EVALUATION OF NATURAL ORGANIC MATTER – METAL OXIDE ADSORPTION ISOTHERMS UNDER INFLUENTIAL STRUCTURAL CONCEPTS

by

ŞERİF ALTAN SÜPHANDAĞ

B.Sc. in Env. E., İstanbul University, 1994

M.Sc. in Environmental Technology, IES, Boğaziçi University, 1998

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APPROVED BY:

Prof. Dr. Miray Bekbölet
(Thesis Supervisor)

Prof. Dr. Bilsen Beler BAYKAL.

Prof. Dr. Nilsun İNCE

Assoc. Prof. Dr. Melek T. SAÇAN

Prof. Dr. Orhan YENİGÜN

DATE OF APPROVAL

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This work is dedicated to the memory of my beloved parents

Selma & Ahmet H. Süphandağ

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I would like to thank everybody who believed in me, and guided me through my journey into the science. I would like to express my gratitude to my advisor Prof. Dr. Miray Bekbölet, for introducing humics to me. I also would like to pay my respects to the members of my jury, for the time and patience they spent to evaluate this work.

I would like to express my warmest feelings and my gratitude for my brother, without whom my life would be much more difficult.

My sincere gratitude goes to my good friends at school, without their support, help and belief; I would not be able to pass through the rough patches of my life. I consider myself a very lucky person, since not many people are blessed with the chance to grow up together like us.

There was a man with tongue of wood
Who essayed to sing.
And in truth it was lamentable
But there was one who heard
The clip-clapper of this tongue of wood
And knew what the man
Wished to sing
And with that the singer was content.

Stephen CRANE

EVALUATION OF NATURAL ORGANIC MATTER-METAL OXIDE ADSORPTION SYSTEMS UNDER INFLUENTIAL STRUCTURAL CONCEPTS

The adsorption of molecules onto a surface is a necessary prerequisite to any surface mediated chemical process. Therefore, the mechanism of binding of humic acids to TiO_2 surface has to be addressed in order to improve the understanding of photocatalytic degradation.

From the fundamental point of view, natural organic matter (NOM) for water scientists can be perceived as very complex entities both in terms of chemistry and comprehension. Especially the fulvic (FA) and humic acids (HA), the soluble portions of NOM, are often considered as oligomeric and polymeric materials. In literature, there are ongoing discussions regarding the high molecular mass is due to aggregation of small units, as in micelles, or due to covalently bound units, as in polymers. The essence of this thesis is to evaluate the adsorption under the light of these two debatable approaches and bring reasonable interpretations of the observed isotherm patterns through the use of proposed structures.

In this dissertation the sorption isotherms of humic acid (HA) on titanium dioxide are analyzed at acidic, neutral, and basic pH ranges. Furthermore the combined effects of pH and increasing ionic strength were evaluated in order to asses the effect of changing solution matrix on the molecular structure of humic acid.

DOĞAL ORGANİK MADDE – METAL OKSİT ADSORPSİYON SİSTEMLERİNİN ETKİN YAPISAL KAVRAMLAR ALTINDA DEĞERLENDİRİLMESİ

Yüzeyde oluşan tüm kimyasal proseslerde, moleküllerin yüzeye adsorpsiyonu gerekli bir esas teşkil etmektedir. Bu yüzden, fotokatalitik arıtma süreçlerindeki anlaşılabilirliği artırmak için, hümik asitlerin TiO_2 yüzeyine bağlanmaları ilgili mekanizmalara değinilmesi gerekmektedir.

Temel bakış açısından yaklaşıldığında, doğal organik maddeler (NOM), su bilimciler için, gerek kimya, gerekse algı boyutunda son derece kompleks bileşikler olarak kabul edilebilirler. Özellikle fulvik (FA) ve hümik asitler (HA), doğal organik maddelerin (NOM) çözülebilir kısımları olan, genellikle oligomerik ve polimerik maddeler olarak kabul edilebilirler. Literatürde, yüksek moleküler ağırlığın, misellerde olduğu gibi, küçük kimyasall birimlerin agregasyonundan; veya polimerlerde olduğu gibi kovalent bağlarla bağlı birimlerden meydana geldiği tartışmaları halen süregelmektedir. Bu tez çalışmasının amacı, adsorpsiyonu bu iki tartışmalı yaklaşım açısından değerlendirmek ve gözlenen izoterm kalıplarına, öne sürülen yapılar aracılığıyla anlamlı yorumlar getirmektir

Bu çalışmada, asidik, bazik ve nötr pH aralıklarında hümik asitin titanyum diyoksit üzerindeki adsorpsiyon izotermleri incelenmiştir.. Buna ek olarak, değişen çözelti matrisinin etkisini değerlendirmek üzere; pH ve iyonik kuvvet (IS) etkisi birlikte izlenmiştir.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Symbol	Explanation
[A]	Adsorbate Concentration
C_e	Equilibrium concentration of adsorbate
CMC	Critical Micelle Concentration
$Color_{436}$	Absorbance at 436 nm
$Color_{400}$	Absorbance at 400 nm
DOC	Dissolved Organic Carbon
DOSY	Diffusion Ordered Spectroscopy
E-R	Eley-Rideal Kinetic Model
FA	Fulvic Acid
HA	Humic Acid
HPLC	High Pressure Liquid Chromatography
HS	Humic Substances
IR	Infrared
IS	Ionic Strength
K_{ads}	Langmuir Adsorption Constant
K_F	Freundlich Adsorption Capacity Constant
L-H	Langmuir-Hinshelwood Kinetic Model
MW	Molecular Weight
n	Freundlich adsorption intensity parameter
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
q_A	Adsorbed amount per unit weight of adsorbent
TOC	Total Organic Carbon
UV_{280}	Absorbance at 280 nm
UV_{254}	Absorbance at 254 nm

1. INTRODUCTION

Varieties of organic compounds are present in most surface and ground water environments. Amongst them, natural organic matter (NOM) have been a focal point for many water scientists with its complexity and omnipresence. Its moderately strong acidity and strong tendency to adsorb, virtually affect all particles in natural waters. The responses triggered by this Particle-NOM binary system in natural waters have been a concern of environmental sciences for the last few decades.

Hydrophobic fraction of the aquatic NOM represents an "operational" definition of humic substances. Almost any description that tends to unite both the structural and the reaction properties of humic substances is bound to fail in giving the most concise information within the definition form. However a molecule cluster of this diverse property sure must have a proper definition which bypasses the structure and yet could give a perfect explanation; such as "humic substances are compounds in humus that are not synthesized directly to sustain the life cycles of the soil biomass" (Sposito, 1989). More specifically, humic substances are the products of the oxidative degradation and subsequent polymerization, of plant and animal matter in the environment. The mechanism of formation of these substances is not well characterized, but they are known to be rich in aromatic, carboxylic and phenolic functionalities. The also possess alkyl moieties, linking the various functional groups, and imparting a measured of flexibility to the polymer chains. The molecular features of the compounds are variable, depending on their age and origin. For this reason, humic substances are operationally, rather than structurally defined (Aiken et al., 1985).

Since the material is very complex and ill defined, in order to develop quantitative chemical analysis, researchers access to such crude measures as envisioning the molecule by different colloid models. Carrying a wide spectra of functional groups; individually contributing a different characteristic, and hydrogen bonds between these functional groups, more or less recalls the tertiary and quaternary structures of proteins, therefore in modeling generally the protein models are taken into consideration supported with colloid and surface chemistry concepts. A vivid example for this sort of consideration was brought to presence by Jones and O’Melia (2000), where protein and humic acid adsorption onto hydrophilic membrane surfaces were analyzed.

Another promising subject for environmental chemistry has been “advanced oxidation"; with photocatalytic oxidation taking the lead. Its excellent pigment quality aside, as a compound with dielectric property, high UV absorption and stability, titanium dioxide has emerged to be the most rewarding semiconductor powder involved in advanced oxidation processes.

Although it is not the major phenomenon, adsorption still occupies an important place in photocatalytic processes when kinetics are involved, excluding E-R. (Eley-Rideal) mechanism, photocatalytic kinetics, namely L-H (Langmuir-Hinschelwood) kinetic model emphasizes that the initiation of a photocatalytic degradation process strongly depends on a preceding adsorption of the substrate on the surface. Although titanium dioxide can not at all be considered as a good adsorbent with respect to specialized adsorbent materials used in wastewater treatment such as activated carbon, or ion exchange resins, its adsorption character still requires consideration owing to its importance as being the generic photocatalyst.

This research aims to draw a detailed adsorption behavior of humic acid on the photocatalyst metal oxide and explain the successive steps of this profile in a deductive manner depending on the structural alterations of humic acids as the conditions change in the medium. The answers were sought within the alternative structural conformations attributed to humics.

2. THEORETICAL BACKGROUND

2.1. Humic Substances

While organic forms of carbon represent only a small proportion of the global carbon reservoir, they are instrumental in many reactions and influence environmental chemistry far beyond their mass contribution. Various ways of classifying organic matter in water help us to understand the relations between the various chemical types of organic matter (OM) and the natural or anthropogenic origins of particular compounds. Where the organic matter is derived from natural sources, it is often referred to as natural organic matter (NOM). It derives from different source materials that have distinctive chemical characteristics.

When the chemistry of organic matter found in the hydrosphere is considered, it is frequently convenient to subdivide the species into two categories based on molecular size (vanLoon and Duffy, 2000)

- Discrete small molecules, like monosaccharides or low molar mass organic acids whose chemical structure and properties are amenable to individual specific study. Individual polluting species like chemical pesticides fall in this category as well.
- Macromolecules, which are treated as classes in terms of their general structural properties and reactivity. Characterization of macromolecules is often based on an operational definition –that is, a definition arising out of a particular analytical protocol, and not based on fundamental structural properties.

Many of the natural forms of organic matter fall in the macromolecule category amongst them humic substance (HS) comprise the highest portion.

Humic substance (also humic matter/material, humate or humus as addressed interchangeably throughout the literature) is naturally occurring organic matter of plant or microbial origin. They are produced and reside in soil and water and form a major component of the terrestrial and aquatic organic carbon pools. In the hydrosphere, humic material typically makes up about 50% of the dissolved organic matter in surface water (vanLoon and Duffy, 2000), as well as much of the organic sediment. Different descriptions of HS are used according to specific environments of origin and research interests. As a consequence, a wide variety of terms such as dissolved organic matter (DOM), NOM, soil organic matter (SOM), and refractory organic substances (ROS) are commonly used in literature. Often they are related to operational definitions based on fractionation procedures. The term “humic substances” is used as a generic name to describe colored material or its fractions obtained on the basis of solubility characteristics (Suffet and MacCarthy, 1989).

Due to their structural versatility, humic substances are involved in many environmental processes, especially in binding, transport, and deposition of inorganic and organic pollutants e.g., heavy metal ions, pesticides (Suffet and MacCarthy, 1989). Imparting undesirable color and acting as precursors for undesirable trihalomethane formation during the chlorination process, their presence in drinking water supplies causes problems, the consequences of which may lead to the deterioration of human health (Reckhow et al., 1990; Rook, 1977).

Humic substances are subdivided in an operational sense into three categories:

- fulvic acid (FA) is the fraction of humic matter that is soluble in aqueous solutions that span all pH values;
- humic acid (HA) is insoluble under acid conditions (pH 2) but soluble at elevated pH;
- humin (Hu) is insoluble in water at all pH values (vanLoon and Duffy, 2000).

Humic acids are the major extractable component of humic substances. They are dark brown to black in colour. Fulvic acid remain in solution after removal of humic acid by acidification. They are light yellow to yellow-brown in colour. Humins are basically black in colour (Suffet and MacCarthy, 1989).

Although it is difficult to obtain a structural analysis about humic and fulvic acids, compositional information can still be achieved through elemental and functional group analysis as presented in Table 2.1

Table 2.1. Elemental analysis of humic substances (Schnitzer and Khan, 1972)

Element	**Humic acid (wt %)**	**Fulvic acid (wt %)**
C	53.6-58.7	40.7-50.6
H	3.2-6.2	3.8-7.0
N	0.8-5.5	0.9-3.3
O	32.8-38.3	39.7-49.8
S	0.1-1.5	0.1-3.6

The elemental analyses from a range of environmental sources show that the atomic H/C ratio is quite low, and is lower for humic acid than fulvic acid, which is consistent with a higher aromatic content for humic acid. The atomic O/C ratio is also lower for humic acid than fulvic acid, reflecting the higher content of polar groups in fulvic acid. The greater water solubility of fulvic acids compared to humic acids can be attributed to the higher content of polar groups, particularly carboxyl groups. Among the other functional groups present in smaller quantities are ether, aldehyde and amine. The major heteroatom in humic and fulvic acids is oxygen. It occurs predominantly in -COOH, phenolic and alcoholic -OH, ketonic and quinoid -C=O, and -OCH_3 (ether). The estimated abundances of these groups are given in Table 2.2.

Table 2.2. Functional groups in humic and fulvic acids (Schnitzer & Khan, 1972)

Functional group (mequiv g^{-1})*	Humic acid	Fulvic acid
Total acidic groups	5.6-8.9	6.4-14.2
Carboxyl, COOH	1.5-5.7	5.2-11.2
Phenolic, OH	2.1-5.7	0.3-5.7
Alcoholic, OH	0.2-4.9	2.6-9.5
Quinoid/keto, C=O	0.1-5.6	0.3-3.1
Methoxy, OCH_3	0.3-0.8	0.3-1.2

*mequiv g^{-1} equivalent to mmol of each group per g of humic substances

Differences between humic acids and fulvic acids can be explained by variations in molecular weight, the number of functional groups (carboxyl and phenolic OH) and the extent of polymerization. The postulated relationships are depicted in Figure 2.1, in which it can be seen that color, carbon and oxygen contents, acidity and degree of polymerization all change systematically with increasing molecular weight. The low molecular weight fulvic acids have higher oxygen but lower carbon contents than the high molecular weight humic acids. The total acidities of fulvic acids (900-1400 meq 100 g^{-1}) are considerably higher than that of humic acids (400-870 meq 100 g^{-1}) (Tipping, 2002).

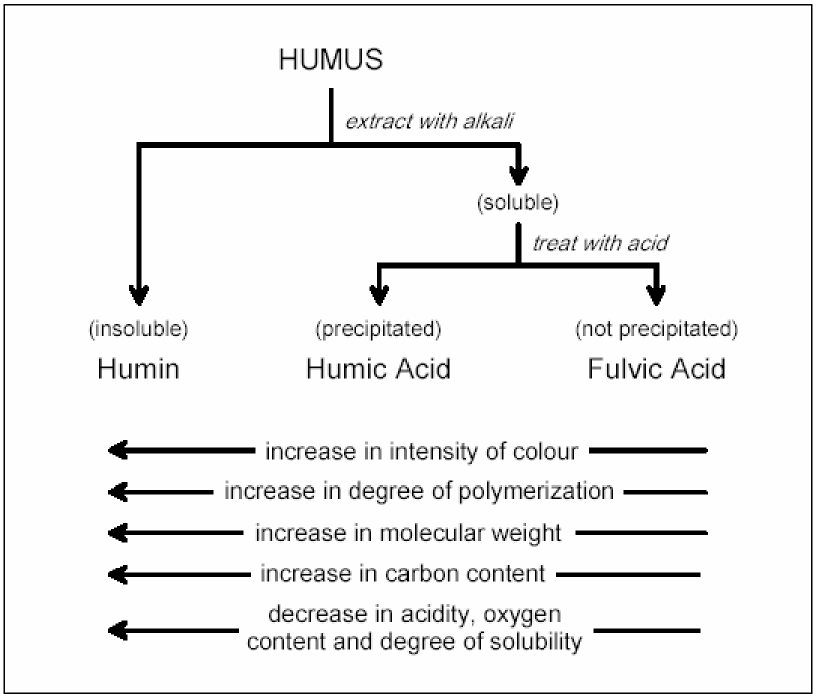


Figure 2.1. Postulated relationships between humic substances (Tipping, 2002).

Humic materials have a wide range of molecular weights and sizes ranging from a few hundred to as much as several hundred thousand atomic mass units. In general, fulvic acids have lower molecular weights than humic acids. It is also known that soil derived humic materials are larger than aquatic humic substances (Gaffney et al., 1996).

Humic acids are thought to be complex aromatic macromolecules with amino acids, amino sugars, peptides, aliphatic compounds involved in linkages between the aromatic groups. The hypothetical structure for humic acid, shown in Figure 2.2 contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings.

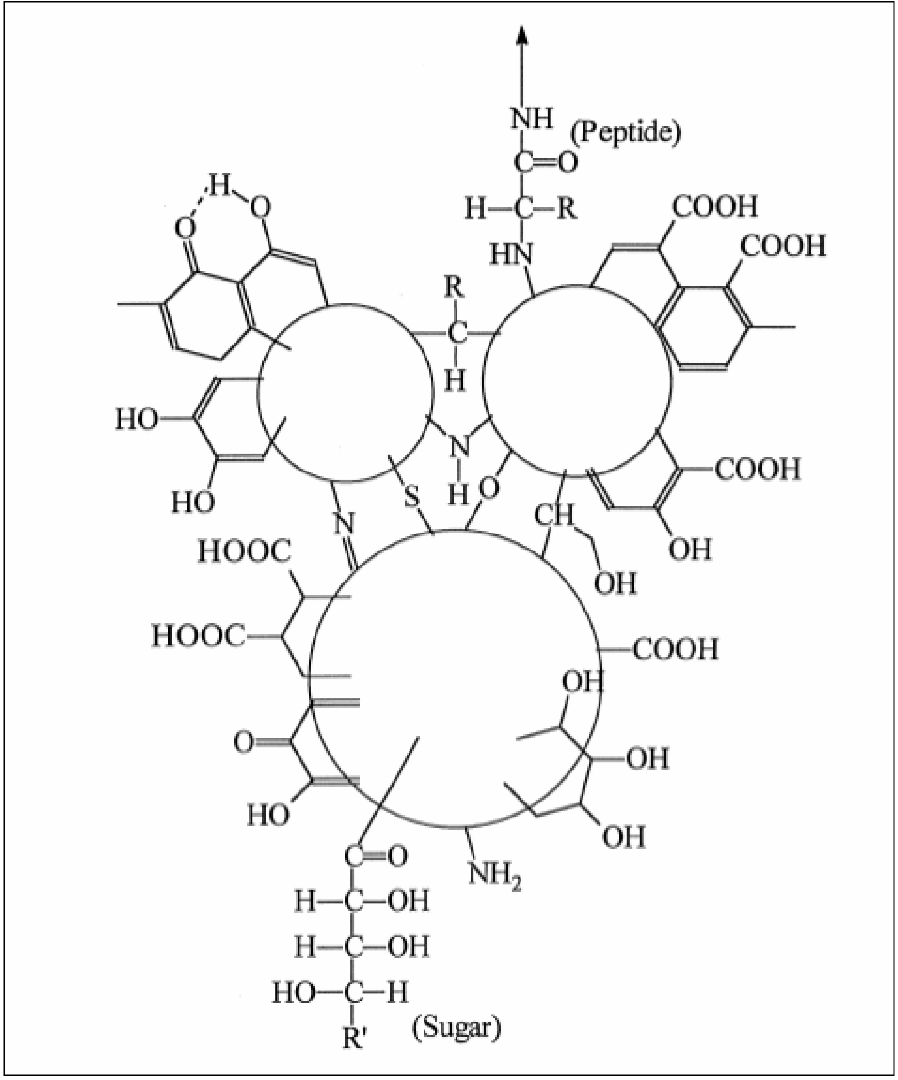


Figure 2.2. Hypothetical structure of model humic acid (Fetsch et al., 1998).

The hypothetical model structure of fulvic acid (Buffle's model) contains both aromatic and aliphatic structures, both extensively substituted with oxygen-containing functional groups (Figure 2.3). However, the structures of fulvic acid are more aliphatic and less aromatic than humic acids. The reason for their high solubility in water at all pH values is mainly due to the presence of carboxylic acid, phenolic and ketonic groups in appreciable amounts.

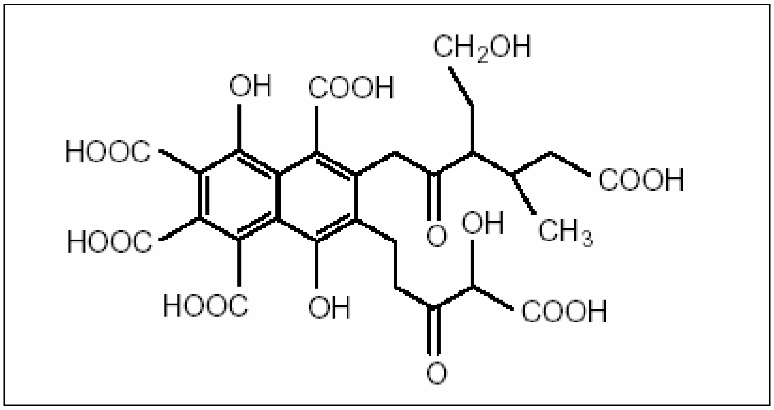


Figure 2.3. Hypothetical structure of fulvic acid (Buffle et al., 1977).

Depending on the pH of the solution, the functional groups in a humic molecule are dissociated or protonated. Dissociated functional groups carry negative charges. Electrostatic repulsions between neighboring negatively charged sites causes stretching of the molecule. Furthermore, the electrostatic forces are influenced by ionic strength, by the presence of cationic species etc. (Ghosh and Schnitzer, 1980). It was reported that humic molecules can change from a large, flexible and linear shape at high pH, low ionic strength and low humic concentration, to a small, rigid and spherocolloidal conformation at low pH, high ionic strength and high humic concentration (Ghosh and Schnitzer, 1980).

Humic substances are mixtures not defined by a single chemical characteristic; hence, their concentrations are difficult to measure. The most useful humic related determinant that provides a useful indication is the dissolved organic carbon (DOC). Concentrations of DOC in freshwater streams, rivers and lakes which are known to be due to the presence of humic substances vary from less than 0.5 mg L^{-1} to 100 mg L^{-1} depending on the nature of the catchment, including the climate, the trophic status of the water body, and pollutant inputs.

Chemical and physical studies of humic substances and their interactions with environmental contaminants are essential in order to explain their impact on the environmental fate, bioavailability and toxicity of organic and metal contaminants in natural water systems. However, elucidation of the important role of humic substances is complicated by their highly heterogeneous nature.

A number of physical and chemical measurements have been employed to characterize humic substances, including elemental analysis, ultrafiltration, UV-*vis* spectroscopy, fluorescence spectroscopy, Fourier transform infrared (FTIR) spectroscopy, pyrolysis-gas chromatography-mass (Py-GC-MS) spectroscopy, ^{1}H and ^{13}C-NMR spectroscopy (Senesi et al., 1991; Westerhoff et al., 1999; Shin et al., 1999; Schulten and Gleixner, 1999; Kalbitz et al., 2000).

Nuclear magnetic resonance spectroscopy (NMR) has been widely used to provide information about humic substances and their chemistry. Applying ^{13}C-NMR spectroscopy appears to be well suited for obtaining an inventory of the chemical composition of humic materials and for revealing differences in functional group content between samples. Spectra can be acquired in solution-state and solid-state NMR-spectroscopy. Information about the presence of functional groups, aromatic systems or branched alkyl groups can be obtained (Pommes et al., 2000).

High pressure liquid chromatography (HPLC) using gels have proved useful in combination with UV-*vis*, fluorescence, light scattering and sensitive dissolved organic carbon detection techniques, yielding information on molecular absorbance, size distribution, molar mass and reactivity. Using both chemical and spectroscopic methods, various studies have been conducted for the characterization of humic substances of different origin (Frimmel, 1998; Shin et al., 1999; Aguer and Richard, 1996).

Despite of the application of powerful analytical methods like Fourier transform infrared spectroscopy, pyrolysis mass spectrometry (Py-MS) and solid phase nuclear magnetic resonance e.g.; ^{13}C-NMR, molecular structure identification in the classical sense has not been successful (Hayes, 1998). Humic materials are still among the least understood and characterized components in the environment. Hence, continued development of new analytical methods and approaches is required for the characterization and analysis of humic substances.

2.2. Titanium Dioxide

Nature does not yield titanium dioxide in a usable form. The compound is associated with iron as either ilmenite or leuxocene ores. It is also mined in one of its purest forms, rutile beach sand. Rutile, ilmenite soaps, Anatase; Titanium Magnetite and Haematite are principle raw materials used in the production of Titanium Dioxide

Aside from its excellent pigmentary properties, Titanium dioxide, as a chemical has dielectric properties, high ultraviolet absorption and high stability which allows it to be used in specialty applications, such as electroceramics, glass, and wastewater treatment.

TiO_2 exists in three modifications or crystal structures, rutile, anatase or brookite. Only the anatase and rutile modifications are of any note, technically, or commercially. Rutile has a density of 4.2 g mL^{-1}, while anatase has a density of 3.9 g mL^{-1}. This difference is explained by their different crystal structures. The rutile structure is more closely packed than the anatase crystal, where each metal center occupies the center of an octahedron of oxygen ligands, each of which is bound to three metals.

Many suspended and colloidal solids encountered in natural waters have surface charge, and that the charge may be strongly affected by pH. The surface charge may arise from chemical reactions at the surface. Many solid surfaces contain ionizable functional groups and the charge transfer of these particles becomes dependent on the degree of ionization (proton transfer) and consequently on the pH of the medium.

In the presence of water, metal or metalloid oxides are generally covered with surface hydroxyl groups. A hydroxylated oxide particle can up to a certain degree be understood as a polymeric oxoacid or -base where surface coordination reactions take place at the oxide-water interface. The pH dependent charge of titanium dioxide results from proton transfers at the amphoteric -hydrated- surface.

$$Ti^{IV}{-}OH + H^{+} \rightarrow \underline{Ti^{IV}}{-}OH_2^{+} \qquad (K_{a1}) \qquad 2.1$$

$$Ti^{IV}{-}OH + OH^{-} \rightarrow Ti^{IV}{-}O^{-}{+}H_2O \qquad (K_{a2}) \qquad 2.2$$

Operationally there is a similarity between H^+ and metal ions (Lewis acids) and OH^- and other bases (Lewis bases). The OH group on a hydrous oxide surface has a complex-forming O-donor group like an OH^- or an OH group attached to another element. Protons and metal ions compete with each other for the available coordinating sites on the surface. The extent of coordination is related to the exchange of H^+ by charged metal ions. Similarly, ligand exchange with coordinating anions leads to a release of OH^- from surface. Because of this Lewis base character of the surface oxide ions of TiO_2, which acts as donor surface states, the chemisorption of water at the Ti^{IV} site is likely to be followed by the proton transfer to the -O- site. Two kinds of surface -OH groups are then formed (Boehm, 1971; van Veen, 1989). The acidic one has a pK_a value of *ca* 2.9, while the remainder behaves as weak acid with a pK_a 12.7 (Boehm, 1971). By using Equations 2.1 and 2.2, the pH where no charge can be attributed to the oxide surface (pH_{zpc}) of TiO2 can be calculated as

$$pH_{zpc} = (pK_{a1} + pK_{a2})/2 \qquad 2.3$$

The measurements of surface charge density of titanium dioxide suspension, having the rutile crystal structure, as a function of pH place the point of zero charge (zpc) at pH 5.8 ± 0.1 (Yates and Healy, 1980). The available data regarding the zpc of anatase are not markedly different from those for rutile and range from pH 6 to pH 6.4 (Bérubé and Bruyn, 1968). Schmelling and his colleagues (1997) measured pH_{zpc} 6.25 for Degussa P-25 TiO_2 brand.

2.3. Adsorption

Adsorption is the accumulation of a substance at or near an interface relative to its concentration in the bulk solution. The process can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The material being concentrated or adsorbed is the *adsorbate*, and the adsorbing phase is termed the *adsorbent*. In principle, these definitions differentiate adsorption from absorption, which is the accumulation of substance in the interior of a non aqueous phase. However, since it is often not possible to distinguish between adsorption and absorption, the two processes are often treated jointly.

In adsorption process, the matter is extracted from one phase and concentrated at the surface of a second phase. This is a surface phenomenon. Surface reactions of this type must occur at least partly as a result of the forces active within the phase boundaries, or surface boundaries; these forces result in characteristic boundary energies. Classical chemistry defines the properties of a system by the properties of its mass; for surface phenomena, however, the significant properties are those of the surface or boundary (Weber, 1972).

2.3.1. Types of Adsorption

There are three general types of adsorption. These are; *physical*, *chemical*, and *exchange* adsorption (Weber, 1972).

Physical adsorption is relatively nonspecific. It is caused by the operation of weak forces of attraction or van der Waals' forces between molecules. In this adsorption type, the adsorbed molecule is not affixed to a particular site on the solid surface, but is free to move about over the surface. The adsorbed material which is bound by van der Waals' forces may condense and form several superimposed layers on the surface of the adsorbent. This type of adsorption is generally quite reversible.

The second type of adsorption is *chemical adsorption*. The forces acting on this kind of adsorption are much stronger than the ones acting on *physical* adsorption. The forces are comparable with those leading the formation of chemical compounds.

Normally the adsorbed material forms a layer over the surface which is only one molecule thick, and the molecules are not considered free to move from one surface site to another. When the surface is covered by the monomolecular layer, the capacity of the adsorbent is essentially exhausted. Chemical adsorption is seldom reversible. Generally the adsorbent must be heated to higher temperatures to remove the adsorbed materials. This type of adsorption is also called “chemisorption” or “activated adsorption”.

The adsorption characterized by electrical attraction between the adsorbate and the surface is called the *exchange* adsorption. In this type; ions of a substance concentrate at the surface as a result of electrostatic attraction to sites of opposite charge on the surface. In general, ions with greater charge, such as trivalent ions, are attracted more strongly toward a site of opposite charge than are ions with smaller charge, such as monovalent ions. Also, the smaller the size of the ion gets (hydrated radius), the greater the attraction is.

Although there are significant differences among the three types of adsorption, there are instances in which it is difficult to assign a given adsorption to a single type. Many adsorption processes involving organic molecules result from specific interactions between identifiable structural elements of the sorbate and the sorbent. These interactions may be designated as “*specific adsorption*” as opposed to adsorption which occurs as a result of simple Coulombic interactions.

2.3.2. Adsorption Equilibrium

Positive adsorption in a solid-liquid system results in the removal of solutes from the solution and their concentration at the surface of the solid. At this point of equilibrium, there is a defined distribution of solute between the liquid and the solid phases. This distribution ratio is a measure of the *adsorption equilibrium* in the adsorption process.

2.3.3. Adsorption Isotherm

For a given system composition, there exists a unique equilibrium distribution of adsorbate between the dissolved and adsorbed states. The equilibrium relationship between the adsorption density and the soluble adsorbate concentration at a given temperetaure is called an adsorption isotherm (Benjamin, 2002). The adsorption isotherm is proportional to the concentration of adsorbate in bulk solution at constant temperature. Frequently, the amount of adsorbed material per unit weight of adsorbent increases with increasing solute concentration, but not in direct proportion. Different solutes show different behavior on the adsorbent. (Weber, 1972), so their adsorption isotherms vary in shape. Letters classifying the isotherm curves according to their form were first introduced by Giles *et al* (1960), and later updated by Sposito in four general categories bearing letters S, L, H and C (Fig.2.4).

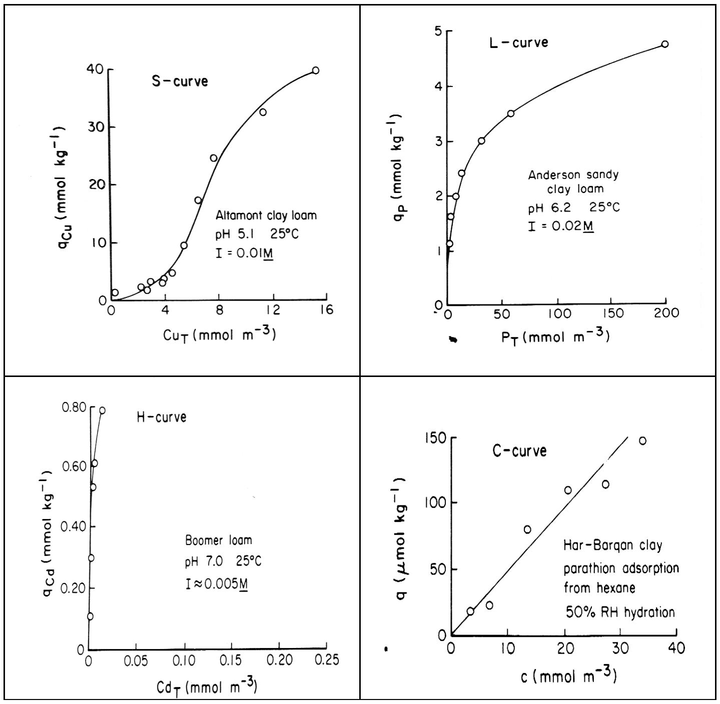


Figure 2.4. The four general categories of adsorption isotherm (Sposito, 1984)

S-curve isotherm is characterized by an initially small slope that increases with adsorptive concentration. This behavior suggests that the affinity of the adsorbent for the adsorbate is less than that of the aqueous solution. In the example in Figure 2.4 below, S-curve is thought to result from competition for Cu^{2+} ions between soluble organic matter and the soil particles. Once the concentration of Cu(II) exceeds the complexing capacity of the organic ligands, the soil particle surface gains in the competition and begins to adsorb copper ions significantly. Thereafter, the isotherm takes on its characteristic S shape. These interactions cause the adsorbate to become stabilized on a solid surface, and thus they produce an enhanced affinity of the surface for the adsorbate as its surface excess increases.

L-curve isotherm is the resultant effect of a high relative affinity of the adsorbent particles for the adsorbate at low surface coverage coupled with a decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increases.

The H-curve isotherm is an extreme version of the L-curve isotherm. Its characteristic large initial slope (in comparison with the L-curve isotherm) suggests a very high relative affinity of the soil for an adsorbate. This condition is usually produced either by inner-sphere surface complexation or by significant van der Waals interactions in the adsorption process. The example of cadmium adsorption at very low concentrations by a kaolinitic soil that is shown in Figure 2.4. above, illustrates an H-curve isotherm caused by specific adsorption. Large organic molecules and inorganic polymers provide examples of H-curve isotherms resulting form van der Waals interactions.

The C-curve isotherm is characterized by an initial slope that remains independent of adsorptive concentration until the maximum possible adsorption achieved. This kind of isotherm can be produced either by a constant partitioning of an adsorptive between the interfacial region and the soil solution, or by a proportionate increase in the amount of adsorbing surface as the surface excess of an adsorbate increases. The example of parathion adsorption in Figure 2.4 above shows constant partitioning of this compound between hexane and the layers of water on a soil at 50% relative humidity.

To describe specific adsorption quantitatively, a variety of mathematical descriptions have been developed for particular cases. Likewise above mentioned shape inspired classifications, many isotherms (or isotherm models) have been derived from isotherms mentioned below:

2.3.3.1. The Langmuir and BET Isotherms. The Langmuir isotherm is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface. In other words, this model is predicated on the assumptions that the energy of sorption for each molecule is the same and independent of surface coverage, and that sorption occurs only on localized sites and involves no interactions between sorbed molecules. (Weber and McGinley, 1991). The BET (Brunauer, Emmet, Teller) model assumes that a number of layers of adsorbate molecules form at the surface and that the Langmuir equation applies to each layer. Further assumption of the BET model is that a given layer need not complete formation prior to initiation of subsequent layers.

2.3.3.2. The Freundlich Isotherm. The Freundlich -or van Bemmelen- isotherm is the most widely used nonlinear adsorption equilibrium model. Despite both its origins and applications for the most part are empirical, the model can be shown to be thermodynamically rigid for special cases of adsorption on heterogeneous surfaces.

Although the Freundlich equation is basically empirical, it is still useful as a means for data description. This equation generally agrees quite well with the Langmuir equation and the experimental data over moderate ranges of concentration, C. Unlike the Langmuir equation, however, it does not reduce to a linear adsorption expression at very low concentrations. Nor does it agree well with the Langmuir equation at very high concentrations, since n must reach some limit when the surface is fully covered.

Further details about the isotherms governed in this study are given in the related sections of discussion section in order to promote the conceptual comprehension.

2.3.4. Factors Influencing Adsorption

Adsorption is mainly affected by factors governing properties of both the adsorbate and the adsorbent (Weber, 1972).

2.3.4.1. Surface Area. Since the adsorption is a surface phenomenon, the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for adsorption. So that, the more finely divided and the more porous the solid, the greater is the amount of adsorption accomplished per unit weight of a solid adsorbent. Because the extent of a surface reaction will vary with available surface area, adsorption rate should exhibit a monotonic increase with some function of the inverse of the diameter of the adsorbent particles.

2.3.4.2. Nature of the adsorbate. Chemical properties of the adsorbate gain importance in considering the nature of the adsorbate. These properties are:

Solubility of the Solute. The solubility of the solute is a controlling factor for adsorption equilibria. In general, there is an inverse relationship between the extent of adsorption of a solute and its solubility in the solvent from which the adsorption occurs. As the solubility increases, the solute-solvent bond gets stronger, which results in a decrease in the extent of adsorption. In the case of an aqueous solution, the more hydrophilic, i.e. the more, substance likes water medium, the less it is adsorbed on solid. Conversely, a hydrophobic, water disliking, substance is adsorbed easily from aqueous solution. A substance may have the “solubility-amphoteric character” where its hydrophobic part is adsorbed at the surface, and the hydrophilic part is directed toward the aqueous phase.

Polarity of the Adsorbate. Solute polarity on adsorption is important. A polar solute prefers the phase which is more polar. In other words, a polar solute is strongly adsorbed from a non-polar adsorbent. But prefers a polar solvent to a non-polar adsorbent.

Dissociation Constant (pK_a) Value of the Adsorbate. Most of the weak acids or bases have pK_a and pK_b values respectively. Their ionization depends on the pH of the solution.

A renowned relationship, the Henderson-Hasselbach equation states the connection between the pH of the medium, the pK value of a weak acid (or base) and the ratio of ionized to unionized forms:

$$\mathrm{pK} = \mathrm{pH} + \log\frac{(\text{unionized molecules})}{(\text{ionized particles})} \qquad 2.4$$

From the known pH and pK_a (or pK_b) values; the anionic, cationic or neutral character of the adsorbent can be found out. For example, for an organic acid, molecular, or anionic form of adsorption.

2.3.4.3. pH. Many organics form negative ions at high pH, positive ions at low pH, and neutral species in intermediate pH ranges. Generally, adsorption increases at pH ranges where the species is neutral in charge. In addition, pH affects the charge on the surface, altering its ability to adsorb materials. Generally, adsorption of typical organic pollutants from water is increased with decreasing pH. In many cases this may result from neutralization of negative charges at the surface of the carbon with increasing hydrogen-ion concentration, thereby reducing hindrance to diffusion and making available more of the active surface of the carbon. This effect can be expected to vary in degree for different carbons, because the charges at the surfaces of the carbon depend on the composition of the raw materials and on the technique of activation.

2.3.4.4. Temperature. Adsorption reactions are normally exothermic; consequently the extent of adsorption generally increases with decreasing temperature. The enthalpy changes for adsorption are usually of the order of those for the condensation or crystallization reactions.

The change in the heat content of the system in which adsorption occurs, the total amount of heat evolved in the adsorption of a definite quantity of solute on an adsorbent, is termed the heat of adsorption, ΔH. Heats of gas-phase adsorption generally are several kcal per mole, but because water is desorbed from the surface when adsorption from aqueous solution occurs, heat effects for the latter process are somewhat smaller than those for gas-phase adsorption.

2.4. Remarks on the Macromolecularity of Humic Substances

The size and shape of humic substances (HS) is still an unresolved issue in humus chemistry. The variability of sources and the chemical heterogeneity of HS have precluded attaining definite knowledge of their secondary chemical structure and absolute molecular weight. There are still divergent opinions about whether humic substances are real polymeric macromolecules or molecular associations of relatively small molecules held together by weak interaction forces (Clapp and Hayes, 1999). Because of this arising difficulty in naming any structure for HS, newer concepts have been put forward in recent years through the use of many conventions and works held by scientist working in the field of water chemistry.

Piccolo et al., (2001) in their comparative study of dissolved humic substance with macromolecular polymers, have proposed the idea that, differences in chromatographic behavior between undisputed polymers and humic samples suggest humic matter reflects, rather than a polymeric nature, a supramolecular association of heterogeneous molecules held together mainly by weak hydrophobic forces. This supramolecular structure compromises the supermixture characteristics of humic substances with the macromolecularity. Furthermore, Piccolo (2001) adds that a large body of evidence shows an alternative understanding of the conformational nature of HS, which should be regarded as supramolecular associations of self assembling heterogeneous and relatively small molecules, deriving from the degradation and decomposition of dead biological material. In the same sense, Hayes and Clapp (2001) have called this structural explanation as "pseudomacromolecularity" and corroborated Piccolo by briefly stating that this concept suggests the macromolecular-like properties arise from associations of smaller molecular species in micellar or pseudomicellar structures or through other forms of molecular associations involving, perhaps, nonpolar molecules such as long chain hydrocarbons, fatty acids/esthers/suberin-type components. In his critical review, Swift (1999) evaluates the macromolecular structure of humic substances under the development of more recent information and defended the concept of macromolecularity.

Based on the accumulated evidence on the origins of humic substances (Stevenson, 1994;; Kögel-Knabner, et al., 1992; and Hayes and Swift 1990) degradation and synthesis processes are equally important in the genesis of HS and lignin is one of the major contributors to humic products when plants are transformed. The most widely accepted concepts of the structures of lignins suggest that the backbone components are linked by C to C bonds and by ether linkages. There are opportunities for internal hydrogen bonding of the lignin structures, which would impart a degree of rigidity to the material. One can thus visualize a structural configuration that might loosely be considered to be net like. On the other hand, Stevenson (1994) points out that HS also contain phenolic moieties that cannot have arisen from lignin precursors but must have been formed, *in situ*, by microbial synthesis. Later, the works of Haider and Martin (Haider and Martin, 1967; and Martin and Haider 1969) have shown how phenolic substances are synthesized by various fungi and some bacteria that can degrade lignin and can release phenols from lignin. Phenols, as well as partially degraded lignins and other reactive compounds, could undergo auto-oxidation or be enzymatically macromolecularized to humic molecules, either extracellularly or within microbial cells. Stressing the role of lignins; their modification and degradation as major processes in the formation of HS, Swift (1999) also states that the products could then be expected to have a range of MW values because of the different extents of cleavage of the altered lignin parent materials.

In an answer posed to the question “Should we expect humic substances to be macromolecular?” Clapp and Hayes (1999) answer that should HS arise only as a result of degradative processes; there would be no logical reason to expect the molecules to be macromolecular, except that the molecules formed are protected from further degradation in the soil environment. That protection might involve entrapment in recalcitrant substances such as long chain fatty acids and esters, binding to inorganic colloids, and held in aggregate or other environments inaccessible to the degradative microorganisms/enzymes. It can be possible that degradative and synthesis processes occur simultaneously. This would preserve macromolecular character as long as the synthesis involves degradation fragments and biologically synthesized molecules, especially macromolecules. Such degradation/synthesis processes might represent the steady state condition in any particular soil where synthesis and decay are in balance. In other words, at any one time there will be a suite or family of HS, some that are fully formed, some that are in the process of formation, and some that are undergoing degradation and decomposition. It should be remembered that the operational approach defining and isolating HS will provide extracts that contain an array of compounds. As a result of these considerations, it is clear that there will be a wide range of closely related substances that exhibit a range of chemical and physical properties in any particular preparation of HS (Swift, 1999).

The macromolecularity can vary depending, possibly, on the substrate materials, on the extent of the biological degradation and synthesis processes, and on the environments in which they are formed and found. However, it is not easy to state the extent to which HS in solution are associations of molecules that are polydisperse or polydisperse macromolecules ranging in size from the relatively small to very large. Nevertheless one can say that these associations can involve cation bridging and interactions with molecules that are relatively nonpolar (Clapp and Hayes, 1999).

Although macromolecularity concept has found echoes within the scientific circles working in the field; the foundation is weakened by various findings which undeniebly provided truthful essentials, i.e. Simpson (2001), although have shown component structures and connectivities in a FA, through the use of NMR techniques; the Diffusion Ordered SpectroscopY (DOSY) results stressed the evidence that HS are not macromolecular with, possibly, some degree of cross linking or branching, but are aggregates of mixtures.

There is no universal structural definition for humic substances. The concepts that are normally chemically meaningful and definite (such as molecular formula and molecular structure) are not applicable to HS as a whole. However pseudo structures offer a means for visualizing and communicating the types of chemical interactions and properties that a humic substance is expected to exhibit based on experimental data, such as carboxylic acid acidity, phenolic acidity, complexation ability, aromatic and aliphatic content, and the presence of ester, ether and other linkages in the system. They can also account for many other properties of HS, such as redox character, free radical nature, the ability to act as cement between clay particles and to sorb nonpolar solutes, the tendency to engage in hydrogen bonding, and infrared (IR) and NMR spectra (McCarthy, 2001).

Macromolecularity, regarding the genesis of humics, is rather a shape or conformation stating notion compared to fictional association of chemical entities that intends to reflect the characteristics of HS. The adsorption studies have found great comfort in considering HS as macromolecules, (Karanfil et al, 1996, 1999; Kilduff et al, 1996; and Vermeer et al., 1998), as it provided a correct interpretation of the evolution of the isotherms in various solution conditions. Besides, the evidences brought to defend macromolecularity of HS by (Swift, 1999; Cameron et al., 1972), remains undisputed in many ways.

2.4.1. Structural Approaches

2.4.1.1 Humic Acids Considered as Flexible Polymers. As mentioned in detail, under most circumstances the organic matter does not fall apart into units, as small as water molecules, so the polymer approach has enough appeal to be often used to gain better understanding of humic and fulvic acid behavior in adsorption.

A generic aspect of HS (or humic and fulvic acids) is its charge. The building units contain acidic groups that can ionize depending on the pH of the solution. Hence, if one approximates HA's as polymers, it would be wise to consider them as polyelectrolytes. Therefore, in discussions about the behavior of HS in solution, it should be recognized that it is dealt with macro-ion or polyelectrolyte and that the amount and distribution of charge on the molecule is the dominant effect influencing its molecular size, shape and behavior. In general, the carboxyl groups encompass vast majority of the acidic sites at HA, and their presence is well established by several analytical techniques, particularly infrared and ^{13}C-NMR spectroscopy and titrimetric methods (Swift 1996). Typically, HS contain four to eight charged (or potentially charged) carboxylate groups per 100 Daltons, depending on the degree of oxidation. This represents a relatively high charge density for a naturally occurring polyelectrolyte, and the extent of development of charge on these sites plays a key role in determining intra- and intermolecular forces.

The macromolecular approach has found support by important scientists in the field that describe the behavior of humic acids in solution as flexible polyelectrolytes. Chen and Schnitzer (1976) mentioned that fulvic and humic acids behave like flexible polyelectrolytes, not exclusively composed of condensed rings but as chains with numerous linkages about which relatively free rotation occurs. Although having taken an opposite view Summers and Roberts (1988), in their research studying the effects of polydispersity of the humic substances on the adsorption isotherms, reported that previously developed concept for well-defined synthetic polymers were also applicable to humic acid adsorption. Gosh and Schnitzer (1980) showed that, under the conditions that normally prevail in natural soils, humic acids can be described as flexible linear colloids. Cameron et al., (1972) visualized the humic acid molecules in solution as a series of charged, occasionally branched hydrated strands and concluded that branching results in an increased coil density within the molecule, giving rise to more compact coils than those for a linear molecule of equivalent weight. Swift, and Posner (1971) in their study for determination of frictional ratio of HS, have come up with results that support flexible linear structure. Although the findings also could have been pointing an alternative structure of condensed, well structured oblate ellipsoid with a high axial ratio, Swift also states that it is difficult, if not impossible to reconcile some of the known chemical and physical properties of HS – such as random tertiary structure, high charge density, rapid ion exchange, and high water uptake- with a condensed, rigid, well ordered structure. In contrast, the proposed flexible, expanding, polymer structure not only explains the observed macromolecular data, it also fits very well with the known chemical and physical properties of HS.

From the viewpoint of genesis of humic acids, Swift (1996) has defended the concept of macromolecularity. He argues that should lignin modification and degradation be major processes in the formation of HS, the products could then be expected to have a range of molecular weight (MW) values because of the different extents of cleavage of the altered lignin parent materials. He also asserts that if microbial synthesis processes are taken into account, it is not reasonable to conclude that the formation of high MW products is not possible in the absence of genetic control, and he refers to evidence of synthesis of HS from plant precursors, but in the absence of lignin as mentioned in previous section by Haider and coworkers (Haider et al., 1975).

To be more specific, flexible polyelectrolyte (or polymer) structure can be visualized as randomly coiled polyelectrolyte structure in solution. Flexible polymers, or flexible polyelectrolytes (as referred HAs are), have a large number of internal degrees of freedom. The typical primary structure of such molecules is linear chain of atoms connected by chemical bonds (“backbone”) and some pendant atoms or groups to satisfy the remaining valencies. By rotation about the (single) bonds in the backbone the molecule changes its shape, and since there are many of these bonds in a polymer a wide spectrum of shapes or conformations is available to long polymer molecule. This rotation may be hindered, notably by bulky pendant groups, so that some of these conformations may be rather unfavorable. In special cases the interaction between neighboring groups leads to preferred sequences of bond orientations, which show up as helical or folded sections in the molecules (*secondary structure*).

A polymer is termed flexible if thermal motion is strong compared to the energy barriers associated with backbone rotation. Such molecules have a randomly fluctuating three-dimensional *tertiary structure*, which can only be described statistically, taking averages over all the numerous allowed conformations (Fleer et al., 1993). To be more precise, one may look upon the conformation of an individual chain in solution as a walk through space. When walking from one end of the chain to the other, one never passes the same position twice. This reflects the fact that the monomers of a given polymer may not occupy the same position in space, which seems obvious. However, in calculations this restriction complicates calculations considerably. Therefore, the chains are described as random walks: when walking from one end of the chain to the other, we do not remember where we have been before. The often sited “random coil structure” term used for humic acids is a result of this fact (Fig 2.5).

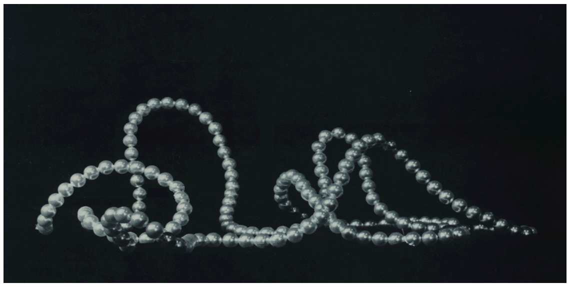


Figure 2.5. Polymers in space (adapted from Rowland et al., 1965)

A randomly coiled HA in solution can be envisaged as a long strand with charged and hydrated functional groups distributed along its length. The molecular strand coils randomly with respect to time and space. At moderate to high molecular weights, this results in a molecular conformation that is bound within a roughly spherical shape in which the mean distribution of molecular mass is Gaussian about the center. That is, the mass density is greatest at the center and decreases to zero at the outer limits of the sphere. The molecule is perfused throughout with solvent that can exchange with the bulk solvent outside the molecule (This portion also explains micellar configuration that will be explained in the coming section). At higher molecular weights, solvent at the periphery of the molecule would move relatively freely, but as the mass density increases toward the center of the molecule, solvent movement will be more restricted and, in some situations, may be effectively trapped. Hence, while the shape of the molecule in solution is essentially spheroidal, it is neither condensed nor rigid. It is important to note also that the nature of the mass distribution within the macromolecule will vary, depending on whether the molecule is tightly or loosely coiled. This, in turn will, depend on factors such as nature of the solvent, the extent of solvent penetration, the charge density of macromolecule, the identity of the counter ion and the surrounding pH (Hayes and Swift 1978, 1990).

Polyelectrolyte Adsorption. Adsorption of polyelectrolytes must imply changes in their shapes. The usual description of conformations at an adsorbing interface, first proposed by Jenkel and Rumbach (1951). The description of adsorbed chains derives to some extent from the solution models and the conformations of the polyelectrolytes in space as illustrated in Fig 2.5, above. This is because the adsorbed polyelectrolytes invariably form loops and tails so that many segments are still in a solution-like environment. The lateral interaction between adsorbed chain molecules is thus expected to be very much like the interaction of coils in solution (Cohen Stuart et al., 1985).

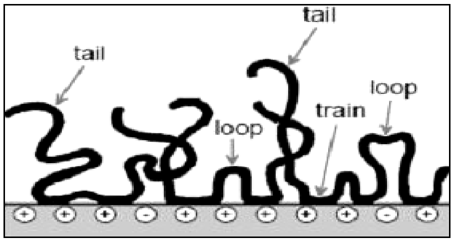


Figure 2.6. Schematic representation of an adsorbed polyelectrolyte layer. Loops, tails and trains are indicated (Cohen-Stuart et al., 1985).

A linear polyelectrolyte molecule adsorbed on a surface is shown schematically in Fig. 2.6. The molecule is represented as an assembly of segments, or subchains. Three different types of segments are identified. Trains are groups of segments in contact with the surface. Loops are groups of segments with no contact with the surface but with two ends connected to two trains. Tails are groups of segments with no contact with the surface and with one end connected to one train.

In polyelectrolyte adsorption electrostatic interactions play a very important role. Since this interaction is of variable range and strength, depending on charge densities (for both the surface and the polyelectrolyte chain) and salt concentration, the adsorbed amount depends strongly on these two variables. At low salt concentrations, one usually finds that highly charged polyelectrolytes adsorb in small amounts, or hardly at all (Cohen Stuart et al., 1991). When salt concentration is increased, the adsorption increases in the majority of cases. A schematic representation of the adsorbed layer for various situations is given in Fig. 2.7. (a – c). The polyelectrolyte is assumed to be negatively charged, and the adsorbent surface charge density is constant. The two left-hand side cartoons (Fig. 2.7 (a) and (b)) refer to low ionic strength solutions where the adsorption is dominated by the electrostatic forces. At acidic pH region (low polymer dissociation degree) the polymer is slightly ionized and exhibits no intrapolymer-chain electrostatic repulsion and therefore assumes a coiled conformation. It is quite common to observe increased adsorption which is attributed to the reduced size of the adsorbate as a result of coiled conformation at this pH range (Fig. 2.7 (a)). At basic pH range, the adsorbed amount lessens due to the ionization of polyelectrolyte which generates negative charges in the polymer chain and reduces the extent of coiling, with the result that less of the polymer is needed for complete surface coverage (Fig. 2.7 (b)). Diagrams in Fig (c) correspond to the high ionic strength, the adsorbed amounts and the conformations of the polymers are the same because the charges associated with the polyelectrolytes are screened by the salt ions and consequently the polyelectrolyte molecules show a tightly coiled and compact conformation in solution.

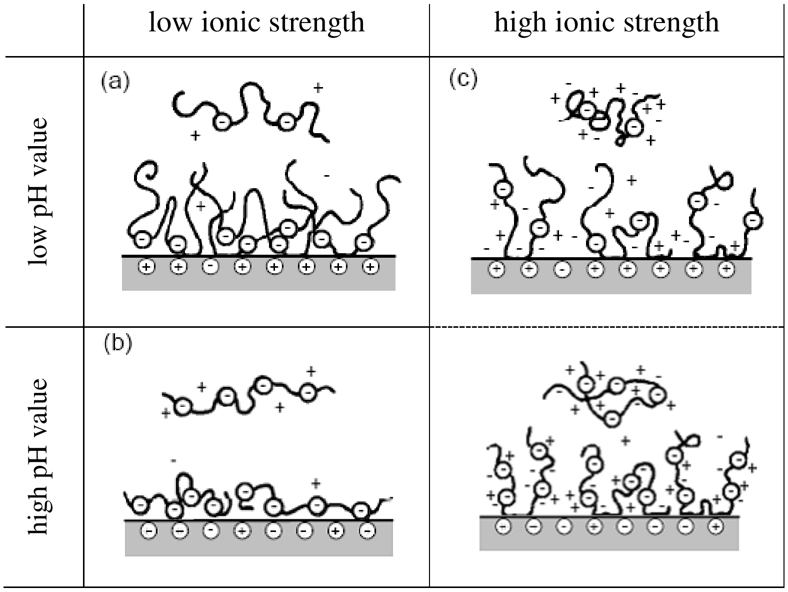


Figure 2.7. Schematic representations of polyelectrolytes at surface under various conditions for the polymer charge density and the ionic strength (after Fleer et al., 1993)

2.4.1.2. Humic Acids Considered as Micelles

Micellar Behavior of Humic Acids from the genesis point of view. As mentioned earlier, it has been proposed that HS are formed by enzymatic depolymerization and oxidation of biopolymers. The depolymerization reactions lead to the formation of relatively unaltered segments of polymers. Further oxidation of polymer fragments produced by depolymerization leads to the formation of carboxylic acid groups on the ends of the fragments (Wershaw, 1994). Wershaw (1993) has proposed that the oxidation of lignin, a major sink for HS, leads to the formation of fragments consisting of relatively unaltered lignin structures attached to one or more carboxylic acid groups. The unaltered segment of such a lignin fragment will be relatively nonpolar (hydrophobic), and the carboxylic groups will be polar (hydrophilic). Molecules with separate hydrophobic and hydrophilic parts are called amphiphiles, and they exhibit surface active properties. The oxidative depolymerization of polyphenolic polymers, such as condensed tannins (proanthocyanidins) that are abundant in leaves of most woody plants, aliphatic plant polymers (i.e. cutins), cuticle fats, waxes and, to a lesser extent, microbial fatty tissue can also lead to the formation of amphiphiles. The amphiphilic molecules are stabilized in soils and sediments by incorporation into membrane like structures that coat mineral grains or by incorporation into micelle-like molecular aggregates (Wershaw, 1993)

General Considerations. Surfactant (amphiphilic / amphipatic compounds) solutions, can adopt many possible modes of organization within a bulk phase. Among them, micellization is thermodynamically driven and is spontaneous. It is therefore often called self-assembly, and the resulting aggregates are known as association colloids. Quite an assortment of bulk surfactant structures is known, including ordinary and reverse micelles, liquid crystals, bilayers, vesicles and microemulsions (Hiemenz and Rajagopalan, 1997). Structural postulates on humic acids primarily concern with micelles, bilayers, and microemulsions; as will be mentioned further on.

Amphiphilic molecules exhibit concentration-dependent aggregation behavior in solutions. At low concentrations they exist almost entirely as monomeric species; however, at concentrations higher than the so-called critical micelle concentration (CMC) they form compact, globular, ordered aggregates called micelles. In aqueous solution, micelles form when hydrophobic portions of surfactant molecules associate as a result of the strong affinity of H_2O molecules -which must be disrupted when any solute is dissolved in water- towards each other constricting these hydrophobic portions in a confined space. The particular attraction of these hydrophobic compartments towards each other is relatively weaker than water-to-water affinity of the solution. This is called the “hydrophobic effect” (Tanford, 1991). As a result in an aqueous solution the aggregate has a hydrophilic exterior and a hydrophobic core.

Undissociated acidic species of humic acid provide an environment in which hydrogen bonding will take place. Hydrogen bonding can be intermolecular and/or intramolecular. For intramolecular hydrogen bonding, however, the interacting species will face the same way, and the configurations and conformations of the molecules will be more rigid than those for intermolecular interactions. Ring strain would also inhibit interactions between closely spaced interacting functionalities. Such considerations make it easier to accept the concept of hydrophobic stretches (or faces) in the cases of intramolecular hydrogen bonding (Clapp and Hayes, 1999). Inherent to this concept, it has been hypothesized that certain functional groups on the humic acid molecule are bound to each other forming pouches filled with hydrophobic constituents of humic acid. Presence of metal ions would induce this formation through “functional group bridging”; meaning:

bonding the functional groups together through their valence electrons. And these pouches were called “pseudomicelles” by Wandruszka et al. (1997). Sometimes, in special situations, polar groups can be found on the interiors of the aggregates. In these instances, ring strain would enlarge because of the diminished hydrophobic bonding affinity which also depends on the distance and distribution of hydrophilic moieties within the humic molecule.

In the case of intermolecular hydrogen bonding, various packing conditions can be employed for micelle formation and hence humics. Typically micelles tend to be approximately spherical but often there are marked transitions to larger, non spherical liquid crystal structure at high concentrations. Possible micelle structures include the spherical, laminar and cylindrical arrangements. Intermolecular hydrogen bond, bridges together individual humic molecules to form aggregates in micellar forms whereas intramolecular hydrogen bonds form similar structures by bridging two different functional groups within a single humic molecule. With different solution conditions and different types of molecules various micellar shapes can result as shown in Figure 2.8 below.

Systems containing spherical micelles tend to have low viscosities, where as liquid crystal phases tend to have high viscosities. The free energies of transition between micellar phases tend to be small and, consequently, the phase diagrams for these systems tend to be quite complicated and sensitive to additives (Shaw, 1994).

De Witt et al., (1993) taken into consideration all possible forms of micelles for humic substances in their research on ion binding to humic substances. Their research primarily assumes humic molecules as an ensemble of small rigid and impermeable cylindrical or spherical particles of a certain size and a variable surface charge density depending on pH and salt concentration.

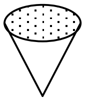
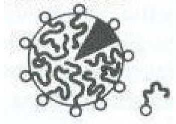
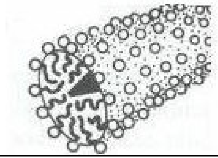
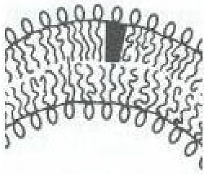
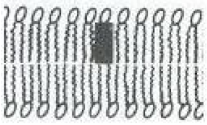
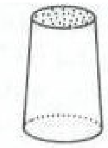
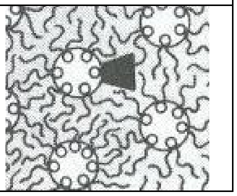
Amphiphilic molecule	Packing Shape	Structures Formed
Single-chained amphiphiles (e.g. lipids) with large head group areas	Cone	Spherical micelles
		
Single-chained amphipiles with small head group areas	Truncated cone	Cylindrical micelles
		
Double chained amphipiles with large head group areas, fluid chains	Truncated cone	Flexible bilayers, vesicles
		
Double-chained amphiphiles with small head-group areas	Cylinder	Planar bilayers, vesicles
		
Double-chained amphiphiles with small head group areas	Inverted truncated cone or wedge	Inverted micelles
		

Figure 2.8. Packing shapes and their relation to aggregate structure

Solubility Enhancement as an Evidence of Micellization of Humic Substances. The presence of hydrophobic core gives micelles the ability to enhance the solubility of hydrophobic organic compounds (HOC), so that the apparent solubility of a HOC in the presence of a micelle is many times that of the HOC in that solvent alone. This ability is the definitive criteria for an evaluation whether a surfactant will or will not, form a micelle (Mukerjee and Mysels, 1971; Mittal and Mukerjee, 1977; Pdopiel, 1978; Tanford, 1991).

Depending on this fact, the micelle formation of humic acid has first been tested by Wershaw et al, (1969). They found that the sodium salt of soil HA enhanced the solubility of DDT in water. However, the concentration of sodium humate solutions used were far higher than the natural DOC concentrations in natural waters. Chiu et al. (1979) measured the enhancement in apparent aqueous solubility of hydrophobic compounds brought about by unextracted DOC in natural waters. They studied the solubility enhancement of DDT and two chlorinated biphenyls in different rivers. They found that the solubility of DDT in these river waters was about 50% greater than that in distilled water. Later, Guetzloff and Rice (1994) also demonstrated the DDT solubility of humic acid and found micelle behavior of humic acid worth mentioning even in comparison with generic surfactant SLS (sodium lauryl sulfate). Wandruszka (1998), benefited from the fluorescence behavior of small non-polar species such as pyrene and diphenyloxazole, which were added to humic acid solutions. As would be the case with detergent micelles, these molecules were found to partition into the hydrophobic domains of the humic acid structure. Sequestered in this manner, they were protected from solution borne fluorescence quenchers (e.g., bromide ion) and were unaffected by the presence of these species.

For further understanding of pseudomicelles, Engebretson and Wandruszka (1997), applied photolysis to aqueous humic acid samples, in order to provide chain scission and trace the pseudomicellization on each individual fraction. The molecular fragments were found to have diminished detergent properties, indicated by a reduced tendency to associate with small hydrophobic species, namely pyrene as in their previous study. It was noted that photolysis is more likely to involve covalent bond breakage than dissociation of hydrogen bonded conglomerates thus disabling further bonding between broken fractions.

3. MATERIALS AND METHODS

3.1. Materials

All chemicals used in this study are analytical grade.

3.1.1. Humic Acid

Humic acid was supplied from Roth GmbH & Co. (Karlsruhe, Germany, Batch no. 485 18307). Stock humic acid solution (1000 mg L^{-1}) was prepared according to the procedure outlined by Urano et al., (1983). 1.000 g powdered humic acid; which was dissolved in 100 mL 0.1 N NaOH solution, and diluted to 1 L after 24 hours, provided 1000 mg L^{-1} stock humic acid solution following filtration. Stock solutions of humic acids were stored in amber glass bottles and were protected from light to prevent decomposition. 50 mg L^{-1} solutions were prepared weekly from the stock solution using distilled deionized water that has conductivity less than 10 μ S cm^{-1}. The UV-*vis* absorbance for 50 ppm HA at 436 nm was 28.6 m^{-1}, and at 254 nm was 170.9 m^{-1}. The TOC value for the same sample was 22.5 mg L^{-1}. pH adjustments were made two days prior and then they were readjusted before the start of the experiments considering altering pH sourced from the complexity of the molecule. The pH adjustments were done by adding standard NaOH (0.1 N) or $HClO_4$ (0.1 N).

3.1.2. Titanium Dioxide

Titanium dioxide powder was provided from Degussa (P25 grade). The qualifications are as given in Table 3.1 below:

Table 3.1. TiO_2 Specifications

Brand	Degussa P25
Crystal Structure	70%Anatase+30%Rutile
BET Surface Area	50 ± 15 m^2 g^{-1}
Primary Particle Size	20 –30 nm
pHzpc	6.25

3.1.3. Ionic Strength Agent

Perchlorate ion (ClO_4^-) was in the form of $NaClO_4$ and supplied from Merck. Different concentrations of perchlorate ion was added into humic acid solution to adjust the ionic strength (IS) to the desired level. The salt of the acid $HClO_4$, which is used to adjust the pH, was used during the experiments in order to avoid the combined effects of different ions in the solution, such as competition, and complexation. Similar technique was applied in a study by Bowers and Huang (1986) in a research about adsorption characteristics of Metal-EDTA complexes on aluminum hydrous oxides.

3.2. Methods

3.2.1. Laboratory Equipment

Shimadzu UV-160A Double Beam Spectrophotometer: Spectrophotometric measurements were done using the instrument.

Shimadzu TOC-V CSH Total Organic Carbon Analyzer: TOC measurements were performed using the instrument.

Bardelin Sonorex RK 100 Sonication: The homogeneous suspension was provided by sonication of slurry for two minutes.

WTW pH Meter-pH 526: pH was measured using the instrument.

Memmert Water Bath Shaker Model WB/OB 7-45: It was used for the adsorption experiments, to provide continuous shaking for 24 hours.

Sartorius BL210S-OCE Balance: Balance was used for weighing measured TiO_2 loadings.

Sterile Millex-HA Millipore Filter: The 0.45µm diameter millipore filters were used for the removal of TiO_2 from the suspension.

Hettich EBA 8S Centrifuge: It was used for the removal of TiO_2. The suspensions were centrifuged for 10 min.

3.2.2. Experimental Procedure

Batch adsorption experiments were held using 100mL Erlenmeyer Flasks. Each flask was filled with 25 ml humic acid solution. TiO_2 was added to each bottle starting from 0.1 mg mL^{-1} and increasing by 0.1 mg mL^{-1} for each bottle up to 5.0 mg mL^{-1}. One extra flask was filled with only humic acid solution for comparative purpose. Each sample was sonicated before being inserted to the shaker for even distribution of TiO_2 in the slurry. The samples were then immersed to water-bath which is equipped with shaking device and the appliance was set to room temperature. The flasks were kept shaking for 24 hours. The samples were centrifuged for 10 minutes in 10000 cycles min^{-1}. The supernatant was then filtered by the 0.45 μm Millipore filter. The procedure was repeated for acidic (pH 5), neutral (pH 7) and basic (pH 9) conditions.

Experiments with increasing ionic strengths were held in the same manner only to the TiO_2 concentrations up to 1.0 mg mL^{-1}. Logarithmically increasing ionic strengths (IS) of 0.001, 0.01, and 0.1 were studied at each pH conditions.

3.2.3. Analytical Methods

3.2.3.1. Total Organic Carbon (TOC) Analysis. Total organic carbon (TOC, mg L^{-1}) contents of the equilibrium humic acid solutions were measured using Total Organic Carbon Analyzer. Calibration of the instrument was done using potassium hydrogen phthalate.

3.2.3.2. UV-*vis* Measurements. UV-*vis* absorption spectra were recorded. Humic acids were characterized by UV-*vis* spectroscopy. Absorbance values at 436 nm ($Color_{436}$), 400 nm ($Color_{400}$), 280 nm (UV_{280}) and 254 nm (UV_{254}) were recorded in solution at the untreated and treated samples to track the change of UV-*vis* parameters after each adsorption experiment.

3.2.4. Parameter Selection and Further Facts

$Color_{436}$ and UV_{254} parameters have found frequent use in NOM studies which can be traced recurrently in the humic literature (Ochs et al.,1994; Bekbölet et al, 2002; Amal et al, 1992). True color is created by the presence of compounds that absorb visible light, or from compounds that fluoresce in the lower ranges of the spectrum. These are compounds of poly-aromatic structure, substituted aromatic structure, polyenia, concentrated hetero-circular molecules or perplex ions. The existence of conjugate bonds (polyenia) is necessary for the absorption in visible light spectrum. Most compounds responsible for color creation contain one or more aromatic rings and start absorbing color at 250 nm.

To support the data acquired by $Color_{436}$ measurements, a supportive absorbance at 400 nm was also followed. With the typical characteristics of color forming moieties, as mentioned above, $Color_{400}$ followed the same trend as its complement $Color_{436}$, and therefore has not been included to the discussion section.

Amongst the key parameters in drinking water quality UV_{254} and TOC are used as representatives organic matter (Krasner, 1999). With its specific wavelength targeting the aromatic carbon functional groups UV_{254} yield good correlation with TOC in monitoring the water quality. In the same sense, it has been reported that for fulvic acids there has been a strong correlation between the molar absorptivity (ε) and aromaticity as determined by ^{13}C NMR measurements (Chin et al., 1994; Gauthier et al., 1987). ε is typically measured at wavelengths between 280-254 nm, because π to π^* transitions occur in this UV range for phenolic substances, aniline derivatives, benzoic acids, polyenes, and polycyclic aromatic hydrocarbons. Chin et al., (1994) proposed that this type of correlation can be used to predict the aromaticity of humic substances with simple spectroscopic measurements. As it can be deduced, from these explanations, parallel to color parameters, UV_{254} and UV_{280} also shares a similar representative quality in NOM detection. Therefore, the correlations derived from UV_{254} were presented throughout this study, along with the $Color_{436}$ parameter.

When regarded as a macromolecular entity, spectrophotometric readings can be employed to represent individual humic molecules in the system, thus making color and UV parameters quantitative factors. However regarding the ill-defined structural properties of humics, the conformation of humics in the adsorbed state, and random distribution of color formers with/within the humic molecule, one should be aware of the dubious nature of these parameters. Therefore, it is necessary to accompany the results with total organic carbon analysis. The constant TOC comparison throughout the various phases of the study has shown that that the $Color_{436}$–TOC relationship, as well as UV_{254}–TOC, holds in the entire adsorption scheme, proving the noninvasive nature of adsorption. Unlike oxidative processes such as photocatalysis or photolysis, adsorption does not break or alter molecule into various forms that would obstruct the nature of spectrophotometric measurements.

In addition to TOC and UV-*vis* data provided, functional group analysis was held as outlined in various articles about identification of humic matter (Balcke et al., 2002; Frimmel et al., 1985; Larive et al., 1996) in order to support the facts stated herein. The prevailing carboxylic and phenolic groups have been sought quantitatively, by titration of the humic sample within the pH range of 2.5-11. The equivalent concentration of NaOH used during the titration up to pH 7.5 quantitates roughly the carboxylic moieties, and the NaOH concentration consumed from pH 7.5 onwards represents phenolic moieties in the same sense. However the repeated trials to prove reproducibility of the data failed because of the limitations concerning limited aliquots produced for each test, and low concentrations of equilibrium humic acid concentration at higher TiO_2 concentrations. The reason about the literature that bears same kind of practice did not fail in reproducibility was because none of them performed titrations after a certain treatment scheme –adsorption in the present study–. The intention of those researches was purely giving clearer chemical profile for NOM of various origins. Whereas in the current study, concentrations were subject to decrease for each batch and experiment. Increasing the concentrations or volumes was out of the question since efficiency in the agitation of the system during adsorption experiments could easily be compromised by this kind of changes and would lead to erroneous interpretations. If the experiments have yielded reasonable results, it would have been possible to comment about the functional groups remaining in equilibrium humic acid solution, and thus would have led further evaluation of the data regarding the role of functional groups in humic acid adsorption onto mineral oxides.

Although the explanations are derived from structural models seem rather simplistic, actually, there exists no research article that evaluates the same observation about humics discretely with different structural models but rather benefiting of them all as the conditions necessitated. With the difficulties in augmenting the data sources such as the example mentioned above, current research evolved around the principle of strong theoretical background with the utmost stress on simplicity and logic.

4. RESULTS AND DISCUSSION

The adsorption of molecules onto a surface is a necessary prerequisite to any surface mediated chemical process. Therefore, the mechanism of binding of humic acids to TiO_2 surface has to be addressed in order to improve the understanding of photocatalytic degradation. (Bekbölet et al., 2002). Extensive work has been carried by Bekbölet and coworkers to elucidate the mechanisms involved in the photocatalytic treatment of humic substances. Assessment of adsorption capacities of natural organic matter (NOM) on various crystal structures of TiO_2 (Süphandağ, 1998); adsorption – desorption studies (Baş, 2001) are worth stressing as examples of adsorption oriented research. Furthermore, photocatalytic degradation kinetics in the presence of various cations, and in different solution conditions were also subject to research where adsorption plays a role in one way or another (Bekbölet and Balcıoğlu, 1996; Bekbölet and Özkösemen, 1996, Bekbölet et al., 1998).

From the fundamental point of view, natural organic matter (NOM) for water scientists can be perceived as very complex entities both in terms of chemistry and comprehension. Especially the fulvic (FA) and humic acids (HA), the soluble portions of NOM, that are often considered as oligomeric and polymeric materials. In literature, there appears an ongoing debate about whether the high molecular mass is due to aggregation of small units, as in micelles, or due to covalently bound units, as in polymers. The essence of this thesis is to discuss the adsorption under the light of these two debatable approaches and bring reasonable interpretations of the observed isotherm patterns through the use of proposed structures.

The discussion covers isotherms of humic acid titanium dioxide adsorption at acidic, neutral, and basic pH ranges in surplus titanium dioxide concentrations exceeding the photocatalytically efficient range, and the combined effects of pH and increasing ionic strengths.

4.1. Evaluating the Effect of pH on Isotherms under different structural approaches

In this section the effects of changing pH conditions were assessed with surplus adsorbent concentrations exceeding the photocatalytically efficient range. The evolution course of the isotherms is evaluated by the view points of both adsorbent and the adsorbate. Micellar and flexible polymer structures, that have been the most frequently proposed molecular models for natural organic matter (NOM) were alternatively approached in explaining the adsorption phenomena.

Freundlich and Langmuir adsorption models were taken into consideration evaluating the isotherms. As it will be discussed accordingly in the following sections; the changes of the isotherms from a layered profile to a concave curve with the increasing pH showed none of these models alone were sufficient to explain the adsorption in this binary system.

In a previous study (Bekbölet, 1996), the effect of change in the concentration of TiO_2 was investigated and a proportionate rise in the degradation percentage was reported, as the concentration of TiO_2 was progressively increased from 0.1 mg $mL^{-1}$to 1.0 mg mL^{-1}. Consecutive photocatalytic experiments held in this manner showed that further increase in the loading resulted in a more opaque solution and a drop in the degradation rate, mainly because of the retardation of the light penetration to the photoactive surface. However, a broader range reaching up to 5 mg mL^{-1} loading ratio was tested, to asses the effect of pH and its reflections on the isotherms, beyond the photocatalytic loading range. The effect of ionic strength will be evaluated discretely within the photocatalytic concentration range later.

4.1.1. Isotherms at acidic pH

In order to follow the course of the isotherms at acidic conditions, pH of the solution is brought to 5, where the surface and adsorbate characteristic alter in favor of adsorption.

4.1.1.1. Polyelectrolyte Approach: In agreement with the polymer adsorption theory (Fleer et al., 1993), highest sorption percentages were attained at acidic condition in the average.

As explained in detail previously, when considered as a macromolecular entity, or namely a flexible polyelectrolyte, humic acid renders a coiled conformation at acidic pH.

Humic acid hosts various moieties with a wide array of dissociation constants - with reference to of prevailing carboxylic groups causing negative charge up to pH 7.5, and phenolic groups up to pH 11 (Frimmel et al., 1985; Frimmel and Abbt-Braun, 1999) respectively- causing a net negative overall charge, however, at acidic pH ranges the dissociated functional groups are less in number which causes a weaker intramolecular electrostatic repulsion. As a result the humic acid molecules form a less rigid and coiled structure causing to occupy a lesser space on the adsorbent surface, in agreement with the Figure 2.7a.

At this pH, the net overall surface charge of titanium dioxide is positive. Fundamentally, this can be explained as follows: in aqueous solution, the titanium dioxide surface consists of amphoteric hydroxyl groups, namely, to the six coordination sites of titanium atom, oxygen molecules are linked by single and double bonds in the hydrous state (Fig. 4.5). The surface group built by double coordinated O_2 atom has acidic character, and the singly coordinated hydroxyl group has basic character. In aqueous systems, titanium dioxide has almost equal distribution of these surface groups that constitute a surface charge close to neutrality, hence the pH_{zpc} for Degussa P25 is given as 6.25 (Schmelling et al., 1997).

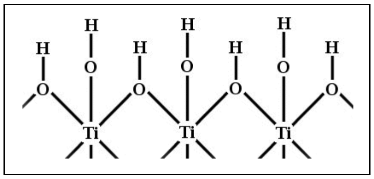


Figure 4.1. Titanium hydrous oxide

At pH 5, the isotherm portrayed a regional profile with a wide span of data points along the Cartesian coordinates (Fig 4.2 and 4.3). The isotherm is divided to three regions in order to observe the different phases of adsorption occurring in the system. The C_e

ranges for ***Region I*** is between 0.0986 to 4.52m^{-1}, ***Region II*** is between 5.82 to 16.7 m^{-1} and ***Region III*** is between 16.7 to 22.5 m^{-1}. For TOC, isotherm is divided in the same manner, with C_e ranges for ***Region I***, between 1.58 to 2.87 mg L^{-1}, for ***Region II***, between 6.24 to 13.10 mg L^{-1}, and for ***Region III***, between 13.69 to16.36 mg L^{-1}.

Region I. The batches with highest TiO_2 concentrations (from 1.25 mg mL^{-1} up to 5.0 mg mL^{-1}) falling in this region make plenty of surface area available for coiled humic acid molecules to adsorb with their reduced size. The opposite charge also enhances the affinity of humic acid molecule for the surface. Thus, the isotherm shows "the resultant effect of a high affinity of TiO_2 surface for the humic acid at low surface coverage coupled with a decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increases"; as given in analogous "L-curve" definition where the adsorption data is interpreted through Langmuir equation (Sposito, 1989).

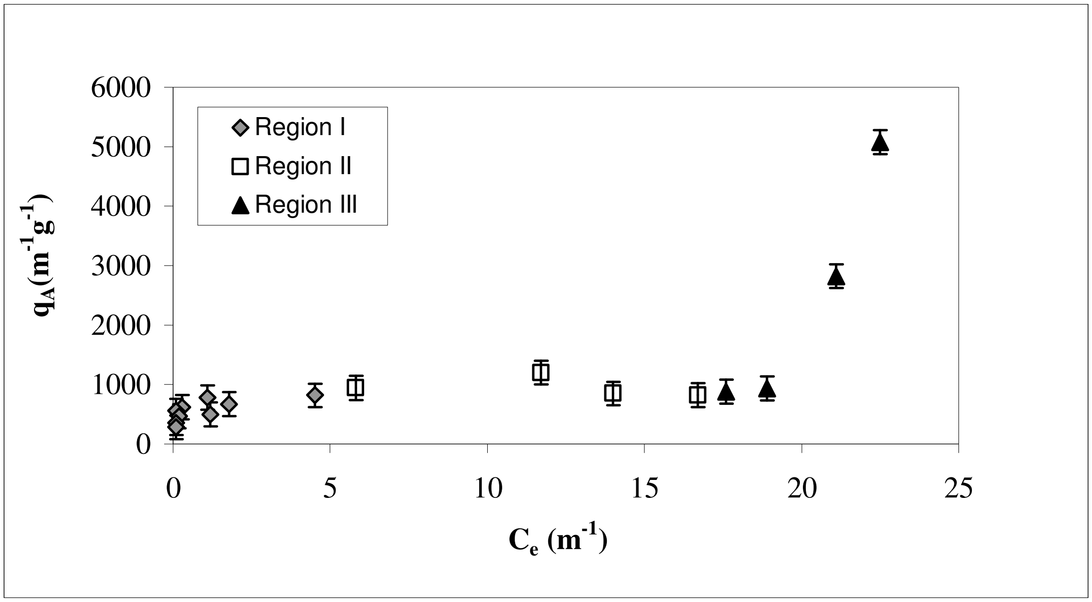


Figure 4.2. Adsorption isotherm at pH 5 for $Color_{436}$

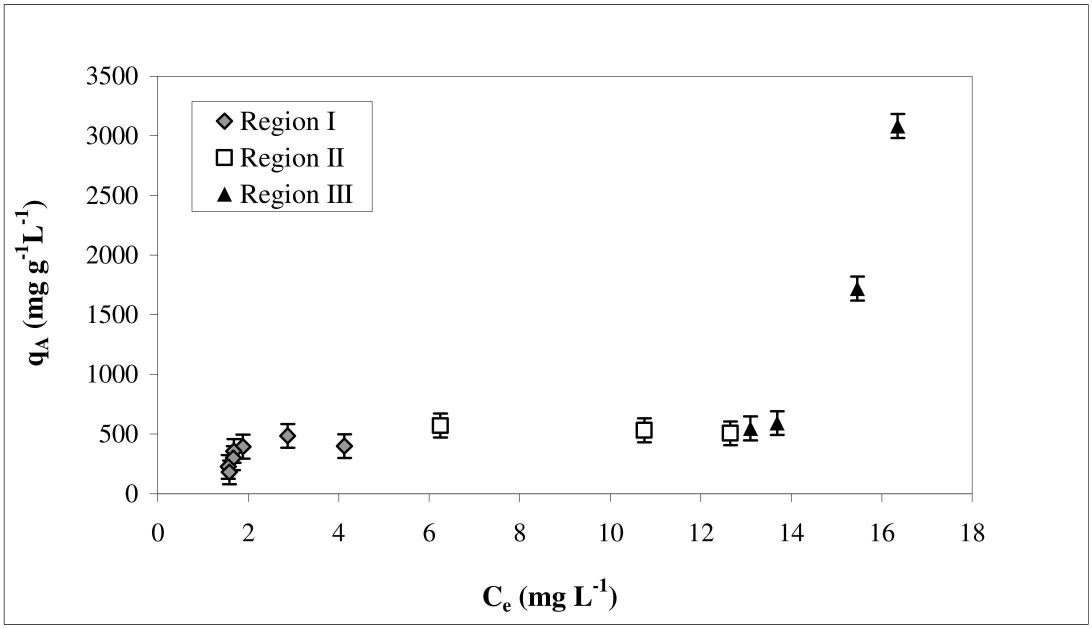


Figure 4.3. Adsorption isotherm at pH 5 for TOC

Validation of the use of Langmuir Equation for Humic Material. Langmuir in his original work (1918) postulated that

1. Adsorption occurs on planar surfaces that have a fixed number of sites which are identical and the sites can hold only one molecule. Thus only, monolayer coverage is permitted, which represents maximum adsorption.
2. Adsorption is reversible.
3. There is no lateral movement of molecules on the surface.
4. The adsorption energy is the same for all sites and independent of surface overage (i.e., surface is homogeneous), and there is no interaction between adsorbate molecules (i.e., adsorbate behaves ideally).

Nevertheless, the adsorption of polymers from solution on liquid-solid interfaces exhibits isotherms which closely resemble Langmuir's. The explanation for this curious finding is probably that if adsorbed particles have a tendency to repel one another within the surface layer, this produces an isotherm similar to Langmuir's but with lower capacity (Rowland et al., 1965). Furthermore it is added that generally, any adsorption process which yields a monolayer will have an initial linear slope proportional to affinity times concentration and show saturation or a plateau, so that at least the low and high concentration sectors of any isotherm can be characterized by two constants as if it were a Langmuir isotherm.

Earlier works on the polymer adsorption have shown preponderance of isotherms whose shapes indicate the presence of monolayer of some kind (Claesson and Claesson, 1948; Gottlieb, 1960; Hobden and Jellinek, 1953; Koral et al, 1958). Koral et al. (1958), in their study about the adsorption of polyvinyl acetate have mentioned the successful fit of their data to Langmuir.

In summary, these works have brought up some basic facts about the application of Langmuir equation to polymer adsorption data. First, the amounts held at the interface at or near equilibrium saturation are, in most cases, appreciably larger than can be accounted for by a monolayer of monomer units, with the exception of the adsorption of polyelectrolytes on surfaces of opposite charge when capacities of monomer monolayers are often approached. Second, the saturation values depend weakly on molecular weight. Finally, there is a strong dependence on the solvent. All these observations were concluded with the emerging polymer adsorption theory which later has been sculptured as explained in Section 1.3 (polyelectrolyte adsorption). However goodness of fit of polymer adsorption data to Langmuir equation keeps being elusive, in view of sophistication of the various treatments, it is almost embarrassing that most polymer adsorption data fit the simple Langmuir Equation, as well as any other, within experimental error (Adamson, 1990).

The Langmuir trend is explained as the resultant effect of high relative affinity of the adsorbent for the adsorbate at low surface coverage coupled with a decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increases (Sposito, 1989).

To show that the experimental records are in agreement this trend, the data is fit to the Langmuir equation:

$$q_A = \frac{K_{ads} C_e}{1 + K_{ads} C_e} q_{max} \qquad 4.1$$

where q_A is the adsorbed humic acid concentration per unit mass of TiO_2 [mg $g^{-1}L^{-1}$ (TOC) $m^{-1}g^{-1}$ ($Color_{436}$)], K_{ads} is the Langmuir adsorption constant [mg L^{-1} (TOC), m^{-1} ($Color_{436}$). C_e is the concentration of humic acid at equilibrium [mg L^{-1}(TOC), m^{-1} ($Color_{436}$)], and q_{max} is the maximum adsorption [mg g^{-1}(TOC), $m^{-1}g^{-1}$ ($Color_{436}$)].

When linearized Langmuir equation takes the form:

$$\frac{1}{q_A} = \frac{1}{q_{max}K_{ads}}\frac{1}{C_e} + \frac{1}{q_{max}} \qquad 4.2$$

where reciprocals of both terms were taken to maintain the simple linear equation "y=ax+b", where the term $1/q_{max}K_{ads}$ substitutes for a and $1/q_{max}$ substitutes for b in Equation 4.2 above.

Table 4.1. Langmuir adsorption model constants at pH 5 for *Region I*

Region I	K_{ads}	q_{max}	R^2
$Color_{436}$	5.5 m	909.1 $m^{-1}.g^{-1}$	0.922
TOC	0.23 mg^{-1} L	769.2 $mg.g^{-1}$	0.914

In the research by Xu and Langford (2000), the maximum adsorption (q_{max}) in terms of TOC was found at 0.12 $mg.g^{-1}$ for acetophenone over Degussa P25. With the same adsorbent, Robert and Weber found, 1.75 $mg.g^{-1}$; 6.05 $mg.g^{-1}$; 3.22 $mg.g^{-1}$; 3.72 $mg.g^{-1}$; for oxalic, malonic, succinic and methylsuccinic acids respectively. The dramatic difference between the values found after humic acid (Table 4.1) in comparison with these simple structured compound can be related to the molecular size of the humic acid and conformation it assumes on the titanium dioxide surface. During adsorption, a single functional group or a few functional groups of humic acid can be enough to establish attachment onto the surface, with the rest extruding into the solution as represented by tails in Figure 2.6., during the separation of the solid phase from the system, the entire body of the adsorbate (humic acid) is removed and this might have caused inflated q_{max} values for humic acid. Parallel to this fact and to the values in Table 4.1, Rowland et al (1965) mentioned that the amounts held at the interface at or near equilibrium saturation are, in most cases, appreciably larger than can be accounted for by a monolayer of monomer units. However one should retain his objectivity since the total carbon amount found for humic acid might have been pointing that either very few molecules of humic acid is enough to fill the surface, or it might imply that many humic molecules stuck to the surface with only one or very few functional groups causing high adsorption maxima.

To supplement evidence about the attachment of humic acid on TiO_2 surface, studies by Wershaw and his colleagues (1995, 1996 a), is worth consideration since they confirm the presence of chemical interaction –or chemisorption – between metal oxides and humic compounds. In their work about the formation of humic coatings on mineral surfaces they studied the sorption of organic acids that represent HA from compost leachate on alumina. Since at acidic pH, the amphoteric hydroxyl groups on the metal oxide exist mainly as the conjugate acids, (-OH), they reacted with the anionic ligands of the organic acid and resulted in surface complexation. Furthermore they showed that carboxyl, phenol hydroxyl, or amino ligands, of the organic acid replaced the hydroxyl groups of the surface. This means that organic acid became attached directly to the metal ions leading to the formation of inner-sphere surface complexes. Again Wershaw et al., (1996b) demonstrated by infrared attenuated total reflectance (ATR) linear dichroism measurements that the carboxylate groups of the organic acids in compost leachate are bound on the alumina surface with a very limited rotation. This limited rotation probably indicates that each carboxylate oxygen atom is bound to an Al ion. The evidences of inner sphere chemical complexation, and limited mobility of the adsorbed functional groups suggest a high relative affinity of adsorbate to the adsorbent. Analogously, these facts successfully explain the large slope in *Region I* and corroborate the presence of L-type isotherm.

Regarding the genesis of humics, a fine detail should not be dismissed without notice: Polymerization need not take place along one axis only. Corollary to this fact, a sheet like structure was proposed by Benedetti et al. (1996). Later this conformation of humic acids covering the surface is supported for low pH in the study by Plaschke et al. (1999). In their in situ atomic force microscopy (AFM) study of sorbed humic acid colloids it is reported that surface coverage increases with decreasing pH. HA covers the oxide surface. Furthermore, it is found that at acidic pH average heights of structures increase compared with alkaline pH. This fact points out the possibility of increased frequency of loops on the surface of TiO_2. The authors stated that at acidic pH colloids arrange to aggregates, chains or networks favored by attractive forces of hydrogen bonding, van der Waals interactions. Therefore, a simultaneous processes of coagulation and adsorption of HA molecules results in branched structures of sorbed species with increased surface coverage and average heights.

Using the presupposed mean molar mass of humic acid, the average number of aromatic rings in a HA molecule, and the aforementioned flat structure (Plaschke et al. 1999) of humic acid in the adsorbed state, Enriquez and Pichat (2001) reached consistency with their adsorption experiment results that affirm the complete surface coverage of TiO_2 by humic acid. Previously on a study about proton binding to humic substances de Witt et al., (1993), have agreed with Chen and Schnitzer (1989) that a sheet like structure of high molecular weight humics is rather favored than a fully flexible linear polyelectrolyte or a rod like structure; since the flexibility of the molecule would be far more restricted than that of a random coil; due to cross-linking of smaller molecules that conform humics. In this manner of approach to humics, the maximum adsorption values can be meaningful.

Region II. When anions adsorb to oxide surfaces, the pH at which the point of net zero proton charge occurs increases (Au et al., 1999). The linear portion observed on isotherms at pH 5 corresponds to this actual phenomenon. Therefore it was found appropriate to dedicate a “region” to this section of the isotherms, in order to stress the criticality of this fact. Otherwise the linear portion can as well be included to the *Region I* and would not change the Langmuir constants, as no change in the slope is observed to cause any change in q_{max} values.

Inferring humic acid would act as an anion in the studied pH ranges; and titanium dioxide is positively charged below its pH_{zpc}, the surface would undergo charge redistribution, upon adsorption of negative humic acid molecules, and thus cause a drift in the pH_{zpc}. As a result, a clear linear pattern on the isotherm is observed at pH 5, *meaning* no matter how much the adsorbent concentration is increased, the adsorbate remains in constant proportion with the adsorbent until the very point that the surface is overwhelmed with the humic acid molecules. In a study about fulvic acid adsorption on hematite particles (Amal et al., 1992), it was reported that as the concentration of FA increased in the interface, the zeta potential decreased significantly until it reached an equilibrium value, after which it remained constant. The writers reasoned this incidence to the presence of both chemical and physical characteristics of fulvic acid adsorption to metal oxides. Electrostatic interaction between the polyanionic organic and the positively charged particles is only one of the driving forces for adsorption. Had this been the only factor involved in the adsorption process, the zeta potential would have been reduced to and remained at zero with increasing organic acid concentration. Instead, in the same study, it was reported that the zeta potential reversed in polarity. This occurrence indicates the presence of some specific chemical interaction supporting the same logic that the surface is coated with the adsorbate and then the adsorbate-adsorbate interaction take on.

The criticality of this linear portion needs to be stressed, since it not only an episode of surface charge drift, but also a statement of a transition between surface complexation and phase transfer type adsorption reactions.

Region III. Although a concave curve facing y-axis is observed at this region, it should be once again stressed that the regions are designated arbitrarily in order to provide an ease in interpretation of the data. Regions are deliberately designated to cover more than three data points so as to impart a further credibility to the trends. Providing further experimental data points were not preferred because of the high possibility of the deterioration in the experimental conditions. However one can easily observe a linear trend for *Region III* by simply ignoring the first data point. Therefore a further explanation is brought to this case, when the trend is linear.

In a research by Chiou et al. (1979), about the sorption of non-ionic organic compounds by soil, the existence of linear isotherms obtained after equilibrium DOC value was reasoned out by a partitioning mechanism. In their study the main adsorbing unit was soil organic matter. The linear trend observed in this study could as well be pointing out a partitioning mechanism, considering that the adsorbent particles were completely covered by humic acids. The present case brings about almost the same occurrence, where instead of soil solution this time the adsorbent is humic acids seeded with TiO_2.

Being loyal to range description of *Region III* (C_e range between 16.7 to 22.5 m^{-1} for $Color_{436}$, and between 13.69 to16.36 mg L^{-1} for TOC.) one can also talk about a Freundlich trend for this portion of the isotherm. The relationship in Freundlich equation has been shown to fit many experimental data sets quite well. In the literature about activated carbon adsorption of humics, similar shaped isotherms (i.e. concave upwards on arithmetic coordinates) are stated to be characteristic of sorption from multicomponent solutions of compounds having different sorption affinities (Karanfil et al., 1999; Karanfil et al., 1996; Kilduff et al., 1996). Neither the Langmuir equation with its original requirements as stated in Section 2.1.1, nor BET equation which represents isotherms reflecting apparent ***multilayer*** adsorption profiles, represents the NOM-activated carbon adsorption data well since they are both limited by the assumption of uniform energies of adsorption on the surface (Weber, 1972). Freundlich equation found common use in modeling adsorption practices, due to its applicability to systems with heterogeneous surface energies, its empirical use and its acceptability in data description.

Freundlich equation is:

$$q_A = K_F C_e^n \qquad 4.3$$

Similar to Langmuir equation, this equation can be linearized as follows, in order to to provide coefficient n from the slope, and K_F from the antilogarithm of intersection with the y-axis.

$$\log q_A = \log K_F + n(\log C_e) \qquad 4.4$$

where q_A is the adsorbed humic acid concentration per unit mass of TiO_2 [mg $g^{-1}L^{-1}$ (TOC) $m^{-1}g^{-1}$ ($Color_{436}$)]; K_F is the parameter that relates to adsorption capacity (or density); C_e is the concentration of humic acid at equilibrium [mg L^{-1}(TOC), m^{-1} ($Color_{436}$)]; n is a parameter which indicates how dramatically the binding strength changes as the adsorption density changes.

Freundlich isotherm assumes that different groups of surface sites reside on the adsorbent, and to each of these surface sites, adsorbate is filled in accord with the Langmuir isotherm. And for any equilibrium concentration of adsorbate, all the surface site groups share the adsorbate to some extend. The high affinity sites get more of the adsorbate, almost to saturation (Benjamin, 2002a). As a cumulative of Langmuir isotherms; Freundlich does not reduce to a linear adsorption expression at very low concentrations. Nor does it agree well with the Langmuir equation at very high concentrations, since n must reach some limit when the surface is fully covered (Weber, 1972). As a result, Freundlich isotherm most correctly represents the data where the constant n is between 0 and 1. A value of "n=1" indicates that the binding strength is the same on all sites, so the equation reduces to a linear isotherm (give $q_A = k\ C_e$). This situation also may be regarded as a confirmation of linear trend mentioned earlier in this section where the surface can be regarded relatively uniform; if it is all consisted of humic molecules, after the surface coverage.

Table 4.2. Freundlich adsorption model constants for *Region III* at pH 5

Region III	K_F	n	R^2
$Color_{436}$	0.0157	3.97	0.943
TOC	0.0095	4.42	0.971

As can be seen from Table 4.2 above, the n value is greater than 1. This increasing trend would have agreed well with the "C-curve" definition (Sposito, 1989), if it was the initial portion of the isotherm; showing increased amounts of humic acid is adsorbed per unit concentration of titanium dioxide. The constant proportion in *Region II* is broken for the favor of the adsorbate in *Region III* where the surface is believed to be fully covered. Encountering a scene in a protracted phase of adsorption with the constant n greater than 1, suggests a possible multilayered adsorption of humic acid over the oxide surface.

In the same vein, previously referred Amal et al., (1992) observed that, after the hematite particle surface appears to be saturated with FA molecules, the capacity to adsorb FA molecules increases again. They discuss that; this may be due to lateral interaction of

FA molecules with other FA molecules through the hydrophobic effect, which promotes further adsorption and hemimicelle formation. Such a phenomenon is consistent with the amphipatic nature of fulvic acid; i.e., it contains both hydrophobic and hydrophilic moieties. In this case, both specific and electrostatic interactions will be operative during the whole adsorption process, but the extent of lateral interaction occurring depends on the extent of adsorption. In a clearer manner; this means that the more humic acid adsorbed on the surface, the larger the new surface is, and therefore adsorption will increase.

Furthermore, n>1 implies that as the adsorption density increases, the affinity of the surface for the adsorbate also increases. Such a result is sometimes used as evidence of multilayer adsorption or conversion of adsorbed species onto a precipitated, separate solid phase at the surface. However, this trend cannot apply indefinitely. There is an upper limit of C_e at which the trend must change, because otherwise it would predict that the affinity of the surface for the adsorbate eventually becomes indefinitely strong, which is thermodynamically impossible. Under the light of this information, most likely the isotherm at pH 5 would be followed by a new plateau (linear region), and a consequent decrease –desorption- in the trend.

4.1.1.2. Micelle Approach.

As detailed earlier on, amphipatic (or amphiphilic) molecules interact in solution with one another giving rise to aggregates. The mechanism driving formation of the surface aggregates is precisely the same one that causes the formation of micelles in aqueous solution, the hydrophobic effect (Ben Naim, 1980)

A second factor determining surfactant adsorption is the surface charge which is known to be a function of the solution pH for ionogenic surfaces, hence titanium hydrous oxide surface being one (Fig 4.1). As detailed previously, the charge on surface is due to protonation or deprotonation of chemically adsorbed water molecules.

Another feature of surfactant adsorption that is of primary importance is the role of surface heterogeneities. As being the subject surface in the latter study, TiO_2 has been known to have a heterogeneous surface character. In a study about inhibition of the adsorption and photocatalytic degradation of an organic contaminant in aqueous TiO_2 suspension by inorganic ions, the observed differences in inhibition levels between adsorption and photocatalytic oxidation was attributed to the surface heterogeneity of TiO_2

(Chen et al., 1997). Supporting the importance of heterogeneity of TiO_2 surface in catalytic reactions, an STM (Scanning Tunneling Microscopy) image of titanium dioxide surface was given by Charmas and Leboda (2000).

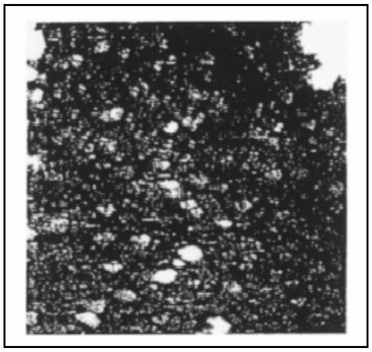


Figure 4.4. STM image of the surface of titanium dioxide (Roher et al., 1992)

As shown above in Figure 4.4, uneven distribution of the surface sites can be traced by the geometric deformation of the surface where darker and brighter fragments of the surface differ in height from one another The shape of the isotherm is in fact sensitively related with these heterogeneities and to the distribution of adsorption energies. A satisfactory theory incorporating humic acid adsorption and micellization covers these mechanisms.

Gaudin and Feurstenau (1955) studied the formation of cationic surfactant coatings on quartz surfaces. They introduced the term “hemimicelle” to represent a monolayer aggregate of amphiphilic molecules that form at low solute concentrations on an adsorbent surface. These aggregates form because hydrophobic interactions cause the nonpolar segments of the amphiphilic molecules to cluster together. Later, Harwell et al., (1985) redefined this notion as a pseudophase and named as “the admicelle” combining terms “adsorption” and “micelle”. Simply expressed, the admicelle hypothesis claims:

- The surfactant aggregation produces a bilayered structure (admicelle).
- Admicelle occurs on a given patch of a heterogeneous surface at a critical solution concentration (CAC, critical admicelle concentration).

- CAC is specific for the heterogeneous surface region that it occurred.
- For concentrations less than the CAC; the adsorbed surfactants do not interact with one another.

According to the hypothesis above, an explanation that would cover the observed isotherm at acidic pH was brought by Harwell et al., (1985). They stated that if the surface is made up of a distribution of patches with different adsorption energies, the overall isotherm will appear as a series of step changes in surfactant adsorption. As mentioned along with the STM image above (Fig. 4.4) titanium dioxide has a heterogeneous surface and thus possessing different adsorption energies. Additionally, isotherms having the characteristic stepwise shape, as in figures 4.2 and 4.3, have also been reported previously (Casas et al., 1982)**.** This viewpoint concerning different adsorption energies is also in corroboration with the use of Freundlich isotherm as detailed in Section 2.3.3.2.

Furthermore Somasundaran et al. (1992) on a research about the adsorption of *p*-octylbenzenesulfonate on alumina; observed that the equilibrium absorbance values constitute a slope that remains high until the critical micelle concentration is reached; at that point the slope of the isotherm changes abruptly to near zero. This is a similar picture to L-type isotherm, the statement also matches to the linear portion explained in Section 2.1.2.

Moreover, Scamehorn et al. (1982) allowed for the possibility of first-layer phase transitions to occur +with subsequent adsorption of surfactant on top of the first layer to complete the bilayered structure. This statement agrees with the Freundlich “n” coefficients–being greater than unity- in Table 4.2, which suggests a possible multilayered adsorption of humic acid over the oxide surface,

4.1.2. Isotherms at neutral pH

At neutral conditions, net charge of the surface has a negative sign, which actually shows the abundance of negative surface sites are slightly over the positive ones. On the other hand, humic acid conserving its overall negative charge sets a lesser affinity profile when compared to the acidic pH. As the fact about high affinity of constituents coupled with high surface area would yield a Langmuir type adsorption profile is not valid at this pH, a Freundlich type adsorption can be foreseeable from the beginning.

A quick scan of increasing, concave upwards profiles (Figures 4.5 and 4.6) can be perceived as a slightly elongated Freundlich isotherm pattern. However when the whole data is fit to Freundlich equation, they did not provide successful curve – fitting.

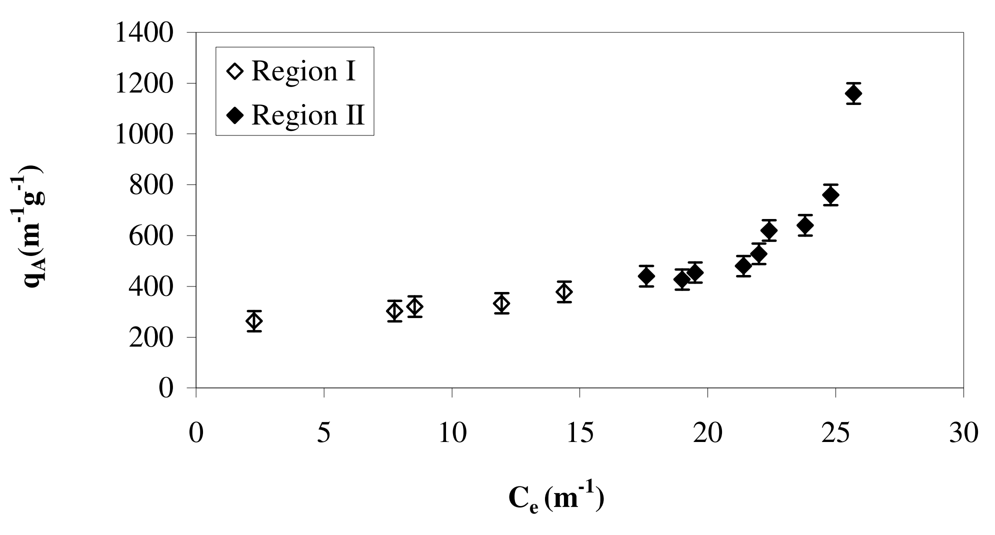


Figure 4.5. Adsorption isotherm at pH 7 for Color_{436}

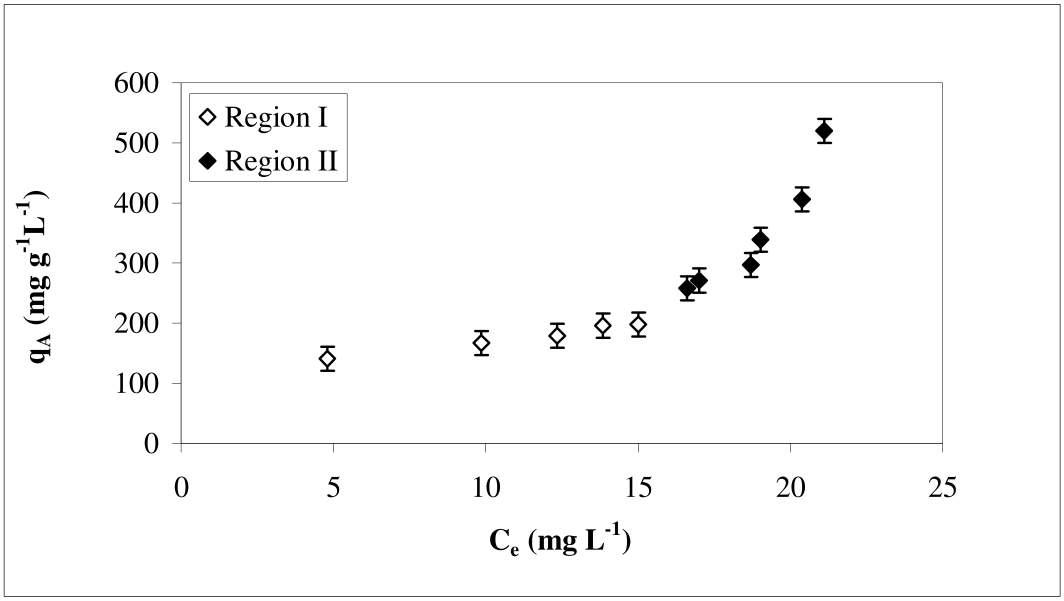


Figure 4.6. Adsorption isotherm at pH 7 for TOC

Further scrutiny of the data brought to attention that, beyond the photocatalytic loading range, the increase in q_A is insignificant in a wider array of C_e (2.27 – 17.6 m^{-1} for Color$_{436}$ and 4.8 – 15.0 mg L^{-1} for TOC) values, while in the photocatalytic range, q_A increases noticeably in a comparatively narrower series of C_e (17.6 – 25.7 m^{-1} for Color$_{436}$ 16.6 – 21.1 mg L^{-1} for TOC). Consequently the region concept is applied to these two sets of data points, *Region II* being the photocatalytic range preceded by *Region I.*

4.1.2.1. Polyelectrolyte Approach.

Region I. Considering the pH$_{zpc}$ of 6.25, at neutral pH, the net overall charge turns slightly negative on the oxide surface, while the humic acid molecule retains its net negative charge, since the pH still permits dissociation of carboxylic moieties residing on it. However as for both constituents of the adsorption system the factors causing electrostatic attraction reach almost their limits at this point. The slightly increasing slope observed in *Region I* shows that the ligand exchange mechanism between the surface and the humic acid molecules win over the electrostatic forces repelling similar charges of both the surface and the adsorbate.

Furthermore, at neutral pH, a common reaction occurs between the carboxylic functional groups of humic acid and the surface of hydrous metal oxide;

$$\equiv \mathrm{SOH} + \mathrm{R} - \mathrm{COO}^{-}(aq) \leftrightarrow \equiv \mathrm{S} - \mathrm{OCO} - \mathrm{R} + \mathrm{OH}^{-}$$

that imparts additional alkalinity to the solution. Consequently, ambient conditions evolve adding up to the opposition between the constituents of the binary system. Throughout the experiments, this effect was pronounced at higher TiO_2 concentrations, at low concentrations of the adsorbent this effect could not be traced, most possibly because of molecular rearrangement of humic acid causing a drop in pH have hindered the smaller increase in pH after TiO_2 is removed.

As a result; the electrostatic forces which draw the humic acid molecules in close proximity of the surface cease, eventually surface complexation decrease, and the initial steep slope complimentary with the linear portion to set "*L-curve*" at pH 5 leaves its place to a weakly increasing linear trend which can be expressed both with Freundlich and Langmuir equations.

The absence of the initial data points that connect the isotherm to the origin is because of the change in the conformation of the humics. As the pH increased, humics adopt a linear and relatively more stretched shape that requires a higher surface area to adsorb. Exercising further experiments with higher TiO_2 concentrations, hence the higher surface area, to provide these points would not be safe since maintaining effective mixing would not be achieved in the current experimental conditions.

Although the data link is missing due to experimental limitations; relating to the fact that unit adsorption (q_A) will approach zero when equilibrium concentration of adsorbate (C_e) is naught; it can still be concluded that isotherms are bound to origin and consequently Langmuir equation can be applied.

When the data are fit to Langmuir isotherm, they yield more reliable constants (Table 4.3), than the Freundlich isotherm for the *Region I* (Table 4.4).

Table 4.3 Langmuir adsorption model constants for *Region I* at pH 7

Region I	K_{ads}	q_{max}	R^2
$Color_{436}$	0.538 m	357.1 $m^{-1}.g^{-1}$	0.814
TOC	0.3088 mg^{-1} L	238.1 $mg.g^{-1}$	0.802

When Freundlich equation is applied, it is practically impossible to reach such high adsorption densities with such small binding strength rates as given in Table 4.4 below.

Table 4.4. Freundlich adsorption model constants for *Region I* at pH 7

Region I	K_F	C_e	R^2
$Color_{436}$	168.2	0.249	0.881
TOC	96.6	0.266	0.963

On the other hand; when compared to the strong L-curve region at pH 5, proportionately smaller values of $\mathbf{K_{ads}}$ and $\mathbf{q_{max}}$ for pH 7, provided in Table 4.3 confirms a weaker Langmuir trend for this region. The inflated q_{max} values derived from Langmuir equation is a characteristic of polymer adsorption when compared to monomolecular compounds (Simha et al., 1953)

Region II. The concave upwards trend at *Region II* portrays a likewise binding strength (n) to that of *Region III* at pH 5 (Table 4.2) . The values found for this region (Table 4.5) are also bigger than 1 for both $Color_{436}$ and TOC. This agreement in the final trends encourages the opinion about multilayered adsorption of humic acid on the TiO_2 surface.

Table 4.5 Freundlich adsorption model constants for *Region II* at pH 7

Region II	K_F	n	R^2
$Color_{436}$	0.134	2.72	0.841
TOC	0.283	2.41	0.902

4.1.2.2. Micelle Approach. The central core of micelle is predominantly hydrocarbon. The expulsion of the hydrophobic tails of the surfactant molecules from the polar medium is an important driving force behind micellization. The amphipatic molecules aggregate with their hydrocarbon tails pointing together toward the center of the sphere and their polar heads in the water at its surface. For the surfactant this mode of organization competes with monolayer adsorption, which it somewhat resembles (Hiemenz and Rajagopalan, 1997). Evidence for a perception, stemmed out of this resemblance was given in Section 3.2 (Somasundaran et al., 1992; and Harwell et al., 1985).

In ionic micelles such as humic acids, the hydrocarbon core is surrounded by a shell that more nearly resembles a concentrated electrolyte solution. This consists of ionic surfactant heads and bound counterions comprising the Stern Layer (Stumm and Morgan, 1996). Water is also present in this region, both as free molecules and as water of hydration. Beyond the Stern layer, the remaining counterions exist in solution. These ions experience electrostatic attraction drawing them toward the micelle and thermal jostling which tends to disperse them. The equilibrium resultant of these opposing forces is a diffuse ion atmosphere, the second half of the double layer of charge at the surface of the colloid. Ionic micelles migrate in an electric field, and the ion atmosphere of the colloidal particle is dragged along with it.

As a result of facts mentioned above, the behavior of micelles in the medium can be compared with the mobility of simple ions with the reservation that both micelle and the ion atmosphere have considerable dimensions. Therefore, electrostatic conditions mentioned in the “polyelectrolyte approach” will still apply for the when humics are perceived as micelles.

Considering the pH_{pzc} for TiO_2 is 6.25, the positively charged surface sites could be considered as equal to the negative ones; causing a weaker net attraction for bulky humic micelles. This fact is reflected to the Cartesian plane with a less enthusiastic trend, compared with the acidic conditions.

4.1.3. Isotherms at basic pH

Rather shifted and compacted manner of the isotherm at basic pH as shown in Figure 4.7 and Figure 4.8 is setting accordance with the evolution of previously discussed isotherms. At pH 5 the data points at the same range were distributed evenly over the x-axis. At pH 7 the array of C_e was relatively narrower and shifted. At pH 9 this effect pronounced in a rather odd fashion not to let any successful curve fitting. The occurrence is more like a cluster of data points concentrated in a narrow C_e span. And in order to stress *this* evolution scheme between studied pH values, the x-axis scales are purposefully not widened into the range of present data, throughout this work.

Although it is necessary to have alkaline conditions to solvate HAs, they will stay in solution when the pH is lowered to values approaching 4 and lower. In these circumstances, carboxyl groups in isolation (which are not activated by neighboring functional groups) will be protonated, but sufficient strong acid functionalities remain dissociated and solvated to keep the molecules in solution and thus also maintains a net negative charge for humics. Charge densities of HS and of the NMR data which indicate that as much as one carbon in five is present as a carboxyl group can be considered in general for HA's (Clapp and Hayes, 1999). At the high pH values, the phenolic and other weakly acidic functionalities can make significant contributions to charge density causing a stretched conformation because of the repellence of same charged functional groups.

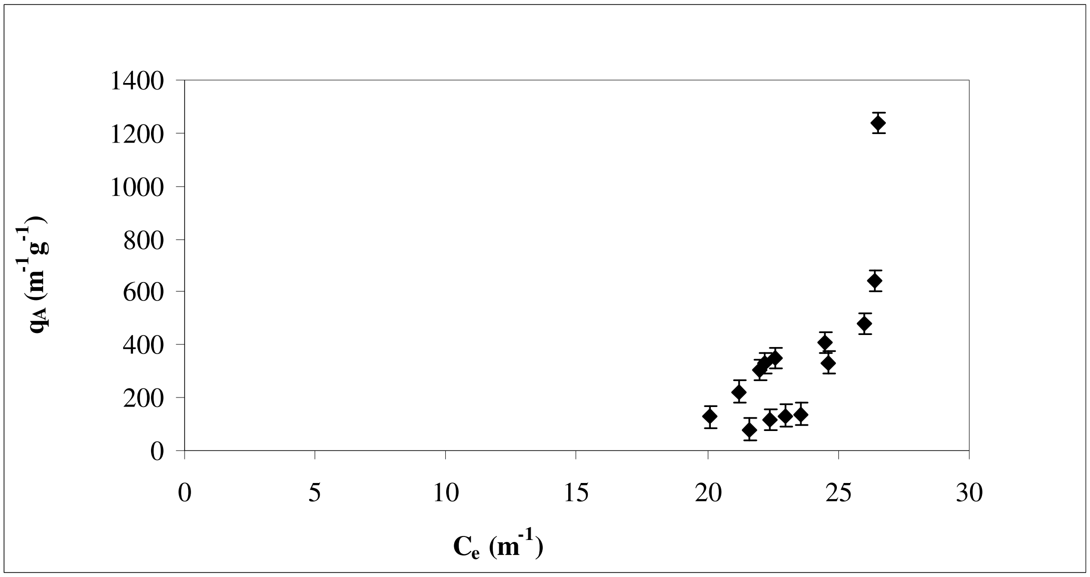


Figure 4.7. Adsorption isotherm at pH 9 for $Color_{436}$

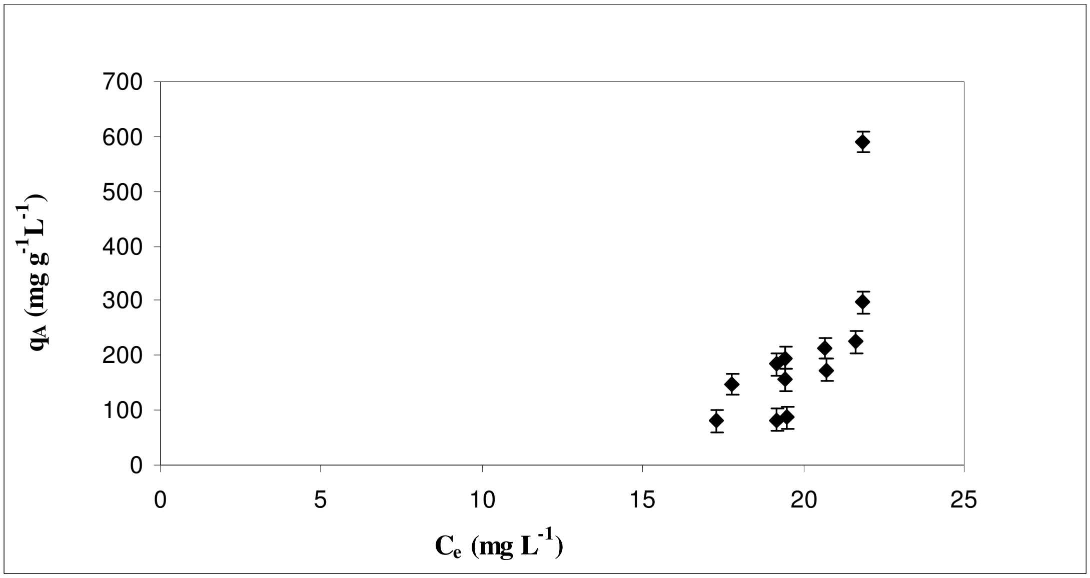
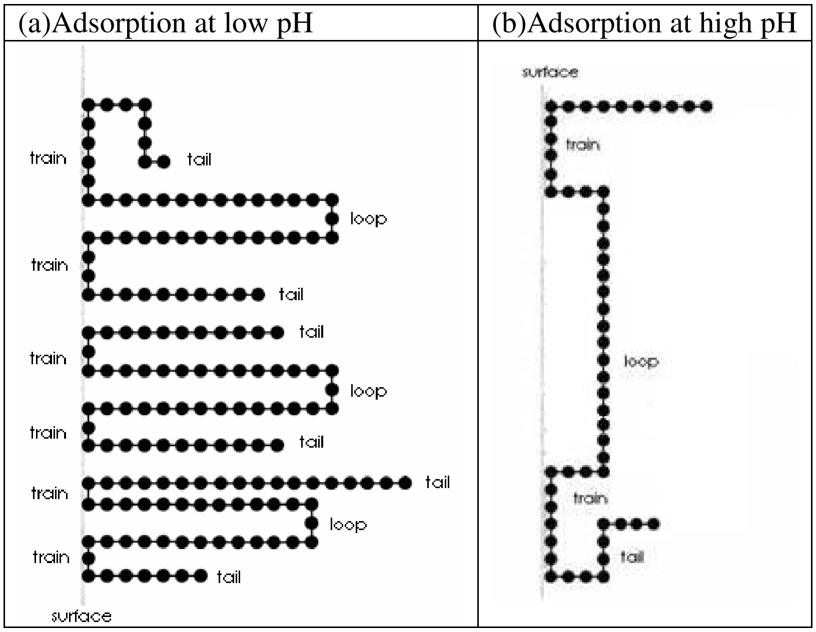


Figure 4.8. Adsorption isotherm at pH 9 for TOC

4.1.3.1. Polyelectrolyte approach. Recapitulating the effect of pH to the course of adsorption so far, it can be said that at low pH, where the polymer is only weakly negative, and the surface is strongly positive, the adsorbed polyelectrolyte molecules protrude relatively far into the solution with loops and tails, and a high adsorbed amount results (Figure 4.9 a). At neutral conditions the charge effect of the surface is not pronounced, where the adsorbate starts to get a more stretched shape, at high pH where the polymer is highly negative and the surface is negatively charged, the adsorption values are relatively low, and a flat and/or stretched conformation of humic acid interacts with very scarce and discretely allocated positively charged surface groups and relatively high fraction of loops (segments that are attached by both ends) determines the adsorption (Figure 4.9 b).



(a)Adsorption at low pH

(b)Adsorption at high pH

Figure 4.9. Schematic representation of humic acid on metal oxide surface at high and low pHs. (Adapted from Au et al., 1999)

With increasing pH the positive surface charge can become overcompensated by the negative charge of the adsorbed polyelectrolyte and an electrostatic barrier arises that minimizes further adsorption (Vermeer et al., 1998). The appearance of clustered data points at a shifted region on the Cartesian plane most likely stems from this fact. On the other hand the array of data points in a narrow C_e range almost reflects an existing near-vertical trend which would yield very high adsorption intensity in a Freundlich equation.

As stressed earlier on, for describing the adsorption of polyelectrolyte to a surface, the attraction between the surface and the polyelectrolyte is a basic parameter. This attraction is counteracted by the loss of entropy of the chain due to adsorption which means that stiff, rod like chains will adsorb more easily than flexible coiled chains. As a result it is still a possibility to talk about an efficient adsorption though the attained molecular architecture disables one to provide valid data points to constitute an isotherm.

4.1.3.2. Micelle Approach. As detailed earlier, the hydrophilic portion of the micelles are considered to be orientated to the exterior, and the interior consist of associations of the hydrophobic components mainly comprised of hydrocarbons. The interiors are normally in the fluid state (Shinitzky et al., 1971; Lindblom and Wennerstörm, 1977). The core of the micelle should be considered as two distinct regions: an inner core that is essentially water-free and hydrated shell between the inner core and the polar heads. This partly aqueous shell is called the *palisade layer* (Fig 4.10).

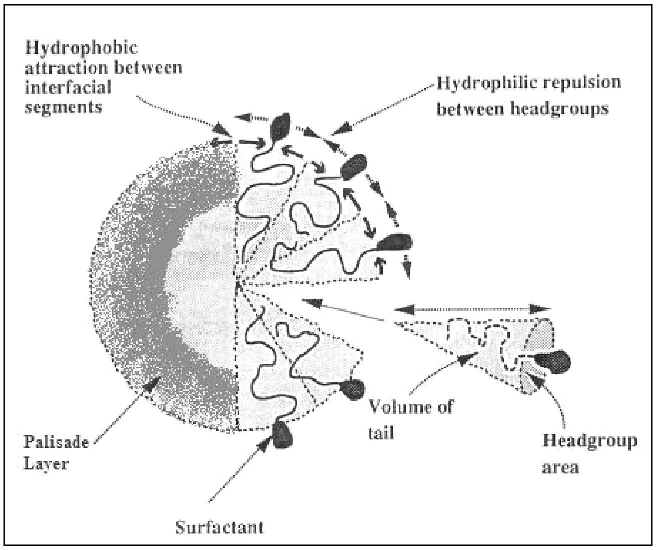


Figure 4.10. Illustration of geometric parameters for surfactant and how they influence the size of micelle (adapted from Israelachvili, 1992)

The surface area taken up by the head group of each surfactant molecule on the surface of a micelle depends on a number of factors, some of which tend to increase the area per head group while others tend to decrease it. This idea of two mutually opposing forces, suggested by Tanford (1991), refers to (a) an attractive force caused by the hydrophobic attraction of the hydrocarbon chain units at the hydrocarbon-water interface, and (b) a repulsive force between adjacent head groups arising from hydrophilic, steric and ionic (in the case of charged head group such as humic acids) forces. These forces together determine the optimal area occupied by the head group as illustrated in Figure 4.10 above.

The hydrophobic attraction is due to the preference of the hydrocarbon units near the surface to be close to its counterparts in the adjacent surfactant molecule. This attraction tends to decrease the effective area occupied by the head group. The repulsive force, on the other hand, is more complex and is not well understood presently. It is only known that, this repulsion is caused by the tendency of the hydrophilic head groups to allow as many water molecules as possible in their neighborhood (i.e. palisade layer) and by simple steric forces. Since the polarity of exterior head groups which would help humic acid molecules to assume a globular shape are lessened by the increased pH. It seems a bilayer, admicelle like formation on the surface of metal oxide is more adequate approach to explain the reaction of humic-oxide interactions at basic pH conditions where hydrophobic domains would be in contact with the metal oxide surface forming an interface, while the polar head groups face outwards to the aqueous solution.

4.1.4. Final Statements on the effect of pH and structural models

As an overall statement, it can be said that, the benefits of each structural approach shows variations with the changing pH. Particularly at acidic pH range, less of the acidic moieties of the humic acid is dissociated and thus provide an environment in which hydrogen bonding will take place which lead to formation of micelles. On the other hand in acidic pH polyelectrolyte model portrays a closely packed, coiled humic acid structure, which also brings about a globular overall structure. As a result for acidic pH, micelle model with attribution to polymer qualities of humic acids can explain the adsorption phenomena well. For neutral pH with the weakened electrostatic forces between the constituents of the system, it gets also difficult to assign any of the models for explaining the adsorption phenomenon. Weaker hydrogen bonding due to fewer amounts of non-hydrolyzed species may jeopardize the formation of micelles at neutral pH. On the other hand polyelectrolyte model can still satisfy the adsorption coefficients found after the experiments. For alkaline conditions, it is hard to talk about the validity of micelle model, since humic acid at this pH assumes a linear (or planar) and almost rigid shape due to dissociation of almost all functional groups that reside on it.

4.2. Evaluating the combined Effect of Ionic Strength and pH on Isotherms under different structural approaches

As well as the effect of pH, covered in detail in the previous section, another pronounced change in the solution matrix that has a major effect on the structural changes of humic acids is the ionic strength. Simply, ionic strength can be defined as a quantity proportional to the amount of electrostatic interaction between ions in solution. It can be expressed mathematically as:

$$\frac{1}{2}\sum m_i Z_i^2 \qquad 4.5$$

where m_i is the molar concentration of the medium i, and Z_i is the ionic charge (Weber, 1972).

In order to observe the ionic strength effect on adsorption of humic acid onto titanium dioxide, ionic strength of the solution is increased between, 0.01 to 0.1 at under acidic (pH 5), neutral (pH 7), and alkaline (pH 9) conditions. The TiO_2 concentration ranges were kept in the photocatalytically efficient range, in order to raise the question, whether the modifications in pH and IS could compensate the limitations caused by restricted TiO_2 usage as a consequence of photocatalytical efficiency limits or not. Because, as the ionic strength is increased, isotherm segments were observed to travel almost along a ghost trend (reminiscing isotherm at acidic pH in Fig 4.3) on the Cartesian plane heading towards high efficiency sectors of the coordinate axis. Conversely, using extended TiO_2 concentrations likewise in section 4.1, was shunned, as they produced regional and wide spanned isotherms, which would limit clarity of the IS effect.

Having discussed, so far the effect of pH on the structures and isotherms, with the salt effect added on this section, it is necessary to mention about a structural model which unifies both polyelectrolyte and micellar approaches under the gel concept

4.2.1. Heterogeneous Donnan Gel Approach

Heterogeneous Donnan gel model has been first introduced by Marinsky and Ephraim (1986). In this model the gel volume is dependent on the salt level and solution composition due to shrinking and the swelling of the gel phase.

To provide further clarity to this expression, the term "gel", as a colloidal state should be explained: Colloidal particles are usually solvated, often to one molecular layer extent, and this tightly bound solvent must be treated as a part of the particle. Sometimes much greater amounts of solvent can be immobilized by mechanical entrapment within particle aggregates. This occurs when voluminous flocculent hydroxide precipitates are formed. In solutions of long thread-like molecules the polymer chains may cross-link, chemically or physically, and/or become mechanically entangled to such an extent that a continuous three-dimensional network is formed. All of the solvent becomes mechanically trapped and immobilized within this network, the system as a whole takes on a solid appearance and is called a "gel" (Shaw, 1966).

Recalling what has been said in Section 2.4.2.1: "*A randomly coiled HA in solution can be envisaged as a long strand with charged and hydrated functional groups distributed along its length. The molecular strand coils randomly with respect to time and space. At moderate to high molecular weights, this results in a molecular conformation that is bound within a roughly spherical shape in which the mean distribution of molecular mass is Gaussian about the center. That is, the mass density is greatest at the center and decreases to zero at the outer limits of the sphere. The molecule is perfused throughout with solvent that can exchange with the bulk solvent outside the molecule.*" it is easier to perceive HA molecules as a separate gel phase that is in suspense with the solution. Further on, the paragraph continues: "*At higher molecular weights, solvent at the periphery of the molecule would move relatively freely, but as the mass density increases toward the center of the molecule, solvent movement will be more restricted and, in some situations, may be effectively trapped. Hence, while the shape of the molecule in solution is essentially spheroidal, it is neither condensed nor rigid (Hayes and Swift 1978, 1990).*"

In summary, when humic acid molecules are considered as linear polyelectrolytes, they may be envisaged as macromolecular entities, forming random coils which are tangled and sealed with each other in a fashion that an effective volume of solvent is trapped inside, which gives them a gel-like characteristic. Furthermore, as mentioned in Section 4.1.2.1, in case of considering a sheet-like structure for humic acids, a gel phase seems more likely than a fully flexible linear polyelectrolyte, due to cross linking and intramolecular interactions. In the same order of reasoning, humic acids may as well be considered as pseudomicellar formations, which was previously mentioned in Section 4.1.1.2.

Having stated the legitimacy of the use of term “gel” for humic acids; osmosis phenomenon should also be outlined to understand the Donnan gel approach.

Osmosis takes place when a solution and a solvent (or two solutions of different concentrations) are separated from each other by a semi-permeable membrane –i.e., a membrane which is permeable to the solvent but not to the solute. The tendency to equalize chemical potentials (and, hence, concentration) on either side of the membrane results in a net diffusion of solvent across the membrane. The counter-pressure necessary to balance this osmotic flow is termed the osmotic pressure. Osmosis also takes place in gels and constitutes an important swelling mechanism (Shaw, 1966).

In a natural water system, ions are ubiquitous, hence conditions for Donnan equilibrium is always present. Considering the humic acids as gels made up of dissimilar elements, it is not wrong to call them “Heterogeneous Donnan Gels”.

Certain complications arise in the osmosis phenomenon when solutions containing both non-diffusible and diffusible ionic species are considered. Gibbs predicted and later Donnan demonstrated that when the non-diffusible ions are located on one side of a semi-permeable membrane, the distribution of diffusible ions is unequal when equilibrium is attained. It is greater on the side of the membrane containing the non-diffusible ions. The main reason for this uneven distribution is to maintain the overall electrical neutrality in the system.

Dissociation of carboxylic and phenolic groups leads to a potential on the humic acid molecule and it is assumed, in Donnan model, that this potential is uniformly distributed within the gel phase. At each charge introduced to the system, the overall electroneutrality of gel phase is entirely preserved by the penetration of salt ions in the gel phase. By this way, Donnan model also provides an appropriate way to account for the effect of salt level on the charge of the humic acid (Benedetti et al., 1995).

Once received, the electrolytes cause shrinkage in the molecular size of humic acids mainly by screening the opposing charges that provides the molecule a stiff, stretched character as a polyelectrolyte. Or imparted ionic strength screens and consequently reduces the polar head group area, thus causing shrinkage in the case of micelles.

4.2.2. Effect ionic strength at acidic pH

At acidic pH the net surface charge is positive while the humic acid molecule preserves an overall negative sign. As a result electrostatic affinity is high at acidic pH.

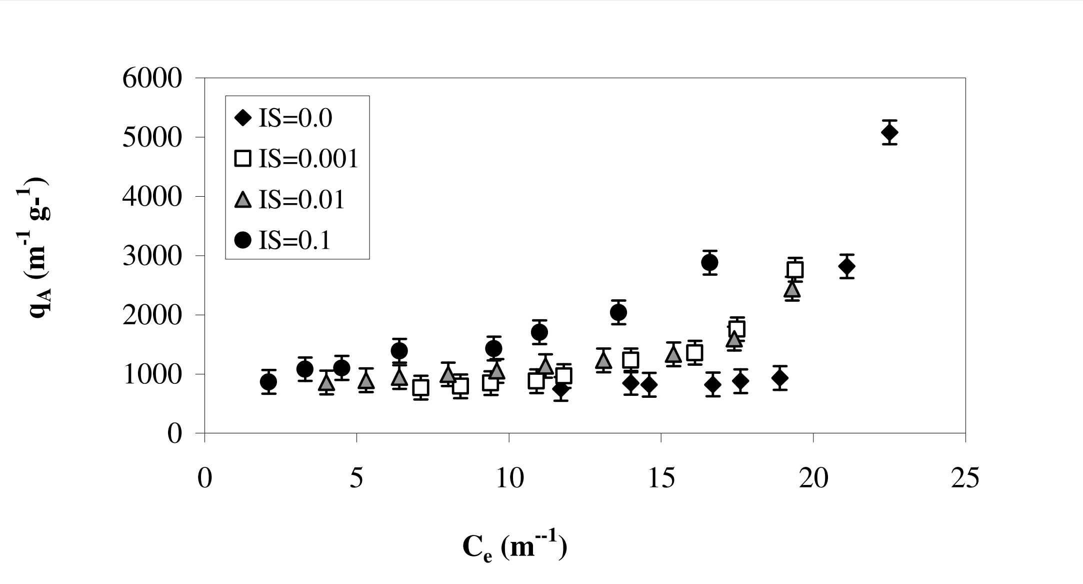


Figure 4.11. Adsorption isotherms of increasing ionic strength at acidic pH forColor$_{436}$

Although the isotherms maintain a C-type isotherm shape at low ionic strength, a transition to an L type can be observed with the increasing ionic strength (Figures 4.11 and

4.12). This points out that the surface is relatively more accessible as the adsorbate shrink due to ionic strength effect.

4.2.2.1 Structural approaches. Under the light of the facts, it can be deduced that the structural approaches discussed up till now; would follow the same logical order with the changing solution matrix. Therefore, from this point on, implications on the structure are not classified discretely, but stressed in the general discussion as they necessitate.

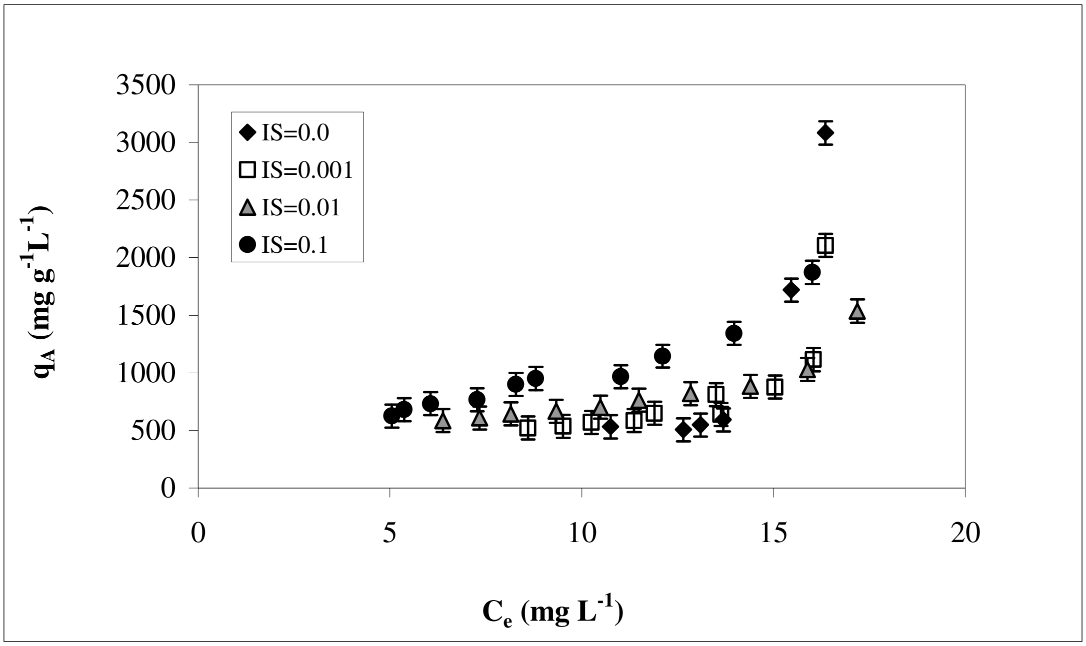


Figure 4.12. Adsorption isotherms of increasing ionic strength at acidic pH for TOC

Once HAs are recognized as macroions or polyelectrolytes, the amount and distribution of charge on the molecule can be regarded as the dominant effect influencing their molecular size, shape and behavior. HAs have a relatively high charge density for a naturally occurring polyelectrolyte and the extent of development of charge on these sites plays a key role in determining intra- and intermolecular forces (Swift, 1999). Depending on the flexibility of this macro-ion, these molecular forces play an important role which must be discussed with an emphasis on ionic strength and pH.

Considering the intramolecular charge effects, if all the charge sites on a flexible humic macromolecule are dissociated, as it occurred at alkaline conditions in Section 4.1.3, the molecule expands and rearranges so as to minimize the electrostatic free energy. If electrolyte is added, the electrostatic repulsion in the diffuse layer surrounding charged functional groups is decreased and the molecules shrink. Thus, the same molecule can exhibit different values for its size, depending on the ionic strength of the medium. The addition of protons by acidification produces similar effects because these are strongly bound. When all charged sites are neutralized, the flexible molecule probably expels solvent and shrinks to its most collapsed state (Swift, 1999).

In regard to intermolecular charge effects, the controlling factors are very similar except that they affect the forces *between* rather than *within* the molecules. When molecules in solution are fully dissociated, they carry a significant charge. When two like-charged molecules approach one another, they experience a mutually repulsive force that keeps them apart as predicted by diffuse double layer theory (Stumm and Morgan, 1996). The extension of the diffuse double-layer into the bulk solution can be decreased by the addition of electrolyte so that the molecules are able to approach each other more closely. In the limit, when the salt concentration is sufficiently high, the electrostatic forces are suppressed and can be superseded by short-range attractive forces. It is under these conditions that various molecular associations (including aggregation, coagulation, and flocculation) can take place (Swift, 1989).

With an emphasis on their perception as association colloids, the structural properties of humic acids can be predicted using three effective geometric parameters of the surfactant. These are the optimal head group area; the volume of the tail (hydrophobic alkyl chain), and the critical chain length. Illustration of these parameters was given in Figure 4.10. Among these geometric concepts, head group area plays a key role. One can change the optimal head group area –polar sections of the amphiphilic molecule- by decreasing or increasing the electrolyte concentration (IS) in the case of ionic surfactants (i.e. HA). As a result, the increasing ionic strength screens the repulsive charges of the head group, and causes formation of smaller micelles.

The effects of increasing ionic strength as outlined above can be traced by the movement of the isotherms towards high efficiency adsorption regions close to origin and in relation; the transformation of isotherms shapes both for Color_{436} and TOC to (Figures

4.11 and 4.12) to Langmuirian curves. Similar trends observed in isotherms of Color_{436} and TOC can be explained by the character of color forming moieties, which probably do not take part in the adsorption process and remain in solution, causing similar trends for TOC and Color_{436} adsorption.

The Langmuirian trend was explained previously as "*the resultant effect of high relative affinity of the adsorbent for the adsorbate at low surface coverage coupled with a decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increases*".

As the adsorbate molecules assume more closely packed structure with the increasing ionic strength, the surface area relatively becomes more accessible This is corollary to the initial condition of the definition above: "*high relative affinity of the adsorbent for the adsorbate at low surface coverage*".

With constant adsorbate concentration, the data points constituting each isotherm are naturally arrayed on the Cartesian plane in decreasing order of TiO_2 concentrations, the highest one being closest to the origin. This meets the secondary condition of the definition "*decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increases*" with the only difference that the "adsorbing surface" was manually decreased while the "adsorbate" was constant in the present case.

Another fine detail which should not be neglected is the difference in the drift of isotherms between Color_{436} and TOC graphs. One can realize the pronounced sidewise drift of the Color_{436} isotherms as the ionic strength increases in Figure 4.10. As the initial Color value decreased with the increasing IS (Table 4.6), isotherms showed regional shifts on the x-axis.

Table 4.6. Color_{436} and TOC values of (50 mg L^{-1}) untreated HA for studied IS' at pH 5

Ionic Strength	Color_{436} Values (m^{-1})	TOC Values (mg L^{-1})
0.00	35.2	22.1
0.001	26.3	21.9
0.01	25.4	21.4
0.1	23.8	21.7

Table 4.6 above, bears decreasing values for Color$_{436}$ for humic acid solution, this decline in the color values can be a result of intricate chemical structure of humic acids and it can be explained as follows: Relating to the complex and source oriented nature of humic matter in general, it is difficult to locate and quantify the color forming chemical associations in it. When IS is increased in the system, more of the negative charged functional groups are neutralized and therefore HA assumes more densely coiled conformation. With the increasing IS, more of the color forming moieties may be trapped within this coiled matrix and cause diminished detection of Color at 436nm. On the other hand, no particular change is observed for TOC. TOC is a global parameter, which stands for the total amount of organic carbon held in the system, as a result, structural alterations caused by the ionic strength and pH does not affect the acquirement of this parameter, since they can not have any effect on the organic content. Therefore variation in parameter Color$_{436}$ and constancy in TOC can be traced comparatively on Table 4.6 above.

Table 4.7. Ionic strength effects on the Freundlich coefficients at pH 5

Ionic Strength	Color$_{436}$			TOC		
	K_F	n	R^2	K_F	n	R^2
0.0	46.6	1.35	0.86	8.73	1.92	0.814
0.001	67.3	1.14	0.807	13.7	1.59	0.811
0.01	356.8	0.527	0.812	122.2	0.784	0.807
0.1	576.5	0.487	0.893	194.2	0.743	0.92

As it can clearly be seen from the dramatic increase of the K_F coefficients on Table 4.7 above, added ion concentrations in the solution caused increased adsorption densities. On the other hand n coefficient showed a contrary decrease. As the previous scrutiny of the graphs in Figures 4.11 and 4.12 revealed, there occurred a transformation of isotherms from Freundlich C-type curves to Langmuirian L-type curves with the increasing ionic strength. Apart from chemical explanations they bring, isotherm equations are mathematical curve fitting equations; therefore the drift of the isotherm patterns towards the origin caused decreased n coefficients of Freundlich equation, however as the increasing ionic strength pulled the isotherms to lower C_e regions, increased capacity is observed.

4.2.3. Effect of ionic strength at neutral pH

The Color$_{436}$ and TOC values acquired from the solution in equilibrium at increasing ionic strengths are plotted on the charts as below (Figure 4.17 and 4.18) at neutral solution pH. At neutral conditions the affinity between the constituents of the system are weaker than acidic conditions, since electrostatic attraction is diminished because of the negative overall surface charge.

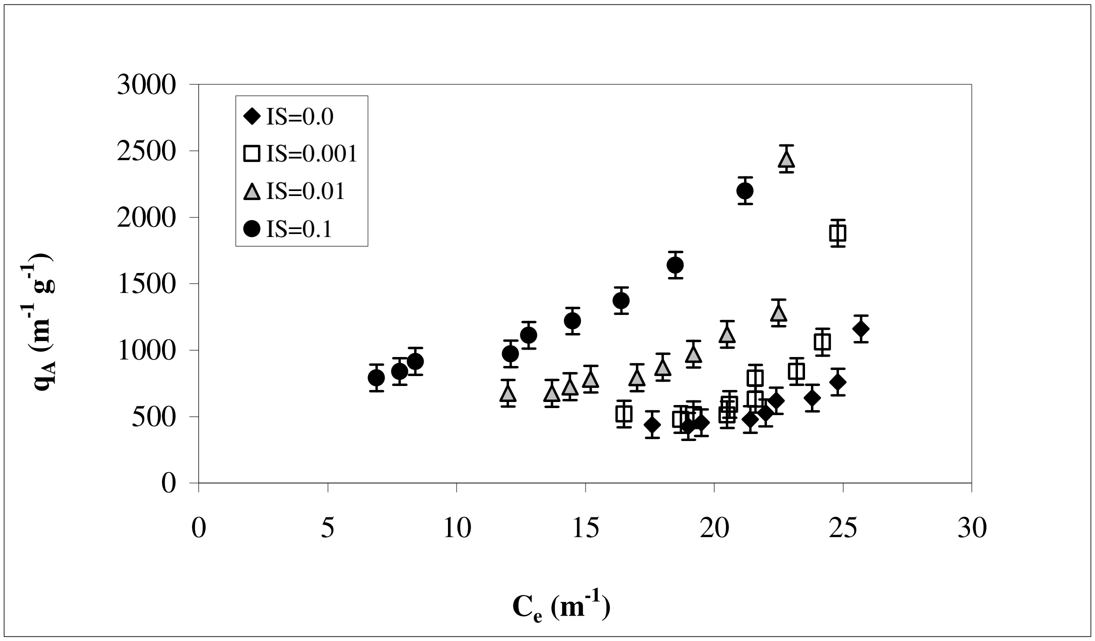


Figure 4.13 Adsorption isotherms of increasing ionic strength at neutral pH for Color$_{436}$

In Figure 4.13 above, it can be followed that as the ionic strength increased in the solution, similar to the observation at the acidic pH, the isotherms are shifted to origin, pointing an efficient adsorption trend. On the other hand, as previously mentioned in the text, increasing the pH caused narrowed spans along x-axis; which apparently points less efficient adsorption. Further inspection of the isotherms in Figure 4.13, reveals that as the ionic strength increased, isotherms are elevated and their span is widened on both coordinates. Under the light of the facts mentioned hitherto, this occurrence is not surprising. As the humic acid molecules shrunk evidently with the increased ionic strength, they were adsorbed more efficiently by the titania. Consequently higher drops in unit adsorption (q_A) were observed as well as bigger differences in the adsorbate concentration remaining in solution (C_e). Isotherms produced after TOC measurements in solution produced similar trends as given below in Figure 4. 14. This picture was not clear at acidic pH, since the effect of pH pertaining as IS was also dominant and thus causing wider spans in all isotherms. When the effect of pH was diminished at the neutral conditions, the drift and elevation is more clearly perceived.

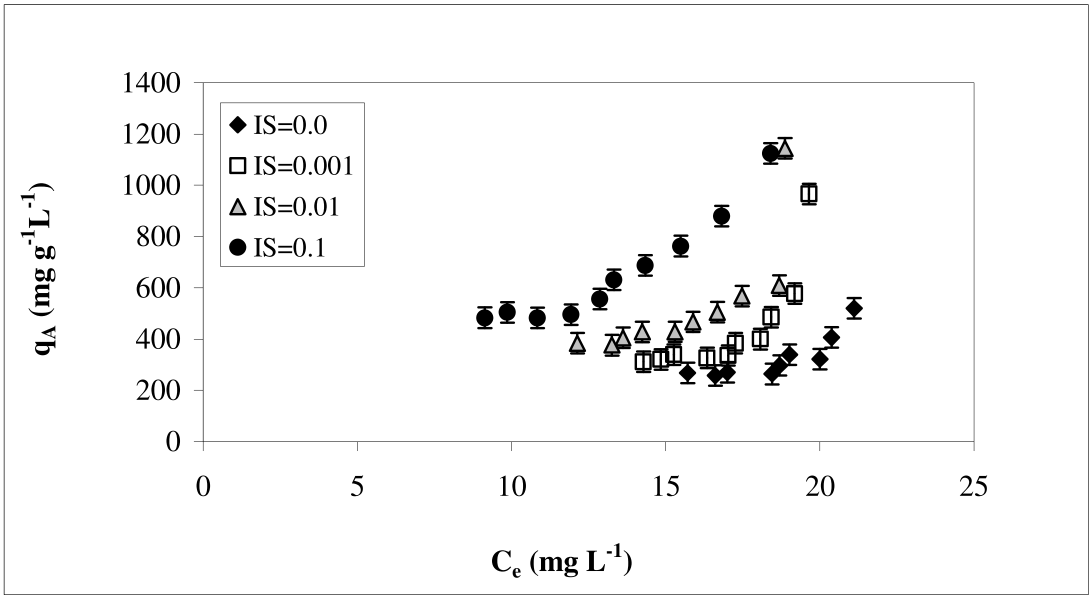


Figure 4.14. Adsorption isotherms of increasing ionic strength at neutral pH for TOC

Discrete interpretation of the coefficients on Table 4.8, would not be any different from what was mentioned about Table 4.7 above. The decrease in the adsorption capacities provided after $Color_{436}$ shows dramatic decrease with the increasing pH when compared with the acidic pH; however for TOC measurements, the drop in the capacities is not as significant. Nevertheless comparison of the coefficients of Table 4.7 and Table 4.8, clearly shows that adsorption of humic acids favors acidic conditions by means of both $Color_{436}$ and TOC, as it is evident from the reduced coefficients.

Table 4.8. Ionic strength effects on the Freundlich coefficients at pH 7

Ionic	$Color_{436}$				TOC	

Strength	K_F	n	R^2	K_F	n	R^2
0.0	0.579	2.25	0.807	1.08	1.96	0.85
0.001	1.64	1.97	0.841	2.3	1.82	0.832
0.01	12.5	1.52	0.791	19.9	1.15	0.87
0.1	157.5	0.79	0.863	40.5	1.08	0.88

Table 4.9. $Color_{436}$ and TOC values of (50 mg L^{-1}) untreated HA for studied IS' at pH 7

Ionic Strength	$Color_{436}$ (m^{-1})	TOC (mg L^{-1})
0.00	28.6	22.4
0.001	29.5	22.1
0.01	28.9	21.7
0.1	26.7	21.2

Similar to Table 4.6, $Color_{436}$ and TOC values are provided for untreated humic acid samples in Table 4.9 above. However the values in the table show any dramatic change neither for $Color_{436}$ nor for TOC for increasing IS. With attribution to polyelectrolyte structure, at neutral solution conditions, humic acid assumes a relatively more stretched shape which does not engulf color forming moieties as effectively as in the acidic pH and therefore displays more of the color forming moieties for detection. At the same time, it can also be said that the effect of ionic strength is not as effective as pH in changing the conformation of humic acid in the solution If ionic strength were more effective, it would be possible to see the same declining trend for $Color_{436}$ values as the IS increases, since the IS would screen the charges and humic acid would assume a densely coiled structure (which also can be perceived as a form of micelle –Section 2.4.2.1–).

4.2.4. Effect of ionic strength at basic pH

A strictly C-type isotherm profiles are present at basic pH as a result of low affinity of surface and adsorbate, with their negative overall charges. The isotherms both measured parameters (Figures 4.15 and 4.16), set similarity with isotherms at neutral pH (Figures 4.13 and 4.14). As explained in detail in the previous sections, with the increasing pH it is expected to observe isotherms related with a reduced adsorptions. This portrayal of isotherms can be explained as the dominance of the effect of ionic strength over the effect of pH. In favor of this verdict, throughout the literature, numerous studies show that the humic substances can shrink and swell as a function of salt. Experimental evidence showed that the intrinsic viscosity of humic substances is more sensitive to changes in salt level than to changes in pH (Hayes, et al., 1989). Similarly, Reuter (1977) used a combination of viscometry and gel permeation chromatography to demonstrate that the size of dissolved humic substances is reduced with increased salt content of the water. Later, Plette et al., (1985), showed with a similar Donnan approach for bacterial cell walls, that the volume was primarily affected by the salt level. These findings contrarily support the assumption that the Donnan volume of humic substances is more sensitive to changes in salt than pH.

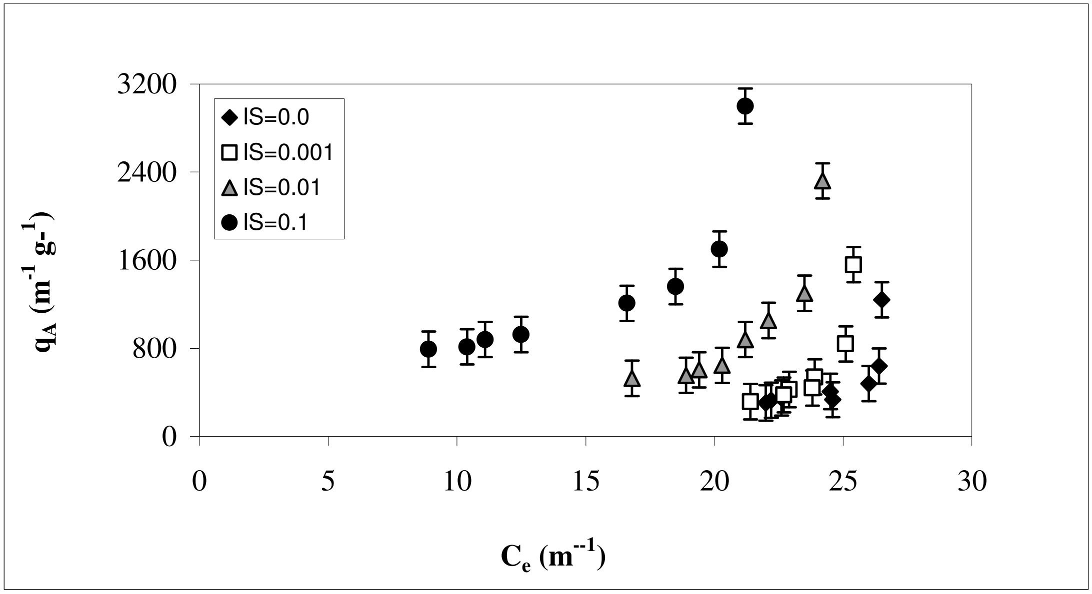


Figure 4.15. Adsorption isotherms of increasing ionic strength at basic pH for $Color_{436}$

Initially no curve fitting was applied to isotherm at alkaline pH, in Section 4.1.3, since it was rather a cluster of data points. Eventually, with the TiO_2 concentration narrowed to photocatalytically efficient range, it was workable on Freundlich isotherm equation. Although the capacity coefficients, namely K_F's, are very small, it is still useful to tabulate the results (Table 4.10) since they provide a basis for comparison. As discussed previously, validity of Freundlich isotherm is compromised when intensity (n) is bigger than unity. Yet, this value still provides valuable information about the course of adsorption. One might talk about multilayered adsorption or conversion of adsorbed species into a separate solid phase in the surface when the coefficient n is greater than one.

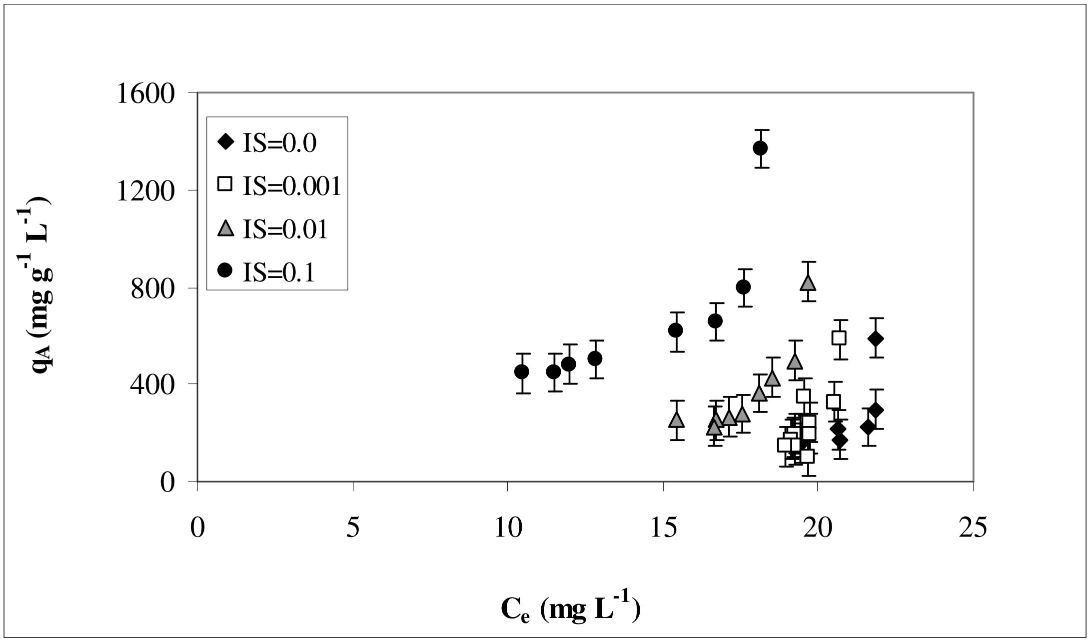


Figure 4.16. TOC Isotherms of increasing ionic strength at basic pH

Table 4.10. Ionic strength effects on the Freundlich coefficients at pH 9

Ionic Strength	Color$_{436}$			TOC		
	K_F	n	R^2	K_F	n	R^2
0.0	1×10^{-4}	4.77	0.806	2×10^{-5}	5.44	0.797
0.001	2×10^{-9}	8.28	0.802	5×10^{-15}	1.82	0.786
0.01	7.6×10^{-3}	3.85	0.822	3×10^{-4}	4.88	0.798
0.1	45.8	1.23	0.798	10.3	1.55	0.807

As ionic strength is raised, with the exception at the ionic strength of 0.001, a decrease in the intensity coefficients is observed while the capacity coefficients are increased. These numerical evidence points that, the isotherms are pulled towards Freundlich boundaries, where $0<n\leq1$, consonant with the size reduction due to increased ionic strength. As a result, the isotherms at basic pH, with the highest ionic strength (Table 4.10), gave almost equal coefficients with the isotherms at acidic pH in the absence of ionic strength (Table 4.7). Referring to the question raised at the beginning of the section if the

modifications in pH and IS compensate the limitations caused by restricted TiO_2 usage, this finding sets a positive answer.

Table 4.11 $Color_{436}$ and TOC values of (50 mg L^{-1}) untreated HA for studied IS' at pH 9

Ionic Strength	$Color_{436}$ (m^{-1})	TOC (mg L^{-1})
0.00	29.6	23.3
0.001	29.3	22.2
0.01	30	21.7
0.1	28.7	21.6

The values $Color_{436}$ and TOC values tabulated above (Table 4.11) shows parallel values as in Table 4.9 further corroborating the effect of stretched polyelectrolyte on the detection of color.

4.2.5. Further notes on ionic strength

In general, it is hard to assign any of the elaborated molecular approaches for better explanation of the ionic strength effect on the adsorption of HA. The "gel" term used for humic acids, helps explaining the imparting of salt ions to the humic acid molecule. Consequently this term brings about the consideration of a three dimensional interwoven matrix perception which also complies both with the micelle and densely coiled polyelectrolyte approaches. Therefore it is possible to talk about the validity of both molecular approaches for acidic pH since the molecule reflects micellar qualities with its coiled polyelectrolyte conformation. For neutral and basic pH, increasing IS allows HA to assume a less rigid polyelectrolyte shape, that also allows micellar point of view to be possible, however, polyelectrolyte approach generally explains this pH conditions better.

In addition to what has been discussed, the ionic strength effect studied in this system also carries parallel points with the findings of previously held studies.

Papenhuijzen et al., (1985) stated that the relative magnitude of the effect of ionic strength depends on the affinity of the sorbate for the surface. When the surface affinity is high, adsorption generally displays a weak dependence on ionic strength. This effect is observed in the IS results at acidic pH in the present study: Relatively higher surface affinity sourced from opposite charges of the system caused drift in the isotherms but no significant drop in the unit adsorptions (q_A) is observed even though the ionic strength is increased.

Randtke and Jepsen (1982), pointed out that when the surface affinity is low, mutual repulsion between charged segments of the adsorbate molecule(s) may limit accumulation in the surface region Increasing ionic strength may increase the extent of adsorption significantly by allowing closer spacing or tighter packing at the surface. For IS experiment results at neutral and basic conditions in the current study, (pH_{pzc} for TiO_2 is 6.25) the surface of TiO_2 is turns to negative, which reduces its affinity for the humic acid; therefore the shift of the isotherms to the efficient regions with increasing ionic strength can actually be explained by closer spacing of the humic acids on the surface.

Electrolytes can influence polyelectrolyte adsorption by changing the charge distribution at the adsorbent surface. As mentioned earlier, indifferent electrolytes can compress the electrical double layer, while specifically adsorbing ions can reduce the surface charge. An increase in ionic strength also increases the potential for complexation with exchangeable cations bound at negatively charged or polar functional groups, which can increase the adsorption of negatively charged polyelectrolytes (Kilduff et al., 1996). This fact may explain the increased efficiency in adsorption with the increased IS at basic pH. The presence of electrolytes may also increase the extent of adsorption by reducing the solubility of humic acids via altering the degree of ionization through common ion, ion pairing, or complexation mechanisms (Randtke and Jepsen., 1982).

5. CONCLUSION

In this dissertation, adsorption characteristic of a coal derived humic acid on the generic semiconductor powder (Degussa P25 TiO_2) was investigated. In order to portray different structural forms that humic acid assume, solution conditions were modified by means of changing the pH and salt concentration. In the light of the attributed structural models, which rooted from colloid chemistry, adsorption phenomenon was reassessed through the use of isotherms and their linked equations. The main emphasis was deducing structural insights about humic acids through the use of these isotherms rather than discussing efficient adsorption alternatives with the changing solution matrix.

Research on the adsorption of humic acids by oxide surfaces provides information about the types of surface reactions in which humic acids may participate. These reactions include ligand exchange, anion exchange, cation bridging, and hydrophobic bonding. In this research, the isotherms acquired for different pH conditions have shown regional phases that successfully evidence various forms of surface reactions.

Solution chemistry has been shown to have significant impact on adsorption of humic substances and deductively on the adsorption of organic polyelectrolytes by a variety of organic and inorganic surfaces. In this research, the extent of humic substance adsorption has been shown to change by changing solution chemistry by the help of increasing ionic strength and pH.

Solution chemistry is important, because at the pH of most natural and engineered systems, humics substances are charged macromolecules and exhibit polyelectrolyte behavior. Negatively charged functional groups distributed throughout single macromolecule cause intramolecular charge repulsion and induced molecular expansion as mentioned copiously throughout the text. In this study, it has been shown that this extent of expansion depends on the solution pH, the solution electrolyte concentration, through the use of adsorption isotherms.

The accumulation of ions in the diffuse layer surrounding charged functional groups reduces intramolecular charge repulsion; therefore, increases in solution ionic strength reduce molecular expansion, causing a reduction in molecular size by coiling, folding or compression. In the case of micelles, the same phenomenon applies to the polar head groups, causing smaller and/or deformed globular structures.

Molecular configuration or size is important, since this feature governs the ability of macromolecules to access adsorbent surface area, which in turn has a significant impact on the extent of adsorption, as shown in the framework of this study.

With vast majority of functional groups, site specific nature, complexities inherent with its genesis poses difficulties in the assessment of humic acids by terms of micelle and polyelectrolyte models discretely. As mentioned previously, presence of divalent cations, including calcium and magnesium, can set a good example to this ambivalence between structural models. Since the cations can bridge functional groups within or between humic acid molecules, a structure once considered as a polyelectrolyte, could easily interpreted as a micelle, a pseudo-micelle, or even as a gel.

With reference to their complex nature, it is not possible to employ a single isotherm model to explain and quantify adsorption of humic acids on mineral oxides. Therefore modified isotherms, or regional approaches, as in this case, may be adopted to explain this phenomenon.

As for the model approaches elaborated throughout the text, it can be said that, the benefits of each structural approach shows variations with the changing pH. However the prevailing superiority of polyelectrolyte model in explaining the adsorption of humic acid can be observed throughout the text. Yet, at acidic pH range, micelle model with attribution to polymer qualities of humic acids can explain the adsorption phenomena well.

In general the IS effect is overcome by pH effect, nevertheless the modifications in solution IS can pull isotherms placed in ineffective ranges to effective regions, and consequently these changes show that IS is a very effective tool in promoting adsorption in systems where no change in the solution pH is possible. In the same vein, increased solution ionic strength can compensate the limitations caused by photocatalytical restrictions of TiO_2 usage (0.1 -1.0 mg mL^{-1}). In other words increased IS pulls the isotherms to higher efficiency regions, which otherwise would only be possible by using higher adsorbent concentrations exceeding the photocatalytically efficient range.

Finally, the structural aspects mentioned throughout this research, and many more facts that can not be covered for the sake of conciseness, shows that the debate about the structure of humic substances; about their presence as macromolecular or polydisperse entities; and about their definition will not seem subside in the future.

This study humbly tries to bring,

- A perspective on the adsorption phenomena of humic acids on semi-conductor powder benefiting from structural approaches that mainly rooted from surfactant theory in general.
- A reflection of changing solution conditions to the electrostatic forces that act upon adsorption
- An incorporation of: colloid and surface chemistry concepts; polymer and self aggregation theories; adsorption as an aquatic chemistry concept, with an emphasis on electrostatic and chemical forces.

6. FURTHER REMARKS

Sorption onto inorganic solids plays a central role in controlling the behavior of NOM as well as many trace inorganic elements in natural systems. And the sorbed species, in turn, affect the behavior of the particles. Apart from its supplementary nature to photocatalytic studies, this research also contributes to the viewpoint of the interaction of NOM with the oxide minerals, since those interactions determine the fate of NOM in conventional water treatment operations.

The adsorption theory in general, considers the increasing adsorbate concentration where the adsorbent is kept in fixed quantities. However, handling a molecule like humic acid upon which the debates in scientific circles have not yet subsided about their being a mixture of small chemical entities or the agglomerates of macromolecules of different size and structures; it was preferred the unorthodox way of increasing the adsorbent concentration instead of the adsorbate. By this way, dilution of non-homogeneous mixture to various concentration gradients was eliminated.

In an investigation held similarly by increasing adsorbent concentration, this phenomenon was named as "Solids Concentration" effect (McKinley and Jenne, 1991). In their study the solids effect was sampled by a span of increasing Cd^{++} concentrations being adsorbed onto iron oxide surface. The oxide surface was gradually increased in each experiment they performed. Their experiments yield isotherms which showed increased slopes as the $[Fe]_T$ (or total iron concentration, namely the adsorbent) increased. This finding is in agreement with the isotherms given in this study. The rising slopes of the isotherms are positively the signs of greater affinity of adsorbate for the solid surface. They furthermore added this positive change in slope may be accounted for by the multiple site adsorption theory and/or "the surface precipitation" model (Benjamin and Leckie, 1980).

Extending this analogy mentioned above -between adsorption and formation of metal/ligand complexes- many important molecules, including NOM molecules, have the potential to bind to several surface sites, however the only case that has been considered in any detail to date is bidentate adsorption by Benjamin (2002a).

According to Benjamin and Leckie (1981); the sites with relatively high affinities for adsorbate dominate the adsorption reaction at low adsorbate concentrations; to the degree that fractional adsorption was independent of the amount of adsorbate available to the adsorbent. In other words, where the adsorbate was present in an amount greater than could be accommodated solely by the adsorbent's high affinity sites, multiple site adsorption occurred and a Freundlich isotherm could describe the behavior of the overall system. Multiple site theory can thus explain the division of each isotherm into segments (shifting from Langmuir to Freundlich behavior) (McKinley et al., 1991). This explanation virtually summons the fragmented explanation about the isotherm at acidic pH in section 4.1.1. as well as the neutral pH in section 4.1.2.

Benjamin (2002b) has stated that the model reactions usually emphasize the interaction between the surface and a single functional group on a NOM molecule. And they do not consider explicitly the fact that most NOM molecules are polyanionic. He adds that this property of the NOM can affect the reaction in two important ways.

First; as discussed above, the different parts of a single molecule might bind to the surface at two or more different sites, increasing the overall binding strength and making it quite unlikely that the molecule will desorb unless solution conditions are changed.

Second, the part of the molecule that does not bind directly to the surface typically carries a negative charge, and the sorption reaction adds negative charge to the surface. This phenomenon was exemplified in this research in section 4.1.2.1, by the occurrence of a linear section in the isotherm, pointing a surface charge drift due to attained negative charges on the surface.

Since the electroneutrality must be maintained near the surface, the reaction must be accompanied by addition of cations and/or release of anions from diffuse layer. The changes can be evaluated by the Donnan Gel effect since it merely considers how the size of NOM change as salts gain access to the NOM matrix to maintain overall neutrality of the system.

The surface precipitation model, on the other hand; treats the curvilinear isotherm as the expression of chemical continuum between adsorption due to surface complexation reactions (the Langmuir portion of the isotherm) and heterogeneous precipitation of a solid phase of the adsorbate. Basically, the adsorption density gradually increases in response to increasing dissolved adsorbate concentration but then, rather than approaching some maximum value, the apparent adsorption density increases without bound. In truth, the latter observation does not reflect continuous adsorption onto the original adsorbent, but rather the formation of increasing amounts of the new precipitate. If the precipitate is a metal hydroxide and solution pH is fixed, the solubility product imposes a limit on the amount of the adsorbate that can be dissolved. As a result, addition of an increment of metal to a system where a surface precipitate has formed leads to precipitation of virtually all the added metal. If adsorption is quantified simply by analyzing the amount of metal that is removed from solution, the precipitation reaction can easily be mistaken for adsorption, causing the apparent adsorption density to increase indefinitely (Benjamin, 2002a).

Although the research done about surface precipitation considers solid –metal-adsorption onto a metal oxide, an analogy can still be made between the occurring precipitate and humics –or more specifically humin-. As explained earlier in the genesis of humic matter within the macromolecularity concept; there are two main approaches regarding the formation of humic substances: a degradative theory and a supramolecular theory (Piccolo, 2001), that focuses on condensation polymerization. The degradative theory proposes that organic macromolecules such as carbohydrates and proteins are degraded or consumed in microbial attack. Whereas biopolymers such as lignin and cutin are degraded into humic substances. Consequently, it can be said that breakdown begins first with the humin fraction -since they comprise the highest proportion in size among the fractions of humic substances and have lower oxygen content, with an insoluble nature-while further oxidation results in humic acid, and ultimately fulvic acid. Humic acid is basically a smaller, more oxidized material, with typical molecular weight ranging from 10,000 - 100,000 Da. This degradation via oxidation explains the increasing oxygen content from humin to fulvic acid. The condensation polymerization on the other hand suggests that all plant materials are initially degraded into small molecules which then polymerize to form humic materials. Contrary to the degradative theory, fulvic acid and humic acid can be considered as precursors to humin in this theory. So actually, a condensation polymerization (polycondensation) that may be occurring in the surface might cause a phenomenon similar to surface precipitation that leads to formation of condensed insoluble humin like paste of humic matter on the surface of the metal oxide which can be reasonably well explained by surface precipitation scenario. This possibility may be worth considering for future research in the field.

Having mentioned two possible scenarios for regional isotherm patterns that were existent throughout this research, it can be concluded that the sorption of humic acids on hydrous oxide TiO_2 is probably controlled by a combination of limited site availability, buildup of negative surface charge, and factors that control the size of humic acid molecules. This study in general focused on the factors that have effect upon the size of humics through the use of most commonly accepted molecular models.

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