exchange capacity, hydrophobic character.
Divinylbenzene-vinylpyrro - lidone copolymers(DVB-VP)	determine polar organic compounds in water samples, can dry out during the extraction procedure without reducing its ability to retain analytes, stable over the entire pH range, but no application related to the preconcentration of trace elements.
Carbon sorbents	large surface areas (300-1000 m <sup>2</sup> /g), well-recognized for their very strong sorption both for trace organic compounds and trace elements, be retained on this sorbent after addition of a proper chelating agent to the sample such as amino acids, dithizone. Main drawback: their heterogeneous surface with active functional groups often leads to low reproducibility, very reactive and can act as catalysts for oxidation and other chemical reactions.

## 2.4 Langmuir isotherm

The adsorption phenomena on solid-liquid interface are commonly described by an adsorption isotherm model. The Langmuir treatment is based on the assumption that the maximum adsorption corresponds to saturated monolayer of adsorbed species on solid surface and there is no other mechanism such as migration of the metal ions in the plane of the surface. The Langmuir model [22], followed to equation 2.4.

$$\frac{C}{N_f} = \frac{C}{N_f^s} + \frac{1}{bN_f^s} \quad (2.4)$$

where  $C$  = the concentration of metal ion solution at equilibrium ( $\text{mol L}^{-1}$ )

$N_f$  = the amount of metal ion per gram of sorbent ( $\text{mol g}^{-1}$ )

$b$  = the Langmuir constant related to energy of adsorption ( $\text{L mol}^{-1}$ )

$N_f^s$  = the maximum amount of metal adsorbed per gram of sorbent ( $\text{mol g}^{-1}$ )

The Langmuir model is used to describe the adsorption isotherm. When the result give a good correlation coefficient ( $r$ ) from the plot of the ratio of the metal ion concentration at equilibrium ( $\text{mol L}^{-1}$ ) and the amount of metal ion per gram of sorbent ( $\text{mol g}^{-1}$ ),  $C/N_f$  versus the concentration of metal ion solution at equilibrium ( $\text{mol L}^{-1}$ ),  $C$ , indicated that the adsorption of metal ion on solid surface was a Langmuir type.  $N_f^s$  is the maximum amount of metal adsorbed per gram of sorbent ( $\text{mol g}^{-1}$ ), can calculated from the slope of the graph. Then,  $b$  value, the Langmuir constant related to energy of adsorption ( $\text{L mol}^{-1}$ ), can calculate from y-intercept value of the graph.

## 2.5 Application of humic acids in heavy metal extraction

The application of humic acids in heavy metal extraction can be summarized below.

The first technique is to blend humic acids with additives to increase the capability of metal removing. In this case, Calcium alginate is often used to increase the extraction efficiency of poisonous heavy metals such as Cd, Cu, Cr, Ni, Mn, Fe and Zn from hazardous solid waste [23]. Another example is the blend of Leonadite humic acid material and the beach sand to treat a wastewater containing Pb, Zn, Ni, Cu, Sr, Cd, As, Ag, Mg [24]. This blend is suitable for the use in the slightly acid condition. The main disadvantage of this technique is the leaching of soluble humic acids in high pH condition.

The second technique is to immobilize or coat humic acids onto solid supports such as activated carbon [25], styrene-divinylbenzene copolymers, cellulose and silica [26], aminopropyl silica [27-30], Fe-Mn nodule material [31], aluminium hydroxide and clays [32]. Some of these solid phases had been used for batch adsorption of metal ions such as As(III). Magnesium oxychloride cement (MOC) was also used to immobilize humic acids for Cr(VI) removal from wastewater [33]. This technique is widely used because humic acid leaching rarely occurred during the extraction and the sorbent can be regenerated and reused.

The third one involves the preparation of insolubilized humic acids (IHA) by heating original humic acids at 330°C. The IHA was used to extract Cu(II) from an aqueous solution in SPE column method [2, 34]. This technique is very new and rarely reported. It seems that the preparation requires time and energy and loss of some active compound occurred during the heating process.

The last technique consists of addition of soluble humic acids into water sample in order to form metallic complexes which can be afterwards removed by adsorption onto a sorbent [35] or ultrafiltration [36, 37].

## **2.6 Conclusion**

Relating works about humic acids mostly presented the production, structure and characteristics of humic substances from different sources including extraction, separation, purification. Other research also includes the use of humic acid as an adsorbent, the kinetics and isothermal of metal adsorption of humic with metal ions as well as the role of humic for environment as an adsorbent for the contaminants in wastewater.