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# Investigation of Constructed Wetlands Capability to Remove Mercury from Contaminated Waters

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# ABSTRACT

## Investigation of Constructed Wetlands Capability to Remove Mercury from Contaminated Waters

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Concordia University, 1999

Wetlands have been known as an efficient and low-cost technology in treating wastewater. It was reported that wetlands (natural and constructed) were used to purify a) municipal; b) industrial; c) acidic; and d) agricultural wastewater. Mercury has been used intensively by wide variety of industries because of its unique properties. Consequently, it was present at various levels in wastewater discharged. The ability of constructed wetlands to serve as a sink of mercury before entering larger aquatic systems has not been investigated. This study focuses on the capability of constructed wetlands (Free Water Surface) to remove mercury from contaminated water / wastewater and reduce the widespread dispersion of the toxic substance to streams, rivers, reservoirs, and oceans. Mercury removal pathways considered in the study are sorption to the solid phase and uptake by plants.

Current design approaches of constructed wetlands lack essential parameters necessary to optimise their capabilities for mercury removal. To evaluate these parameters a combination of experimental and numerical modeling approaches were undertaken.

Experimental investigations were conducted to investigate the ability of Water Hyacinth (Eichhornia crassipes) - floating plants - and Reeds (Phragmites communis) – rooted plants- to remove inorganic mercury compounds from water. Kinetics of mercury removal by floating and rooted plants in the concentration range of 5 to 150 ppb were investigated and the apparent removal rate coefficients were determined for a first order kinetic model.

Numerical modeling investigations were then carried out to: a) expand the results obtained in the experimental phase by examining the distribution of mercury forms in water including: $HgOH^{+1}$, $Hg(OH)_3^{-1}$, $Hg^{+2}$, $HgCl^{+1}$, $HgCl_2$ (aq), $HgCl_3^{-1}$, $HgCl_4^{-2}$, HgClOH (aq) and evaluating the amount of bioavailable mercury for plant uptake; b) verify the effects of pH, temperature, and chloride concentrations in water on Hg speciation; c) assess characteristics of mercury adsorption on four different sediment materials (kaolinite, natural soil, glokonite, and bentonite) at three pH values and three different adsorbent medium for five initial mercury concentrations (1E-7 to 1E-3 moles) using a triple layer adsorption model.

The major results suggest that - properly designed - constructed wetlands can remove up to 95% of mercury discharged within short period of 3 days. The removal process occurs at in two phases fast and around 10 times slower thereafter. The uptake of the bioavailable form of mercury ($Hg_2^{+2}$) was influenced mainly by the pH of the water discharged. Higher adsorbent mass concentration in sediments and higher pH result in less amount of bioavailable mercury. The amount of bioavailable mercury was proportional to the initial mercury concentrations. It was concluded also that mercury has high affinity to be sorbed on all tested sediment mediums.

The findings of this research could be also applied in preparing environmental risk impact assessments and could be considered as the first nuclei of establishing regulations (codes) governing the design of constructed wetlands to remove mercury from contaminated waters. However, a pilot field study is still necessary to validate the experimental results.

***To My Parents:***

***Here is your dream came true***

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# LIST OF SYMBOLS

| | |
|---|---|
| a : | resistance factor |
| $a_{i\sigma}$ | stoichiometry of the electrostatic component pertaining to $\sigma$ in species i |
| $A_s$: | loading surface area of wetland |
| BCF: | Bioconcentration factor the ratio between the concentration of mercury in an organism and the concentration in the medium to which the organism was exposed |
| BOD: | Biological Oxygen Demand |
| $BOD_5$: | Biological Oxygen Demand after 5 days |
| $C_{cap}$: | constant capacitance term |
| $C_{cap1}$,$C_{cap2}$: | capacitances associated with the zones between the o- and $\beta$-planes and d-planes, respectively |
| $C_{ci}$ : | measured mercury concentration in the control solution at time i |
| $C_{eff}$ : | effluent mercury concentration |
| $C_{inf}$ : | influent mercury concentration |
| $c_p$: | specific heat |
| $C_{pi}$: | mercury concentration removed by the plants at time i |
| $C_s$: | concentration of solid in the suspension |
| $C_{wi}$ : | measured mercury concentration in water at time i |
| DOC: | Dissolved Organic Carbon |
| E: | the activation energy constant |
| e: | space available for water to flow through the wetland (vegetation and litter occupy some space in the Free Water Surface wetland). |
| F: | Faraday constant |
| I : | ionic strength |
| k: | first order reaction rate constant |
| $K_d$: | the ratio of the concentration of metal bound on the surface to total dissolved metal concentration at equilibrium. |
| $K_d^{act}$: | equilibrium constant in terms of activity |
| $K_{ex}$: | Selectivity coefficients |
| $K_f^{act}$: | Freundlich equilibrium constant in terms of activity |

| | |
|---|---|
| $K_L^{act}$: | Langmuir equilibrium constant in terms of activity |
| L: | length of the wetland cell |
| $LC_{50}$: | effluent concentration in dilution water that causes mortality to 50% of test population |
| M: | molarity |
| n: | Manning's coefficient |
| $N_A$: | Avogadro's number |
| $N_s$: | analytically determined surface site density |
| p: | pressure in mm Hg |
| PCB: | Polychlorinated biphenyls |
| Q: | average flow through the wetland |
| R: | the gas constant |
| S: | hydraulic gradient, or the slope of the water surface |
| $S_A$: | specific surface area of the solid |
| T: | absolute temperature |
| $T_{1/2}$: | biological half-life |
| $T_{air}$: | average air temperature |
| $T_d$: | the higher of 3 °C or the minimum allowed temperature for vegetation's survival. |
| TKN: | Total Kjeldahl Nitrogen |
| TN: | Total Nitrogen |
| $T_o$: | water temperature at distance $x_o$, the entry point for the wetland segment |
| TOC: | Total Organic Carbon |
| TP: | Total Phosphorus |
| $t_r$: | hydraulic residence time |
| TSS: | Total Suspended Solids |
| $t_{tot}$: | total experimental period |
| $t_{tot}$: | total experimental period |
| $T_w$: | water temperature |
| $T_{\sigma o}$, $T_{\sigma\beta}$, $T_{\sigma d}$: | total charges associated with the o-, $\beta$ -, and d-planes |
| $U_p$: | plant's water uptake rate |
| $U_s$: | heat transfer coefficient at wetland surface |

| | |
|---|---|
| $v$: | flow velocity |
| $v$: | flow velocity in wetland |
| $V_{ci}$: | water volume in the control's container at time i |
| $V_{eva}$: | total volume of water evaporated from the control container |
| $V_{fin}$: | the final volume of solution measured in the control container |
| $V_{fin}$: | the final volume of solution measured in the control container |
| $V_{ini}$: | the initial volume of solution measured in the control container |
| $V_{ini}$: | the initial volume of solution measured in the control container |
| $V_o$: | initial water volumes at time zero |
| VSS: | Volatile Suspended Solids |
| $V_{wi}$: | water volume in the plant's container at time i |
| W: | width of the wetland cell |
| $\{X_s^z\}$: | activity of an ion X of charge z near the surface |
| $\{X^z\}$: | activity of X in bulk solution outside the influence of the charged surface |
| $y$: | depth of water in the wetland cell |
| $y$: | depth of water |
| $y$: | water depth inside the wetland |
| $Z$: | ion charge |
| $Z$: | valency of the symmetrical electrolyte |
| $\Sigma V_{sp}$: | total volume of samples taken |
| $\Sigma V_{sp}$: | total volume of samples taken |
| $\alpha$: | mass action stoichiometric coefficient |
| $\varepsilon$ : | dielectric constant |
| $\varepsilon_o$: | permittivity in free space |
| $\gamma_m$: | activity coefficient of dissolved species |
| $\theta$: | is a temperature coefficient |
| $\rho$: | density of water |
| $\sigma_o, \sigma_\beta, \sigma_d$: | surface charge at the o-, $\beta$ -, and d-planes |
| $\psi_o, \psi_\beta, \psi_d$: | electrostatic potentials at the o-, $\beta$ -, and d-planes |

# CHAPTER 1

# INTRODUCTION AND LITERATURE REVIEW

Mercury is one of the heavy metals that has been used intensively in different industries due its unique chemical and physical properties. Industrial wastes containing mercury residuals have severe impacts on the surrounding environment, particularly on human health because of mercury toxicity. Elevated mercury levels in fish from remotely located lakes have generated public concern about the scope of mercury contamination in the environment. This study introduces and investigates constructed wetlands as a potential treatment system for mercury contaminated waters.

Wetlands have been known as an efficient and low-cost technology in treating wastewater. It was reported that wetlands (natural and constructed) were used to purify a) municipal waste water: both sewage (Brix and Schierup 1989) and leachate from municipal landfills (Staubitz et al 1989); b) industrial wastewater from a wide variety of industries such as: auto manufacturing (Barnett et al 1991), clam processing water (Guida and Kugelman 1989), oil refining (Lichfield and Schatz 1989), paper mills / pulp mills (Tettleton et al 1993), sugar refinery waste water (Gambrell et al 1987), textiles dyes (Davies and Cottingham 1994), and thermal discharge (Ailstock 1989); c) acidic waste water which comes from: acid drainage (Howard et al 1989), ash pond seepage (Brodie et al 1989); and d) agricultural waste water: milk house waste, animal waste (Hammer et al 1993).

The focus of this study is to assess the responses of the sediments, suspended material and plants of Free Water Surface constructed wetlands to mercury contaminated waters, and to evaluate removal processes. This in turn will shed some light on the extent of removing mercury from polluted waters and produce much needed information for designing constructed wetlands to remove mercury from contaminated waters. This investigation will assess the possibility of using wetlands for polishing mercury contaminated wastewater coming from various sources such as: electrolytic production of chlorine and caustic soda in mercury cells (Chlor-Alkali Industry), manufacturing of wiring devices and switches, pulp and paper industries, waste water which contains dental materials, paints, and the manufacturing of agricultural pesticides.

The literature reviewed in this chapter could be classified into three main streams. Section 1.1 covers mercury, its properties, transformations, behaviours in aquatic environments, toxic aspects, and regulations of its dosage limits. On the other hand, section 1.2 focuses on wetlands and their use as wastewater treatment facilities for various types of wastewater, along with the reported values of removal rates for different contaminants. Section 1.3 demonstrates current approaches adopted for designing constructed wetlands for wastewater treatment pointing out their deficiencies in quantifying wetlands' mercury removal characteristics.

## 1.1 Mercury

### 1.1.1 Physical and Chemical Properties

Elemental mercury has an atomic number of 80, an atomic mass of 200.59, a specific gravity of 13.55, a melting point of -39.8°C and a boiling point of 357°C. The vapour pressure of liquid mercury is 0.0012 mm Hg at 20°C. Thermal conductivity of mercury is 8.34 W $m^{-1}$ $K^{-1}$ at 27°C (300°K). The electrical resistivity of mercury is 94.1 x $10^{-8}$ m at 0°C (273°K). Several other metals can dissolve in mercury to form various amalgams. However, the most important forms of mercury to which living organisms are exposed can be placed into three broad categories having different properties with regard to sorption, bodily distribution, accumulation, and toxic hazards. These categories are: metallic mercury (e.g. $Hg^o$), inorganic ions of mercury (e.g. $Hg^I$, $Hg^{II}$), and organic mercury compounds (e.g. $CH_3Hg^+$).

Metallic mercury: elemental mercury ($Hg^o$) is usually referred to as mercury vapour when present in the atmosphere or as metallic mercury in liquid form. This form is of considerable importance toxicologically because of its high water solubility (20 mg/L) and high vapour pressure. For industrial applications, the following formula could be used to approximate the vapour pressure between 0 and 150°C:

$$\text{Log } p = (-321.5 / T) + 8.025 \tag{1.1}$$

Where p is the pressure in mm Hg and T the absolute temperature (Patty, 1981). Saturated atmosphere at 24°C contains approximately 18 $mg/m^3$. Stumm and Morgan (1981) reported a large value of 8.5 atm. $M^{-1}$ for the Henry's law constant for $Hg^o$ (aq).

Inorganic ions of mercury: mercury exists in ionic form as $Hg^{II}$ *(mercuric salts)* and $Hg^I$ (mercurous salts). The former readily forms complexes with organic ligands notably sulfhydryl groups (-SH). The most important salts are: mercuric chloride, ($HgCl_2$), a poison which is highly soluble in water (69 g/L at 20°C); mercurous chloride, ($Hg_2Cl_2$), occasionally still used in medicine and has low water solubility (2 mg/L at 25°C); and mercuric sulphide, (HgS), which is known commercially as cinnabar, (a high-grade paint pigment), and has the least water solubility of 10 ng/L (Weast, 1978).

Organic mercury compounds: consist of diverse chemical structures in which mercury forms a covalent bond with carbon. These compounds include three main groups: a) alkylmercurials such as: methylmercury ($CH_3Hg^+$) and ethylmercury ($C_2H_5Hg^+$); b) arylmercurials such as phenylmercury ($C_6H_5Hg^+$); and c) the family of alkoxyalkyl mercury diuretics.

Organic mercury cations form salts with inorganic and organic acids, e.g., chlorides and acetates such as: methylmercury chloride ($CH_3HgCl$) and phenylmercury acetate ($C_6H_5HgOCOCH_3$). They react readily with biologically important ligands, notably sulfhydryl groups (-SH), and also they pass easily across biological membranes (Hochster and Quastel 1963) perhaps since the halides (e.g., $CH_3HgCl$, although it is not clear if this exists in a stable form in tissues at physiological pH) and dialkymercury are lipid soluble. Organomercuric ions hydrolyse in water and form corresponding hydroxides, e.g. $CH_3HgOH$ and $C_6H_5HgOH$. The major difference among these various organomercury cations is that the stability of carbon-mercury bonds varies considerably.

### 1.1.2 Mercury Distribution in the Environment

Mercury is a unique metal that is found in air, water, and soil. One form of naturally occurring mercury is cinnabar ore, primary composed of mercuric sulphide. Mercury is the only heavy metal that exists as a liquid at room temperature, has high electrical conductivity and high volatility, alloys with other metal and is toxic to living organisms. Because of its physical and chemical properties, mercury has been used in thousands of industrial, agricultural, medical, and household applications.

In rocks and soils, mercury occurs as various combinations of oxides, sulphides, halides, organic complexes and native metal. The Hg concentration in some soils (Stock and Cucuel (1934) were:

| | |
|---|---|
| Humic horizon of forest soil | 0.03 - 0.08 ppm |
| Forest soils | 0.10 - 0.29 ppm |
| Cultivated soils | 0.03 - 0.07 ppm |
| Clay soils | 0.03 - 0.034 ppm |
| Sand | 0.001 - 0.029 ppm |

Mercury concentration in the oceanic waters has increased as a result of increasing human activities. Sediment cores from lakes and estuaries indicate that there are two to five times higher levels of mercury in recent sediments compared to those in sediments laid down in pre-human culture times (UK Department of Environment, 1976).

About 20000 tons of mercury per year are released by industry and this eventually becomes distributed in water (ground-, river-, and sea-). Over the past 100 years, anthropogenic activities have led to the discharge of about 100 million kilograms of mercury into natural waters, and about five times this amount each into the land and atmosphere (Mitra 1986).

Over the last decade investigations to determine mercury in natural waters have established that the typical total dissolved mercury concentration (i.e., inorganic and organic forms in the solution) are at the picomolar level (0.2 - 100 ng/L) and in some cases even lower (Bloom and Crecelius 1983; Dalziel and Yeats 1985; Gill and Bruland 1990; Mason and Fitzgerlad 1990).

Measurements of mercury in aquatic systems have given the following concentration ranges (Lindquist et al 1984):

| | |
|---|---|
| Open Ocean | 0.5 - 3 ng/L |
| Coastal sea water | 2 - 15 ng/L |
| Rivers and lakes | 1 - 3 ng/L |

Gill and Bruland (1990) found that the mercury concentration range in fresh water is 0.5-100 ng/L as total dissolved mercury in pristine and contaminated Californian lakes.

Unpolluted air contains less than 1, to about 10 ng/m$^3$ of mercury. In the Northern hemisphere, higher concentrations of mercury have been observed in air (Slemr et al, 1981), in seawater (Gardner, 1975), and in human hair. It was suggested that mercury concentrations in the air (background level) was at about 2 ng/m$^3$ in the lower troposphere of the northern hemisphere and about 1 ng/m$^3$ in the southern hemisphere (Lindquist et al. 1984). In European areas remote from industrial sources, such as rural parts of southern Sweden and Italy, concentrations most often lie in the range from 2 to 3 ng/m$^3$ in summer and 3 to 4 ng/m$^3$ in winter (Ferrara et al 1982, Brosset 1983). Natural pollution caused by the volatilisation of mercury from ore deposits of mercury or base metals contributes up to 62 ng/m$^3$. Very large amounts of mercury reach the atmosphere from volcanic gases (Mitra 1986).

On average, air, rainwater, spring-water contain about $2 \times 10^{-8}$ ng/L, $2 \times 10^{-4}$ mg/L, and $2 \times 10^{-5}$ mg/L of Hg, respectively (Mitra 1986).

### 1.1.3 Sources of Mercury in the Environment

Twenty-five or thirty percent of the atmospheric burden of mercury comes from anthropogenic sources (Mitra 1986). The industries which are responsible for the dispersion of mercury are the burning of fossil fuels, compost incinerators, mining and extraction of mercury from cinnabar, the chlor-alkali-industries, pulp and paper industries, paints, fungicides, electrical equipments, instrumentation, amalgamation and dental use.

The Chlor-alkali industry is a potential source of mercury in the environment since its output (chlorine, caustic soda and potash) are widely used in other industrial processes and products. Nearly all chlorine is manufactured by the electrolysis of brine, using mercury cells in which the cathode is a flowing sheet of elemental mercury. A typical, modern 30 $m^2$ Hg-cell can contain up to 5424 kg (12000 lb.) of Hg, which is circulated in a closed system and reused indefinitely. However, due to the circumstances of its operation, there is a loss of 150-250 gm Hg per kg of chlorine produced (Environment Canada 1994).

### 1.1.4 Mercury Cycling in the Environment

There are two cycles believed to be involved in the environmental transport and distribution of mercury. The first one is global in scope and represents the atmospheric circulation of elemental mercury vapour from sources on land to the water bodies (lakes, oceans...etc.). The second cycle is local and depends upon the methylation of inorganic mercury mainly from anthropogenic sources. Many steps of this cycle are poorly understood.

Mercury cycling pathways in aquatic environments are very complex. The various forms of mercury can be converted from one to the next; most important is the conversion to methylmercury ($CH_3Hg^+$) because of its high toxicity. Ultimately, mercury ends up in the sediments, fish and wildlife, or evades back to the atmosphere by volatilisation.

Once in the atmosphere, mercury could be deposited again into the aquatic ecosystem. Atmospheric deposition contains the three principal forms of mercury, although the majority is as inorganic mercury ($Hg^{II}$, ionic mercury) (Hudson et al 1994).

Once in surface water, mercury enters a complex cycle in which one form can be converted to another. It can be brought to the sediments by particle settling and then later released by diffusion or resuspension. It can enter the food chain, or it can be released back to the atmosphere by volatilisation. The concentration of dissolved organic carbon (DOC) and pH have a strong effect on the ultimate fate of mercury in an ecosystem (Hudson et al 1994). For the same species of fish taken from the same region, increasing the acidity of the water and/or the DOC content generally results in higher body burdens in fish (Greib et al,1990; Spry and Wiener, 1991). The higher acidity and DOC levels enhance the mobility of mercury in the environment, thus making it more likely to enter the food chain. Many of the details of the aquatic mercury cycle are still unknown, however, and remain areas of active research.

During the last decade a new pattern of Hg pollution has been discovered, mostly in Scandinavia and North America (Lindquist 1991). Fish from low productivity lakes, even in remote areas, have been found to have high Hg content. For water bodies not directly impacted by a discharge, the dominant sources of Hg are through direct runoff and precipitation (Fitzgerald and Watras 1989; Wiener et al 1990). A large number of waters are affected by widespread air pollution and the long-range transport of pollutants. It is estimated that 40-50% of the $Hg^0$ cycling through the atmosphere is initially of anthropogenic origin, largely due to combustion of coal (Brosset1983; Lindquist et al 1984; Lindquist 1991). Additionally, acidification of surface waters further enhance the bioavailability of Hg by leading to increased in-water methylation (Lindquist et al 1984; Bjorklund et al 1984; Watras and Bloom 1992).

### 1.1.4.1 Modelling Mercury Cycle in Lakes

Mercury Cycling Model (MCM) represents a theory of mercury cycling in lakes, and one of the most important uses of MCM is the prediction of methylmercury in fish. This simulation model was developed for the cycling of Mercury in Temperate Lakes, MTL project, (Hudson et al 1994). The model is bounded by the atmosphere, the lake margins, and a deep sediment layer. Reactions in the watershed and the atmosphere were not modelled; volumetric inflows and concentrations are measured to provide mercury input at the model boundary. MCM tracks all three major forms of mercury ($Hg^o$, $Hg^{II}$, and $CH_3Hg^+$) in three physical compartments of levels: an upper mixed layer (epilimnion), a lower layer (hypolimnion), and the sediments. At one time dimethylmercury was considered as a possibly important chemical species, but so far it has been observed only at extremely low levels in marine environments (Mason and Fitzgerlad, 1990). Four biotic compartments are defined: phytoplankton, zooplankton, a forage fish population, and a piscivorous fish population. Simulation output can include any variable, however the target of interest is mercury concentration in piscivorous fish population. MCM has monthly time step and runs on Macintosh computers.

Although MCM simulates the mercury cycling in temperate lakes, it couldn't be used for the simulation of other aquatic systems with different conditions. Wetlands for example, have shallow water layer, aquatic plants, and living microorganisms. These components are not included in the MCM. On the other hand, wetlands usually do not support fish populations and can have relatively small water surface areas.

#### 1.1.4.2 Mercury Methylation

Inorganic mercury is converted to the toxic methylmercury compounds in the aquatic ecosystems. Microbial methylation can occur under aerobic or anaerobic conditions (Bisogni and Lawrence, 1975; Olsson et al, 1979). Factors which have been reported to affect rates of methylmercury production include sediment type (Miller and Agaki, 1979), water temperature (Bisogni and Lawrence, 1975; Wright and Hamilton, 1982; Nagase et al, 1982), pH (Fagerstrom and Jernelov, 1972, Langley, 1973; Wood, 1979; Nagase et al, 1982), redox potential (Ridley et al 1977; Wood, 1979), inorganic mercury concentration in sediments (Wright and Hamilton, 1982; Nagase et al, 1982), bioturbation of the sediments by macroinvertebrates (Langley 1973), and availability of a chemical precursor or methyl donor (Ridley et al 1977; Wood 1979). Nagase et al (1982) reported that in aquatic environments, humic substances can provide a methyl donor and may stimulate methylmercury production from the sediments; however, this conclusion was based on results obtained under very high mercury conditions (1 mg/L).

Abiotic (chemical) methylation has been reported in the literature. An example is the chemical reaction of methyl groups from other compounds (e.g. water soluble methyl silicon compounds (De Simmone 1972) with $Hg^{+2}$ to give methylmercury). Abiotic methylation is reported to be directly proportional to temperature and concentration of $Hg^{+2}$ and inversely proportional to pH, (at pH >5), (Rogers 1978).

The form of Hg that is methylated is $Hg^{+2}$, however Hg (aq), phenylmercury, and most other Hg species are available for methylation, since they can be converted to $Hg^{+2}$ upon release into the environment. Cinnabar (HgS) is the least accessible to methylation because of its extreme insolubility (Bodek et al 1988 and the literature cited there).

Most of the $CH_3Hg^+$ in the aquatic ecosystems resides in fish (85%). Nearly all mercury in fish flesh (>95%) occurs as $CH_3Hg^+$ (Grieb et al 1990, Bloom, 1992). Usually, the percentage of $CH_3Hg^+$ in sediments does not exceed 1.5% of the total Hg available. The concentration measured, however, represents the approximate equilibrium between concurrent methylation and demethylation processes (Craig and Bartlett 1978). On the other hand, a delicate balance of methylation and demethylation is maintained in nature by bacterial activity.

Normally methylation takes place in bottom sediments and is restricted to the upper 5 to 10 cm. The most intense mercury methylation occurs in the transitional oxidising anaerobic zones of natural sediments (Mitra 1986). The rate of methylmercury production from bottom sediments is greatly affected by sediment type, which includes proportion of organic matter and nutrients. Nutrients concentration in mercury methylating sediments may not be as important as the amount of nutrients available for microbial activity near the sediment water interface. This may explain why the covering of methylmercury producing sediments with clean, nutrient-poor, sediments effectively reduces the production of methylmercury (Jernelov, 1970; Rudd et al, 1983)

The following conclusions have been drawn by Bisogni and Lawrence (1973) concerning methylation by microorganisms:

a. Mono methylmercury is the predominant product of biological methylation near neutral pH.

b. The rate of methylation is greater under oxidising conditions than under anaerobic conditions.

c. The output of methylmercury doubles for a ten-fold increase in inorganic mercury.

d. Temperature affects methylation as a result of its effect on overall microbial activity.

e. Higher microbial gross rate increases mercury methylation.

f. Methylation rate is inhibited by the presence of sulphide in anaerobic systems.

After its biomethylation in the environment, mercury is known to be bioconcentrated up the food chain. Total and $CH_3Hg^+$ levels in surface water are extremely low (1 ng/L of total Hg; 0.05 ng/L of $CH_3Hg^+$) but bioconcentration of factors up to $10^7$(Craig 1986; Zvonaric et al 1987; Bloom and Watras 1989) often lead to $CH_3Hg^+$ levels in fish which exceed the WHO health standards (0.5 mg $g^{-1}$ flesh weight).

### 1.1.5 Toxic Aspects of Mercury

Intake: the typical Western diet yields approximately 0.015 mg Hg/day in a 70 kg reference man. An additional 0.001 mg/day comes from inhalation in exposed population. The WHO has suggested that the intake for adults should be less than 0.3 mg total Hg per person per week, of which no more than 0.2 mg should be methylmercury (O'Neill 1993).

Once absorbed, mercury is generally distributed about the body, binding to sulfhydryl groups (-SH) in many proteins. The soft tissue body burden is approximately 13 mg; kidneys are the major sites of deposit following exposure to inorganic salts whereas kidney and brain are primary depots (OECD 1974; Mitra 1986) after mercury vapour exposure. The target organ of methylmercury in humans is the brain, where it disrupts the blood brain barrier, upsetting the metabolism of the nervous system (WHO 1976). Elimination of methylmercury follows first order whole body kinetics, with elimination occurring primary through the faeces. The biological half-life of methylmercury is long and species dependent. In humans, the $T_{1/2}$ is approximately 70 days which lead to accumulation of methylmercury in tissues.

Acute Toxicity is the toxicity which is severe enough to produce a response rapidly (typically a response observed in 48 or 94 hours). The $LC_{50}$ is the effluent concentration in dilution water that causes mortality to 50% of test population. Acute mercury poisoning is usually characterised by pharyngitis, abdominal pain, nausea, vomiting, bloody diarrhea, and shock. Nephritis, anuria, and hepatitis occur, followed by death from gastrointestinal and kidney lesions (WHO 1976).

Chronic Toxicity is the toxicity impact that lingers or continues for a relatively long period of time. Humans exposed to excessive levels of methylmercury may develop central nervous system symptoms collectively known as Minamata disease. Any group of people who consume large amount of fish, such as native Indians, are potentially susceptible to methylmercury intoxication.

End point classification of toxic actions and effects of metals is commonly used for classifying the toxic actions of chemical substances. The term "genotoxic" precisely groups both "*carcinogenic*" and "mutagenic" effects. This term would include all chemical substances that can alter genes or chromosomes, possibly initiating cancer in somatic cells (all cells other than reproductive cells) or leading to heredity changes due to actions on germ cells (reproductive cells). Skerfving et al. (1974) found a positive correlation between chromosomal aberrations and blood methylmercury levels in a fish eating population. The term "teratogenicity" refers to the pathological effects during the sensitive development phase after implantation of the embryo up to the first three months of pregnancy in humans when major tissues and organs differentiate and develop, while the term "fetotoxicity" represents various disturbances, like growth depression, that may occur to a developing fetus during the later stages of pregnancy. Teratogenic activity in human, so far, could definitely be demonstrated for methylmercury (Gebhart and Rossman 1991).

Humans generally uptake mercury in two ways: a) in consumption as methylmercury ($CH_3Hg^+$), or b) by breathing vaporous mercury ($Hg^o$) emitted from various sources such as metallic mercury, dental amalgams, and ambient air. Elemental mercury ($Hg^o$) itself can be toxic especially if inhaled, but this element can also be methylated by microorganisms in aquatic systems into its most toxic organic form, methylmercury ($CH_3Hg^+$) which biomagnifies through the food chain especially in fish tissue. Human bodies are much more adapted for reducing the potential toxicity effects from vaporous mercury, so health effects from this source are relatively rare. The major pathway to human body is through ingesting (e.g.: fish, shrimps, etc.).

As mentioned before, mercury is efficiently transformed into the most toxic form (methylmercury) in the aquatic environment. Methylmercury, which affects the central nervous system and in severe cases irreversibly damages areas of the brain, can bioaccumulate from 100,000 to 1,000,000 times in fish tissue posing a threat to humans and wild life that consume that contaminated fish (Cole et al 1992). Small pan fish, such as perch, rock bass and crappie (less than 9 inches) are very low in methylmercury. However, larger, older predatory fish such as bass and pike often contain higher levels of methylmercury. Unlike PCBs, dioxin or other fish contaminants, mercury concentrates in the muscle, not the fat. Therefore, trimming the fat or grilling will not significantly reduce methylmercury levels.

Many mercury-poisoning cases have been reported. The most well documented cases of severe methylmercury poisoning are from Minamata Bay, Japan in 1956 (industrial release of methyl-mercury) and in Iraq (Damluhi and Tikriti 1972) where seed grains treated with an ethylmercuric compound were supplied to farmers. In each case, hundreds of people died, and thousands were affected, many with permanent damage. Other milder poisoning cases were reported in Guatemala, New Mexico, and USA (D'itri and D'itri 1977). In Canada, the Cree Indians have been reported to suffer from what they call "fish decease" (Rauber 1992).

In milder cases of mercury poisoning, adults complain of reductions in motor skills and dulled senses of touch, taste, and sight. These milder effects are generally reversible if exposure to mercury is halted. Unborn children are at greatest risk from low-level exposure to methylmercury.

#### 1.1.5.1 Regulations Related to Dosage Limits

##### 1.1.5.1.1 World Health Organisation

Regulatory agencies focus on fish as the target organism to protect the health of humans. For example, the U.S. Food and Drug Administration set an advisory standard of 1 ppm wet weight in fish flesh, and the World Health Organisation (WHO) recommends that the dose should not exceed 30 mg/day to protect adult humans. Some states of the U.S.A use 0.5 ppm wet weight in fish flesh to set fish consumption advisories (Michigan Mercury Pollution Prevention Task Force, 1996). Table 1.1 summarises the national standards of mercury levels in the environment in Canada, Japan, Sweden, and the United States.

Table 1.1: National Standards for Mercury *(after OECD 1974)*

| | Japan | Sweden | Canada | U.S.A. |
|---|---|---|---|---|
| **Environment Quality Standards** | | | | |
| fish, for sale (wet weight) | 1.0 [b] | 1.0 [c] | 0.5 | 0.5 |
| fish from natural waters | - | - | - | 0.5 [d] |
| food, excluding fish | - | 0.05 | 0.02 | - |
| drinking water [e] | nd [f] | - | - | 0.005 [g] |
| bottom sediments (dry weight) | - | - | - | 1.0 |
| **Emission Standards** | | | | |
| liquid effluents[h] | nd [f] | * | - [i] | * |
| gaseous effluents | - | * | - | - [j] |

a. All figures are maximum tolerable values in mg/kg of total mercury unless otherwise stated. A dash (-) indicates no standard has been established; an asterisk (*) refers to a standard not expressible numerically (see Note h).

b. A measured concentration of 1.0 mg/kg in one fish is used to indicate the need for more extensive sampling. If then more than 5 fish in a sample of 25 contain more than 1.0 mg/kg, mercury pollution alert is issued for the waters concerned.

c. This figure refers to methylmercury. The level of methylmercury in fish is almost identical to that of total mercury.

d. When a range of fish species in an inland or estuarine body of water contains more than 0.5-mg/kg mercury on average, gross mercury pollution is considered indicated. When such a range contains between 0.2-0.5 mg/kg on average, while consumption may not represent a hazard, mercury pollution and a need to find the mercury source is considered to exist.

e. The WHO International Standards for Drinking Water (1971) has assessed a tentative limit for total mercury in drinking water at 0.001 mg/kg.

f. nd in Japanese legislation means not detectable by the defined method of analysis. At the present time this implies an upper limit for total mercury of 0.02 mg/kg, and in addition, an upper limit of 0.001 mg/kg for alkylmercury.

g. This standard is being re-valued for possible reduction

h. Japanese practice is to specify the maximum permissible limit to be achieved by liquid effluents (Note n. Swedish policy has not included the setting of liquid effluent standards, but requires that firms install the "best available technology" to abate mercury pollution (this refers in addition to gaseous effluents). The policy of the USA is that all man-made discharges of mercury to public waters should be prohibited. (For Canada, see Note i).

i. The emission standard established for liquid effluents from mercury cell chloralkali plants is 0.005 lb./day/ton $Cl_2$ produced.

j. The policy of the U. S. is that as knowledge of sources and control technology becomes available it is believed that all man-made emissions should be controlled. Proposed emission standards for chlorine production and primary processing of mercury-bearing materials would limit mercury emissions to 5 lb./day.

### 1.1.5.1.2 Canada

Canada has established several regulations and guidelines concerning mercury use and release to the environment. The federal mercury regulations and guidelines include:

1. Pest Control Products Act.
2. Metallurgical Industries Mercury Information Regulations.
3. Chlor-Alkali Mercury National Emission Standards Regulations.
4. Chlor-Alkali Mercury Liquid Effluent Regulations. This regulations states that:

> "The owner of a plant may deposit mercury contained in effluent if the actual deposit of mercury in any day does not exceed 0.00250 kilograms per tonne of chlorine times the reference production rate of that plant".

5. Liquid Effluent Discharges from Smelters and Base Metal Refineries.
6. Fish Inspection Act.
7. Ocean Dumping Control Act.
8. Food and Drug Act.
9. Labour Code.
10. Hazardous products Act.
11. Pollutant Substances Regulations.
12. Canada-U.S. Great Lake Water Quality Agreement.
13. Northern Inland Waters Act.
14. Arctic Waters Pollution Prevention Act.

In 1988, Quebec has established its classification of mercury-contaminated soils and ground water. The classification has three classes: A, B, and C (Ministere de l' Environnement, Gouvernement du Quebec, 1988). Class A represents the detection limit for the contaminant, class B represents the limit at which intensive analyses have to be done, whereas class C represents the limit at which corrective actions have to be undertaken. If the mercury concentrations fell between A and B, that indicates that the soil or the ground water is slightly contaminated. Between the limits B and C, the ground water and the soil are contaminated. Beyond C the ground water and the soil are heavily contaminated. Mercury concentrations in soils corresponding to classes A, B, and C are 0.2, 2, and 10 mg/kg (ppm) respectively. For ground water, the mercury concentrations corresponding to A, B, and C are 0.1, 0.5, 1.0 mg/L (ppb) respectively. For potable water, the maximum permissible concentration of mercury is 0.001 mg/L (Gazette officielle du Quebec 1993).

#### 1.1.5.1.3 U.S.A.

In the U.S.A., a permissible limit for mercury (methylmercury) has been established for air and drinking water. The limit was set to 0.05 mg of Hg vapour per m$^3$ of air for industrial atmospheres; in drinking water, this limit has been set at a higher limit of 50 ppb (Mitra 1986).

U.S. Federal Pollution Prevention Act of 1990 endorses the reduction of a polluting source as the preferred approach. The pollution prevention hierarchy, as set in the 1990 Act, Section 6602(b) is as follows:

" 1) Pollution should be prevented or reduced at the source whenever feasible;

2) Pollution that can not be prevented should be recycled in an environmentally safe manner whenever feasible;

3) Pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and

4) Disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner."

However, this hierarchy may need to be re-evaluated regarding the recycling of mercury.

#### 1.1.5.1.4 Sweden

In 1991 Sweden's parliament decided that all uses of mercury should be stopped by the year 2000. The Swedish Environmental Protection Agency (EPA) has also recommended that mercury not be reclaimed for recycling or reuse. The Swedish EPA believes that the only feasible long term solution is that mercury be stored permanently in a geological repository (Michigan Mercury Pollution Prevention Task Force, 1996).

### 1.1.6 Preventive Actions to Decrease the Use of Mercury in U.S.A. and Canada

Domestic consumption of mercury has been in downward trend since the early 1970's. However, the industrial consumption of refined mercury metal in the U.S. in 1994 and 1995 are 483 and 436 metric tons respectively (Table 1.2). The largest commercial use of mercury in the United States was for electrolytic production of chlorine and caustic soda in mercury cell, accounting for 35% of domestic mercury consumption in 1995. It was followed by manufacturing of wiring devices and switches, which accounted for 19%; and dental equipment and supplies, which used 7% (Plachy, personal communications, 1995).

Table 1.2: U.S. Industrial Consumption of Refined Mercury Metal
*(USGS, Personal Contact 1996)*

| Use | 1994 | 1995 |
|---|---|---|
| **Chemical and allied products:** | | |
| Chlorine and caustic soda manufacture | 135 | 154 |
| Laboratory uses | 24 | [1] |
| Other chemical and allied products [2] | 25 | [1] |
| **Electrical and electronic uses:** | | |
| Electric lighting | 27 | 30 |
| Wiring devices and switches | 79 | 84 |
| Batteries | 6 | [3] |
| **Instruments and related products** | | |
| Measuring and control instruments | 53 | 43 |
| Dental equipment and supplies | 24 | 32 |
| **Other uses** [4] | 110 | 93 |
| **Total** | 483 | 436 |

[1] With held to avoid disclosing company proprietary data; included in “Other uses”.
[2] Includes pharmaceutical uses and miscellaneous catalysts.
[3] Less than 0.5 unit.
[4] Includes other electrical and electronic uses, other instruments and related products, and unclassified uses. For 1995, it also includes “Laboratory uses” and “Other chemical and allied products”

Chlorine, the primary output of this industry, has been used as a bleaching agent for linen, cotton and paper. Chlorine and chemicals related to its production, soda ash, and caustic soda are among the most important industrial chemicals with applications that cover the production of soap and detergents, plastic, glass, petrochemicals, fertilisers, and water/waste water treatment. In 1892, the process of producing chlorine and caustic soda in an electrolytic cell was developed. This process employed the electrolysis of brine (NaCl) using a moving liquid mercury cathode to produce chlorine at the anode and a sodium mercury amalgam at the cathode. This so called "mercury cell process" constituted the main commercial production process for chlorine and caustic soda from the 1890s to the middle of 20th century. Although mercury cells are still in operation throughout the world, they are being increasingly replaced with alternative, mercury free electrolytic process. These processes, the diaphragm cell and membrane cell processes, produce chlorine and caustic soda, use the same raw materials (brine, water, and electricity), and are similar in terms of generating and treating product gases. The primary difference from the mercury cells is the absence of mercury in effluents of coming from diaphragm and membrane cells.

In Canada, chlorine was produced from 15 mercury cells plants from 1935 to mid 1970s. By 1979, only five operating mercury cell plants remained (Environment Canada, 1994). During 1986-1989, total mercury losses from Chlor-Alkali industry to effluents decreased from 88.07 kg (1986) to 46.29 kg (1989) and the losses to emissions were also decreased from 680.56 kg (1986) to 547.19 kg (1989). On contrast, the mercury losses to solid wastes have increased over the same period. In 1986 the total losses to solid wastes were 449.3 kg while in 1989 the losses were 1196.11 kg.

### 1.1.7 Efforts Done in Canada for Pre-treatment of Mercury-contaminated Soils

Due to the harmful impacts of mercury on the environment and human health, some efforts have been done in Canada in previous times to improve this situation. A pre-treatment process for mercury contaminated soil has been developed and demonstrated by PPG Canada Inc., in implementing the restoration plan for its industrial site at Beauharnois, Quebec. This process, which uses gravimetric and flotation technologies, was developed in collaboration with Biogenie SRDC Inc., and tested in the summer of 1992. The contaminated soil treatment process allows mercury that would otherwise be disposed of in a landfill cell to be removed and recycled. However, the process is applicable in removing heavy metals prior to other types of treatment. During the testing period, the process recovered 1350 kg of the metallic mercury initially present in the 5000 $m^3$ of soil treated, with a residual concentration of less than 900 mg/kg (Environment Canada 1993).

The governments of Canada and Quebec have established a joint program, the St. Lawrence Vision 2000 action plan or SLV 2000 (1993-1998) to protect and rehabilitate the St. Lawrence ecosystem. SLV 2000 builds on the work of its predecessor, the first St. Lawrence Action Plan (1988-1993). Since 1988, both governments have invested close to $400 million toward reducing the discharge of industrial effluents into the river, safeguarding habitats, developing environmental technologies, and rehabilitating degraded environments. One hundred and six industrial plants have been targeted to reduce their wastewater discharges as part of SLV 2000.

St. Lawrence Action Plan and SLV 2000 have many concrete accomplishments such as:

1. The 50 most polluting industrial plants targeted by the St. Lawrence Action Plan have reduced their toxic effluent discharges by 96%.
2. Discharges of 56 other polluting plants have been characterised.
3. A program has been established to emphasise the participation of industry in protecting the environment and to promote the exchange of information among private sector partners.
4. The "State of the Environment Report on the St. Lawrence River" has been published, the product of many years of research.
5. Recovery plans have been prepared for six threatened species.
6. Knowledge has been acquired of various key elements of the St. Lawrence ecosystem including its degree of contamination and the effect of disturbance on different ecosystem components.

## 1.2 Wetlands

### 1.2.1 Introduction

The U.S. Fish and Wild life service adopted the following definition of wetlands: "Wetlands are lands transitional between terrestrial and aquatic systems where the water table is usually at or near the surface or the land is covered by shallow water. For purpose of this classification wetlands must have one or more of the following three attributes: (1) at least periodically, the land supports predominately hydrophytes; (2) the substrate is predominantly undrained hydric soils; and (3) the substrate is nonsoil and is saturated with water or covered by shallow water at some time during the growing season each year".

The Canadian National Wetlands Working Group has established another definition of wetlands. Under the definition of the Canadian National Wetlands Working Group, a wetland must have all the three components mentioned above.

Wetlands cover approximately 14% of the area of Canada, or 127,200,000 ha (National Wetlands Working Group 1988). There are five wetland classes in the Canadian classification system: bog, fen, swamp, marsh, and shallow open water.

Bogs are peat-covered wetlands in which the vegetation shows the effect of high water table levels and a general lack of nutrients. *Fens* are peatlands with water table usually just at or above the ground surface; they are much richer in nutrients than bogs. *Swamps* are mineral wetlands or peatlands with standing water or water flowing slowly through pools or channels; water is rich in nutrient and the associated soils consist of mixtures of mineral and organic materials. *Marshes* are mineral wetlands that are periodically inundated by standing water or gently moving water; water is rich in nutrients and the substrate is predominantly mineral soils. *Shallow water wetlands* are non-fluvial bodies of standing water representing a transitional state between lakes and marshes. They could be distinguished from deep water by midsummer water depth of less than 2 m, and from other wetlands by summer open water zones occupying 75% or more of the wetland surface area.

Wetlands could be *fresh water wetlands* or *coastal wetlands*. Frayer et al (1983) reported that about 95% of the wetlands in the United States are inland fresh water. Most of these wetlands are either fresh water marshes or riparian woodlands. Fresh water wetlands develop at elevations above open water aquatic habitat and below uplands. They are found in a wide range of hydrologic conditions, from permanently flooded (to a depth of 1 m) to seasonal saturation of the root zone. Fresh water wetlands occur in wide variety of soil types including both organic and mineral soils, as well as in non-soil conditions.

Coastal wetlands are generally defined as those wetlands that lie within the realm and effects of salt water. As such, coastal wetlands include sea grass meadows, mangrove forests, and salt marshes. Sea grass meadows are the only type of coastal wetlands subject to nearly constant submergence.

Natural and constructed (artificial or engineered) wetlands treatment systems have distinctive characteristics that strengthen their application on a site-specific basis. They are relatively easy systems to operate and maintain, they are extremely energy efficient when compared to mechanical systems, and they provide beneficial habitat for a variety of wildlife. Both European and U.S. investigators provided research into wetlands treatment in northern climate (Doku and Heinke 1995).

Natural and constructed wetland systems provide waste water treatment by significantly reducing oxygen demanding substances such as BOD and ammonia, suspended solids, nutrients such as nitrogen and phosphorus, and other pollutants such as metals. Primary, secondary, and incremental removal mechanisms include: physical, chemical, and biological operations as well as plant uptake (Sherwood et al 1979, Reed et al 1988, U.S. Environmental Protection Agency 1988, Hammer 1989, Water Pollution Control Federation 1990)

Most natural or constructed wetlands have five principal components:

1. Substrate with various rates of hydraulic conductivity
2. Plants adapted to water saturated anaerobic substrates
3. Water column (water flowing in above the surface of the substrate)

4. Invertebrates and vertebrates
5. Aerobic and anaerobic microbial population

Aquatic plants are divided into free floating and rooted forms. The rooted class is then subdivided into emergent, floating and submerged classes. Wetland plants have two important functions: 1) the stems and the leaves increasing the surface area for attachment of microbial populations, and 2) creating an aerobic region (called rhizosphere) surrounding root hair. This aerobic region is a result of oxygen leakage during its transport down into the roots.

Microorganisms remove heavy metals from solution by two general mechanisms: metabolism-dependent uptake into the cell and binding of metal ions to the cell wall (Wilkinson 1957; Kelly et al 1979; Shumate and Strandberg 1985).

Wetland hydrology affects their performance and should be taken into consideration. For example: rainfall can cause two opposing effects: 1) dilution of wastewater and 2) increased velocities, reducing retention times within the wetland.

Wetlands provide a number of functions that meet ecological and human needs. They provide life support (climatic regulation, absorption of toxic materials, stabilisation of biosphere processes, water storage, cleansing, nutrient cycling, food chain support, habitat, biomass storage, and genetic and biological diversity), social and cultural opportunities (research specimens, viewing, photography, bird watching, hiking, canoeing, and community, religious, or cultural traditions), and production functions (natural production of birds, plants, fish, fibre, and soil supplements), (Sheely 1993).

Although wetlands provide a greater water surface area for mosquitoes to breed, this potential can be controlled. The most effective method is the use of mosquito fish that eat the mosquito larvae before they reach the adult stage. Nesting boxes can be set up for purple martins and swallows, which consume adult mosquitoes as they emerge from the wetland. Dragon fly larvae can be introduced into the system that, once they reach the adult stage, will feed on the adult mosquitoes. Maintaining the design water level will reduce the formation of stagnant, mosquito hatching sites.

### 1.2.2 Waste Water Treated in Wetlands

The success of employing wetlands functions in purifying wastewater relates to the metabolism of the wetlands ecosystem. Stems and leaves of wetlands plants provide surface area for microbes, whereas below ground transport of oxygen by these same plants produces an oxidised zone in the rhizosphere where additional microbial populations exist. This complex of wetlands plants and microbes has a high efficiency in modifying nutrients, metals and other compounds.

Certain plant/substrate combination appear to be more efficient in constructed wetlands treatment systems (Gersberg et al 1986) and others may be more tolerant of high pollutant concentrations (Brix and Schierup 1989).

#### 1.2.2.1 Municipal Wastewater

Sewage: Sewage treatment with emergent aquatic macrophytes was introduced in Denmark in 1983. The results show a $BOD_5$ reduction of 70-90%. Total nitrogen was reduced 25-50% and total phosphorus was reduced 20-40% (Brix and Schierup 1989). In Florida, two constructed wetland systems for sewage treatment were reported, one in the city of Lakeland and the other in the city of Orlando. Total phosphorus was reduced by 50% in the Lakeland system (Jackson 1989). In South Africa, available data from Olifantsvlei wetland system (near Johannnesburg) indicates significant removal of suspended solids and pathogens (Wood and Hensman 1989). In July 1980, The Ontario Ministry of Environment (MOE) initiated the Listowel Marsh project in southern Ontario, Canada. The northern community of Cobalt was selected to check the suitability of march wetlands for wastewater treatment in Northern Ontario. $BOD_5$ concentrations were reduced by 80% (Miller 1989).

Landfill leachate: The construction of eight wetland plots at municipal solid waste landfills in Allegancy County and Tompkins County, New York began in the spring of 1988 as a part of investigating the feasibility of constructed wetlands for landfill leachate treatment (Staubitz et al 1989). The chemical quality of landfill leachate is different from one landfill to another, even for the same landfill it fluctuates seasonally. Metal accumulation in the wetland plots is an important factor for the long-term use. Metals may accumulate in the wetland plots by: 1) bioaccumulation in the aquatic plants, 2) adsorption to the substrate, 3) microbially mediated oxidation of metals, 4) formation of insoluble sulphide precipitation, and 5) chelation by organic material and incorporation into the biofilm. The first two processes have limited capacities to retain metals, if dominant in controlling metals retention, may indicate poor long-term treatment performance (Staubitz et al 1989).

### 1.2.2.2 Industrial Wastewater

Auto manufacturing: A study has been performed by the University of Tennessee and Saturn corporation to search for a feasible way of managing the blow down water. The cooling tower at General Motor's Saturn Plant in Spring Hill, Tennessee produces blow down wastewater at rate reaching 1893 $m^3$/day (Barnett et al 1991). Treatment of the blow down water on site in a constructed wetland was recommended. The constructed wetland system is to be supplemented with plant storm water run off, spray irrigation of crops farmed by Saturn. The study recommended that the treatment of the blow down water in a constructed wetland followed by spray irrigation of the crops is a viable alternative.

Clam processing water: High strength, low toxicity, saline wastewater from seafood processing could be treated in natural tidal salt marshes. Salt tolerant micro biota, plants, and animals in salt marshes facilitate the treatment of saline clam processing. Experiments were performed at the Wetlands Institute near Stone Harbour, New Jersey to investigate the efficiency of treating the clam processing wastewater. Removal of $BOD_5$ from the effluent ranges from 29% to 100%; TSS from 58% to 108%; TN from 69% to 98%, and TP from 30% to 73%(Guida and Kugelman 1989)

Oil refining: Amoco Oil company has used constructed wetlands for wastewater treatment at its refinery in Mandan, North Dakota. Primary treatment of wastewater from the refinery process units is done in a conventional American Petroleum Institute separator in which oil and other contaminants are separated and recovered. Then, water is discharged into a lagoon for initial secondary treatment and pumped to a high point for distribution among many routes through a series of cascading ponds and ditches before discharge to the Missouri River (Litchfield and Schatz 1989).

Paper mills / Pulp mills: In 1989, the University of Southern Mississippi participated in a study of the efficiency of tertiary treatment of bleach kraft pulp mill effluent by constructed marshes. A two years pilot study has revealed that except for TP in the second year, concentrations for all water quality contaminants were reduced through the march system (Tettleton et al 1993). Thut (1993) reported that the overall quality of wetland effluent from pulp mill was very high and could be compared to the receiving water. However, a constructed wetland would have no effect on the colour and small effect on the chlorinated organic found in bleached kraft effluents.

Sugar refinery wastewater: A sugar refinery in Gramercy, LA, has been using water from the Mississippi River for cooling. During the cooling process, some quantities of sucrose are dissolved in the cooling water. This cooling water (which leaves the refinery with a variable concentrations of soluble organic carbon) is to be finally disposed to the Blind River or Lake Maurepas. There has been concern by federal and state agencies that the organic carbon loading from the refinery may increase the $BOD_5$ in the receiving waters (Gambrell et al 1987). A study was performed to estimate the capacity of a refinery-owned swamp to effectively treat its effluent. Wetlands have been known for their ability to purify wastewater, however, they should be properly designed. The study recommended that the area of the treating wetland be increased to allow adequate retention time. Having done that, the effluent TOC would be degraded.

Textiles dyes: Constructed wetlands are capable of treating industrial waste water containing a wide range of chemicals, including priority pollutants such as phenols and cresols, by processes such as absorption and bacterial breakdown, chemical oxidation, adsorption onto the bed matrix and sedimentation (Davies and Cottingham 1994). Experiments have been carried out in a constructed wetland located in Melbourne, Australia. The textile dye wastewater was discharged at a rate of 10 l/min. Results show that breakdown of the visible dye occurred in the first one third of the wetland. It was concluded that constructed wetlands have the potential to treat industrial effluents containing priority pollutants and dyes.

Thermal discharge: Thermal discharges have been treated by wetlands. Nevamar Corporation, located in Denton, Maryland produces decorative building surfaces for counter tops, furniture and other interior applications. The water temperature can reach 51.6°C during the manufacturing process. The regulations in Maryland required the discharge temperature not to exceed 32.2°C. The manufacturer has introduced an aquatic plant nursery/ thermal treatment pond (Ailstock 1989). This has reduced the effluent temperature to permit limitations and provided plants for constructing other wetlands.

#### 1.2.2.3 Acidic Wastewater

Acid drainage: Acid mine drainage is a very common problem related to coal and metal mining. Effluents from these systems have low pH and high dissolved metal concentrations that could harm aquatic ecosystems. Concentrations of metal ion in acid mine drainage flowing through Sphagnum- dominated peat bogs and natural wetlands have been reduced by cation exchange process (Howard et al 1989). Several hundred wetlands have been constructed in the coal bearing states of Maryland, West Virginia, Pennsylvania, and Ohio to reduce impacts from acid mine drainage. 50% of the incoming iron has been removed by a wetland constructed by Windsor Coal Company, West Virginia (Kolbash and Romanoski 1989).

Treatment of ash pond seepage: Processing and transporting of coal and the storage of coal ash frequently result in acid drainage similar to seepage from mine areas. Seepage from ash storage pond has concentrations of metallic ions similar to acid mine drainage, but the cumulative flow from many seeps along one ash pond dike may be orders of magnitude greater than individual mine drainage seeps. Tennessee Valley Authority ash pond seeps have pHs of 3-6, Fe of 100-200 mg/L, Mn of 5-10 mg/L and it may also contain Se, and heavy metals (Brodie et al 1989). Constructed wetlands for treatment of ash pond seepage were investigated at three locations. Results at one of these locations show that over 97% of Fe were removed but only 9% of the Mn, and average discharge pH decreased 2.1 s.u.

### 1.2.2.4 Storm Water

Storm water runoff from roofs, parking lots, roadways and landscapes impacts and degrades water quality. However, temporary detention of storm water run-off can improve it. Runoff from parking lots and roadways contains high concentrations of suspended solids, nutrients, trace metals, oil and grease, and de-icing salts. Constructed wetland have been used to treat storm water runoff from a regional shopping mall in Massachusetts (Dukes et al 1989). The range of pollutant removal efficiencies was estimated for that shopping mall as follows: suspended solids 80-95%, TP 60-85%, TN 40-70% $BOD_5$ 50-80%, lead 80-95%, and mercury 50-90%.

### 1.2.2.5 Agricultural Wastewater

Non Point Sources of pollution (NPS) was reported as a principal cause of water quality problems in six of ten EPA regions in 1982 (USEPA 1984). Agricultural activities (i.e., animal waste, and tillage practices) were considered the most dominant problems in all regions. In 1984, officials from 49 states reported that 29% of lakes and reservoirs assessed were moderately to severely impacted by NPS pollution, mainly from agricultural activities (ASIWPCA 1984).

Livestock and Dairy Animal waste waters: A constructed wetlands waste water treatment system for swine waste was developed at Auburn University's experimental station in DeKalb County, Alabama. Wastes from 500 animal furrowing and finishing operation is routed to two cells in series lagoon system, with a separate single cell lagoon collecting waste from one barn. The wetlands (constructed in 1988) are surface flow type located below the lagoons. The constructed wetlands demonstrated effective and reliable treatment of swine lagoon effluent. The percentage of removal were: $BOD_5$ 90.4%, TSS 91.4%, Fecal coliform 99.4%, TP 75.9%, and TKN 91.4% (Hammer et al 1993).

In Ireland, Lough Gara Farms Limited has an intensive dairy farm to produce milk for direct retail sale built in 1961. The existing treatment system employs a natural wetland formed as a result of successive drainage schemes carried out in the region. The wetlands wastewater treatment system is divided into two parts: the first part has peat as a substrate and covered by vigorous vegetation. A boundary drain receives outlet waters from the first part to avoid short circuits and to serve as a distribution channel to the second zone. The system was designed so that the treatment takes place in the first zone. Results show that the system produced: 99.95% reduction in $BOD_5$, 95.4% reduction in ammonia concentrations, 91.3% reduction in orthophosphate concentrations (Costello 1989).

Runoff and sediment control: Most wetlands are designed to treat domestic wastewater and focus on $BOD_5$ and nutrient removal. Systems for mitigating agricultural (cropland) non-point runoff are directed to sediment and nutrients. The application of constructed wetlands in treating agricultural wastes differs from those used to treat wastewater. The hydraulic loading is intermittent and usually there is no significant organic load. Also, agricultural runoff carries heavy load of sediments as well as high nutrient and pesticides levels. This would limit the capacity of a constructed wetland to treat agricultural runoff. A proper design should allow for a sedimentation basin, grass filter strip, constructed wetland, and retention pond. Four systems consisted of sediment basins, grass filters, and constructed wetlands pond components have been constructed in the Long Lake watershed in the St. John valley of northern Maine. The results show that, in 1990, the average removal of TP was 82%, TSS 97%, and VSS 94% (Higgins et al 1993).

### 1.2.3 Wetlands in Canada for Wastewater Treatment

An intensive investigation was carried out in early 1994 to determine the locations of wetlands in Canada used for storm water and waste water treatment with the exception of acid mine drainage treatment systems and a literature search was carried out to identify Canadian literature on wetland waste water and storm water treatment systems (Pries 1994).

Wetlands for waste water and storm water treatment in Canada are primarily located in the temperate and boreal wetland regions. The high boreal region, which stretches into the central part of the Yukon and Northwest Territories, has at least 10 wetlands for waste water treatment that are currently operating on a seasonal basis or have been approved for operation by the regulating authorities. The climate in this region is typified by long winters, high accumulations of snow, and short summers with short growing seasons. The status and location of each of these wetlands is summarised after Pries (1994) in Table 1.3.

In Canada, the problem associated with wetland technology is operation at cold temperatures. It seems logical that treatment processes may slow or stop at cold temperatures, as they do in conventional treatment plant operations.

Table 1.3 Location and Status of Treatment Wetlands in Canada (*after Pries 1994*)

| Location | Wetland Region | Application | Full-Scale | Pilot-Scale | Designed[1] |
|---|---|---|---|---|---|
| ***Yukon*** | | | | | |
| Old Crow | SH | Municipal, Lagoon | * | | |
| Destruction Bay | BH | Municipal, Lagoon | * | | |
| Haines Junction | BH | Municipal, Lagoon | * | | |
| Crestview | BH | Municipal, Lagoon | * | | |
| Faro | BH | Municipal, Lagoon | * | | |
| Ross River | BH | Municipal, Lagoon | * | | |
| Teslin | BH | Municipal, Lagoon | * | | |
| ***Northwest Territories*** | | | | | |
| Hay River | BH | Municipal, Lagoon | * | | |
| Pine Point | BH | Municipal, Lagoon | * | | |
| ***British Columbia*** | | | | | |
| West Moberly | BM | Municipal, Lagoon | | | * |
| Portage | BM | Municipal, Lagoon | * | | |
| Stellaquo | BM | Municipal, Lagoon | * | | |
| Coal Creek | TP | Industrial, Fish Hatchery (two sites) | * | | |
| Rosewall Creek | TP | Industrial, Fish Hatchery | * | | |
| Pinecrest Estates | MC | Municipal, Wastewater Treatment Plant Secondary Effluent | * | | |
| Richmond | TP | Landfill, Leachate | * | | |
| Burnaby | TP | Stormwater, Rural | | * | |
| Frances Garden | TP | Municipal, Wastewater Treatment Plant Secondary Effluent | * | | |
| Throup Road | TP | Municipal, Wastewater Treatment Plant Secondary Effluent | * | | |
| Fishtrap Creek | TP | Stormwater, Urban | * | | |
| Chilliwack | TP | Industrial, Oil | | * | |
| ***Alberta*** | | | | | |
| Fort McMurray | BH | Industrial, Oil | | * | |
| St. Paul | BM | Municipal, School | * | | |
| Stettler | PC | Farm, Stormwater | | * | |
| Frank Lake | PC | Industrial, Meat Packer/Municipal, Lagoon | * | | |
| Stirling | PC | Municipal, Lagoon | * | | |
| ***Saskatchewan*** | | | | | |
| Meadow Lake | BM | Municipal, Lagoon | * | | |

| Location | Wetland Region | Application | Full-Scale | Pilot-Scale | Designed[1] |
|---|---|---|---|---|---|
| Saskatoon | PC | Stormwater, Urban | * | | |
| Aberdeen | PC | Municipal, Lagoon | * | | |
| Humbolt | PC | Municipal, Lagoon | | * | |
| Shaunavon | PC | Municipal, Lagoon | * | | |
| Regina | PC | Stormwater, Urban | * | | |
| Estevan | PC | Municipal, Lagoon | * | | |
| ***Manitoba*** | | | | | |
| Oak Hammock | PC | Municipal, Lagoon | * | | |
| ***Ontario*** | | | | | |
| Cobalt | BL | Municipal, Lagoon | | * | |
| Listowel | BL | Municipal, Lagoon | | * | |
| Fullerton Township | BL | Farm, Manure Runoff | * | | |
| Sarnia | TE | Landfill, Leachate | * | | |
| Lambton | TE | Stormwater, Industrial | * | | |
| Essex | TE | Farm, Manure Runoff | * | | |
| Hamilton | TE | Farm, Manure Runoff | | | * |
| Niagara-on-the-Lake | TE | Municipal, Lagoon | | * | |
| Mississauga | TE | Stormwater, Urban | * | | |
| East York | TE | Stormwater, Urban | | | * |
| North York | TE | Stormwater, Urban | | | * |
| Scarborough | TE | Stormwater, Urban | | | * |
| Port Perry | TE | Municipal, Lagoon | * | | |
| Storrington | TE | Landfill, Leachate | | * | |
| Rideau Township | TE | Farm, Manure Runoff | * | | |
| Kanata | TE | Stormwater, Urban | | | * |
| ***Quebec*** | | | | | |
| Lac Simon | BL | Municipal, Single Family Dwelling | * | | |
| Lac Simon | BL | Municipal, Septic Tank | * | | |
| Carillon | TE | Municipal, Septic Tank | | | * |
| Mirabel | TE | Municipal, Septic Tank | * | | |
| Rivière Beaudette | TE | Municipal, Septic Tank | | | * |
| Ile Ste. Hélène | TE | Recreational, Beach | * | | |
| Montreal (Biosphere) | TE | Municipal, Septic Tank | * | | |
| Stoke | TE | Municipal, Septic Tank | * | | |
| Grand-Saint-Esprit | TE | Municipal, Lagoon | | | * |

| Location | Wetland Region | Application | Full-Scale | Pilot-Scale | Designed[1] |
|---|---|---|---|---|---|
| Fontages | SL | Municipal, Lagoon | * | | |
| Saint-Felicien | BL | Municipal, Zoo, Lagoon | * | | |
| Saint-Henri de Taillon | BL | Municipal, Lagoon | | | * |
| Saint-Vianney | BA | Municipal, Lagoon | * | | |
| ***New Brunswick*** | | | | | |
| Moncton | BA | Municipal, Lagoon | * | | |
| ***Prince Edward Island*** | | | | | |
| New Annan | BA | Industrial, Potato Processor Tertiary Effluent, Wastewater Treatment Plant | * | | |
| ***Nova Scotia*** | | | | | |
| River Hebert | BA | Municipal, Lagoon | | | * |
| Hwy. 101 Landfill | BA | Landfill, Leachate | * | | |

Legend/Notes:

[1] System has been designed and approved by the regulating authorities. Construction to begin when weather permits.

Wetland Regions:

| | | | |
|---|---|---|---|
| BA | Atlantic Boreal | OP | Pacific Oceanic |
| BH | High Boreal | PC | Continental Prairie |
| BL | Low Boreal | SH | High Subarctic |
| BM | Mid-Boreal | SL | Low Subarctic |
| MC | Coastal Mountain | TE | Eastern Temperate |
| MI | Interior Mountain | TP | Pacific Temperate |

Applications:
Municipal - Treated (Primary/Secondary) Municipal Wastewater
Lagoon - Primary/Secondary Lagoon Treatment (Facultative or Aerated)
Industrial - Treated Industrial Wastewater
Oil - Treated Wastewater from the Oil Industry
Fish Hatchery - Treated Fish Hatchery Wastewater

Wetlands, however, are far more complex than conventional wastewater treatment facilities and they perform many treatment functions efficiently in winter (Miller, 1989).

Treatment does not have to rely on slow winter processes. Many northern systems store water for the duration of the non-growing season and then discharge to the wetland during the warm spring, summer, and fall months (Doku, and Heinke, 1995). The advantage of this approach is the availability of warm weather design information; the disadvantage is the cost of the storage lagoons (Doku, and Heinke, 1995).

Challenges for wetland waste water treatment in northern communities in the Yukon and Northwest Territories include permafrost (damage to berms), low precipitation, extreme temperatures, 24 hours of sunshine during the summer, and 24 hours of darkness during the winter that can lead to septic conditions.

Information pertaining to winter operation is now significant and increasing rapidly. Canadian research has contributed valuable knowledge. Pioneering work on surface flow wetlands was conducted at Listowel, Ontario in 1980 to 1984. Five wetlands were continuously operated throughout the winter by controlling the insulation in a way unique to wetland ecosystems. Water levels were raised at freeze-up, and a layer of ice was allowed to form. The water level was then lowered to provide an insulating air gap above the water, but below the ice. The stems of the dense stand of emergent cattails served as supports to keep the ice layer elevated. The dead cattails trapped snow and added an insulating snow blanket (Herskowitz et al 1986). Temperature effects were significant for nitrogen reduction, slight for phosphorus, and non-existent for BOD and total suspended solids (TSS). Many northern peatlands exhibit this behaviour, with unfrozen water below a snow blanket trapped by the plants. A subsequent project at Cobalt, Ontario reinforced much of the knowledge gained at Listowel (Miller, 1989).

### 1.2.4 Design Elements of Wastewater Treatment Wetlands

Natural Wetlands: Design criteria for natural wetlands have been very much empirically based. The design criteria available do not predict reliably the performance or the required size of natural wetlands for wastewater treatment systems. Design criteria are insufficient because the characteristics of natural wetlands such as climate, hydrology, soils, and vegetation are site specific. The critically employed parameter in design is the hydraulic loading rate (Reed et al, 1995). The organic loading rate is used as a check to ensure that aerobic conditions necessary for microbial activity prevail in the wetland ecosystem. The hydraulic loading rates for the treatment of secondary effluent using natural wetland systems range from 100 to 200 $m^3$/ha.d, and the maximum organic loading rate is 4 kg $BOD_5$/ha.d (Water 1990).

Constructed Wetlands: Constructed wetlands are man made wetlands, establishing the required vegetation and hydrologic conditions in locations where previously they did not exist. There are two types of constructed wetlands, free water surface (FWS) wetland and subsurface flow (SF) wetlands. The design criteria for both types range from empirical to more rationale mathematical models.

## 1.3 Review of Design Concepts for Designing Constructed Wetlands

Constructed wetlands are designed according to many criteria. Some designers utilise multiple regression analysis of performance data from operating systems to establish design criteria (Knight et al 1993). Other designers suggest the areal loading approach, in which the treatment performance is related to the volume of water or mass of particular pollutant divided by the surface area of the wetland (Smith, 1980). A third group of designers assumes that the biological reactions which occur in wetlands are similar to those describing the same type of reactions in other attached growth wastewater treatment processes (Knight et al 1993).

All three concepts can produce valid results if the procedures are developed properly. However, designing engineers (Tchobanoglous and Burton 1991) agreed that the last approach for constructed wetlands design - which assumes that wetland's performance can be described using familiar biological design models (first order design model where the response is a function of the residence time and the temperature of the system) – gives better and more reliable results.

### 1.3.1 Characteristics of Flow Pattern Through Constructed Wetland Systems

The two extremes of reactor flow patterns are identified as either plug flow or completely mixed. In a plug flow reactor, the effluent is envisaged as passing along the length of the reactor without experiencing any longitudinal mixing. As there is no intermixing, every element in the reactor experiences treatment for the same amount of time (the theoretical retention time). In a completely mixed reactor the influent is instantaneously mixed with the entire contents of the reactor and the contents of the reactor are homogeneous at every point. In addition each particle will have a different retention time. If a number of completely mixed reactors are connected in series, their behaviour changes from completely mixed towards plug flow.

The plug flow conditions are approached as the number of tanks in series approaches infinity (Horan, 1990). A wetland system is not an ideal plug flow reactor, but the response tends to be closer to plug flow than to the complete mix reactor.

In the areal loading design method, wastewater is applied uniformly over most of the land area involves by sprinklers or similar devices resulting in a uniform unit loading on a unit area. However, that is not the case in most wetlands systems, where typically all of the influent is applied at the head of the channel, so the unit loading per unit area of the wetland is not uniform. Another limitation of the areal loading method is that it does not take into account the depth of the water and the related hydraulic residence time in the wetland. The areal loading of water or any pollutant could be constant for a particular system, whether the water depth was only a few centimetres or almost a meter. The hydraulic residence time and the system performance in such a wetland would vary significantly with the depth of the water even though the areal loading were constant.

### 1.3.2 Major Processes for Mercury Removal by Constructed Wetland Systems

The major processes of mercury removal from wastewater in constructed wetland systems are expected to be sorption on sediments (or water column's suspended solids), and uptake by floating and rooted plants. Assuming that mercury is immediately (after being introduced) sorbed to the sediments and the suspended solids in the wetland system, the only time dependent removal process would be the plant uptake. However, no information is available regarding the reaction rate of mercury removal by wetland's plants, critical effect of some environmental factors such as pH and chloride concentration on mercury speciation in the water column/pore water, and characteristics of mercury adsorption by sediments. Having obtained these information (one of the objectives of the current research work), the process of removing mercury by plant's uptake could be modelled as attached growth biological reactor, and its performance can be estimated with first order plug flow kinetics.

The basic relationship for plug flow reactors (Reed et al, 1995) is given by:

$$C_{eff}/C_{inf} = \exp(-k\,t_r) \qquad (1.1)$$

Where:

$C_{eff}$: effluent mercury concentration, mg/L
$C_{inf}$: influent mercury concentration, mg/L
k : first order reaction rate constant, $d^{-1}$ (or $h^{-1}$)
$t_r$: hydraulic residence time, d (or h)

The hydraulic residence time in the wetland system can be calculated by:

$$t_r = L\,w\,y\,e\,/\,Q \qquad (1.2)$$

where:

L: length of the wetland cell, m
w: width of the wetland cell, m
y: depth of water in the wetland cell, m
e: the space available for water to flow through the wetland, dimensionless (vegetation and litter occupy some space in the Free Water Surface wetland).
Q: the average flow through the wetland, $m^3/d$

$$Q = (Q_{in} + Q_{out})\,/\,2 \qquad (1.3)$$

It is necessary to determine the average flow to compensate for water losses or gains through evapotranspiration or precipitation as the wastewater flows through the wetland. For conservative design, reasonable values of evapotranspiration and precipitation should be obtained from local records for each month or season of the year.

It is then possible to determine the loading surface area of the wetland from equations (1.1) and (1.2):

$$A_s = LW = [Q \ln (C_{inf}/C_{eff})]\,/\,[k\,y\,e] \qquad (1.4)$$

where

$A_s$: loading surface area of wetland, $m^2$

The value used for k in equations (1.1) or (1.4) depends on the plant type, as discussed in Chapter 3, and on the temperature as discussed in section 1.3.2.2.

This approach of design ignores the role of wetland sediments in removing contaminants such as mercury from contaminated waters. Another shortcoming in this approach is that it does not show which form of the contaminant is being removed.

#### 1.3.2.1 Hydraulic Aspects

To ensure successful performance of a constructed wetland treatment system, special attention must be paid to hydraulic designs. Currently, all design models assume uniform flow conditions and unrestricted opportunities for contact between wastewater constituents (pollutants) and the vegetation responsible for treatment.

Flow through wetland systems must overcome the frictional resistance in the system. This resistance is imposed by the vegetation and the litter layer in the Free Water Surface wetlands. The energy to overcome this resistance is provided by the head differential between the inlet and the outlet of the wetland. Some of this differential can be provided by constructing the wetland with a sloping bottom. However, it is neither cost effective nor prudent to depend on just a sloping bottom for the head differential required, since the resistance to flow might increase with time and the bottom slope is fixed for the life of the system (Reed et al, 1995). The alternative approach (Reed et al 1995) is to construct the bottom with sufficient slope to ensure complete drainage when necessary and to provide an outlet, which permits adjustment of the water level at the end of the wetland. This adjustment can then be used to set the required water surface slope and to drain the wetland.

Short-circuiting can be minimised by careful construction and maintenance of the wetland bottom, by use of multiple cells, and with intermediate open water zones for flow redistribution. Attention should be paid to capture storm runoff and redirect it. If not captured, it would move randomly to the wetland damaging berms and causing overflow problems.

The flow of water in a free water surface wetland is described by the Manning's equation, which defines flow in open channels. Flow velocity (equation 1.5) depends on the depth of the flow, the slope of the water surface, and the vegetation density. Other applications of the Manning's equation to open channel flow assume that the frictional resistance occurs only at the bottom and the sides of the channel. This is not the case in wetland systems where the resistance is distributed over the entire depth of water column because the emergent plants and litter are present in the entire depth.

$$v = (1/n)\, y^{2/3}\, S^{1/2} \qquad (1.5)$$

where

$v$: flow velocity, m/s
$n$: Manning's coefficient, s/m$^{1/3}$
$y$: water depth inside the wetland, m
$S$: hydraulic gradient, or the slope of the water surface, m/m

In wetland systems, Manning's coefficient is a function of the depth of the water because of the resistance imposed by the emergent vegetation. The resistance in turn depends on the density of the vegetation and the litter, which can vary with location and season. The relationship is defined by :

$$n = a / y^{1/2} \qquad (1.6)$$

where

a : resistance factor, $s.m^{1/6}$

$= 0.4\ s.m^{1/6}$ for sparse, low standing vegetation, $y > 0.4$ m (Reed et al, 1995)

$= 1.6\ s.m^{1/6}$ for moderately dense vegetation, $y \cong 0.3$ m (Reed et al, 1995)

$= 6.4\ s.m^{1/6}$ for very dense vegetation, $y \leq 0.3$ m (Reed et al, 1995)

In most situations, with typical emergent vegetation, it is acceptable to assume for the design purposes that: $1 < a < 6$. Substituting equation (1.6) in (1.5) gives:

$$v = (y^{1/2}/a)\ y^{2/3}\ S^{1/2}$$

or

$$v = (1/a)\ y^{7/6}\ S^{1/2} \qquad (1.7)$$

After Reed et al (1995), it is possible to develop an equation for determining the absolute maximum length of the wetland cell, since

$$v = Q/\,(Wy), \qquad W = A_s/\,L, \qquad \text{and} \qquad S = my\,/\,L$$

where:

Q: flow, $m^3/d$
W: width of wetland cell, m
L: length of wetland cell, m
m: fraction of depth serving as head differential.

substitution of these terms in equation (1.7) gives:

$$L = [\{(A_s)(y)^{8/3}(m)^{1/2}(86{,}400)\}/\ \{(a)(Q)\}]^{2/3} \qquad (1.8)$$

The surface area of the wetland ($A_s$) is first determined with the mercury kinetics removal model, then the maximum allowable length of the wetland cell (which is compatible with the hydraulic gradient) is calculated using equation (1.8). The smallest possible hydraulic gradient is recommended for the design processes to provide a reserve for future adjustments if necessary. The (m) value used for design in equation (1.8) will typically be between 0.1 and 0.3 of the potential head available. The maximum potential head is equal to the total water depth (y) of the wetland when m = 1. This is not recommended for design configuration as the wetland would be dry at effluent end and there would be no reserve energy if the flow resistance in the wetland would increase further in the future (Reed et al 1995). The Q value in equation (1.8) is the average flow through the wetland (equation 1.3). For a preliminary design it is generally acceptable to assume that $Q_{in} = Q_{out}$, however the final system design should take into consideration water losses and gains.

### 1.3.2.2 Thermal Aspects

Temperature is one of the most important parameters, which affect chemical and biochemical reactions in a predictable way. In the extreme cases, sustained low temperature conditions and the resulting ice formation could result in a physical failure of the wetland. The biological reactions responsible for mercury removal are temperature dependent as demonstrated in section (1.3.2.2.1). Calculation techniques for determining the water temperature in the Free Water Surface wetlands are presented in section (1.3.2.2.2).

#### 1.3.2.2.1 Effects of Temperature on Biological Reaction Rates:

The effects of temperature on reaction rate may be described by the following equation:

$$d(\ln k) / dt = E / RT^2 \qquad (1.9)$$

where k is the reaction rate constant (1/time), E the activation energy constant (J), R the gas constant (J/°C), and T the absolute temperature (Horan 1990).

Integrating the previous relation between the limits $T_o$ and T, one can obtain the following relation:

$$\ln (k/k_o) = E (T - T_o)/ RTT_o \qquad (1.10)$$

where k and $k_o$ are the rate constants at T and $T_o$. If the temperature change is over a small range, as it is the case in wastewater treatment systems, thus (E / $RTT_o$) can be considered as a constant, the previous equation can therefore be approximated by:

$$k = k_o\, \theta^{(T-To)} \qquad (1.11)$$

where θ is a temperature coefficient characteristics of a particular wastewater process. The previous equation is used widely in wastewater treatment systems to model the effect of temperature on reaction rate.

#### 1.3.2.2.2 Water Temperature in Wetlands

Although some data exist supporting that the wetland treatment system for BOD and nitrogen removal are functional during winter months under freezing conditions, no data is available to support their ability to treat mercury contaminated waters under severe winter conditions. Therefore, the critical temperature that will govern the wetland ability to treat mercury contaminated wastewater would be the minimum survival temperature of the vegetation employed in the wetland. Ice formation is expected in locations experiencing subfreezing air temperatures.

The presence of some ice can be a benefit in that the ice layer acts as a thermal barrier and slows the cooling of the water beneath. In ponds, lakes and most rivers, the ice layer floats freely and can increase in thickness without significantly reducing the volume available for flow beneath the ice cover. This is not the case in free Water Surface wetlands where the ice may be held in place by the stems and leaves of the vegetation, so the volume available for flow can be significantly reduced as the ice layer thickens. In the extreme case, the ice layer may thicken to the point where flow is constricted, the stresses induced cause cracks in the ice, and flow commences on top of the ice layer. Freezing of that surface flow will occur and the wetland will then be in a failure mode until warm weather returns. The biological activities will also stop at this point. This situation is to be avoided when designing constructed wetlands. In such conditions, the solution would be to utilise seasonal wetland component with wastewater stored in a lagoon during the extreme winter months (Reed et al 1995). For any project in a northern climate, thermal analysis has to be conducted to ensure that the wetland will be stable during the winter month.

Ashton (1986) suggested using equation (1.12) to calculate the water temperature at the point of interest in the wetland. Ice formation begins when the bulk temperature in the liquid approaches 3°C, because of density differences and convection losses at the water surface. The equation is repeated until a temperature of 3 °C is reached or until the end of the wetland cell is reached. If the wetland is composed of vegetated zones interspersed with deeper open water zones, the equation must be used sequentially, with the appropriate heat transfer coefficients ($U_s$), to calculate the water temperatures.

$$T_w = T_{air} + (T_o - T_{air}) \exp [\{-U_s(x - x_o)\} / \{(\rho)(y)(v)(c_p)\}] \qquad (1.12)$$

where

$T_w$: water temperature at distance x, °C
$T_{air}$: average air temperature during period of interest, °C
$T_o$: water temperature at distance $x_o$, the entry point for the wetland segment, °C
$U_s$: heat transfer coefficient at wetland surface, $W/m^2.\ ^\circ C$
  $1.5\ W/m^2.\ ^\circ C$ for dense marsh vegetation
  $10 - 25\ W/m^2.\ ^\circ C$ for open water, high value for windy conditions
$\rho$: density of water, $1000\ kg/m^3$

$y$: depth of water, m
$v$: flow velocity in wetland, m/s
$c_p$: specific heat, 4215 J/kg

If the first iteration shows a temperature of less than 3 °C or the minimum allowed temperature for vegetation survival, which ever higher, the equation would be rearranged and solved for the distance x at which the temperature reaches the desired value:

$$(x - x_o) = - [\{(\rho)(y)(v)(c_p)\} / \{U_s\}] [\ln \{(T_d - T_{air}) / (T_o - T_{air}) \}] \qquad (1.13)$$

where

$T_d$: 3 °C or the minimum allowed temperature for vegetation's survival, which ever higher.

### 1.3.3 Construction and Operation Costs

There are no specific data for the construction and operation o constructed wetlands for treating mercury contaminated wastewater. However, there have been some estimates for wetland systems built to treat mining effluents including metals. The costs reported to build the integrated wetland treatment system was estimated at $2.0 million as opposed $3.0 million to $3.5 million for a comparable conventional lime treatment system for waste water containing zinc, silver, and iron from the Mike Horse Mine, Montana where the spring peak flow ranges from 265 to 284 L/min (Sanders et al 1999). The long term (30-year) costs are estimated at $5 million, compared with about $15 million for lime treatment. Cost savings primarily come from much lower annual operating and maintenance costs (approximately $200,000 per year, versus $800,000 for lime treatment). Although actual savings are difficult to predict accurately, available information suggests that the long-term savings may be in the order of $10 million.

# CHAPTER 2

# RESEARCH OBJECTIVES AND GENERAL APPROACH

## 2.1 Scope of the Problem

It was concluded from chapter 1, section 1.2 that wetland ecosystems both natural and constructed have been employed successfully to treat various types of wastewater. Total nitrogen, total phosphorus, suspended solids, and BOD were removed efficiently from wastewater using the wetland ecosystems. It should be mentioned that many environmental agencies do not encourage the use of natural wetlands in wastewater treatment, on the other hand they try to preserve them to protect the wild life habitat. That will leave constructed wetlands (CW) to be the potential type of wetlands recommended for wastewater treatment.

Chapter 1, section 1.1 has shown the uses of the mercury in many industrial applications because of its physical and chemical properties. Toxic effects of mercury and its compounds that present in the waste effluent have caused many environmental crises that led to the establishment of very strict regulations of mercury disposal. However, even after precautions, mercury residuals appear in industrial and municipal wastewater.

The ability of constructed wetlands to remove mercury from contaminated waters has not been investigated. Therefore, the performance of the CW for mercury removal has to be evaluated and the removal rates estimated. The most important factors to be examined are mercury uptake by plants, mercury speciation in the water column, and mercury sorption on sediments and suspended solids in the water column. Obtaining these vital information (which have never been verified) will complement the deficiencies in current design procedures for mercury removal by constructed wetlands, as outlined in Chapter 1, section 1.3.

Having investigated the capability of constructed wetlands to capture mercury, it will be possible to introduce the system as economic and energy-efficient technology for removing mercury from contaminated waters. The principal of using CW for mercury removal will satisfy both industrial needs and environmental requirements. The environment downstream would be greatly protected due to the accumulation of (the otherwise dispersed) mercury within the natural buffering system of wetlands. Mercury captured within wetlands could be - with precautions - recycled.

## 2.2 Objectives and Expected Results

The main objective of this study is to investigate the potential of Constructed Wetlands (CW) to purify mercury-contaminated waters, evaluate their performance, and estimate essential design parameters to improve CW's mercury removal capabilities.

The secondary objectives of this research are:

- Evaluate essential conditions for the design of CW's for mercury removal and improving their capabilities.
- To estimate the amount of mercury removed by wetland and the partial removal by individual component within the system.
- To determine the influences of some environmental factors on the removal processes, and incorporate the results to the CW design.
- To collect and document of some critical information necessary to optimise the design of constructed wetlands designated to mercury removal and to pose

restrictions on the quality of wastewater discharged to the system. This scientifically proofed data will be of great value in designing constructed wetland and it will serve as a starting point for future attempts.

The potential applications of the study are:

- To optimise the design of constructed wetlands to remove mercury from contaminated waters.
- To introduce a novel methodology that could be followed to evaluate the removal of other metals (e.g. cadmium, lead, arsenic) using constructed wetlands.
- To introduce an economical factor for treating mercury contaminated wastewater and encouraging the industry to utilise a new buffering technology.
- To establish of an environmental criterion for protecting downstream from mercury contaminated wastewater.

## 2.3 Methodology

In this study, Free Water Surface Wetlands were investigated. Two main pathways of mercury removal were considered: 1) sorption to sediments and the suspended solids in the water column, and 2) uptake by aquatic plants. Consequently, the interaction of components with mercury through different processes (e.g.: physical, chemical, and biological) have to be considered. Investigating these interacting processes within the multimedia of CW will determine the influence of some external and internal factors on the removal efficiency of CW for mercury contaminated water. Consequently, the results of this investigation can be applied to the design of CW.

To carry out this investigation it was necessary to combine both experimental and theoretical techniques to provide comprehensive, flexible, and efficient alternatives for a wetland's designer as illustrated in Figure 2.1.

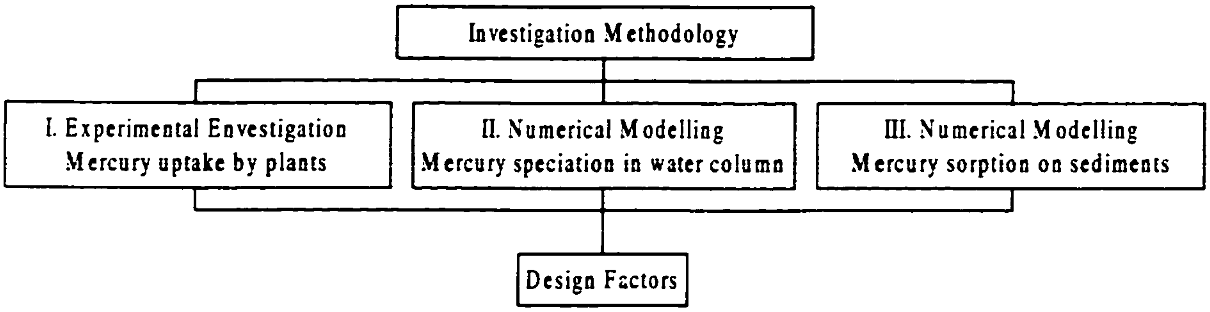


Figure 2.1: The investigation methodology adopted in this study combining both experimental and theoretical work.

Experimental investigations will answer questions such as the time dependence of mercury by plants, the possibility of modelling the uptake process using first order kinetics, and if so what would be the values of the removal coefficients. The results of the experimental investigation were then extended using numerical modelling to evaluate the bioavailable form of mercury for plant uptake and the impact of some environmental factors on mercury bioavailability. Mercury sorption on sediments and suspended solids on the water column were then modelled and the influences of some factors affecting the sorption process were assessed.

The following sections discuss briefly the general approach proposed for designing constructed wetlands to remove mercury from contaminated waters and the necessity of conducting both experimental and theoretical investigations.

### 2.3.1 The General Approach Proposed for Designing Constructed Wetlands to Remove Mercury from Contaminated Water

There are many factors required to conduct a comprehensive design of a constructed wetland system to treat mercury-contaminated water, among them the influence of removal kinetics, hydraulic and thermal factors. The most important factor, which affects the entire design procedure, is the residence time inside the treatment system. This factor depends on the type of the plants used in the system and the properties of the material constituting the suspended solids in the water column and sediments and the change in these properties due to external factors. Subsequently, those factors have to be investigated.

In this study, the input for the wetland treatment system is the wastewater with different mercury concentration (including industrial sources e.g. Pulp and paper Mills). The output from the system would be the effluent to the receiving water body (e.g. river) within acceptable (allowed) mercury levels as determined by regulating agencies.

Amounts and forms of mercury that will be uptaken by plants, suspended solids in the water column, and sediments have to be evaluated. To prevent the possibility of contaminating groundwater with mercury captured by wetland components it was assumed that the bottom of the wetland is lined with an impervious layer.

Data related to mercury content in sediments, plants, and water column can be found in publications such as conferences proceedings, reports, publications from Environmental agencies such as: U.S EPA and Environment Canada, and results from experimental studies performed at SLV 2000. Unfortunately, these data collected by a vast diversity of researchers with various backgrounds (including chemistry, biology, and agriculture) reflect different environmental conditions or serve their specific interests and are not complete.

Therefore, the combination of experimental and theoretical studies was necessary to achieve the research objectives. Experimental studies were conducted on wetland's plants, while theoretical studies extended the information collected during the experiment and were conducted on sediments and suspended solids in the water column as described below.

### 2.3.2 Experimental Investigations

In this study, an experimental investigations were conducted to: a) evaluate the plants reaction to mercury contaminated waters, b) describe their ability to remove mercury, and c) estimate the removal rate constant for different conditions as described in chapter 3.

Two types of wetland's plants were considered: floating and rooted. The most significant factors in choosing the types of plants are the efficiency of these plants in removing mercury from the water and their tolerance to its toxicity. Based on the literature reviewed, the use of specific plants for the purpose of treating wastewater in constructed wetlands, including Water Hyacinth (*Eichhornia crassipes*) and Reeds (*Phragmites communis*), was recommended.

In addition to their efficiency in removing many pollutants from wastewater, Water Hyacinth and Reeds have the capability to accumulate different mercury compounds. Water Hyacinth was chosen as a representative of the floating plants, while Reeds were chosen to represent rooted plants. The World Health Organisation (1989) has published some data regarding mercury's Bioconcentration Factor (BCF) by both plants.

Water Hyacinth has the capability to accumulate mercury in the form of mercuric chloride up to a BCF of 580; and Reeds accumulate mercury in the form of phenyl mercuric acetate to a BCF of 850.

Water Hyacinth is a perennial, fresh water aquatic macrophyte (water tolerant vascular plant) with rounded upright, shiny green leaves and spikes of lavender flowers. Optimum growth conditions are pH: 5- 7, and temperature: 20°C (where 30°C is desirable and 10°C is survival temperature). Maximum salinity tolerance is 800 mg/l. Size varies with habitat. Root length varies with the nutrient status of the water and the frequency of plant harvest. In nutrient rich wastewater with regular harvest, the roots might extend 10 cm below the central rhizome. When they are grown in wastewater, individual plant range from 50 to 120 cm from the top of the flower to the root tips. Hyacinths are one of the most productive photosynthetic plants in the world. It has been estimated that 10 plants could produce 600,000 more during 8-month growing season and completely cover 0.4 ha of a natural fresh water surface (Reed et al, 1995).

After Reed et al (1995), the optimum growth conditions for Reeds are: pH: 2- 8, salinity tolerance < 45 ppt. Very rapid growth, via rhizomes, is observed (lateral spread around 1 m/year) and very dense cover in one year with plants spaced at 0.6 m. Deep root penetration in gravel is around 0.4 m. Annual yield is reported to be around 40 (dry weight) Mt/ha. Reed's tissue contain 45 % C, 20 % N, 2% P; 40 % solids (dry basis). During Hydroperiod it can be permanently inundated (up to ~ 1m), it is also very drought resistant. It is considered by some to be an invasive pest species in natural wetlands in the United States. Very successful utilization of Reeds at constructed wetlanlds was reported in the United States.

### 2.3.3 Theoretical Investigations

In order to complement the results obtained experimentally, theoretical investigations were carried out to answer the questions regarding the extent of mercury uptake by plants, since the uptake is associated with mercury speciation in liquid phase and its adsorption on solid phase. Subsequently, the theoretical study should cover two main aspects: mercury speciation in the water column (chapter 4), and mercury sorption on suspended solids in the water column and sediments (chapter 5). Thus, it was important to incorporate software that is able to perform both tasks, reliable, and was previously tested and calibrated.

MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems (version 3.0), developed by the U.S. Environmental Protection Agency, was chosen. The software satisfies the previously mentioned conditions as well as computing equilibrium among the dissolved, adsorbed, solid, and gas phases in an environmental setting using an extensive database of reliable thermodynamic data.

Clay is the most common component of wetland sediments due to its low permeability. Clay mineral particles are colloids having a high specific surface area (i.e. high surface area to mass ratio) influencing their properties (Yong et al, 1992). The basic structural units of clay minerals consist of sheets of silica tetrahedron and alumina octahedron. The various clay minerals are formed by the stacking of combinations of the basic sheet structures with different forms of bonding between the combined sheets. The surfaces of clay mineral particles carry residual negative charges mainly as a result of the isomorphous substitution of aluminum or silicon atoms by atoms of lower valances, due to disassociation of hydroxyl ions and broken ends at the edges of the particles. The negative charges result in cations (present in the pore water) being attracted to the particles. The sorbed ionic layers are complex and sensitive to water quality changes (e.g. cation exchange).

On one hand, MINTEQA2 was used to study the different mercury compounds that would exist at each time step of the experimental investigation. Influences of some environmental factors (such as the ambient temperature and chloride concentration in water) on the distribution of mercury compounds in water are presented (chapter 4). On the other hand, MINTEQA2's Triple Layer Adsorption Model was employed to evaluate mercury sorption on soil surfaces for four different clay types namely: Kaolinite, Natural clay, Glokonite, and Bentonite under different pH, initial Hg concentration, and the concentration of the adsorbent medium in solution (chapter 5).

## 2.4 Research Originality and Main Contribution

Many aspects of mercury behaviour in wetlands are still unknown and great gaps of information still exist. The concept of introducing wetlands as an efficient and cost-effective technology in wastewater treatment is very recent (Brix and Schierup 1989; Barnett et al 1991). The fate of mercury and its compounds within the constructed wetlands has not been considered.

Having finished the present study, the role of main constructed wetlands components in removing mercury from contaminated water will be clearly understood and evaluated. Mercury's bioavailable species for CW's particular components will be specified. Effects of different environmental factors on the rate of mercury sorption on sediments will be reported. The information (obtained through out the investigation) would be employed in developing a unique approach for designing constructed wetlands to removal of mercury from contaminated water.

The findings of this research could be also applied in environmental impact assessments and could be considered as the first nuclei of establishing regulations (codes) governing the design of constructed wetlands to remove mercury from contaminated waters.

Those aspects demonstrate the originality and the significant contribution of the current research work to the environmental science and engineering.

# CHAPTER 3

# EXPERIMENTAL INVESTIGATION

The literature review demonstrated a lack of information regarding the response of floating and rooted plants grown in constructed wetlands to mercury contaminated water. To verify the rate of mercury uptake in constructed wetland's simulated conditions, series of experiments were performed in the laboratory. This chapter summarises the methodology applied for the experimental investigation. Description of the analysis of the samples for their mercury content using Cold Vapour Atomic Absorption Spectrophotometer (CVAAS) is included in this chapter and appendix A. The results obtained are discussed and analysed in section 3.4.

## 3.1 Materials and Experimental Set-up

As it has been mentioned in section 2.3.2, two types of wetland's plants were used in the experiment: Water Hyacinth (*Eichhornia crassipes*) representing the floating plants, and Reeds (*Phragmites communis*) representing the rooted plants. Six week old plants were obtained from "*A fleur d'eau*" Stunbridge East, Quebec in October 1997. The plants were similar in regard to their size, age, and number of leaves. Plants were washed in tap water to eliminate any residues sticking to their roots prior to the starting of the experiment. Thereafter, they were placed in plastic water containers with diluted nutrients (10-15-10, all-purpose liquid plant food, Schultz) in water and maintained for a climatization period of two weeks before the experiments.

The preliminary series of experiments were conducted in the green house. These experiments permitted to observe no changes in the growth among Water Hyacinths subjected to low mercury levels (5 and 10 ppb) for 96 hours. The green house did not provide uniform conditions (e.g. changes of temperature, light intensity) therefore the final series of experiments were conducted inside the fume hood. It provided continuous ventilation, under the following controlled conditions: 14 hours light / 10 hours dark cycle, 25 °C temperature, and pressure close to 1 atm. Figure 3.1 shows a few photos of the experimental set-up. Lighting was provided inside the fume hood by two bulbs (Gro & Sho Bright Stick, 25 inch Fluorescent Plant Light Unit, GE) and the light cycle was controlled by a timer (Time Controlled Outlet Strip, Model 1451 N, Grasslin Controls Corporation). For each exposure, Water Hyacinth plants (three replicates) were placed in plastic buckets (Figure 3.2) diameter 17 cm and depth 13.5 cm containing 2 litre of the experimental solution. Reed plants (three replicates) were placed in higher (26 cm) plastic buckets, due to plants height. The buckets containing 1 litre of experimental solution had diameter of 9 cm. Prior to use, all the buckets were washed overnight with 10% $HNO_3$.

Generally, the mercuric halides (with the exception of $HgF_2$) and pseudo-halides have considerable covalent character to their bonding (Cotton and Wilkinson, 1972). As a consequence of this, $HgCl_2$ has a lower melting point and higher vapour pressure than the ionic $HgF_2$, and in aqueous solution has a strong tendency to exist in molecular form. In contrast, species such as $HgSO_4$ and $Hg(NO_3)_2$ are highly ionic in character and thus dissociate in aqueous solution to form hydrated $Hg^{2+}{}_{(aq)}$ ions. However, depending on the concentrations of complexing ligands such as $Cl^-$ or $OH^-$ that may be present, $Hg^{2+}{}_{(aq)}$ ions will form complexes of the form $HgX_n{}^{2-n}{}_{(aq)}$. Consequently $HgCl_2$ and $Hg(OH)_2$ are taken to be representative of most Hg (II) compounds in the environment (Lindqvist et al., 1984). The inorganic mercury form - used for tested solution - in the experiments is mercuric chloride (2594, 99.9% ACS Certified, Baker Analysed Reagent).

Literature data (Lenka et al 1990) indicated that solution containing mercury concentration of 1 ppm was toxic to plants and recommended lower concentrations to be used for experimental testing. Therefore, the spectrum of concentrations from 5 to 150 ppb was incorporated for the tests. Tap water was used to prepare aqueous solutions in the experiments. Two containers (with large and smaller diameters) were used to calculate the evaporation losses and the correction factors. The measured value of the aqueous solution's pH was around 5.4.

### 3.2 Methodology of Measurements

Water samples of 15 ml each were collected each three hours for the first 12 hours, then at 24, 48, and 72 hours from the beginning of the experiment. The samples were preserved and stored (as described later in this chapter) prior to analysis for mercury content.

Mercury uptake by the plants was calculated using the following formula:

$$C_{pi} = [(C_{ci} * V_{ci}) - (C_{wi} * V_{wi})] / V_o \qquad (3.1)$$

i = *0, 3, 6, 9, 12, 24, 48, 72 hours*

where:

$C_{pi}$: mercury concentration removed by the plants at time i, ppb
$C_{ci}$ : measured mercury concentration in the control solution at time i, ppb
$C_{wi}$ : measured mercury concentration in water at time i, ppb
$V_{ci}$: volume of water in the control's container at time i, litre
$V_{wi}$: volume of water in the plant's container at time i, litre
$V_o$: initial water volumes at time zero (2 litre for Water Hyacinth, 1 litre for Reeds)

In order to calculate the mercury uptake by the plants at specific time, two sets of water samples were taken and analysed: those from the control's container, and those from the plant's container. Mercury concentrations in plant's containers were always less than those of the control's containers at every time step. Their offsets from the corresponding control values were resulting from plant's uptake.

The rate of removal is mainly associated with the uptake by plants. However, other processes can influence the mercury removal such as volatilisation or photodegradation.

The experiments conducted inside a fume hood, could be subjected to evaporation, consequently all the measured concentrations were corrected to accounting for the evaporation effect. Each measured concentration was multiplied by a correction factor calculated in the following way: $V_{ci} / V_o$ in case of control's samples, and $V_{wi} / V_o$ in case of plant's sample.

The average evaporation rate calculated for the Water Hyacinth's control containers was calculated from the average of the evaporation rate of different experimental sets. For any experimental set, the evaporation rate was calculated using the following formula:

$$\text{Evaporation rate (ml/hour)} = (V_{ini} - V_{fin} - \Sigma V_{sp}) / t_{tot} \tag{3.2}$$

where:

$V_{ini}$: the initial volume of solution measured in the control container = 2000 ml
$V_{fin}$: the final volume of solution measured in the control container, ml
$\Sigma V_{sp}$: total volume of samples taken, ml
$t_{tot}$: total experimental period, 72 hours

The calculated value for the average evaporation rate from the Water Hyacinth control containers in the fume hood was 9.375 ml/hour.

Similar formula was used to calculate the average evaporation rate from the Reed's containers using 1000 ml initial water volume. The average evaporation rate from the Reed's control containers in the fume hood was 1.736 ml/hour, much smaller than that of the Water Hyacinth's control containers. The main reason for this difference would be the difference in exposed surface area of solution inside the fume hood.

Those values where later used to calculate the hourly rate of water uptake for each plant. The plant's water uptake rate, over 72 hours, is calculated from the following:

$$U_p = (V_{ini} - V_{fin} - \Sigma V_{sp} - V_{eva}) / t_{tot} \qquad (3.3)$$

where:

$U_p$: plant's water uptake rate, ml / hour
$V_{ini}$: the initial volume of solution measured in the control container (2000 ml in case of Water Hyacinth and 1000 ml in case of Reeds).
$V_{fin}$: the final volume of solution measured in the control container, ml
$\Sigma V_{sp}$: total volume of samples taken, ml
$V_{eva}$: total volume of water evaporated from the control container, ml
$t_{tot}$: total experimental period, 72 hours

Several results (Wallace and Romney, 1977) confirmed that the largest amount of many metals (e.g. Pb, Sn, and Ag) uptaken by plants was recovered from the rooted part of the plants. Therefore, to compare the performance of Water Hyacinth at different initial mercury concentrations and perform comparison between Water Hyacinth and Reeds, it was necessary to introduce another factor to the mercury concentration sorbed by the plants. This factor was incorporated in the calculations through normalising all the concentration values with respect to the dry weight of roots.

Having finished the experiment, all the plants were air dried for a period of three weeks in the room temperature (25 °C) inside the fume hood. Following the drying period, the roots were carefully separated, packed, and weighted (Figure 3.3).

### 3.2.1 Sampling and Preservation of Samples

Sampling was performed using 10 ml glass pipettes (Fisher). Samples were taken at levels close to the half depth of solutions in each individual container. Immediately after the water samples were taken from the containers, they were acidified and stabilised as the stability of mercury solutions could be affected due to adsorption on the walls of the storage vessel. To preserve a 10 ml sample, the following procedures were followed: for each sample prepared, two drops of potassium permanganate (P270-500, 99%, $KMnO_4$- 5% solution: ACS Certified, Fisher Chemicals) and 2.5 ml of 70% nitric acid (A509SK-212, Trace Metal Grade, 68% $HNO_3$: ACS Certified, Fisher Chemicals) were added to the sample, then the volume was brought up to 10 ml using the collected samples.

## 3.3 Analysis of Samples for Total Mercury

Analysis of total mercury was carried out using CVAAS (Perkin Elmer AAnalyst 100), (Figure 3.4) equipped with MHS 10 attachment. The MHS 10 Mercury Hydride System is used primarily to reduce mercury with tin (II) chloride ($SnCl_2$) or sodium borohydride ($NaBH_4$). When sodium borohydride is used as a reducing agent, the violent reaction and the liberation of hydrogen aid the release of metallic mercury from solution and the transport of mercury vapour to the quartz cell. When tin (II) chloride is used as a reductant, on the other hand, an increased inert gas stream is required to drive metallic mercury from solution and transport it to the quartz cell, and hence the concentration is measured by the Spectrophotometer. More technical details are provided in Appendix A.

### 3.3.1 Preparation of Reductant & Standard Solutions

The tin (II) chloride solutions were freshly prepared on the same date of performing the determination. As specified in the Operator's Manual, the tin (II) chloride was prepared to be 5% $SnCl_2.2H_2O$ in 10% HCl. The procedures followed to prepare a 250 ml of the solution were: 12.5 gm of $SnCl_2.2H_2O$ (S 6620, 98% ACS Certified, ACP) was dissolved in 25 ml concentrated HCl (BDH: ACS 393-41, 36.46% ACS Certified), then the solution was brought up to volume (250 ml) with deionized water (18 mΩ $H_2O$). After the determinations were performed for one day, the rest of the solution was disposed in toxic disposal container according to the health and safety regulations. For determinations on subsequent days, fresh solutions were prepared as needed on each required date.

Standards for these experiments were prepared from the stock solution (SCP science, Hg 1000 μg/ml in 10% $HNO_3$) by serial dilution. The standard solutions were prepared exactly the same as the samples in terms of acidification and preservation. All solutions less than 1 mg/ml were prepared daily. A blank and three standards of 10, 20, and 50 ppb Hg were used to obtain the calibration curve of the spectrophotometer. The volume for each prepared blank or standard was 10 ml.

Detection limit in solution was calculated as follows (Perkin Elmer, 1978):

(0.0044 / Abs. of first significant standard) x Concentration of that standard.

A standard with mercury content of 1ppb Hg gives 0.032 Abs., therefore the detection limit is (0.0044 /0.032 x 1) = 0.14 ppb.

## 3.4 Results of Experimental Investigations

### 3.4.1 Mercury Removal from Water

The results were calculated by averaging the three replicate values obtained from Atomic absorption analysis for each experimental set. Standard deviations from the averages were in the range of 5 – 15%. Generally, the results indicate that plants can remove mercury from water efficiently and within reasonable amount of time. The ability of plants to remove mercury changed with both time and initial concentrations. The following is the discussion of the results obtained for both Water Hyacinth and Reeds.

#### 3.4.1.1 Removal of Mercury by Water Hyacinth

Water Hyacinth demonstrated high ability to remove mercury from water at different concentration levels and in a considerably short period. The general behaviour of mercury removal by Water Hyacinth was characterised by two phases: a rapid phase followed by a much slower phase. When an initial mercury concentration in solution was 5 ppb, the plant was able to reduce this concentration to 1.8 ppb in the first three hours following exposure. This value was further decreased to values below detection limit at the end of the 72 hours experimental period. As the initial concentration increased to 10 ppb, the mercury concentration in water has dropped to 4.5 ppb after the first three hours. This value was further decreased to a minimum of 1.6 ppb at the end of the experimental period (Figure 3.5).

At a much higher initial mercury concentration in solution of 50 ppb, mercury concentrations has dropped to 8.5 ppb after the first three hours and reached 2.8 ppb at the end of the 72 hours. The superior performance of Water Hyacinth was reported when the initial mercury concentration in solution was 150 ppb. After 3 hours, there was only

19.1 ppb mercury left in the solution, which was even decreased to 7.1 ppb at the end of the experimental period (Figure 3.6).

In terms of efficiency, Water Hyacinths remove 64 %, 83%, and 87 % of the initial mercury concentrations of 5, 50, and 150 ppb respectively within the first three hours following exposure. These values were even improved by the end of the experimental period, were they reached 94%, 94%, and 95 % for the initial concentrations of 5, 50, and 150 ppb respectively.

### 3.4.1.2 Removal of Mercury by Reeds

Reeds demonstrated less ability (compared to Water Hyacinth) to remove mercury from water in short run, but as the time advances, their behaviour was comparable to that of Water Hyacinth. As it was the case in Water Hyacinth, removal is characterised by two phases: a rapid phase followed by a much slower phase. When an initial mercury concentration in solution of 50 ppb, the plant was able to reduce this concentration to 16.5 ppb in the first three hours following the exposure. This value was further decreased to 4.2 ppb at the end of the 72 hours experimental period. As the initial concentration increased to 150 ppb, the mercury concentration in water sample has dropped to 35.0 ppb after the first three hours. This value was further decreased to a minimum of 4.3 ppb at the end of the experimental period (Figure 3.7).

In terms of efficiency, Reeds remove 67%, and 77 % of the initial mercury concentrations of 50, and 150 ppb respectively in the first three hours following exposure. These values were even improved by the end of the experimental period, were they reached 92%, and 97 % for the initial concentrations of 50, and 150 ppb respectively.

#### 3.4.1.3 Comparison of Mercury Removal from Water by Water Hyacinth and Reeds:

At an initial mercury concentration in solution of 50 ppb, both plants achieved over 90% removal efficiency by the end of the 72 hours for initial mercury concentration of 50 ppb (Figure 3.8) and 150 ppb (Figure 3.9). However, Water Hyacinth was faster in removing mercury on the short run. As the time advances, the difference between the removal efficiency for both plants was decreasing.

It was also observed that the uptake rate (ppb/hour) - calculated by dividing: a)the difference in concentration at the beginning and the end of any time period (ppb) by b)that period (hour) - is proportional to the initial mercury concentration used for both plants at the two uptake phases (Figure 3.10: A, B). At the first phase (after 3 hours) the uptake rate of Water Hyacinth were higher than those of Reeds specially when the initial concentration used is higher. For the highest initial mercury concentration of 150 ppb, the uptake rate for Water Hycinths was 43.6 ppb/hour compared to 38.3 ppb/hour for Reeds. During the second phase, the uptake rate for Reeds (0.44 ppb/hour) was higher than that of Water Hycinths (0.17ppb/hour) for initial mercury concentration of 150 ppb, but the relationship between the uptake rate and the concentration remains linear.

### 3.4.2 Removal Rate Coefficient (k)

Mercury removal rates for Water Hyacinth and Reeds were calculated and the results are shown in Figure 3.11: A, B, C through Figure 3.12: A, B. For initial mercury concentrations ranging from 10 to 150 ppb, the removal processes could be classified into two phases: a rapid phase, followed by a slower phase. The rapid phase takes place in the first three hours, and the slower phase extends until the end of the 72 hours of the experimental period.

### 3.4.2.1 Removal Rate Coefficient for Water Hyacinth

For an initial mercury concentration of 10 ppb, the removal rate coefficient (k) was found to be 0.265 $h^{-1}$ in the rapid phase and 0.0137 $h^{-1}$ for the slower phase. Increasing the initial mercury concentration to 50 ppb resulted in an increase in the removal reaction rate in the rapid phase only, where it has increased to 0.589 $h^{-1}$, while the value calculated for the slower phase remains almost unchanged at 0.0128 $h^{-1}$. This observation was typical when the initial mercury concentration was increased to 150 ppb. Once again, the removal rate coefficient has increased to 0.686 $h^{-1}$ in the first three hours, while it remains almost unchanged at 0.0122 $h^{-1}$ for the rest of the 72 hours.

### 3.4.2.2 Removal Rate Coefficient for Reeds

For an initial mercury concentration of 50 ppb, the reaction rate coefficient (k) was found to be 0.369 $h^{-1}$ in the rapid phase, and 0.018 $h^{-1}$ for the slower phase. As the initial mercury concentration increases to 150 ppb, the values calculated for the rate coefficient (k) are: 0.485 $h^{-1}$ in the rapid phase, and 0.030 $h^{-1}$ for the slower phase, suggesting that the initial mercury concentration affects its removal from water by Reeds (i.e. higher initial concentration results in higher values of the removal rates).

When comparing the reaction rates obtained for both Water Hyacinth and Reeds, it could be concluded that as the initial mercury concentration in the water increases the value of the rate coefficient increases in the rapid phase with higher values obtained for the Water Hyacinth. In the slower phase, the values of the reaction rate coefficient slightly increased for the Water Hyacinth, while they have considerably increased as the initial mercury concentration increased for Reeds.

### 3.4.3 Ratio of Mercury Removed to Plants Roots (Dry Weight)

To estimate mercury uptake by plant roots the following assumptions were made: a) The weight of plants roots remains constant over 3 days period, b) All mercury removed (after evaporation correction) from water is sorbed by the roots of the plants. The amount of mercury removed by roots of the plant was then calculated as the ratio of the amount of mercury removed (micro gram Hg) to the dry weight of the root (gram-dry weight).

#### 3.4.3.1 Ratio of Mercury Removed to Water Hyacinths Roots (Dry Weight)

The ratio of mercury removed to the dry roots of Water Hyacinths are shown in Figure 3.13 for the initial mercury concentration in solution of 5 and 10 ppb, and Figure 3.14 for the initial mercury concentration in solution of 50 and 150 ppb. For the initial mercury concentration in solution of 5 ppb, the ratio was found to be 7.61 µg/g of dried roots after the first three hours. This ratio has increased from 7.61 µg/g to 11.11 µg/g at the end of the 72 hours.

The ratio for Water Hyacinth increased as the initial mercury concentrations in solutions increased. Increasing the initial mercury concentration to 50 ppb resulted in an increase in the ratio to 110.55 µg/g after the first three hours. Further increase in the initial concentration from 50 ppb to 150 ppb increased the ratio to 443.61 µg/g for the same period of time. After the first three hours and up to the end of the experiment, the ratio for Water Hyacinths has increased from 110.55 µg/g to 125.84 µg/g in the case of initial mercury concentration of 50 ppb, and from 443.61 μg/g to 484.46 μg/g when a 150 ppb initial mercury concentration was used.

### 3.4.3.2 Ratio of Mercury Removed to Reeds Roots (Dry Weight)

The ratios of mercury removed to the dry roots of Reeds are shown in Figure 3.15 for the initial mercury concentration in solution of 50 and 150 ppb. For the initial mercury concentration in solution of 50 ppb, the ratio for Reeds roots was found to be 28.9 μg/g of dried material after the first three hours. The ratio for the plant's roots shows an increase from 28.9 μg/g to 39.5 μg/g at the end of the 72 hours.

Accumulations of mercury in the roots of Reeds increased as higher initial mercury concentrations in solutions were used. Increasing the initial mercury concentration from 50 ppb to 150 ppb resulted in an increase in the ratio from 28.9 μg/g to 90.5 μg/g during the first three hours. During the second phase up to the end of the experiment, the ratio for the roots of the Reeds has increased from 90.5 μg/g to 114.7 μg/g when the 150 ppb initial mercury concentration was used.

### 3.4.3.3 Comparison of the Ratios of Mercury Removed to Plants Roots (Dry Weight) for Water Hyacinths and Reeds:

Both plants show a positive response towards an increasing mercury concentration in solution from 50 to 150 ppb. Mercury contents in the roots of both plants have considerably increased as the initial mercury concentrations increased.

For the initial mercury concentration in solution of 50 ppb, average mercury contents in the roots of Water Hyacinths were 3.5 times higher than those of Reeds. After the first three hours, the Water Hyacinths roots accumulate 110.55 μg/g compared to only 28.9 μg/g accumulated in the roots of the Reeds. As the time increases from 3 to 72 hours, the values of mercury contents in the roots of Water Hyacinths were 3 times higher than those of Reeds (Figure 3.16).

Similar behaviour of the plants was detected as the initial mercury concentration increased to 150 ppb. However, the average mercury contents in the roots of Water Hyacinths were 4.5 times higher than those of Reeds. After the first three hours, the Water Hyacinths roots accumulate almost 5 times more mercury than the roots of Reeds. As the time increases from 3 to 72 hours, the values of mercury contents in the roots of Water Hyacinths were 4.5 times higher than Reeds roots (Figure 3.17).

One of the factors which explains why the amounts of mercury accumulated in the roots of Water Hyacinths were much higher than those accumulated in the roots of Reeds is roots structure. The Water Hyacinths have generally massive root system composed of numerous root meristems offering considerably more surface area for mercury uptake (Figure 3.4). Another factor is the water content in the roots of each plant. Water almost constitutes 90 ~ 95% of the total weight of Water Hyacinth. When dried out, the remaining solid residue are considerably less than those of Reeds. Consequently, this results in more mercury contents value per gram weight of Water Hyacinths than those of the Reeds.

### 3.4.4 Bioconcentration of Mercury by Plants

The results obtained indicate clearly that Water Hyacinth and Reeds are able to bioconcentrate mercury. There is a general tendency for Hg to accumulate in the roots of the plants (Gracy and Stewart 1974, Beauford et al 1977, Fang 1978, Hogg et al 1978). Mercury concentration in alfalfa roots was 133 times higher than its concentration in alfalfa foliage (Gracy and Stewart 1974) suggesting that the roots serve as a barrier to Hg uptake by plants.

### 3.4.4.1 Bioconcentration of Mercury by Water Hyacinths

During the first three hours of exposure, Water Hyacinth plants were able to bioconcentrate mercury. The values of mercury contents are 7.61, 19.59, 110.55, and 443.61 µg/g dry weight of roots for the initial mercury concentration in solution of 5, 10, 50, and 150 ppb respectively. Bioconcentration rate decreases as the time increased. At the end of the 72 hours experimental period, the mercury contents in dry roots were 11.11, 29.99, 125.84, and 484.46 µg/g for an initial mercury concentrations of 5, 10, 50, and 150 ppb respectively (Figure 3.18).

### 3.4.4.2 Bioconcentration of Mercury by Reeds

During the first three hours of exposure, Reeds were able to bioconcentrate mercury up to 28.9, and 90.5 (µg/g dry weight of roots) for the initial mercury concentration in solution of 50, and 150 ppb respectively. These ratios seem to be proportional to initial mercury concentrations in solution. Bioconcentration rate decreases as the time increased. At the end of the 72 hours experimental period, the mercury contents in dry roots were 39.5 and 114.7 µg/g for an initial mercury concentrations of 50, and 150 ppb respectively (Figure 3.19). For an initial mercury concentration of 50 ppb, the rate of decrease in the ability of reeds to bioacumulate mercury dropped from 9.63 µg/g per hour (during the first phase) to 0.15 µg/g per hour (during the second phase). The corresponding values of rate decrease for an initial mercury concentration of 150 ppb are 30.17 and 0.35 µg/g per hour, respectively.

#### 3.4.4.3 Comparison of Bioconcentration of Mercury in the Roots of Water Hyacinth and Reeds:

Water Hyacinth demonstrated greater ability than that of Reeds to bioconcentrate mercury for all the range of the mercury concentrations used in the investigation (5 to 150 ppb). At an initial mercury concentration of 50 ppb, Water Hyacinth bioconcentrate 110.55 µg/g (root dry weight) compared to only 28.9 µg/g after the first three hours of exposure. The values were further increasing with time, at a slower rate, to reach a maximum of 125.84 µg/g (root dry weight) for Water Hyacinth, compared to only 39.5 µg/g in the case of Reeds.

At the maximum initial mercury concentration of 150 ppb, similar behaviour was observed (Figure 3.20). Water Hyacinth bioconcentrate 443.61 µg/g (root dry weight) compared to 90.5 µg/g after the first three hours of exposure. The values were further increasing with time to reach a maximum of 484.46 µg/g (root dry weight) for Water Hyacinth, compared to 114.7 µg/g in the case of Reeds (Figure 3.21).

### 3.5 Conclusion

In this chapter it was clearly demonstrated that both floating and rooted plants have high capacity of mercury accumulation. The differences in mercury removal by different plants were visible. The process of mercury uptake is generally short, where most of the mercury is removed from water in the first three hours, then the process continues but at slow rate until the end of experimental period at 72 hours.

Mercury removal process is a function of a) the initial mercury concentration in solution: bioconcentration increased as the initial mercury concentration increased in the range of tested concentrations. It was visible that both plants did not achieve their saturation capacities; b) the structure of roots: Reeds roots - due to their structure - needed longer exposure time as a result of not having a root system as well developed as Water Hyacinths; and c) the exposure time: almost 87% of the mercury removed instantaneously while the remaining 13 % were removed during 3 days period suggesting that the time factor is not the most important factor for both plants. Only during that period of time (the first few hours after discharging mercury), ideal growing conditions for the plants should be maintained.

The use of rooted plants provides two functions to the process of mercury removal: a) allow the bioavailable mercury which was not captured by the floating plants to be uptaken by rooted plants roots from pore water; and b) allow for multi component removal system within sediments where mercury could be sorbed on the solid phase and/or captured by the Reeds roots. Subsequently, the amount of bioavailable mercury for microorganisms is decreased and the quality of water in constructed wetlands is increased.

Frequent removal of plants would increase the cost of operating a constructed wetland system to treat mercury-contaminated water but it will increase its efficiency. Mercury removal by both types of plants was excellent for the tested range of mercury concentration. However, it is necessary to determine the maximum mercury concentration in water that will not affect the plant growth in order to optimise the design of constructed wetlands.

To evaluate the bioavailable form of mercury for plant uptake and to study the effect of other environmental factors on mercury removal, the experimental results were extended using computer modelling as described in Chapter 4. Mercury speciations in water column distinguished between available and unavailable mercury forms for both Water Hyacinth and Reeds.

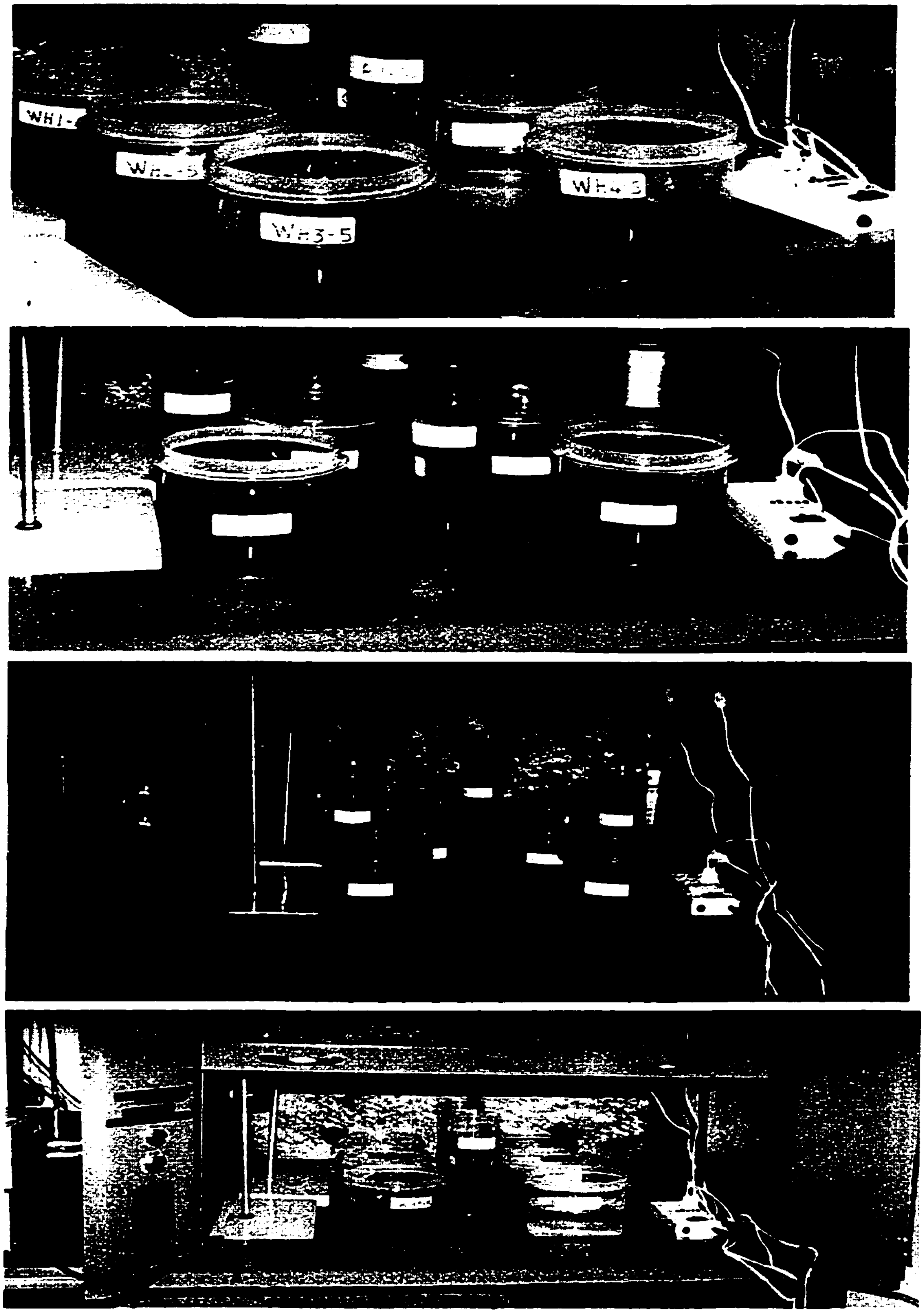


Figure 3.1 The experimental setup with Water Hyacinths and Reeds.

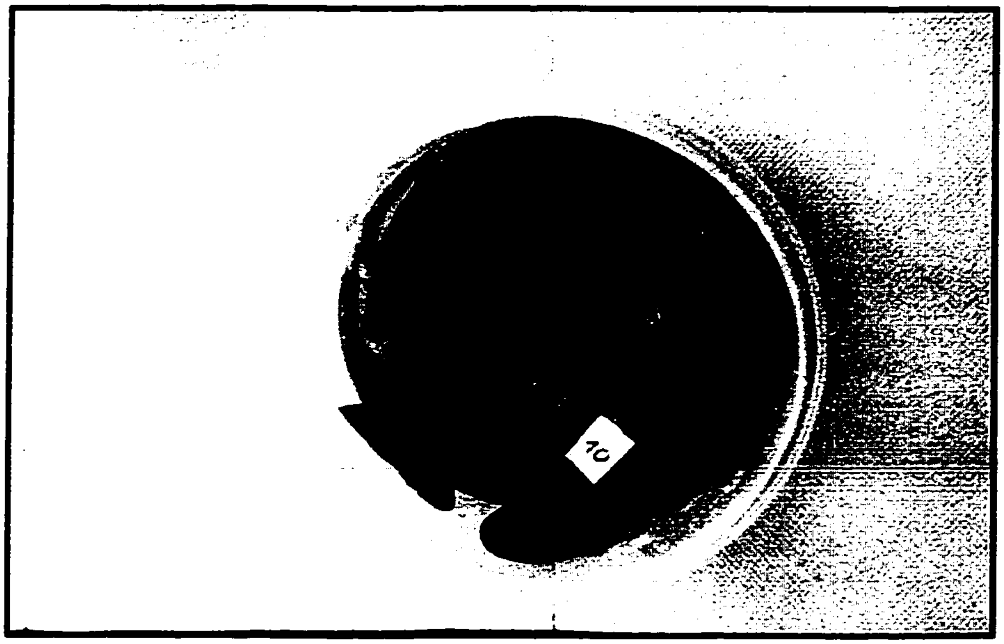


Figure 3.2 Pot with mercury solution and Water Hyacinth

Figure 3.3 Dry roots of plants roots during and after the experiment.

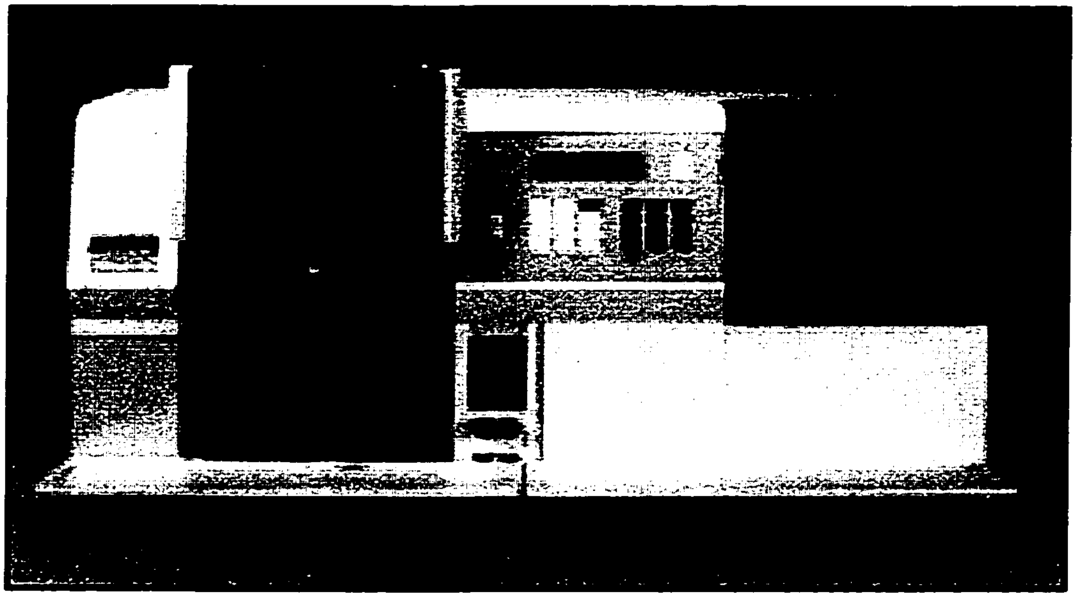


Figure 3.4: Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst 100) used to analyse total mercury.

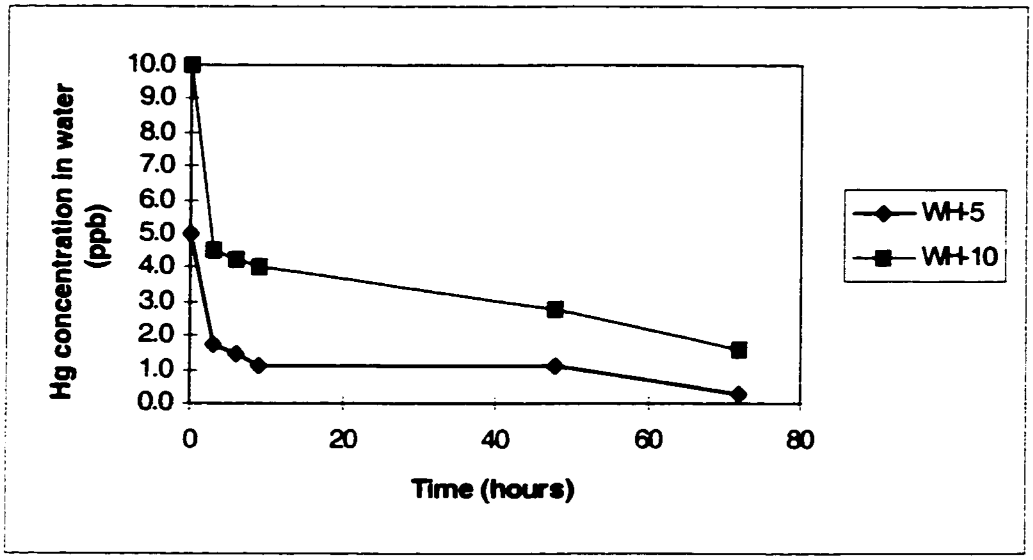


Figure 3.5 Mercury removal from water by Water Hyacinth (WH) as a function of time for the initial mercury concentrations of 5, and 10 ppb.

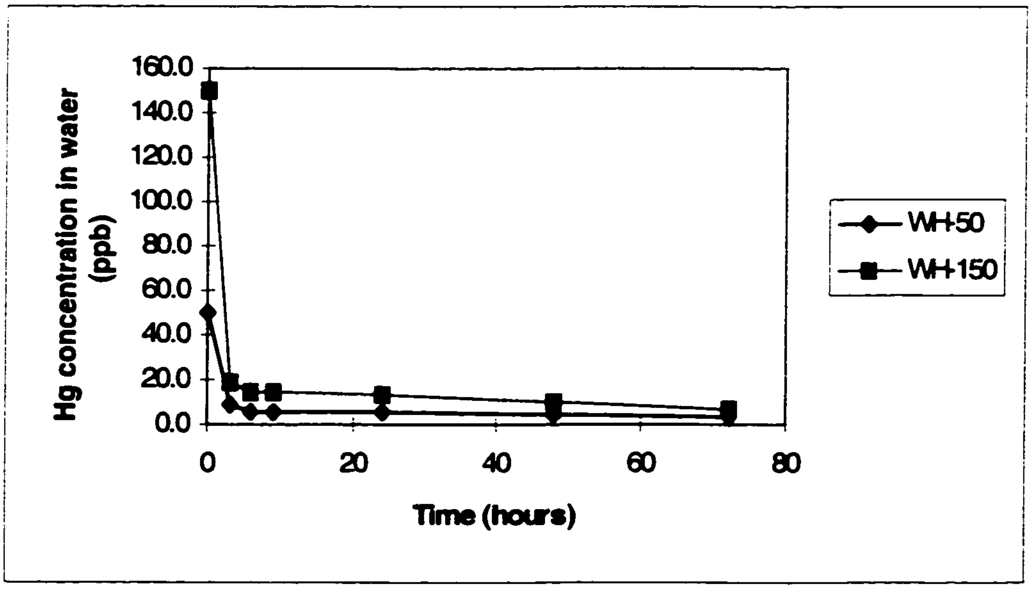


Figure 3.6 Mercury removal from water by Water Hyacinth (WH) as a function of time for the initial mercury concentrations of 50, and 150 ppb.

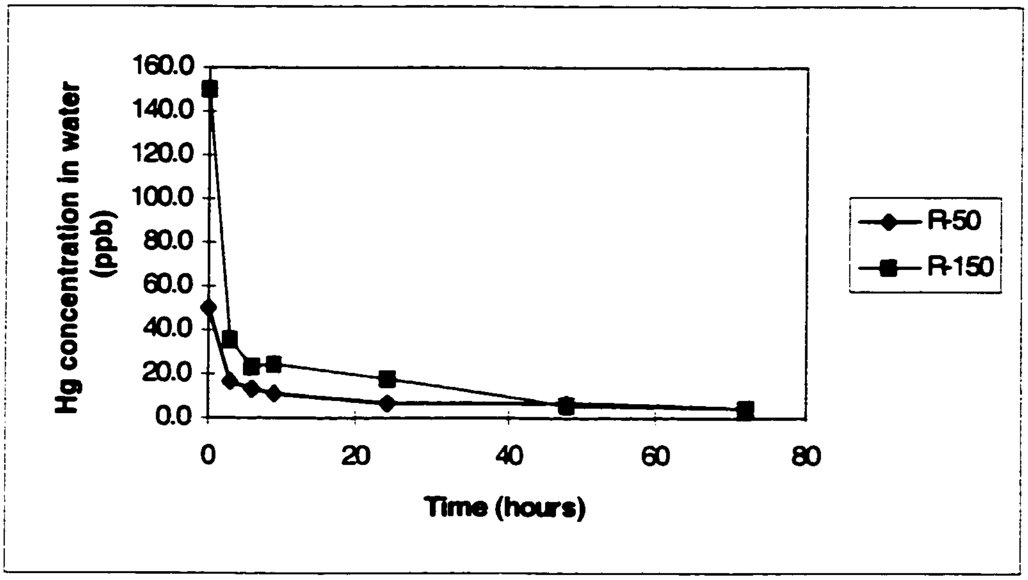


Figure 3.7 Mercury removal from water by Reeds (R) as a function of time for the initial mercury concentrations of 50, and 150 ppb.

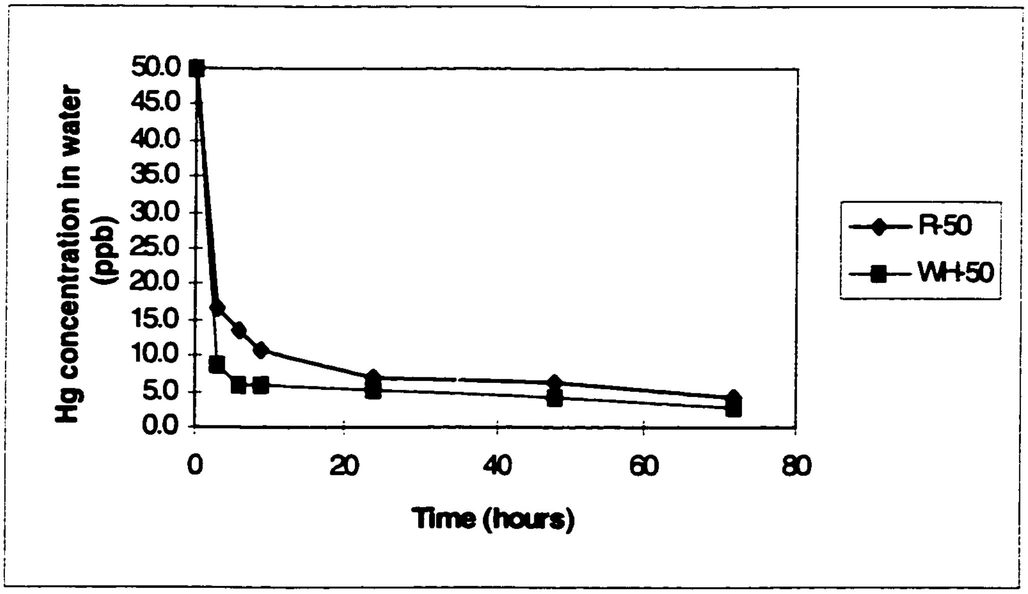


Figure 3.8 Comparison between mercury removal from water by Water Hyacinth (WH) and Reeds (R) as a function of time for the initial mercury concentrations of 50 ppb.

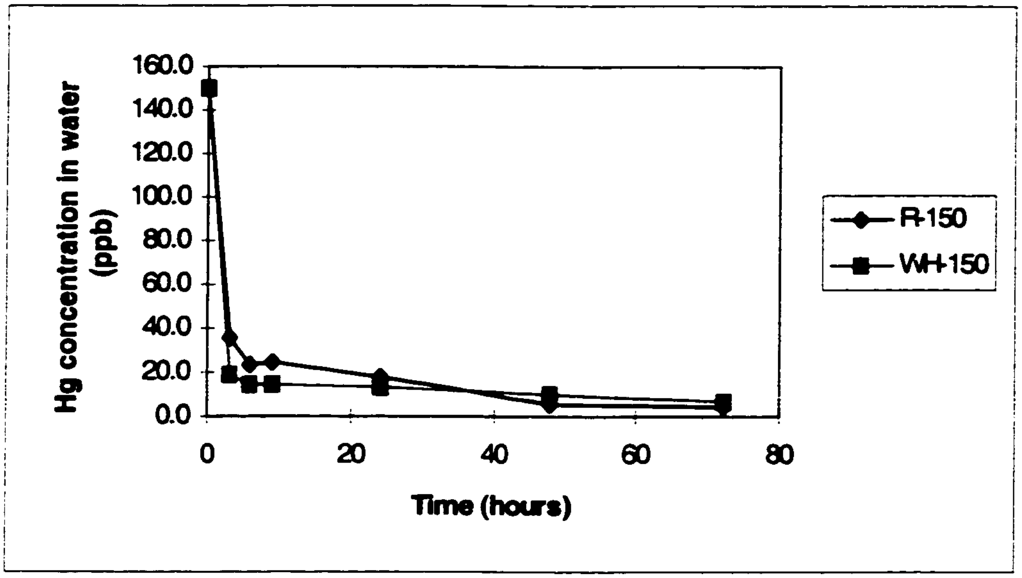


Figure 3.9 Comparison between mercury removal from water by Water Hyacinth (WH) and Reeds (R) as a function of time for the initial mercury concentrations of 150 ppb.

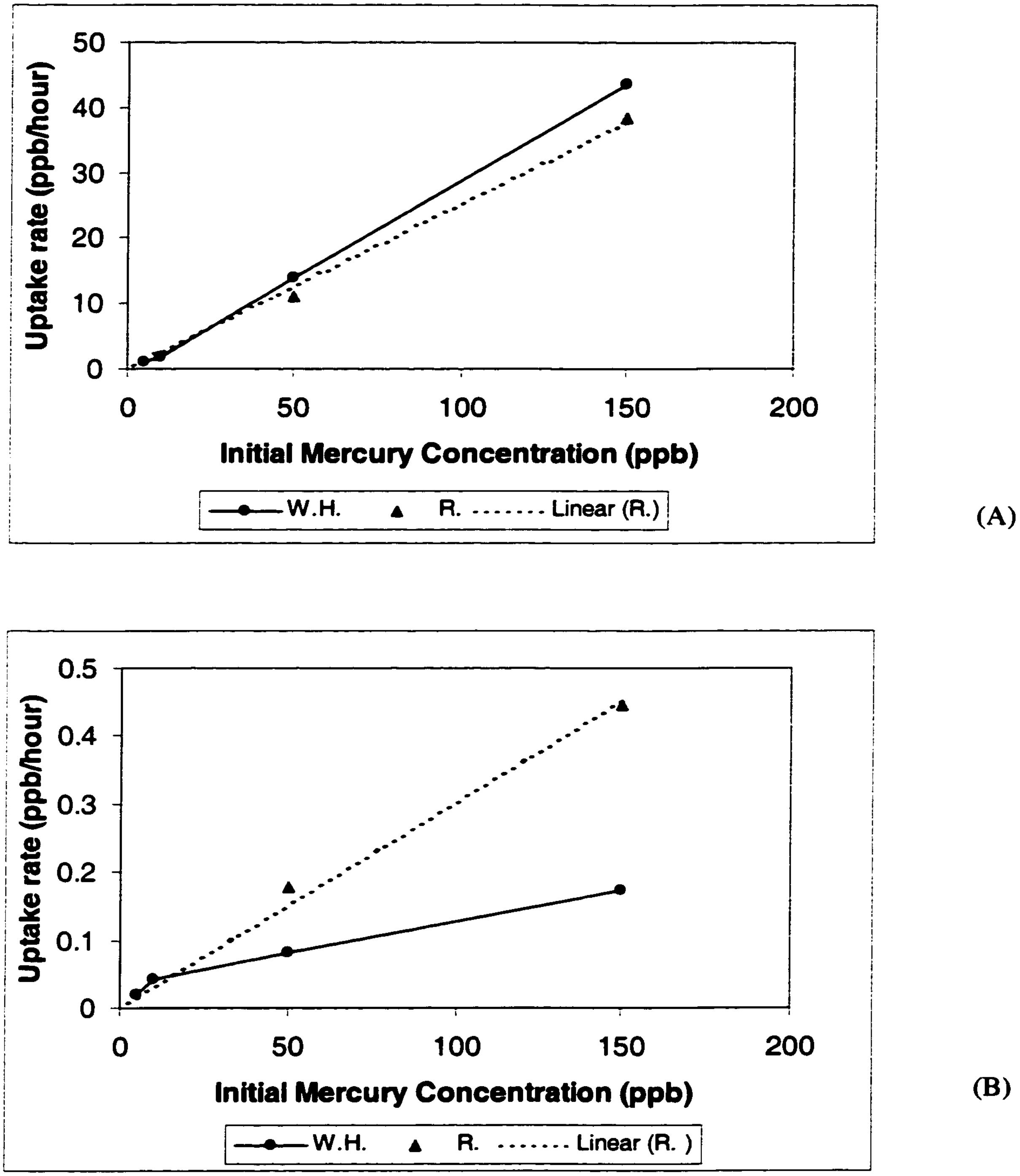


Figure 3.10 Relationship between mercury uptake rate and initial mercury concentration for Water Hyacinths and Reeds at: (A) First phase (First 3 hours of exposure) and (B) Second phase (exposure between 3 hours and 3 days).

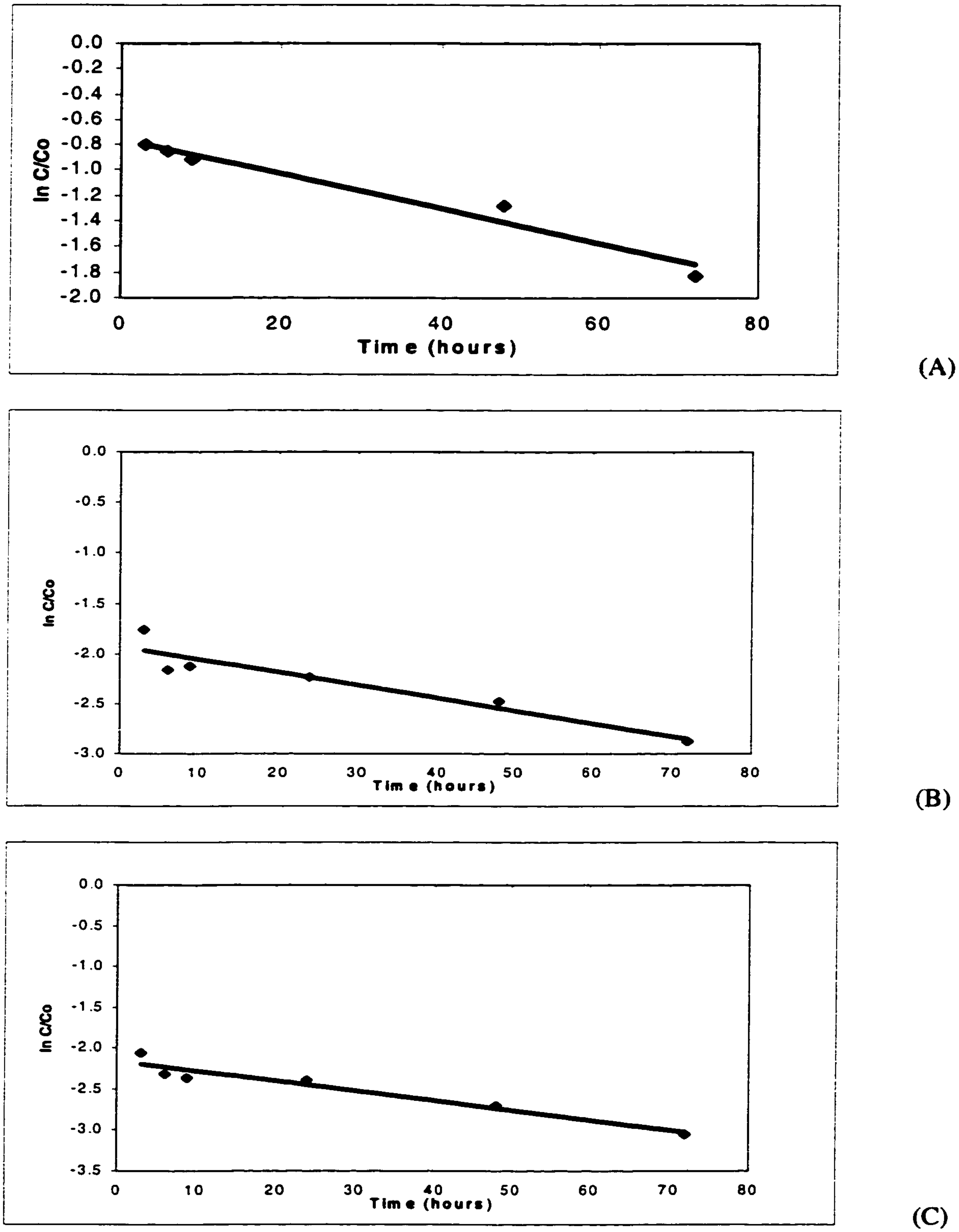
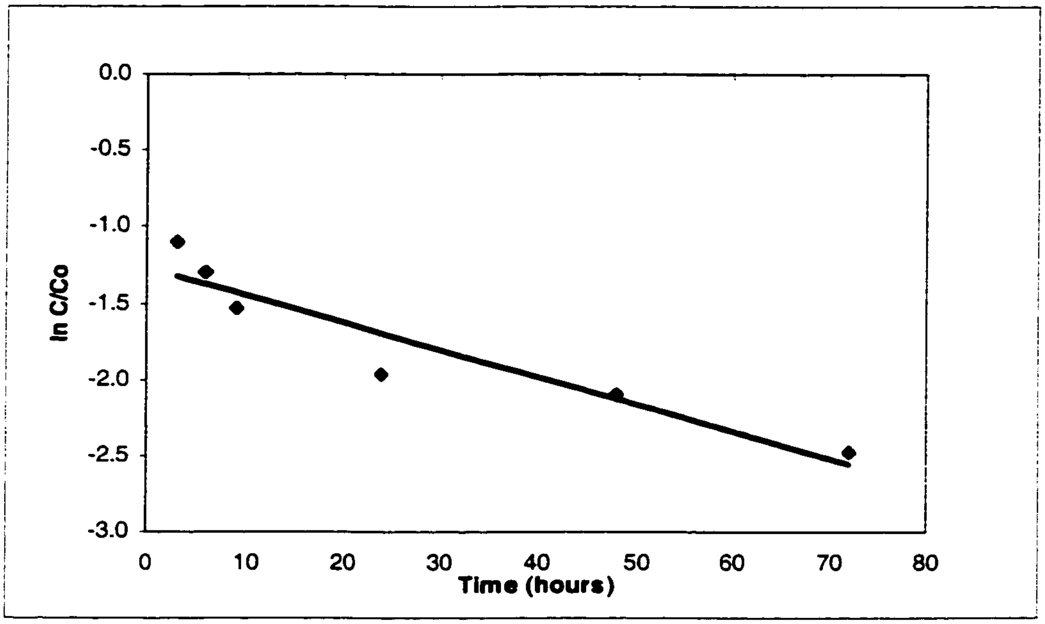
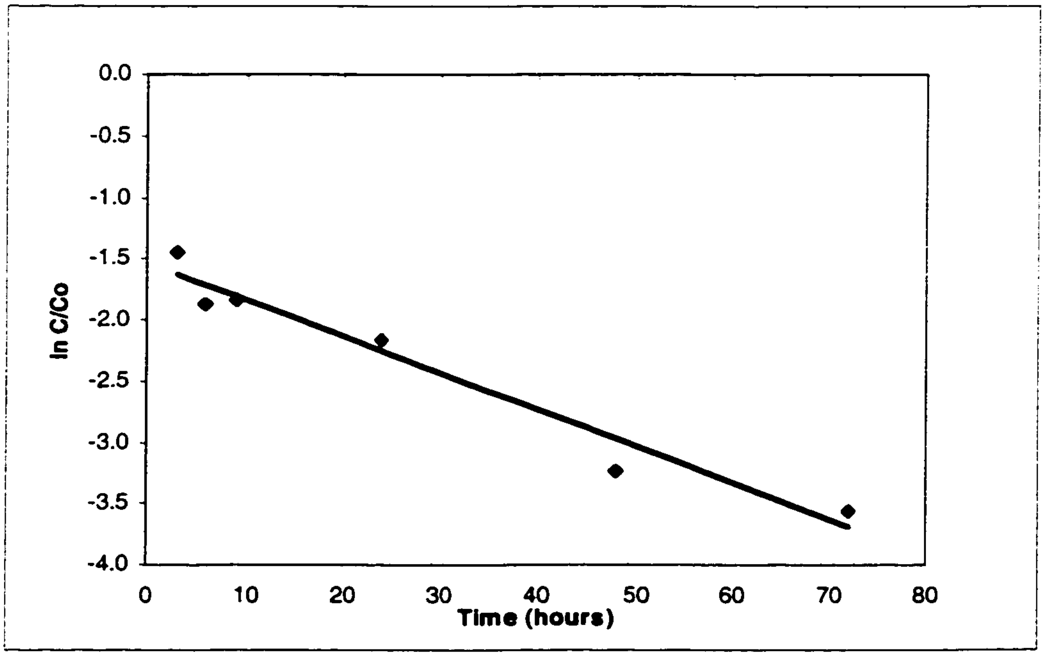


Figure 3.11 Reaction rate constant relationship for mercury removal from water by Water Hyacinth for initial mercury concentrations in solutions of: (A) 10 ppb, (B) 50 ppb, and (C) 150 ppb.



(A)



(B)

Figure 3.12 Reaction rate constant relationship for mercury removal from water by Reeds for initial mercury concentrations in solutions of: (A) 50 ppb, and (B) 150 ppb.

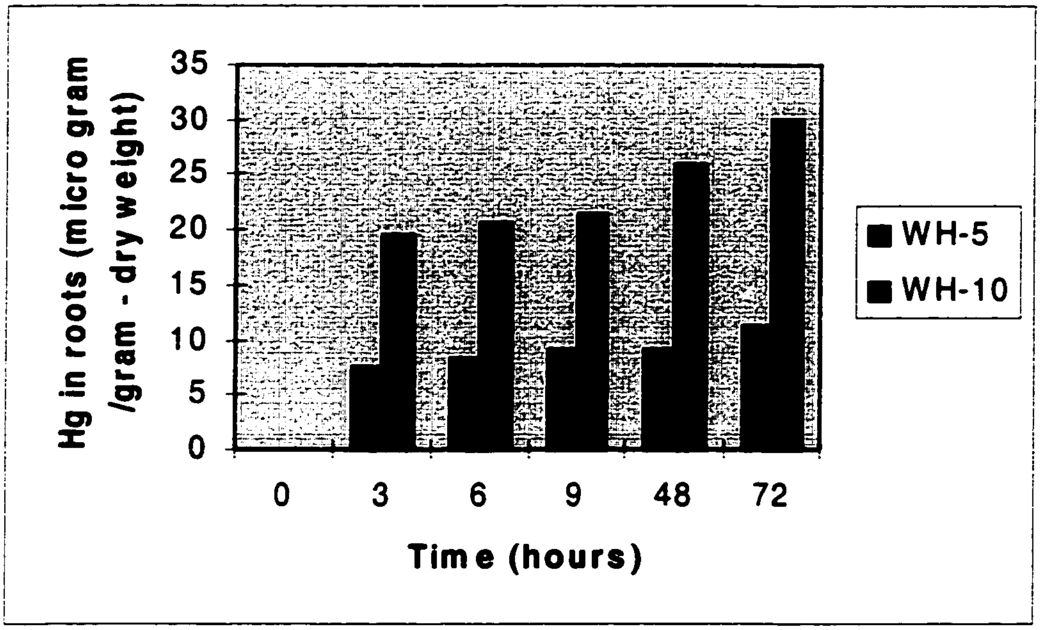


Figure 3.13: Mercury removal by Water Hyacinth (WH) per gram of dry roots for initial mercury concentrations in solutions of 5 and 10 ppb, respectively at different time steps.

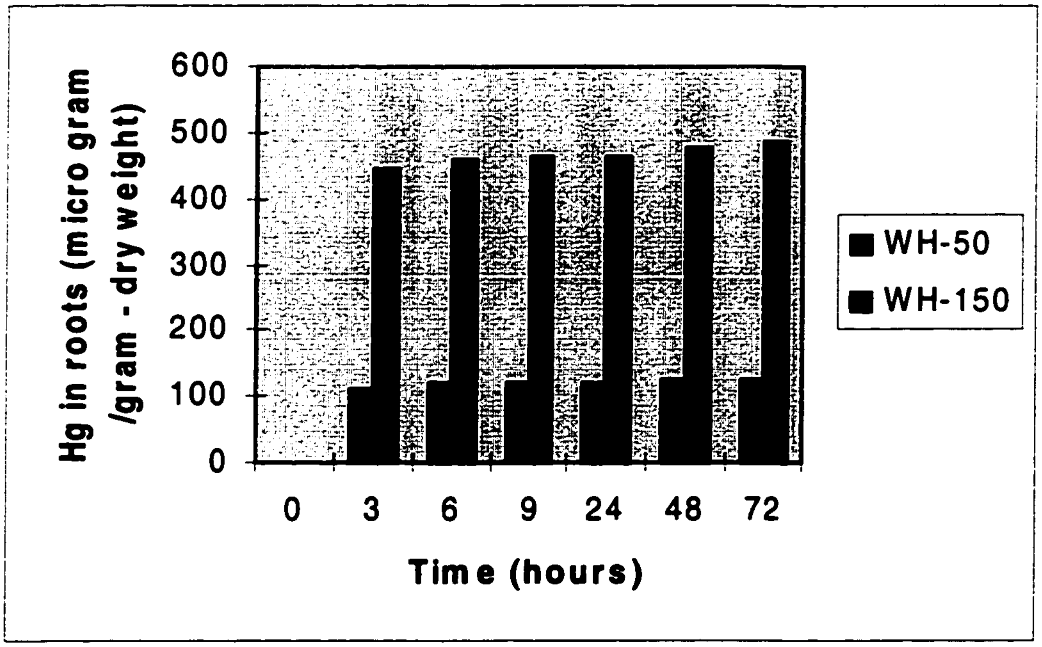


Figure 3.14: Mercury accumulation by Water Hyacinth (WH) per gram of dry roots for initial mercury concentrations in solutions of 50 and 150 ppb, respectively at different time steps.

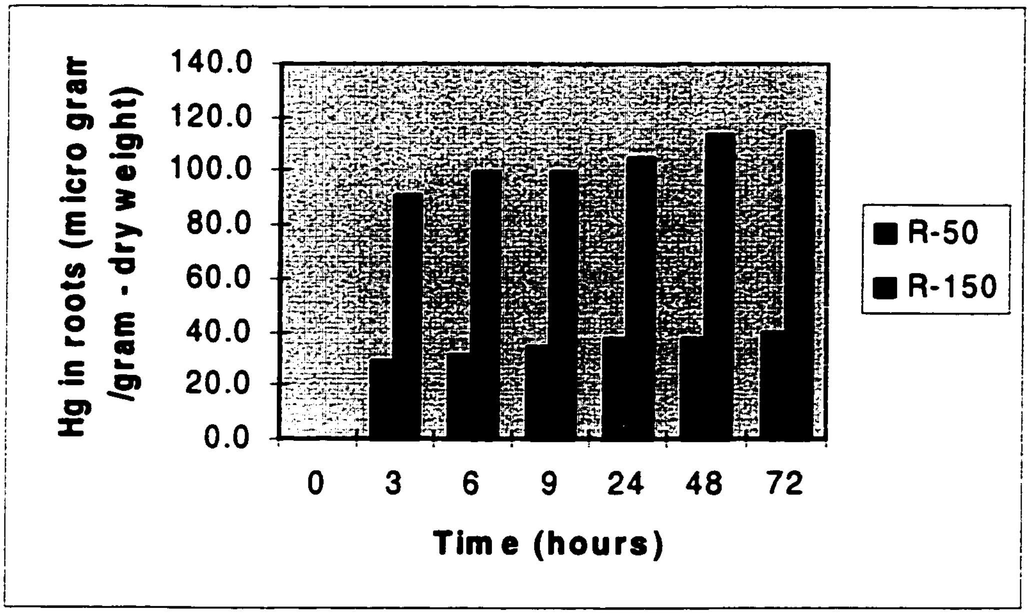


Figure 3.15: Mercury accumulation by Reeds (R) per gram of dry roots for initial mercury concentrations in solutions of 50 and 150 ppb, respectively at different time steps.

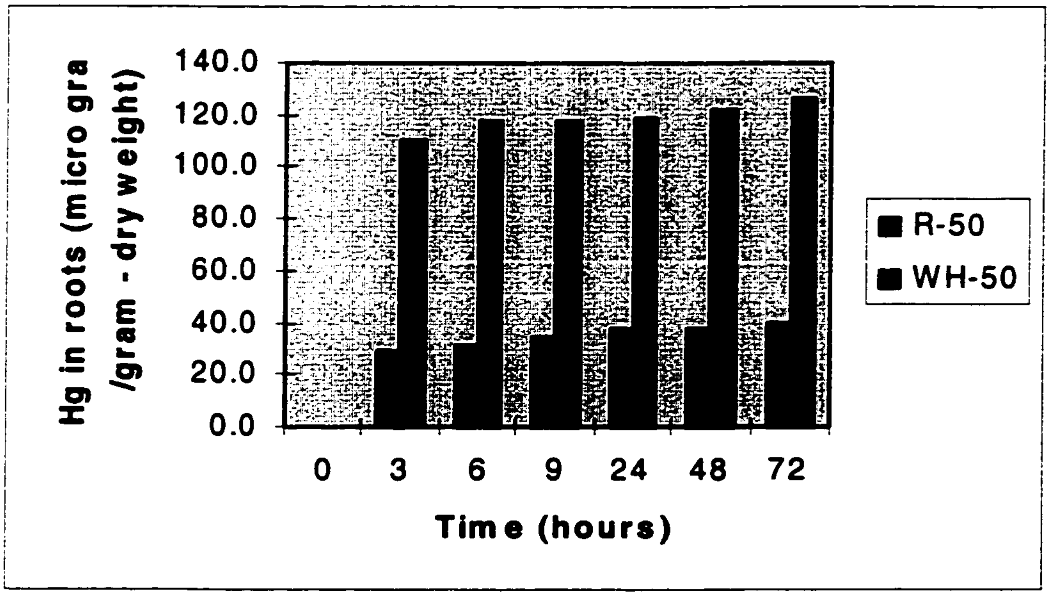


Figure 3.16: Comparison between the levels of mercury accumulation by Water Hyacinth (WH) and Reeds (R) per gram of dry roots for initial mercury concentrations in solutions of 50 ppb at different time steps.

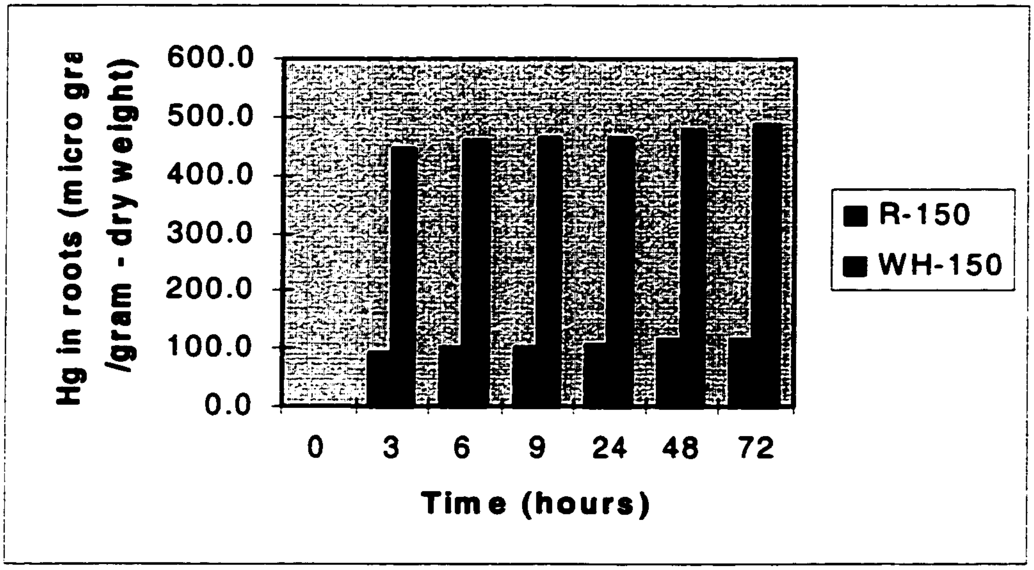


Figure 3.17: Comparison between the levels of mercury accumulation by Water Hyacinth (WH) and Reeds (R) per gram of dry roots for initial mercury concentrations in solutions of 150 ppb at different time steps.

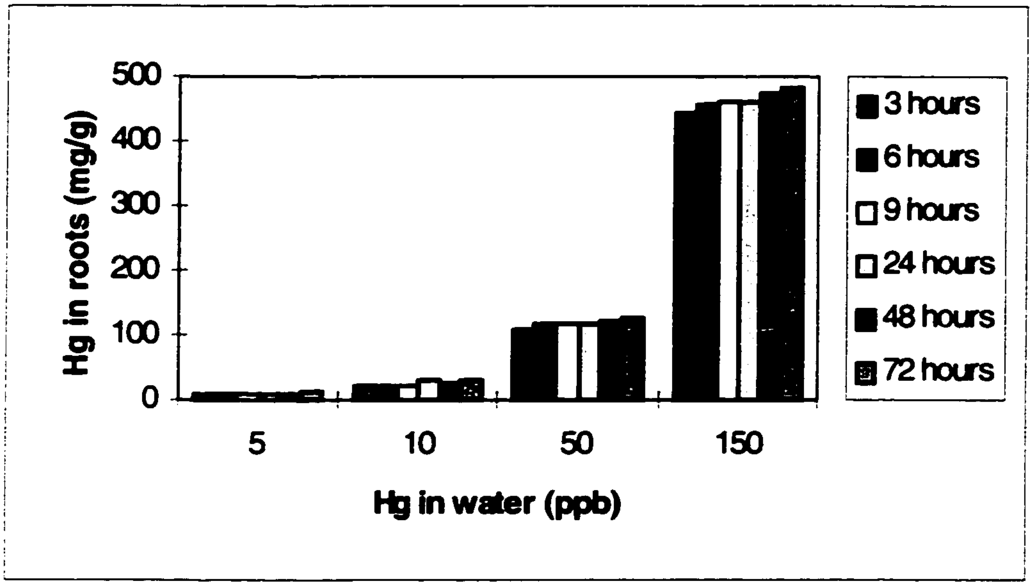


Figure 3.18: Accumulation of mercury by Water Hyacinth at different experimental periods for initial mercury concentration in solution of: 5, 10, 50, and 150 ppb, respectively.

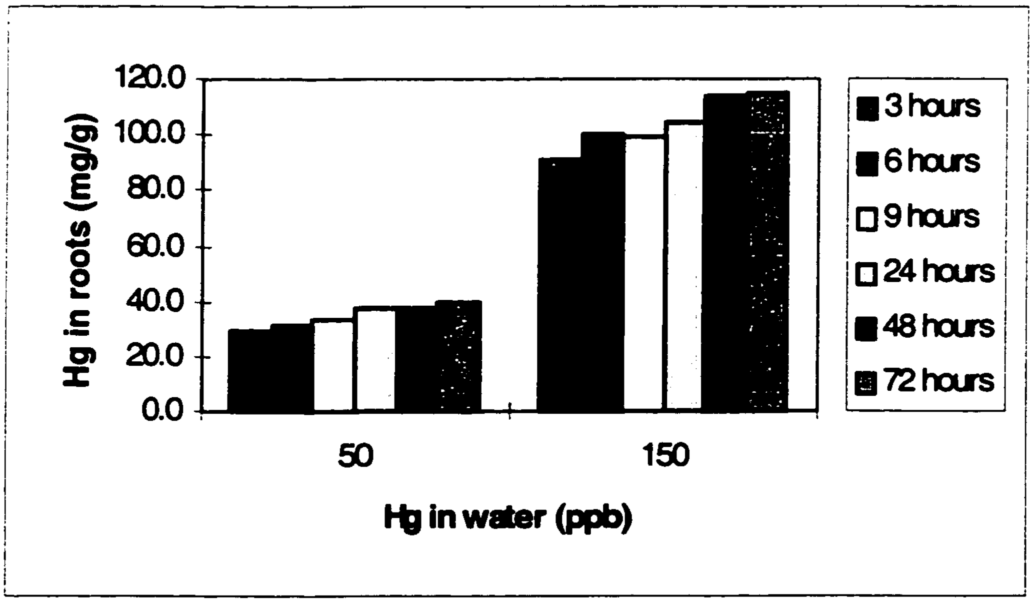


Figure 3.19: Accumulation of mercury by Reeds at different experimental periods for initial mercury concentration in solution of: 50, and 150 ppb , respectively.

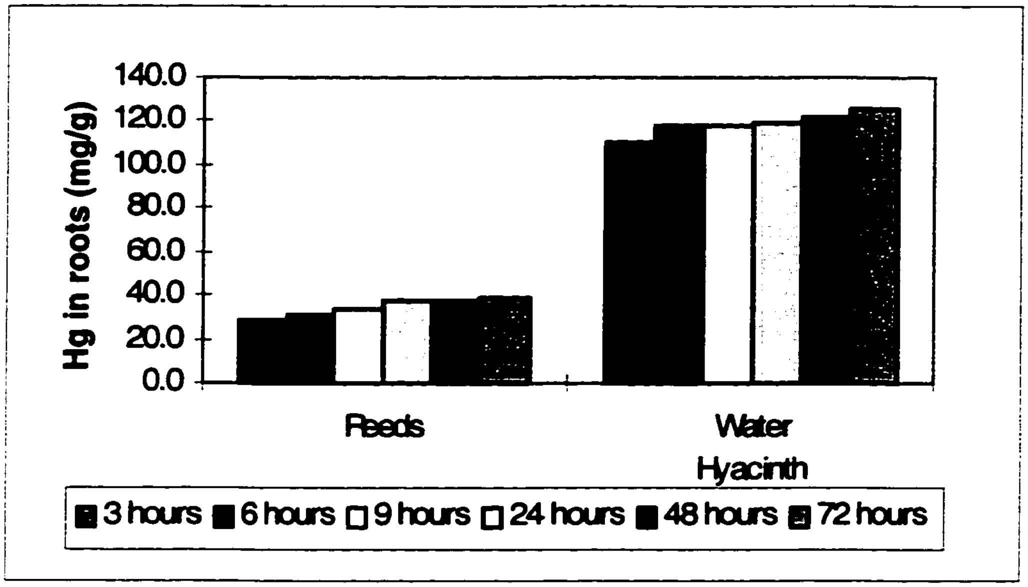


Figure 3.20: Comparison between accumulation of mercury by Water Hyacinth and Reeds at different experimental periods for initial mercury concentration in solution of: 50 ppb.

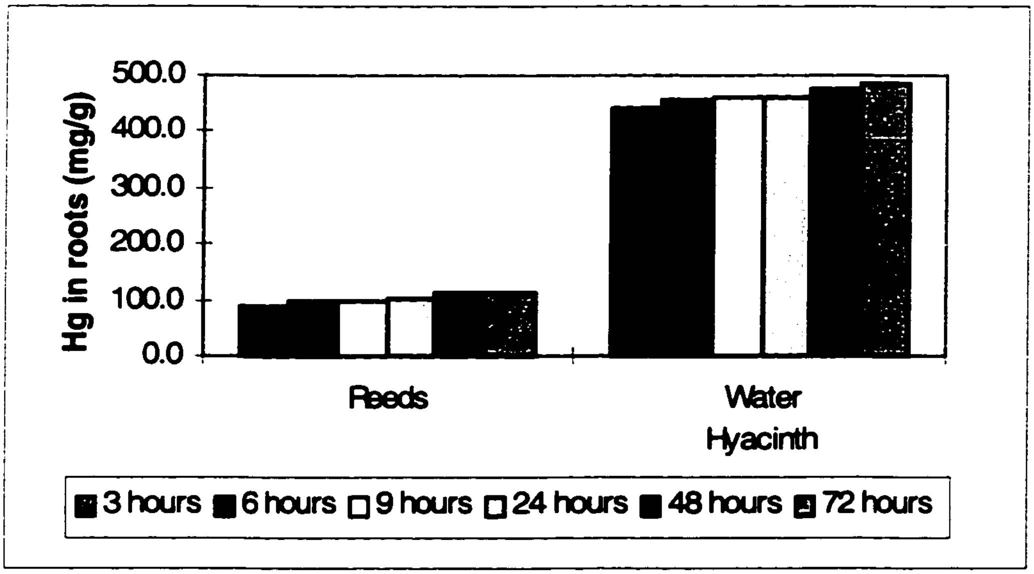


Figure 3.21: Comparison between accumulation of mercury by Water Hyacinth and Reeds at different experimental periods for initial mercury concentration in solution of:150 ppb.

# CHAPTER 4

# IMPACT OF MERCURY SPECIATION ON WETLAND'S DESIGN

Mercury could be found in different forms in surface and ground water depending on environmental conditions. The experimental study (chapter 3) concluded that the uptake of mercury by plants is classified by a rapid phase followed by a much slower phase. It was shown that total mercury was uptaken up to 98% by Reeds and 99% by Water Hyacinth. However, those investigations were not able to show if remaining mercury is bioavailable. This chapter describes the investigations carried out to specify the forms of mercury available and unavailable for plants depending on some environmental parameters (e.g. water quality, climatic changes, and characteristics of wastewater discharged). The objective of these investigations was to provide supplementary information (to the experimental results) for the optimum design of wetlands, and to enhance the extend of wetland involvement in the removal of particular mercury species.

As there are many factors affecting mercury speciations in water, the analysis was then extended to explore and quantify the effect of some of these factors. Wider ranges of mercury concentrations in water and pH values were applied. The investigation was based on changing one variable while the other factors were kept unchanged. The influence of each of these factors on mercury speciations was described. The mercury compounds considered in the final equilibrium solution, throughout all the investigations, are $Hg_2^{+2}$, $HgOH^{+1}$, $Hg\ (OH)_3^{-1}$, $Hg^{+2}$, $HgCl^{+1}$, $HgCl_2$ (aq), $HgCl_3^{-1}$, $HgCl_4^{-2}$, and HgClOH (aq).

The analysis was carried out using MINTEQA2, a geochemical software developed by the USEPA. For the two plant types tested in the experiment, mercury compounds were calculated at time: 0, 3, 6, 12, 24, 48, and 72 hours. The results show the distribution of mercury species with respect to time and mercury concentration range used in the experiment. As the ambient temperature and chloride concentration in water would affect the distribution of mercury forms, their influences were also investigated.

## 4.1 Mercury Speciation in Water Column for Water Hyacinth

The results obtained from the experimental investigation on Water Hyacinth were employed to calculate mercury speciation in water column at the end of each time step. The values of pH and temperature throughout the experiment were 5.36 and 25°C, respectively. The results show the influence of time and mercury uptake by Water Hyacinth on the distribution of mercury compounds in water column. Various mercury speciations in water column were detected for the experimental data obtained for Water Hyacinth at initial Hg concentrations of 5, 10, 50, 150 ppb respectively (Figure 4.1:A, B, C, D).

For all the initial mercury concentrations used in the experiment, a similar pattern of mercury distribution could be easily identified. The least concentration present in the equilibrium solution is $HgCl_4^{-2}$ at the level of 6.48 E-30 moles. Next to this form, $HgCl_3^{-1}$ is present at a concentration of 2.51 E-22 moles. Significantly higher than these forms, $Hg(OH)_3^{-1}$ is present at the level of 2.27 E-17 moles. Those three forms are the least dominant forms. In the middle domain, one can identify $HgCl_2$ (aq), $HgCl^{+1}$ , HgClOH (aq), $Hg^{+2}$, $HgOH^{+1}$ in the increasing order of 3.14 E-15, 1.35 E-13 , 9.01 E-12, 2.39 E-12, 2.17 E-10 respectively. The most dominant form of mercury in solution is $Hg_2^{+2}$. It was also noticed that, as the time increases, or the initial mercury concentration, there was no effect on other mercury compounds except for $Hg_2^{+2}$ which was decreasing with time (Figure 4.2). This information shows that bioavailable form of mercury is the ionic form.

The rate of decrease of $Hg_2^{+2}$ concentration in solution is faster during the first three hours, then it slows down at the end of the 72-hours experimental period. For an initial mercury concentration of 50 ppb (2.5 E-7 moles), the rate of decrease in the first three hours is 6.91 E-8 compared to 2.92 E-10 moles/hour at the end of the experiment. Similar trend was noticed when the initial mercury concentration was increased to 150 ppb (7.5 E-7 moles), where the rate of decrease at the initial three hours is 2.18 E-7 moles/hour (43.6 ppb/hour) compared to 6.17 E-10 moles/hour (0.12 ppb/hour) at the end of the experiment.

### 4.2 Mercury Speciation in Water Column for Reeds

The results obtained from the experimental investigation on Reeds were employed to calculate mercury speciation in water column at the end of each time step, in the same fashion as those of Water Hyacinth. The values of pH and temperature, throughout the experiment, were 5.36 and 25°C, respectively. The results show the influence of time and mercury uptake by Reeds on the distribution of mercury compounds in water column. Different mercury speciations in water column were detected for the experimental data obtained for Reeds and initial Hg concentrations of 50, 150 ppb respectively (Figure 4.3: A,B).

For all the initial mercury concentrations used in the experiment, a similar pattern of mercury distribution could easily be identified. The least concentration present in the equilibrium solution is $HgCl_4^{-2}$ at the level of 6.48 E-30 moles. Next to this form, $HgCl_3^{-1}$ is present at a concentration of 2.51 E-22 moles. Significantly higher than these forms, $Hg(OH)_3^{-1}$ is present at the level of 2.27 E-17 moles. Those three forms are the least dominant forms. In the middle domain, one can identify $HgCl_2$ (aq), $HgCl^{+1}$, HgClOH (aq), $Hg^{+2}$, $HgOH^{+1}$ in the increasing order of 3.14 E-15, 1.35 E-13, 9.01 E-12, 2.39 E-12, 2.17 E-10 respectively. The most dominant form of mercury in solution is $Hg_2^{+2}$. It was also noticed that, as the time increases, or the initial mercury concentration, there was no effect on all mercury compounds except for $Hg_2^{+2}$ which was decreasing with time (Figure 4.4). The order of presence of the other compounds in the solution remains the same, suggesting that $Hg_2^{+2}$ is the only form that is being uptaken by the plant as it was the case for the Water Hyacinth.

The rate of decrease of $Hg_2^{+2}$ concentration in solution, is faster in the first three hours, then it slows down at the end of the 72-hours experimental period. For an initial mercury concentration of 50 ppb (2.5 E-7 moles), the rate of decrease in the first three hours is 5.58 E-8 moles/hour compared to 3.96 E-10 at the end of the experiment. Similar trend was noticed when the initial mercury concentration was increased to 150 ppb (7.5 E-7 moles), where the rate of decrease in the initial three hours is 1.92 E-7 moles/hour compared to 3.46 E-10 moles/hour at the end of the experiment.

### 4.3 Chloride Concentration (1E-8 to 1E-4 moles)

To examine the effect of chloride concentration in solution on mercury speciation, which exists at equilibrium, five values of the chloride were investigated starting at a low of 1 E-8 moles and increasing evenly one fold at a time to a maximum of 1E -4 moles. The other parameters used in the analysis: pH 5.36, temperature 25 °C, and initial mercury concentration 7.5 E-7 moles were the same that applied during the experimental period.

As the chloride concentration increased in the solution, various distributions of mercury speciations were detected (Figure 4.5). It was observed that some mercury compounds had increased and others had decreased as the chloride concentration increased. At the extremely high values of chloride concentration (1E-5, and 1E-4 moles), the solid Calomel ($Hg_2Cl_2$) has appeared (and precipitated) for the first time in solution. The following is a detailed analysis for the behaviour of each mercury compound.

The group of mercury compounds that experienced less concentration in solution as the chloride concentration increased includes: $Hg(OH)_2$, $HgOH^{+1}$, $Hg(OH)_3^{-1}$, and $Hg^{+2}$. As the initial chloride concentration increased from 1E-8 to 1E-7, the rates of decrease calculated for $Hg(OH)_2$, $HgOH^{+1}$, $Hg(OH)_3^{-1}$, and $Hg^{+2}$ are : 8.89 E-4, 2.33 E-6, 2.22 E-13, and 1.11 E-8 moles per one fold increase in chloride concentration. Increasing the chloride concentration from 1 E-7 to 1 E-6 moles resulted in the following rates of decrease: $Hg(OH)_2$ : 9.33 E-3, $HgOH^{+1}$: 2E-5, $Hg(OH)_3^{-1}$: 2.11 E-12, and $Hg^{+2}$ : 2.11 E-7 moles per one fold increase in chloride concentration. Further increase in the chloride concentration from 1 E-6 to 1 E-5 moles, resulted in the following rates of decrease: $Hg(OH)_2$ : 9.12 E-2, $HgOH^{+1}$: 1.98 E-4, $Hg(OH)_3^{-1}$: 2.06 E-11, and $Hg^{+2}$ : 2.14 E-6 moles per one fold increase in chloride concentration. As the chloride concentration has increased to reach its maximum value, the rates of decrease calculated are: $Hg(OH)_2$ :

7.81 E-1, $HgOH^{+1}$: 1.70 E-3, $Hg(OH)_3^{-1}$: 1.77 E-10, and $Hg^{+2}$ : 1.87 E-5 moles per one fold increase in chloride concentration.

The group of mercury compounds that experienced more concentrations in solution as the chloride concentration increased includes: $HgCl^{+1}$, $HgCl_2$ (aq), $HgCl_3^{-1}$, $HgCl_4^{-2}$, and HgClOH (aq). $HgCl_4^{-2}$ is the compound that demonstrated the highest rate of increase as the chloride increase. Its concentration in solution, has increased from 6.48 E-30 moles at the lowest chloride concentration to 1.24 E-14 moles at the highest chloride concentration. The rates of increase for this compound are: 7.19 E-19, 7.12 E-15, 3.47 E-11, and 1.38 E-7 moles per unit increase in the chloride concentration.

Mercury form: $HgCl_3^{-1}$ has demonstrated also, fairly high increase in concentration as the chloride increased. The rates of increase for this compound are: 2.78 E-12, 2.75 E-9, 1.57 E-6, and 5.33 E-4 moles per unit increase in the chloride concentration.

$HgCl_2$ (aq) was the next compound to demonstrate high rates of increase as the chloride increased. The rates of increase for this compound are: 3.45 E-6, 3.42 E-4, 2.27 E-2, and 6.58 E-1 moles per unit increase in the chloride concentration.

At the lowest end of rate increase of mercury compounds, one can identify both HgClOH, and $HgCl^{+1}$. The rates of increase for HgClOH are: 9.00 E-4, 8.91 E-3, 6.77E-2, 1.22 E-1 and those for $HgCl^{+1}$ are: 1.34 E-5, 1.33 E-4, 1.01 E-3, 1.84 E-3 1 moles per unit increase in the chloride concentration.

As mentioned above, Calomel ($Hg_2Cl_2$) did not exist at the low chloride concentrations used. It was formed only at the high $Cl^-$ initial concentrations of 1 E-5, and 1E-6 moles, and it was found in solution at the concentration of : 7.3 E-7 moles, and 7.5 E-7 moles, respectively. It was noticed that as this compound forms, a drop in the concentration of $Hg_2^{+2}$ took place. $Hg_2^{+2}$ concentrations were constant at the low initial chloride concentrations, but as the chloride reach a value of 1 E-5 moles, a noticeable drop was encountered. The calculated $Hg_2^{+2}$ concentrations are 2.01 E-8 and 1.56 E-10 moles corresponding to an increase in the chloride from 1 E-5 and 1E-4 moles. Presence of chloride at the level of (1E-5 moles) decreases the available mercury for plants by 97.32%. Further increase of the chloride concentration to 1E-4 moles resulted in a decrease of 99.98% of the available mercury. Consequently, more unavailable mercury will remain in wetland water. Wastewater discharged should have a controlled value of $Cl^-$ content. The increased value of $Cl^-$ can also decrease mercury available for methylation.

## 4.4 Effect of Temperature Change on Mercury Distribution

The effect of temperature variation on mercury speciation in water was investigated. Three different values for temperature were used: the experimental value of 25 °C, 15 °C, and 35 °C. The analysis were performed for the highest experimental concentration (7.5 E-7 moles) of mercury, and three pH values are used (5.36, 6.5, and 8).

### 4.4.1 Effect of Temperature Change at pH 5.36

For the experimental pH: 5.36, as the temperature increased from 15 °C to 35 °C, all mercury species had increased concentrations in solution except those for $Hg_2^{+2}$, and HgClOH (aq) (Figure 4.6). Increasing the temperature from 15 °C to 25 °C resulted in the following rates of increase in mercury compounds concentration: $HgCl^{+1}$: 3 E-16, $HgCl_2$ (aq): 9 E-17, $HgCl_3^{-1}$: 1E-22, $HgCl_4^{-2}$: 3.1 E-29, $Hg(OH)_2$ : 1 E-11, $HgOH^{+1}$: 2 E-14, and $Hg(OH)_3^{-1}$: 2 E-21 moles / °C. Both HgClOH (aq) and $Hg^{+2}$ had a rate decrease in their concentration of 9.66 E-12, and 2.18 E-13 moles / °C increase in temperature. The temperature had no effect on the concentration of $Hg_2^{+2}$. $Hg_2(OH)_2$ was not present at pH 5.36.

Increasing the temperature from 25 °C to 35 °C resulted in lower rates of changes. The rates of increase in mercury compounds concentration are: $HgCl^{+1}$: 1 E-16, $HgCl_2$ (aq): 4 E-17, $HgCl_3^{-1}$: 4E-23 , $HgCl_4^{-2}$: 1.5 E-29, $Hg(OH)_2$ : 4 E-12, $HgOH^{+1}$: 1 E-14, and $Hg(OH)_3^{-1}$: 1 E-21 moles / °C. While the rates of decrease in both HgClOH (aq) and $Hg_2^{+2}$are: 4.5 E-12, and 1.1 E-13 moles / °C increase.

No effect on the concentration of $Hg_2^{+2}$ was observed. $Hg_2(OH)_2$ was not present at pH 5.36.

### 4.4.2 Effect of Temperature Change at pH 6.5

At pH 6.5, the increase of temperature from 15 °C to 35 °C affected some mercury species (increase and decrease in concentration) but some left without changes (Figure 4.7). Increasing the temperature from 15 °C to 25 °C resulted in the following rates of increase in mercury compounds concentration: $HgCl^{+1}$: 1 E-19, $HgCl_4^{-2}$: 2E-32, and $Hg(OH)_2$: 1E-12 moles per unit increase in temperature (°Centigrade). Species such as $HgCl_2$ (aq), $HgCl_3^{-1}$, $HgOH^{+1}$, $Hg(OH)_3^{-1}$, $Hg_2^{+2}$, and $Hg_2(OH)_2$ did not have changes in their concentrations as the temperature was increased. Both HgClOH (aq) and $Hg_2^{+2}$ had a rate of decrease in their concentrations of 7.06 E-13, and 1.14 E-15 moles per unit increase in temperature.

Increasing the temperature from 25 °C to 35 °C resulted in lower rates of changes. The rates of increase calculated are: $HgCl^{+1}$: 1 E-19, and $Hg_2^{+2}$: 1 E-12 moles per unit increase in temperature (Centigrade). Species such as $Hg(OH)_2$ , $HgCl_4^{-2}$, $HgCl_2$ (aq), $HgCl_3^{-1}$, $HgOH^{+1}$, $Hg(OH)_3^{-1}$, and $Hg_2(OH)_2$ had no change in their concentrations as the temperature was increased. Both HgClOH (aq) and $Hg^{+2}$ had a rate of decrease in their concentration of 3.2 E-13, and 5.7 E-16 moles per unit increase in temperature, respectively.

### 4.4.3 Effect of Temperature Change at pH 8

At pH 8, as the temperature increased from 15 °C to 35 °C, mercury species existed in different way (Figure 4.8). Increasing the temperature from 15 °C to 25 °C resulted in the following rates of increase in mercury compounds concentration: $HgOH^{+1}$: 1 E-17, $Hg(OH)_3^{-1}$ : 2 E-19, and $Hg_2^{+2}$ : 2 E-15 moles per unit increase in temperature (Centigrade). Concentrations of the following species: $HgCl^{+1}$, $HgCl_4^{-2}$, $Hg(OH)_2$ and $Hg_2(OH)_2$ did not change as the temperature was increased. Species such as: HgClOH (aq), $HgCl_2$ (aq), $HgCl_3^{-1}$, and $Hg^{+2}$ had a rate decrease in their concentrations of 2.24 E-14, 1 E-22, 1 E-28, and 1.14 E-18 moles per unit increase in temperature.

Increasing the temperature from 25 °C to 35 °C resulted in different rates of changes. The following rates of increase calculated were calculated: $Hg(OH)_3^{-1}$ : 4 E-19, $HgOH^{+1}$ : 2 E-17, and $Hg_2^{+2}$: 3 E-15 moles per unit increase in temperature (Centigrade). Species such as: $Hg(OH)_2$ , $HgCl_4^{-2}$, $HgCl^{+1}$, and $Hg_2(OH)_2$ had no change in their concentrations as the temperature was increased. Species such as HgClOH (aq), $HgCl_2$ (aq), $HgCl_3^{-1}$ and $Hg^{+2}$ had a rate decrease in their concentration of 1 E-14, 1 E-22, 1 E-28, and 5.7 E-19 moles per unit increase in temperature.

### 4.5 Effect of Initial Mercury Concentration on Mercury Distribution

The effect of initial mercury concentration on the distribution of mercury species in solution is investigated in this section. Five initial mercury concentrations were chosen in the analysis spanning from a high of 1 E-3 moles and decreasing evenly by one fold to a low of 1 E-7 moles. For each of these concentrations, three different values of equilibrium pH were considered. The lowest value (5.36) reflects the actual pH that exists during the experimental investigation, and represents slightly acidic environment. The highest value is 8.0 representing a slightly basic environment and the nearly neutral value of 6.5. The temperature was set to simulate the room temperature value at 25 °C. All other parameters remain unchanged.

### 4.5.1 Initial Mercury Concentration of 1 E -3 moles

Mercury compounds that exist for an initial mercury concentration of 1 E-3 moles and different pH values are shown (Figure 4.9:A). Except for $Hg(OH)_3^{-1}$, $Hg(OH)_2$, and $Hg_2(OH)_2$, all mercury compounds had less concentration in solution as the pH increased from 5.36 to 8.0. This decrease was offset by an increase in the three mentioned compounds. The rates of change were however different. As the pH increased from 5.36 to 6.5 the following rates are observed: 1) decrease: $Hg_2^{+2}$ (3.07 E-6 moles/pH unit), $HgOH^{+1}$ (1.77 E-10 moles/pH unit), $Hg^{+2}$ (2.1 E-12 moles/pH unit), $HgCl^{+1}$ (1.17 E-13 moles/pH unit), $HgCl_2$(aq) (2.73 E-15 moles/pH unit), Hg $Cl_3^{-1}$ (2.18 E-22 moles/pH unit), $HgCl_4^{-2}$ (5.65 E-30 moles/pH unit), HgClOH (aq) (7.32 E-12 moles/pH unit).

2) increase: $Hg(OH)_2$ (1.84 E-10 moles/pH unit), $Hg_2(OH)_2$ (3.07 E-6 moles/pH unit), $Hg(OH)_3^{-1}$ (2.55 E-16 moles/pH unit).

As the pH increased from 6.5 to 8.0 the following rates were noticed: 1) decrease: $Hg_2^{+2}$ (1.22 E-8 moles/pH unit), $HgOH^{+1}$ (1.02 E-11 moles/pH unit), $Hg_2^{+2}$ (8.34 E-15 moles/pH unit), $HgCl^{+1}$ (4.71 E-16 moles/pH unit), $HgCl_2$(aq) (1.1 E-17 moles/pH unit), Hg $Cl_3^{-1}$ (8.82 E-25 moles/pH unit), $HgCl_4^{-2}$ (2.28 E-32 moles/pH unit), HgClOH (aq) (4.23 E-13 moles/pH unit). 2) increase: $Hg(OH)_2$ (1.33 E-11 moles/pH unit), $Hg(OH)_3^{-1}$

(6.4 E-15 moles/pH unit). The increase of pH from 6.5 to 8.0 did not have any effect on the concentration of $Hg_2(OH)_2$ in solution.

Increasing the pH from 5.36 to 6.5 and from 6.5 to 8.0 have decreased the bioavailable form of mercury: $Hg_2^{+2}$ suggesting that the highest bioavailability is at pH 5.36. As the pH increases, the rate of removal by plants decreases.

### 4.5.2 Initial Mercury Concentration of 1 E -4, 1 E-5, 1E-6, and 1E-7 moles

Mercury compounds that exists for an initial mercury concentration of 1 E-4, 1 E-5, 1 E-6, 1 E-7 moles and different pH values are shown (Figures 4.9: B, C, D, E).

As the initial mercury concentration increased, there was no change in the distribution of the different mercury compounds in solution, nor in the rates of changes previously noticed in the case of 1E-3 moles except for $Hg_2^{+2}$ (the bioavailable form), and $Hg_2(OH)_2$.

An increase in the equilibrium pH from 5.35 to 6.5 resulted in a decrease of $Hg_2^{+2}$ concentration in solution of 3.07 E-6, 3.07 E-6, 8.61 E-7, and 7.17 E-8 moles/ pH unit for the initial mercury concentrations of 1 E-4, 1E-5, 1E-6, and 1E-7 respectively. These rates of decrease were compensated by the following rates of increase of $Hg_2(OH)_2$ concentration in solution : 3.1 E-6, and 3.1 E-6 for initial mercury concentrations of 1 E-4, and 1E-5 moles respectively. This compound was not present in solution for the initial mercury concentration of 1E-6, and 1E-7 moles at pH 5.36. At pH 6.5, the corresponding concentrations observed for $Hg_2(OH)_2$ were 9.82 E-7, and 8.18 E-8 moles for initial concentration of 1E-6, and 1E-7 moles respectively.

As the pH increased from 6.5 to 8, there was no change in the distribution of the different mercury compounds in solution, nor in the rates of changes previously noticed in the case of 1E-3 moles except for $Hg_2(OH)_2$. There was no change in its concentration in solution as pH changed in the case of initial mercury concentration of 1E-4 moles. However, it was observed that its rate of concentration increase in solution was almost the same at 1.2 E-8 moles/pH unit for the lower initial concentrations used (1 E-5 to 1 E-7 moles).

### 4.6 Effect of the pH of the Equilibrium Solution on Mercury Distribution

The effect of the pH of equilibrium solution on the formation different speciation is investigated in this section. Using the same parameters and values employed previously for pH and initial mercury concentrations, the following results were obtained and shown (Figure 4.10:A, B, C).

#### 4.6.1 Effect of Initial Mercury Concentration at pH 5.36

Initial mercury concentrations are expected to affect mercury distribution in water. The highest mercury concentration used in during the experiment was 7.5E-7 moles. In the numerical investigation it was possible to use higher mercury concentrations of: 1E-6, 1E-5, 1E-4, and 1E-3 moles.

$Hg_2(OH)_2$ was not present at the low initial mercury concentrations of 1 E-6 and 1E-7 moles. The compound starts to exist when initial mercury concentrations of 1 E-5 and higher were used (Figure 4.11:A). The concentrations observed for this compound are 6.48 E-6, 9.65 E-5, and 9.97 E-4 moles, at initial mercury concentrations of: 1E-5, 1E-4, and 1E-3 moles. The composition of mercury speculation in solution is as follows: $Hg_2^{+2}$: 3.52E-06 moles, $Hg(OH)_2$: 9.98E-08 moles, $HgOH^{+1}$: 2.18E-10 moles, $Hg(OH)_3^{-1}$: 2.27E-17 moles, $Hg^{+2}$ :2.41E-12 moles, $HgCl^{+1}$: 1.35E-13 moles, $HgCl_2$(aq) :3.13E-15 moles, $HgCl_3^{-1}$ :2.50E-22 moles, $HgCl_4^{-2}$ :6.48E-30 moles, HgClOH (aq) :9.00E-12 moles. The concentration of the bioavailable form of mercury ($Hg_2^{+2}$) has decreased by 64.8% as the initial mercury concentration reached 1E-5 moles. Increasing the initial mercury concentration to 1E-4 moles resulted in a decrease of 96.48% of the available mercury. As the initial mercury concentration reached 1E-3 moles, the bioavailable mercury was reduced by 99.65%.

### 4.6.2 Effect of Initial Mercury Concentration at pH 6.5

As the initial values of mercury concentration in solution changed from 1 E-3 to 1 E-7 moles, neither changes in the distribution of mercury speciation, nor in the rates of changes were observed except for $Hg_2(OH)_2$ as shown (Figure 4.11:B). Unlike the case of pH 5.36, this compound was present at all initial concentration levels and its concentration was increasing as the initial mercury concentration increases. The concentrations observed for this compound are: 1.00E-03, 1.00E-04, 9.98E-06, 9.82E-07, and 8.18E-08 moles for the initial mercury concentrations of 1E-3 to 1E-7 moles. The composition of mercury speciation in solution is as follows: $Hg_2^{+2}$ : 1.83 E-08 moles, $Hg(OH)_2$ : 1.0 E-7 moles, $HgOH^{+1}$ :1.58 E-11 moles, $Hg(OH)_3^{-1}$ :3.13 E-16 moles, $Hg^{+2}$ :1.25 E-14 moles, $HgCl^{+1}$ :7.08 E-16 moles, $HgCl_2$(aq) :1.66 E-17 moles, Hg $Cl_3^{-1}$ :1.32 E-24 moles, $HgCl_4^{-2}$ :3.42 E-32 moles, HgClOH (aq) :6.56 E-13 moles.

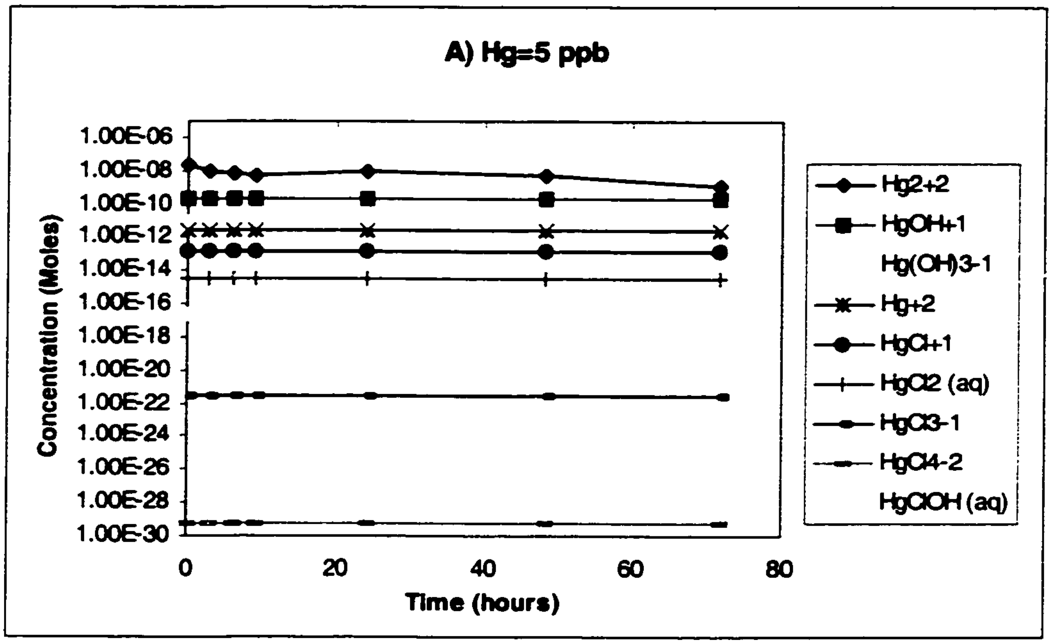
### 4.6.3 Effect of Initial Mercury Concentration at pH 8

Similar to the case of pH 6.5, as the initial values of mercury concentration in solution changed from 1 E-3 to 1 E-7 moles, neither changes in the distribution of mercury speciation, nor in the rates of changes were observed except for $Hg_2(OH)_2$ as shown (Figure 4.11:C). Unlike the case of pH 5.36, this compound was present at all initial concentration level and its concentration was increasing as the initial mercury concentration increases. The concentrations observed for this compound are: 1.00E-03,1.00E-04, 1E-05, 1E-06, and 1E-07 moles for the initial mercury concentrations of 1E-3 to 1E-7 moles. The composition of mercury speciation in solution is as follows: $Hg_2^{+2}$: 1.83 E-08 moles, $Hg(OH)_2$: 1.0 E-7 moles, $HgOH^{+1}$: 4.99 E-13 moles, $Hg(OH)_3^{-1}$: 9.91 E-15 moles, $Hg_2^{+2}$: 1.25 E-17 moles, $HgCl^{+1}$: 7.08 E-19 moles, $HgCl_2(aq)$: 1.66 E-20 moles, $HgCl_3^{-1}$: 1.32 E-27 moles, $HgCl_4^{-2}$: 3.42 E-35 moles, HgClOH (aq): 2.07 E-14 moles.

## 4.7 Conclusion

It could be concluded from this chapter that mercury speciation in water does not change as the initial concentration changes. However, the amount of each form could be different. The rates of change calculated for the experimental investigation could be applied as presented in section 4.1 and 4.2.

Changing pH in the range acceptable for plant (5.36 to 8.0) resulted in an impact on $Hg_2^{+2}$ and $Hg_2(OH)_2$ concentrations in water. As the pH increases the concentrations of bioavailable mercury form ($Hg_2^{+2}$) decreases while the concentrations of $Hg_2(OH)_2$ increases (unavailable for uptake by the plants). As the initial mercury concentration increased to 1E-5 moles, the bioavailable mercury was decreased by 64.8% at pH 5.36. For the same pH conditions, further increase in the initial mercury concentration to 1E-4 and 1E-3 moles resulted in a considerable decrease in the bioavailable mercury by 96.48% and 99.65% respectively. The presence of chloride in water influences the mercury distribution. An increase in the chloride concentration decreases the concentration of ($Hg_2^{+2}$), the bioavailable form. At the level of 1E-5 moles the bioavailable mercury was reduced by 97.32%. Further increase in the chloride concentration to 1E-4 moles reduced the bioavailable mercury by 99.98%. As the temperature changed from (15 °C to 35 °C), the concentrations of bioavailable form of mercury ($Hg_2^{+2}$) remain unchanged at pH 5.36 and 6.5, but caused an increase at pH 8.0. The rates of changes are presented in sections 4.4.1 through 4.4.3. An optimum design of a constructed wetland's system for mercury removal should consider the presence of $Cl^-$, pH, and initial mercury concentration as they affect the bioavailable mercury forms for plant uptake.



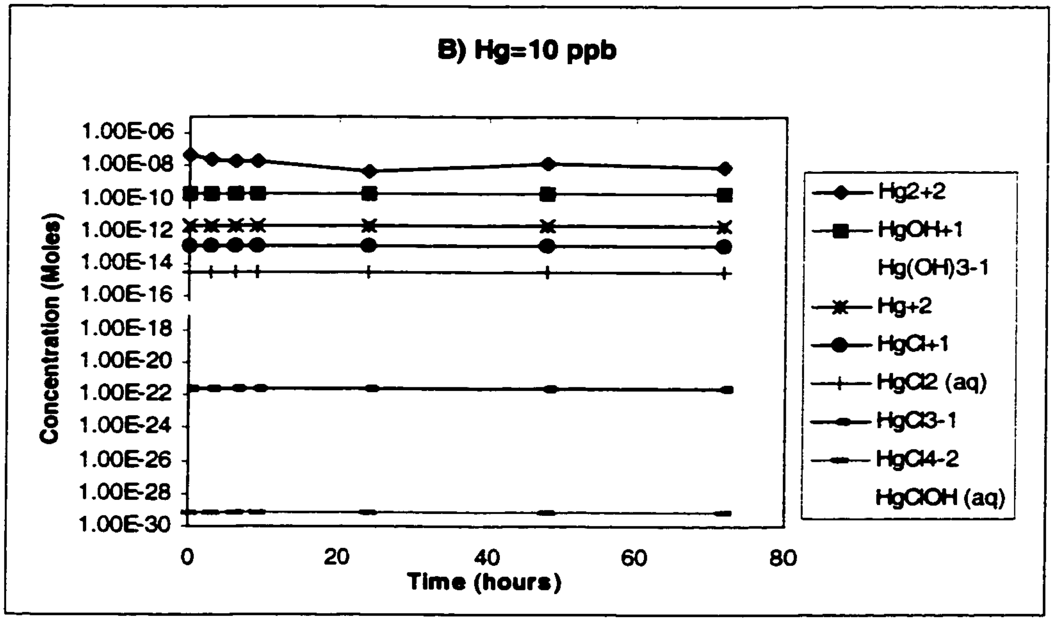
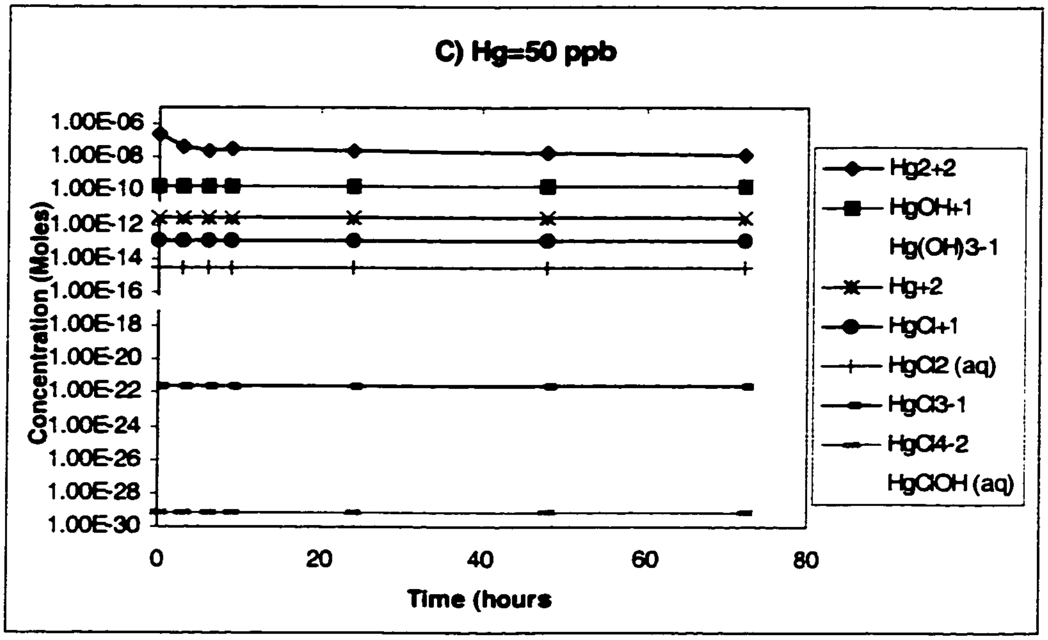


Figure 4.1 (A, B) show mercury speciation in water column for the experimental data obtained for Water Hyacinth and initial Hg concentrations of 5 and 10 ppb, respectively.



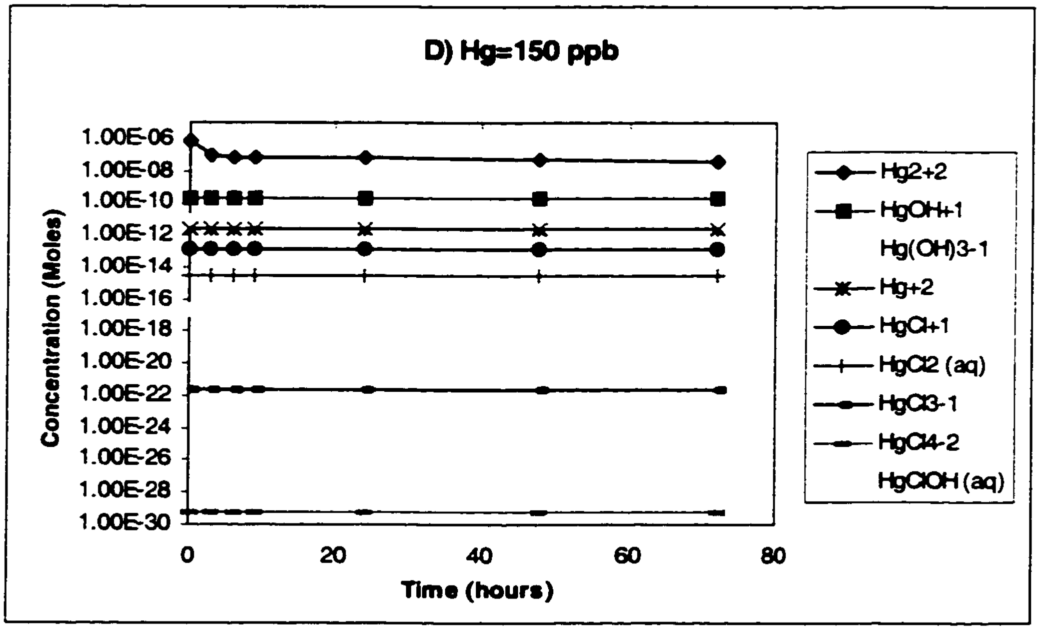


Figure 4.1 (C, D) show mercury speciation in water column for the experimental data obtained for Water Hyacinth and initial Hg concentrations of 50 and 150 ppb, respectively.

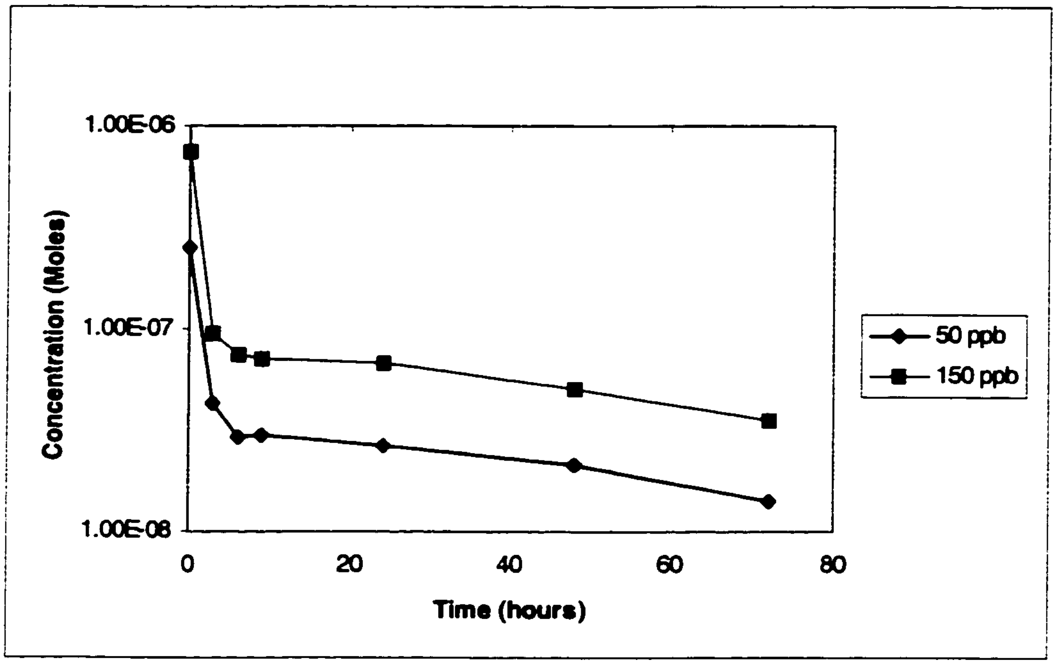


Figure 4.2: Concentration of $Hg_2^{+2}$ in solution as a function of time in the case of Water Hyacinth and initial mercury concentrations of 50, 150 ppb.

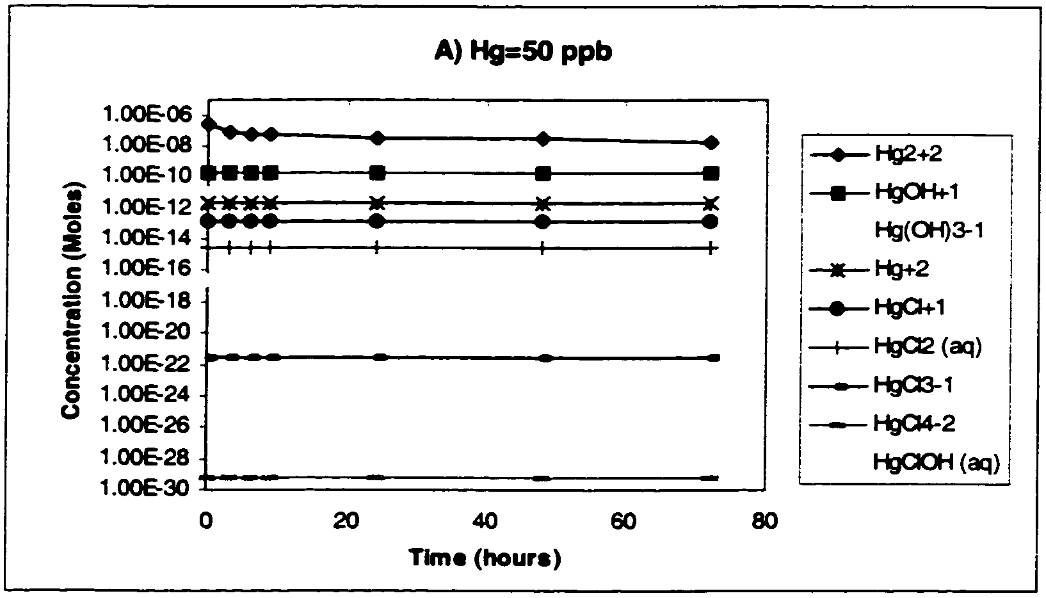


Figure 4.3 (A) show mercury speciation in water column for the experimental data obtained for Reeds and initial Hg concentrations of 50 ppb.

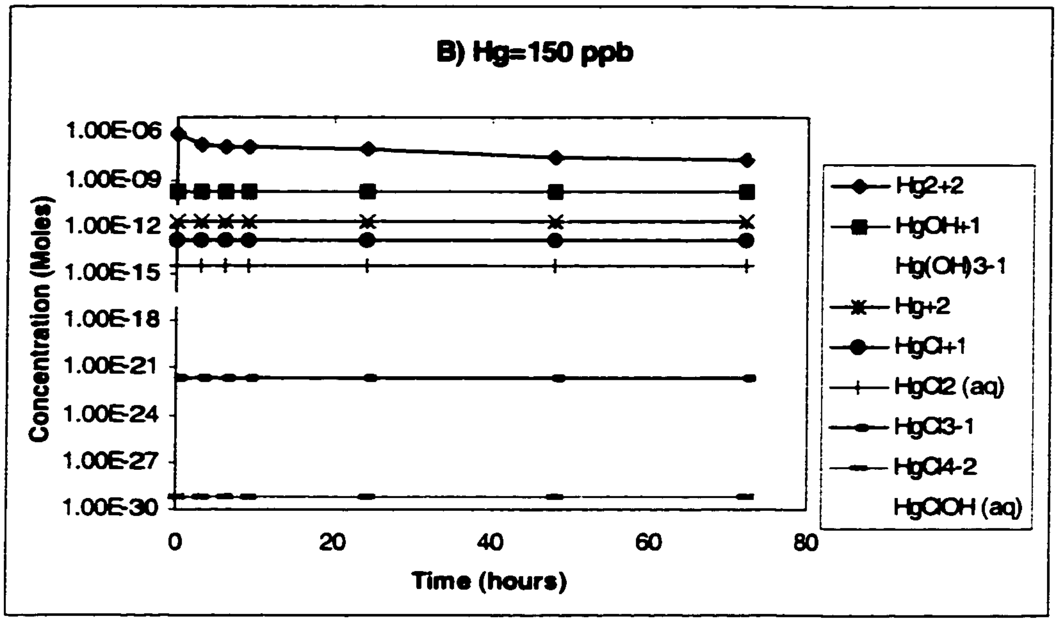


Figure 4.3 (B) show mercury speciation in water column for the experimental data obtained for Reeds and initial Hg concentrations of 150 ppb.

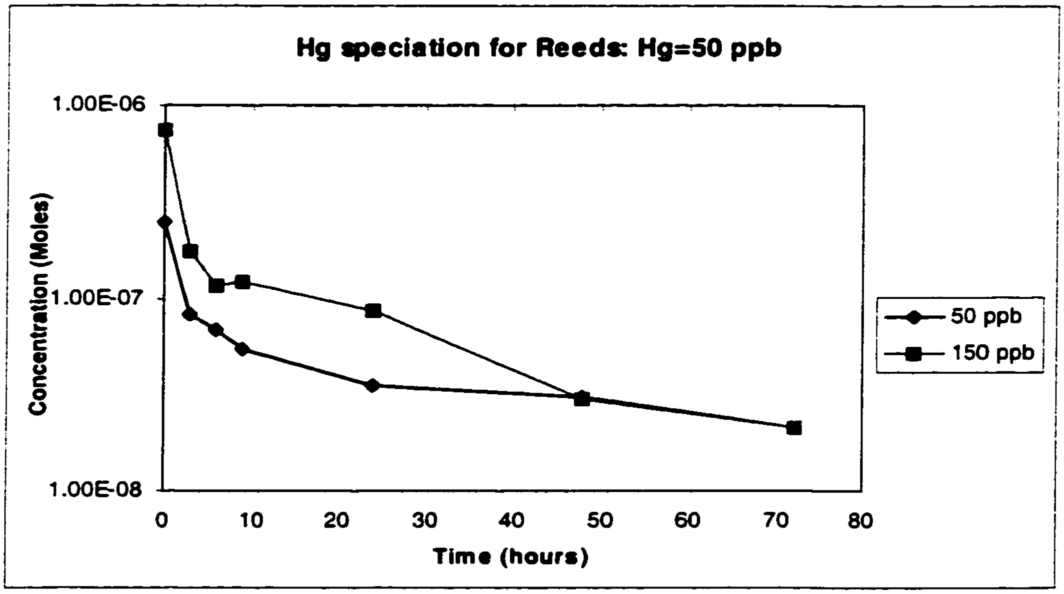


Figure 4.4: Concentration of $Hg_2^{+2}$ in solution as a function of time in the case of Reeds and initial mercury concentrations of 50, 150 ppb.

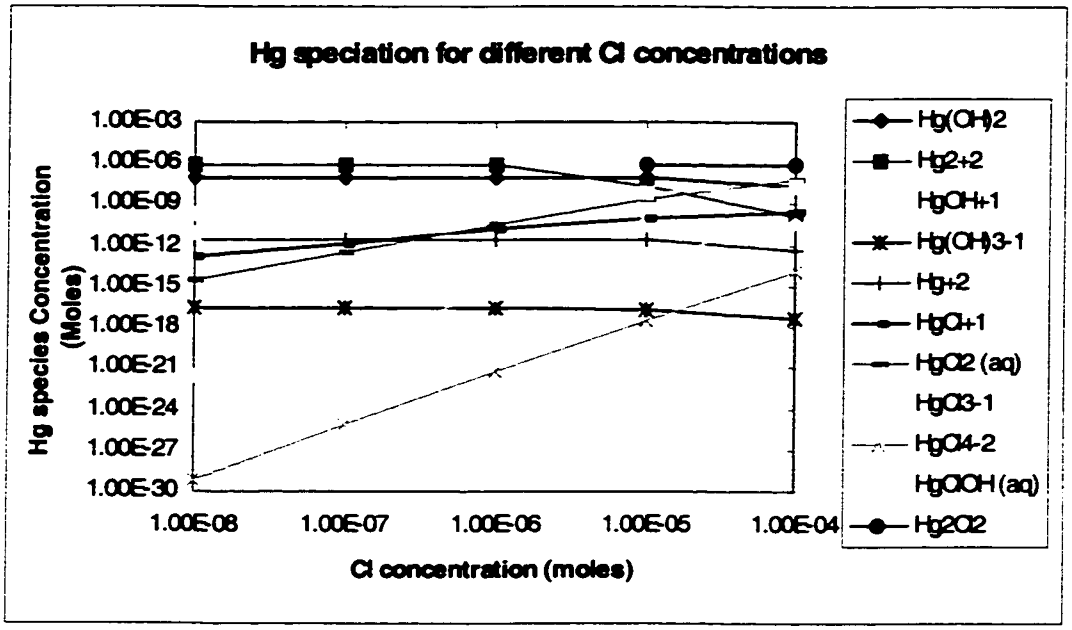


Figure 4.5 Behaviour of different mercury compounds in solution as the chloride concentration increases from 1 E-8 to 1E-4 moles.

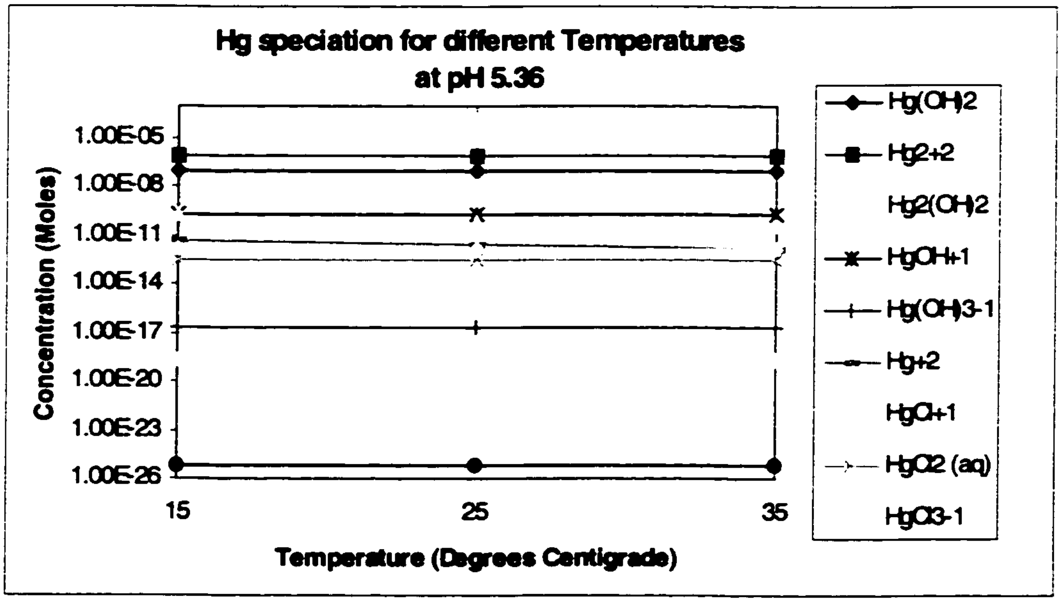


Figure 4.6 Effect of temperature increase on mercury speciation in solution at pH 5.36 (Experimental Condition).

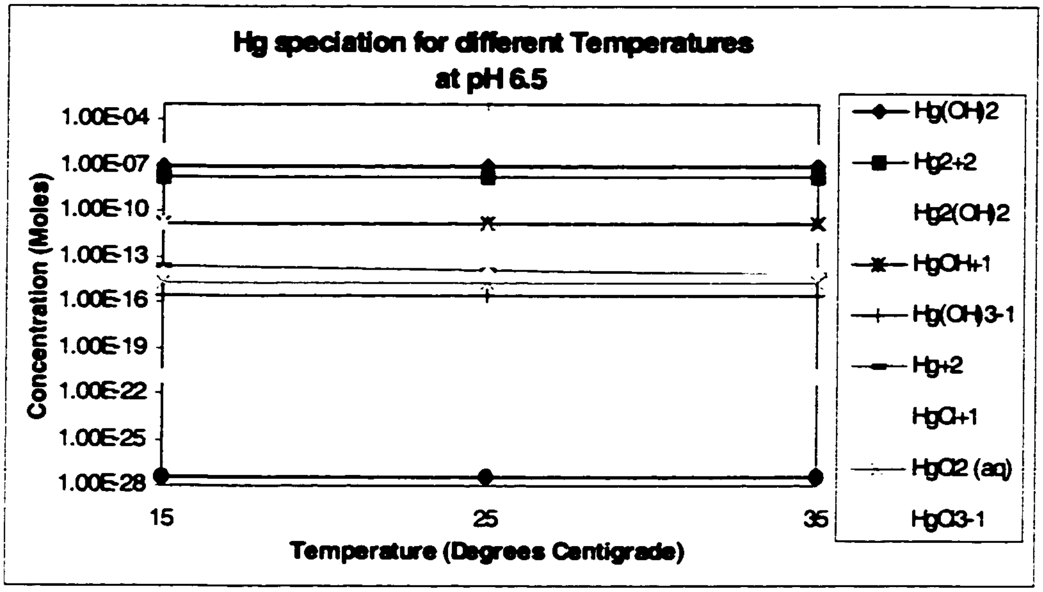


Figure 4.7 Effect of temperature increase on mercury speciation in solution at pH 6.5.

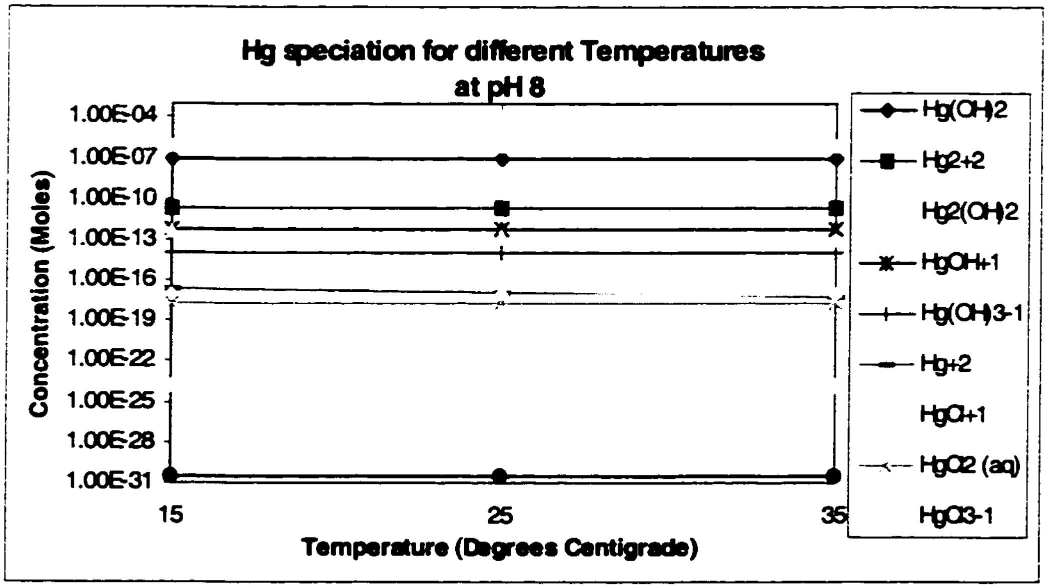
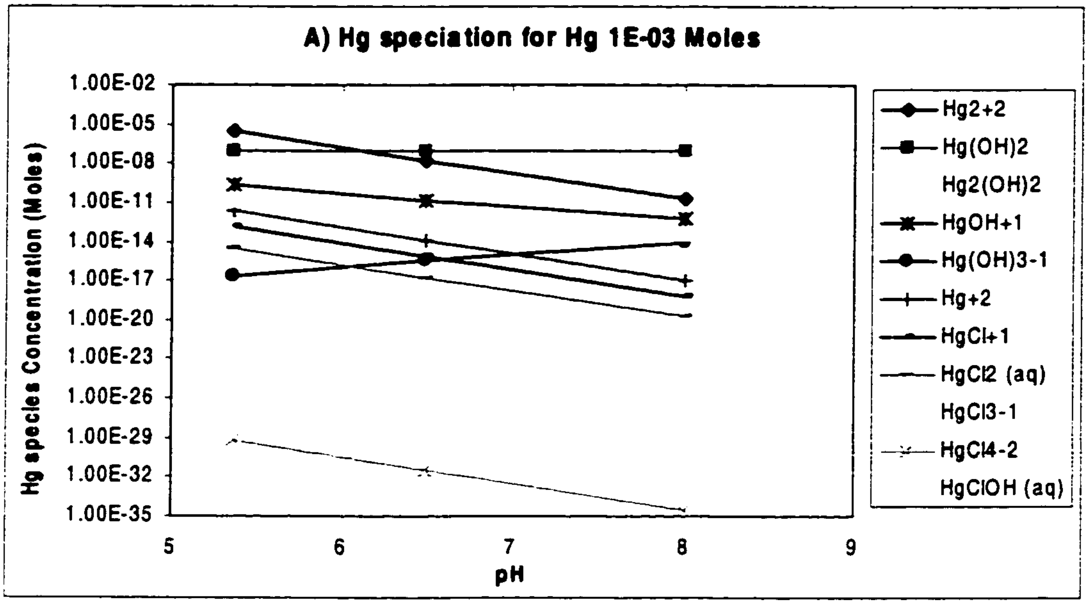


Figure 4.8 Effect of temperature increase on mercury speciation in solution at pH 8.



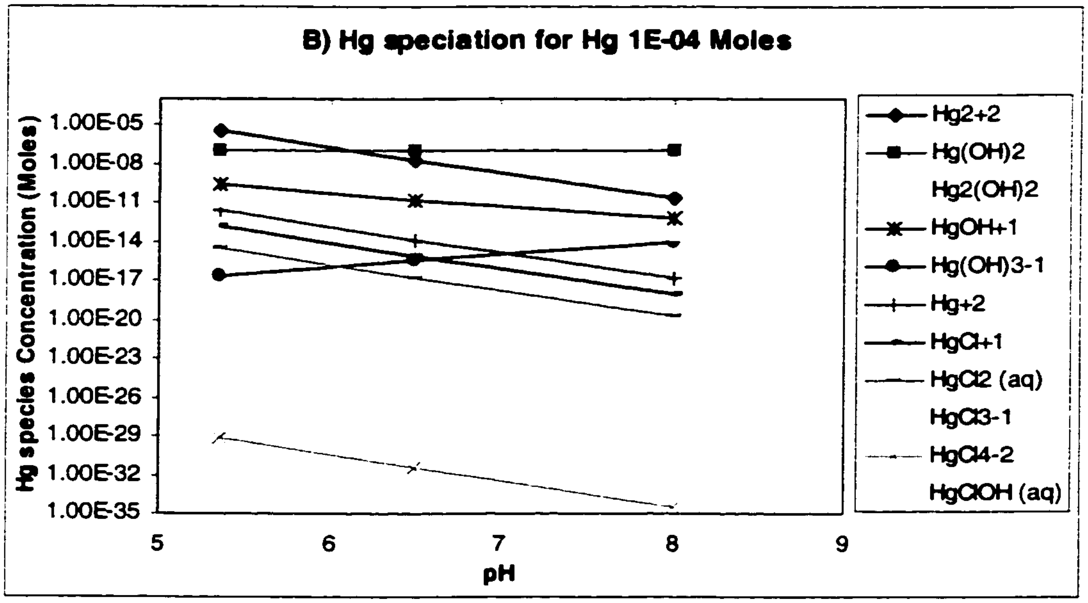
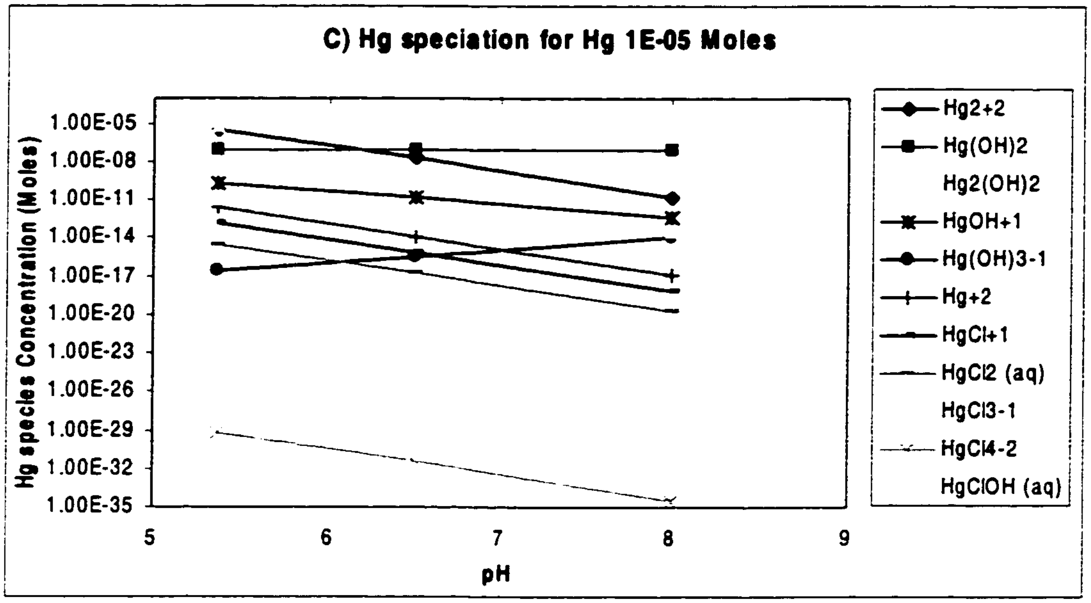


Figure 4.9 (A, B) Mercury compounds in solution that exist for initial mercury concentration of 1 E-3, and 1 E-4 moles and different pH conditions.



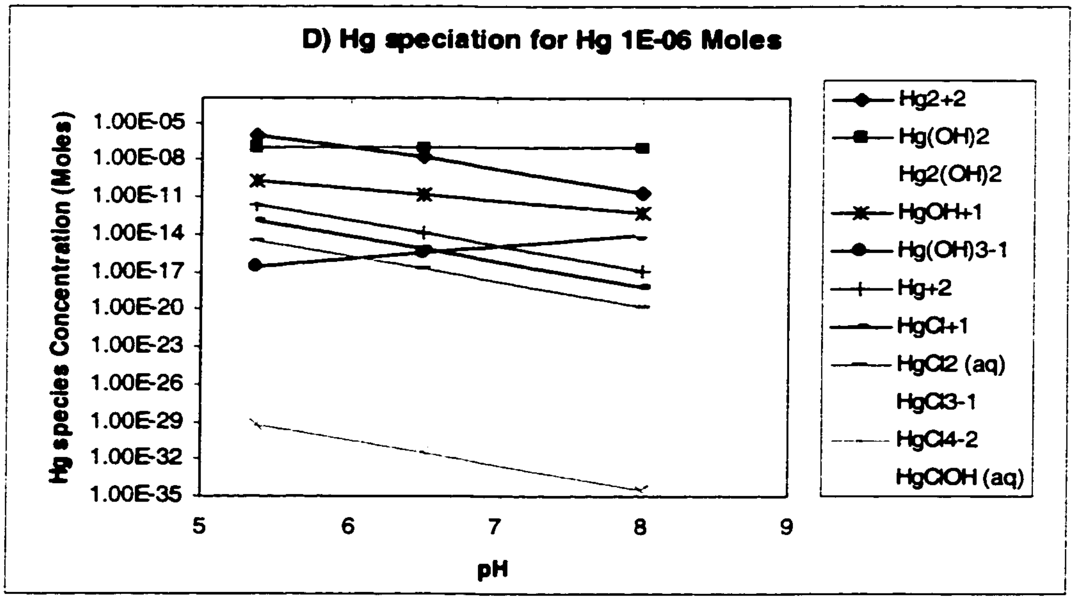


Figure 4.9 (C, D) Mercury compounds in solution that exist for an initial mercury concentration of 1 E-5, 1 E-6 moles and different pH conditions.

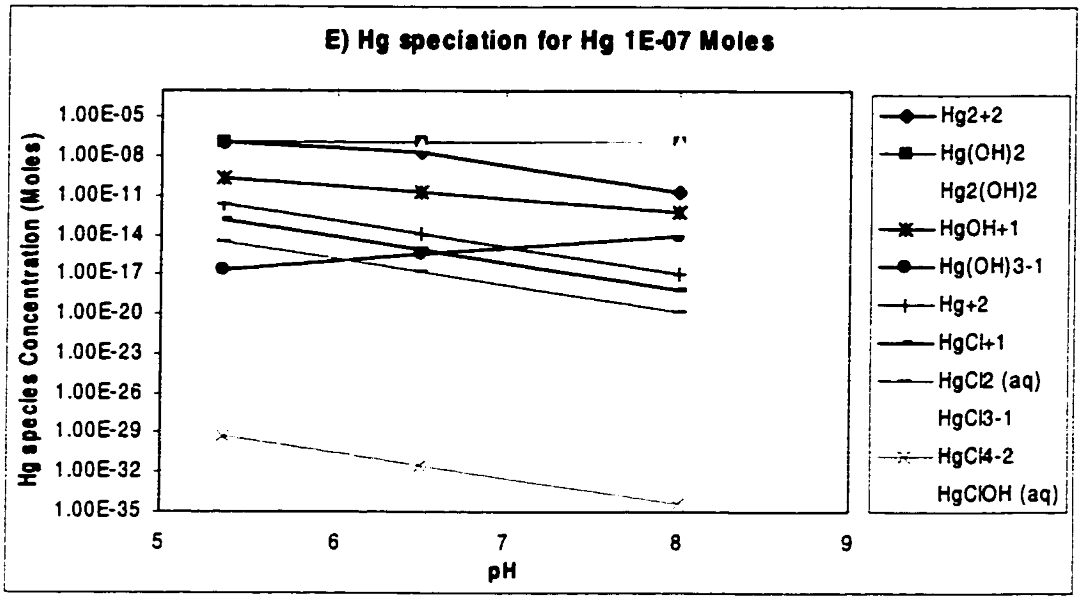
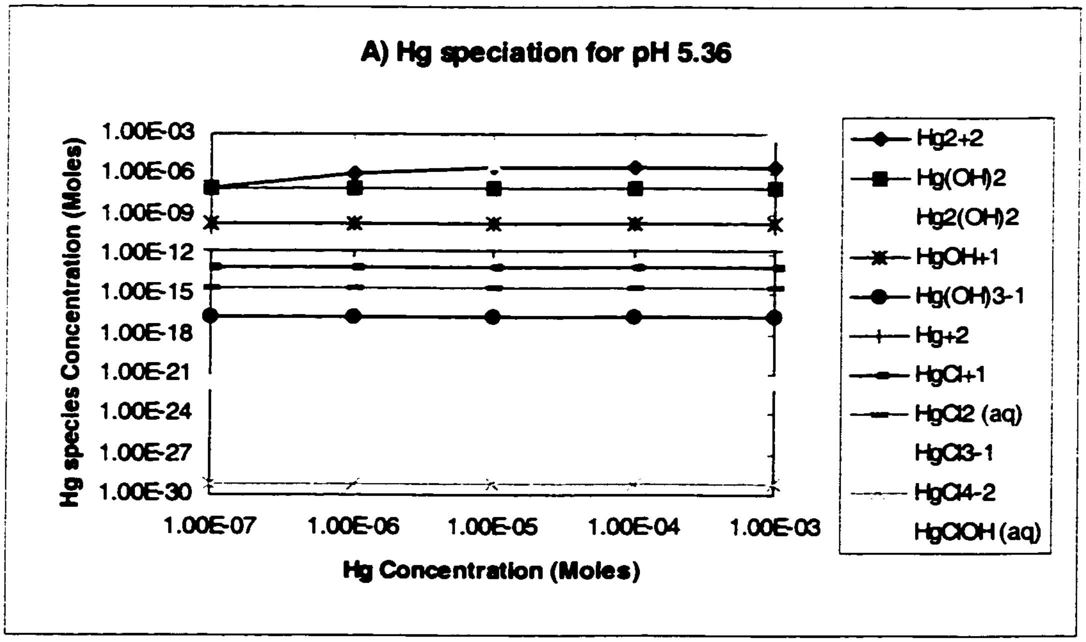
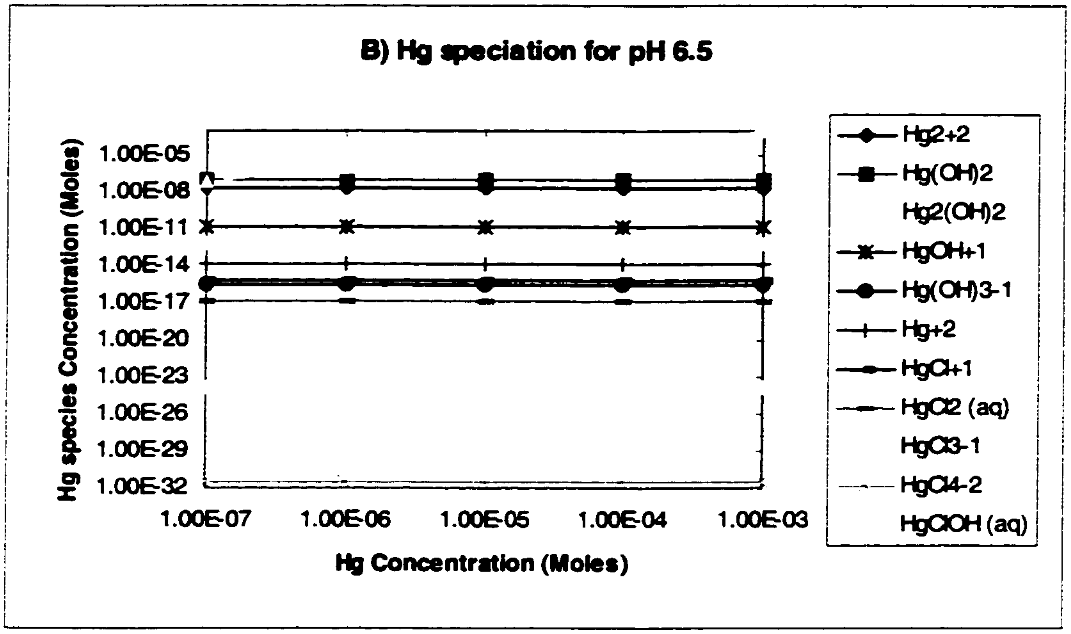
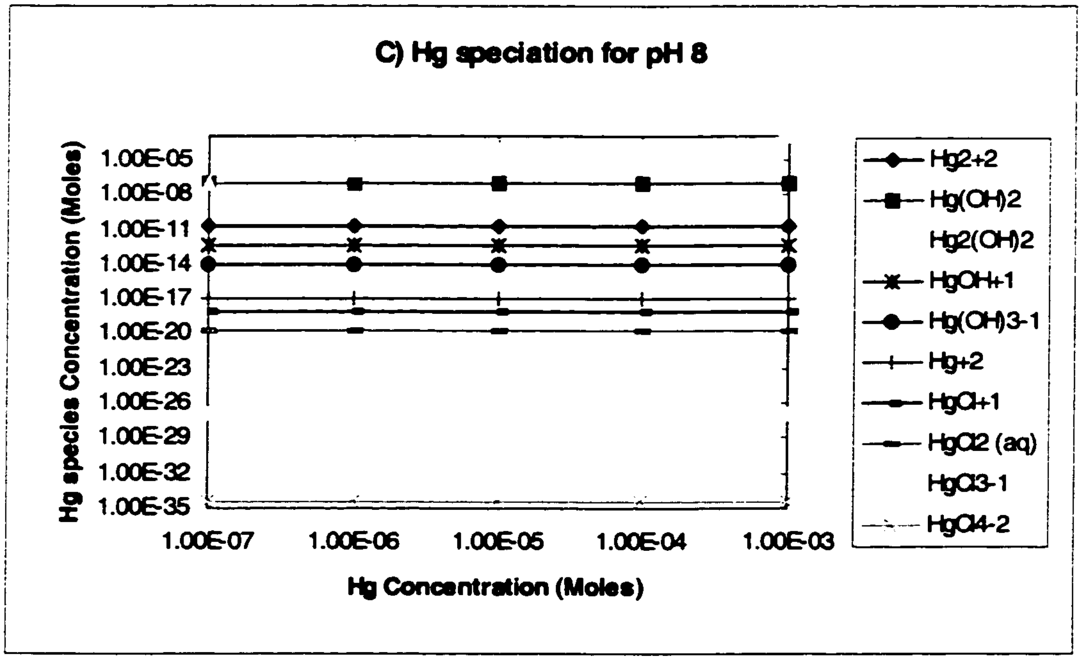


Figure 4.9 (E) Mercury compounds in solution that exist for an initial mercury concentration of 1 E-7 moles and different pH conditions.



Figures 4.10 (A) different mercury speciation in solution for pH values of 5.36





Figures 4.10 (B, C) Different mercury speciation in solution for pH values of 6.5 and 8

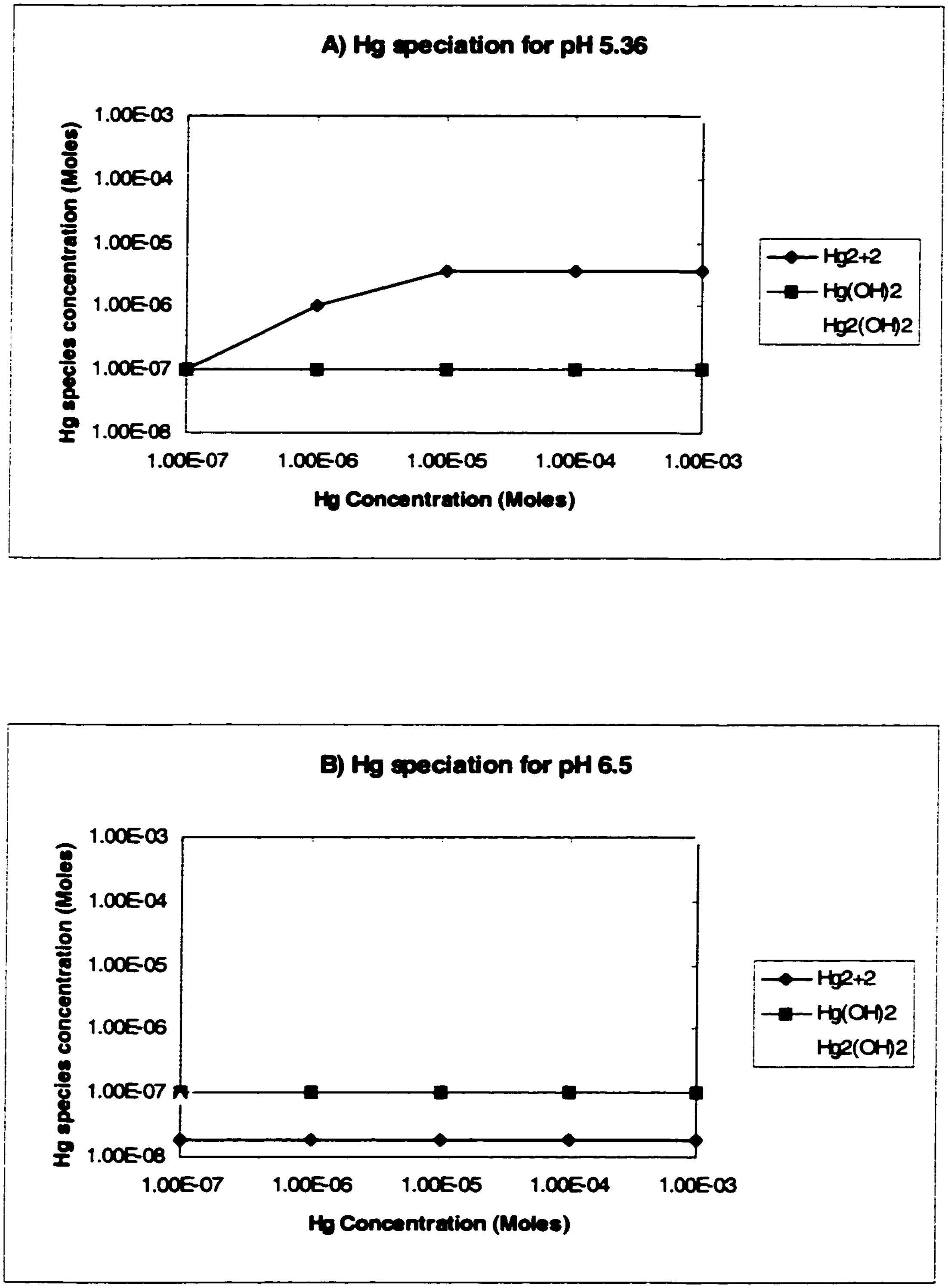


Figure 4.11 (A, B) distribution of $Hg_2^{+2}$, $Hg(OH)_2$, $Hg_2(OH)_2$ in solution for different initial mercury concentrations at the pH 5.36 and 6.5

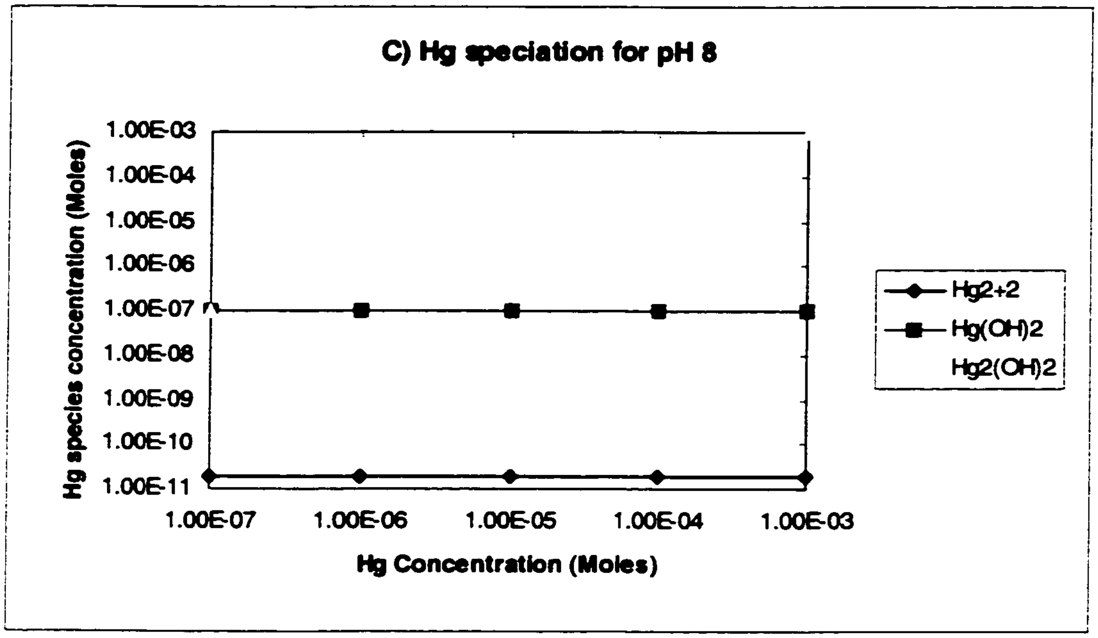


Figure 4.11 (C) distribution of $Hg_2^{+2}$, $Hg(OH)_2$, $Hg_2(OH)_2$ in solution for different initial mercury concentrations at pH 8

# CHAPTER 5

# CHARACTERISTICS OF MERCURY SORPTION ON SOILS

Water discharged to constructed wetlands engage in direct contacts with all particular components of the wetland. Mineral composition of the bottom sediments has an important impact on the dynamics of mercury cycle within the wetland. The adsorption phenomena appear to be a factor that governs mercury fate (Yong et al 1992). Therefore, this phenomenon has to be investigated to provide a basic information for modelling and subsequently for an accurate assessment and design.

Chapter five gives a theoretical review of modelling techniques currently used in modelling metal's sorption on soils. Detailed comparisons suggested that a Triple Layer Model would be most suitable to conduct a comprehensive parametric study of mercury sorption on soil surfaces. Factors affecting the sorption process such as solution pH (Andersson 1979 and Semu et al. 1987), the initial mercury concentration in solution (Yujun Yin et. al. 1997), particle's specific surface area (Di Toro et. al. 1986; Christensen 1989), and concentration of the adsorbent medium in solution (Thomann and Mueller 1987) are discussed thoroughly.

The current study suggests an estimate of the expected capacity of sediments to sorb mercury under numerous environmental conditions. In addition, the study simulates the mineral colloid suspension in water column that also has an important effect on the total amount of mercury adsorbed. It also shows a strong interrelation between mineral solid characteristics and mercury adsorption.

## 5.1 Modelling Metal's Sorption on Soil Surface

Metals sorption on soil surfaces can be modelled by computer software. MINTEQA2 developed by the USEPA incorporates various modelling theories for calculating metal's sorption on soil surfaces such as: 1) the activity $K_d$ model, 2) the activity Langmuir model, 3) the activity Freundlich model, 4) the ion exchange model, 5) the constant capacitance model, 6) the triple layer model, and 7) the diffuse-layer model (Allison et al 1991).

The general modelling approach is to create a component to represent a sorbing site and then to write reactions between other components and that site. When the equilibrium composition is determined, the equilibrated mass distribution between the dissolved, sorbed, and solid phases is computed and reported. The differences between any type of surfaces and between the sites on a surface are established by identifying the surface concentration, specific surface area, and reactions.

Developing a coherent system for characterising the surface sites and the species that pertain to them is an essential task. The notation frequently used in the literature for the electrostatic models seems to be primarily applicable to oxide surfaces. However, it does provide a coherent naming system, therefore "SOH" was used to designate a surface site throughout this chapter.

For the explanation and discussion of the adsorption models that follows, the simpler notation of SOH is used to designate a surface site and electrostatic terms are referred to in accepted notation of $\sigma$ and $\psi$ to represent surface charge and potential, respectively.

### 5.2 Non-Electrostatic Adsorption Models

Adsorption models reviewed could be grouped into those that involve electrostatic terms and those that do not. The non-electrostatic models have been in common use and certain conventions as to their use have become accepted (Morel, 1983). The specifics of each model are explained below.

#### 5.2.1 Activity $K_d$ Adsorption Model

For an adsorbing metal M, $K_d$ is conventionally defined as the ratio of the concentration of metal bound on the surface to total dissolved metal concentration at equilibrium. That is,

$$K_d = \quad [SOH{\cdot}M] \, / \, [M]_T \tag{5.1}$$

where [SOH•M] represents the concentration of adsorption sites occupied by an ion M or surface-bound metal and $[M]_T$ is the total dissolved equilibrium concentration of M.

In the activity $K_d$ model,

$$K_d^{act} = \{SOH{\cdot}M\} / \, \{M\} \tag{5.2}$$

where {M} is the free activity of M in the equilibrium solution. Following convention and because there is no generally accepted method of computing activity coefficients for unreacted or reacted adsorption sites, those coefficients were defined as unity so that {SOH-M} = [SOH-M]. Then in terms of concentrations, equation (5.2) becomes

$$K_d^{act} = [SOH{\cdot}M] / \, \gamma_m [M] \tag{5.3}$$

where $\gamma_m$ is the activity coefficient of dissolved species M and $K_d^{act}$ may be thought of as the equilibrium constant of the surface reaction

$$\mathrm{SOH} + \mathrm{M} \longleftrightarrow \mathrm{SOH{\cdot}M} \qquad (5.4)$$

SOH represents unreacted surface sites and is present at a fixed activity (or fixed concentration assuming that the activity coefficient pertaining to SOH is unity). Taking the activity of SOH as 1.0, equation (5.3) may be thought of as a mass action expression for reaction (5.4). The constraint is that there is an unlimited supply of unreacted sites; the surface cannot approach saturation no matter how much M adsorbs. This constraint also renders competition between different metals (M1, M2,...) meaningless. Equation (5.2) defines the equilibrium constant actually used for an activity $K_d$ reaction in the model. This value is calculated from the more common expression of $K_d$ in L/kg and solid concentration in kg/L (e.g., the number of kg of soil with which one liter of solution is equilibrated) (Allison et al 1991).

### 5.2.2 Activity Langmuir Adsorption Model

In the Langmuir adsorption model, the number of surface sites available for adsorption must be specified at the outset. The surface reaction can be written identically as for the activity $K_d$ model

$$\mathrm{SOH} + \mathrm{M} \longleftrightarrow \mathrm{SOH{\cdot}M} \qquad (5.5)$$

where the equilibrium constant in terms of activities is expressed by

$$K_L^{act} = \{\mathrm{SOH{\cdot}M}\} / \{\mathrm{M}\}\,\{\mathrm{SOH}\} \qquad (5.6)$$

When assigning the value of unity to the activity coefficients pertaining to unreacted and reacted surface sites, the mass action equation (5.6) could be written as

$$K_L^{act} = [\mathrm{SOH{\cdot}M}] / \gamma_m[\mathrm{M}]\,[\mathrm{SOH}] \qquad (5.7)$$

To understand the correspondence between this implementation of the Langmuir model and the defining equation to which that model is commonly described, the mass balance equation written for the surface sites is

$$[SOH]_T = [SOH{\cdot}M] + [SOH] \tag{5.8}$$

where $[SOH]_T$ = total concentration of surface sites available. The combined mass balance and mass action expressions yield the Langmuir relationship in terms of activities

$$[SOH{\cdot}M] = K_L^{act}\,[SOH]_T\,\gamma_m[M]\,/\,(1 + K_L^{act}\,\gamma_m[M]) \tag{5.9}$$

To express equation (5.9) in terms of concentrations, replace $K_L^{act}$ with $K_L$ and let $\gamma_m = 1$. The competitive Langmuir model for the competing metals M1, M2,... is derived in a similar manner with additional reactions defined:

$$SOH + M1 \longleftrightarrow SOH{\cdot}M1 \qquad K_{L1}^{act}$$

$$SOH + M2 \longleftrightarrow SOH{\cdot}M2 \qquad K_{L2}^{act}$$

$$SOH + Mn \longleftrightarrow SOH{\cdot}Mn \qquad K_{Ln}^{act}$$

Modeling such competition requires defining these separate reactions on the surface. The only difference between the Langmuir and activity $K_d$ models is that the Langmuir equation accounts for the finite concentration of surface sites. It is also important to mention that the $K_L$ used is an "activity" $K_L$ rather than the conventional concentration-based constant (Allison et al 1991).

### 5.2.3 Activity Freundlich Model

The mass action equation representing the Freundlich model can be written

$$SOH + \alpha M \longleftrightarrow SOH{\cdot}M \qquad K_f^{act} \tag{5.10}$$

$$K_f^{act} = \{SOH{\cdot}M\} / \{M\}\alpha\{SOH\} \tag{5.11}$$

Like the activity $K_d$ model, an unlimited supply of unreacted sites is assumed and the activity and concentration of surface species are considered to be equal. Imposing the condition {SOH} = 1.0.

$$[SOH{\cdot}M] = K_f^{act}\,\{M^{m+}\}^{\alpha} \qquad (5.12)$$

[SOH-M]: equilibrium concentration of reacted sites or surface-bound metal
{M}: equilibrium activity of the free metal species M
$\alpha$: mass action stoichiometric coefficient pertaining to M

This is similar to the activity $K_d$ relationship except that the stoichiometric coefficient of the reacting species M is $\alpha$. For the special case where $\alpha = 1$, the Freundlich and activity $K_d$ mass action equations are identical (the mass balance stoichiometry for M is 1.0, just as it is for the activity $K_d$ model, while the mass action stoichiometry is $\alpha$) (Allison et al 1991).

### 5.2.4 Ion Exchange Adsorption Model

Ion exchange sorption is defined as the process by which an ion from solution is exchanged for one on the solid surface. The relative abilities of solute ion species to compete for surface sites is governed by intrinsic factors and their solution activities. The ion exchange model assumes that the surface site is initially occupied by an exchangeable ion that is released into solution during the exchange process. The ion exchange reaction and its corresponding mass action equation can be expressed as

$$SOH{\cdot}M1 - M1 + M2 \longleftrightarrow SOH{\cdot}M2 \qquad (5.13)$$

$$K_{ex} = \{M1\}\,\{SOH{\cdot}M2\} \,/\, \{M2\}\,\{SOH{\cdot}M1\} \qquad (5.14)$$

where M1 is the ion initially occupying the exchange site, $M_2$ is the replacing ion to be adsorbed, and $SOH{\cdot}M_1$, $SOH{\cdot}M_2$ are surface sites occupied by the respective ions. As for the previous models, activity coefficients for the occupied sites are arbitrarily taken as unity and $K_{ex}$ is written in terms of concentrations by replacing activity of each species in equation (5.14) with the product of concentration and activity coefficient.

Selectivity coefficients ($K_{ex}$) can be derived from the literature for most common ions such as $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ , etc., but are seldom available for trace metals. In using the ion exchange algorithm, the reaction stoichiometries, selectivity constants and the ion that initially occupies the exchange sites must be supplied. The reaction stoichiometries may be related to ion charge. For example, a single $Ca^{2+}$ ion may replace two $Na^+$ ions and thus occupy two sites (Allison et al 1991).

### 5.3. Electrostatic Adsorption Models

All four adsorption models discussed thus far neglect the electrostatic influence of charged surfaces on the solution and the counter ions influence due to solution composition. Many colloidal particles carry a significant surface charge that creates electrostatic potentials extending into the suspending solutions. Solution ions with charge of the same polarity as the surface are repelled and ions of opposite charge are attracted. Because of this phenomenon, the electrostatic potentials associated with charged surfaces may greatly influence the adsorptive behaviour of charged species. This influence is incorporated in electrostatic adsorption models by including terms in the mass action equations that modify the activities of sorbate ions approaching charged surfaces by the electrical work necessary to penetrate the zone of electrostatic potential ($\psi$) present in vicinity of a particle.

Several models are available to account for these effects in various degrees of detail. Westall and Hohl (1980) provided a review for clear comparisons of presently available surface complexation/ electrostatic models.

Brief description of surface complexation models such as: the constant capacitance, diffuse-layer, and triple-layer models are reviewed in MINTEQA2 software (Allison et al 1991). These three models are closely related in many ways. Each treats adsorption as a surface complexation reaction (the reaction is treated as analogous to a solution phase complexation reaction governed by a mass action equation) and each accounts for the electrostatic potentials at the charged surface. They differ primarily in the types of surface species that are allowed within specific physical locations or layers extending away from the surface and in the parameters of the electrostatic model that each employs.

All models (the constant capacitance, diffuse-layer, and triple-layer) treat trace metal surface reactions as complexation reactions analogous to the formation of complexes in solution. Surface sites are represented as SOH groups where S is the metal associated with the solid structure and located at the solid-liquid interface. Some ions, such as $H^+$, $OH^-$, and a variety of trace metal ions are presumed to be specifically adsorbed at the surface via complexation with the surface sites. In all three models, a charge ($\sigma$) associated with the surface is assumed to be balanced by a charge ($\sigma_d$) associated with a diffuse layer of counterions. These charges are such that $\sigma + \sigma_d = 0$. In the constant capacitance and diffuse-layer models, all specifically adsorbed ions contribute to the surface charge ($\sigma$). However, in the triple-layer model, the net charge due to adsorption is the sum of the charges associated with two adsorbing planes rather than one. The innermost of the two planes (the o-plane) specifically adsorbs $H^+$ and $OH^-$ and is characterised by charge $\sigma_o$. The other plane ( $\beta$-plane) has charge $\sigma_\beta$ resulting from the adsorption of other ions. The net surface charge is given by $\sigma = \sigma_o + \sigma_\beta$ and is balanced by the charge in the diffuse layer such that $\sigma + \sigma_d = 0$. Because the electrical potential gradients extending away from the surface are the direct result of the surface charge, the specifically adsorbed potential determining ions also govern distributions of counter-ions in the diffuse layer.

Activities of ions in solution and near the surface are influenced by the presence of electrostatic potentials arising from the surface charge. The activity difference between ions near the surface and those far away is the result of electrical work in moving the ions across the potential gradient between the charged surface and the bulk solution. The activity change between these zones is related to the ion charge (z) and the electrical potential ($\psi$) near the surface and can be expressed using the exponential Boltzmann expression,

$$\{X_s^z\} = \{X^z\}\,[e^{-\psi F/RT}]^z \tag{5.15}$$

Where:

$z$ : charge of ion X
$\{X_s^z\}$: activity of an ion X of charge z near the surface
$\{X^z\}$: corresponding activity of X in bulk solution outside the influence of the charged surface
$e^{-\psi F/RT}$: Boltzmann factor
F: Faraday constant
R: ideal gas constant
T: absolute temperature

### 5.3.1 General Algorithms of the Electrostatic Models

The general algorithm is similar for all three of the electrostatic models. Specific details for each model are discussed separately below. As mentioned below, for the constant capacitance and diffuse-layer models, there is only one layer or plane within which specifically adsorbed ions define the surface charge $\sigma$. Accordingly, that plane is commonly referred to as the o-plane and the surface charge and potential are denoted $\sigma_o$

and $\psi_o$. These notations as well as the notations $\sigma_d$ and $\psi_d$ , will be retained for their counterparts in the diffuse layer. The o-plane is defined differently in the triple layer model and those parameters subscripted with "o" in that model should not be regarded as equivalent to the o-plane parameters of the former two models. Also, with regard to the constant capacitance and diffuse-layer models, $\sigma_o$ and $\psi_o$ are referred to as "surface" charge and "surface" potential. This is not true of the triple-layer model because there are two planes ("o" and "$\beta$") associated with the surface. Thus, the charge at the beginning of the diffuse layer is defined in terms of $\sigma_o + \sigma_\beta$ .

The Boltzmann factor of equation (5.15), with the potential $\psi$ subscripted to indicate the layer to which it applies, is incorporated as a scaling factor by assigning it a component number and writing the surface reaction so as to include it as a reactant of appropriate stoichiometry. It is only a mathematical way to incorporate the parameters of the desired model into the computational scheme. The mass action equations for surface reactions will contain those components (referred to as electrostatic components) that are really the Boltzmann factors. The term $T_\sigma$ is used to refer to a specific plane as the total charge for that plane but note that it does not imply a measured input value. Also, MINTEQA2 (Allison et al 1991) will seek to perform mass balance calculations on all components. It is necessary, therefore, to direct otherwise for the electrostatic components by excluding them from the mass balance calculations. Charge balance equations that are analogous to mass balance are defined for the electrostatic components and have the form

$$Y_\sigma = \Sigma\ a_{i\sigma}C_i - T_\sigma \tag{5.16}$$

where $a_{i\sigma}$ is the stoichiometry of the electrostatic component pertaining to $\sigma$ in species i. The overall approach of the electrostatic calculations for a given plane is:

1) Calculate the total charge $T_\sigma$ from the potential on the plane by using a functional relationship appropriate for the model. Initial guesses for the potential of each plane are provided in the input file.

2) Calculate the total charge on the plane by a different method, namely, by summing the charges of all species specifically adsorbed on that plane. Operationally, this becomes a summation of the charge contribution from all species in which the stoichiometry of the component representing the plane is non-zero ($\Sigma\ a_{i\sigma}C_l$).

3) Obtain the difference in the total charge pertaining to the plane as in equation (5.16). Test whether the difference is less than some small tolerance value. If not, adjust the potential for that plane and repeat. The potentials are always adjusted simultaneously with the activities of other components. Calculations involving the surface sites themselves are exactly as described for other real chemical entities by the mass action equations and mass balance equations.

The activity coefficients of both the reacted and unreacted surface sites are taken as unity. As some components have been created to represent the Boltzmann factors, activity coefficients for them have to be created as well. Imaginary though they be, it is possible to make them innocuous by setting them to unity.

All surface reactions in MINTEQA2 are written in terms of the neutral surface site SOH and the equilibrium constants appropriate for MINTEQA2 are formation constants. The constants for many reactions found in the literature are intrinsic constants, which sometimes are referenced to the protonated surface site $SOH_2^+$ (for adsorbing anions) and to the deprotonated site $SO^-$ (for adsorbing cations). Such reactions must be re-written in terms of MINTEQA2 components and their equilibrium constants adjusted accordingly. The surface reactions, which are generally model specific, must be provided to MINTEQA2 through its input file. The correct stoichiometry for the electrostatic components of surface reactions that are created for an input file, are computed automatically.

The analytical input concentration for the surface site, $T_{SOH}$, is expressed in moles of sites per litre and is calculated from

$$T_{SOH} = N_s \, S_A \, C_s \, / \, N_A \tag{5.17}$$

Where:

$N_s$: the analytically determined surface site density (number of sites/$m^2$)
$S_A$: specific surface area of the solid ($m^2/g$)
$C_s$: concentration of solid in the suspension (g/L)
$N_A$: Avogadro's number ($6.02 \times 10^{23}$)

### 5.3.2 Constant Capacitance and Diffuse-Layer Models

The constant capacitance and diffuse-layer models have many similarities. Both define specific adsorption of all ions on the "o" plane. Also, their mass action and charge balance equations are identical (except for the numerical value of the equilibrium constants). The difference in these two models is in the function relating total surface charge $\sigma_o$ to surface potential o. For the diffuse-layer model

$$T_{\sigma o} = 0.1174 \; I^{1/2} \; \sinh(Z\psi_o F/2RT) \tag{5.18}$$

where Z is the valency of the symmetrical electrolyte (which was taken as unity), I is ionic strength, and all other parameters are defined as in equation (5.15). This expression is used in evaluating equation (5.16) (Allison et al 1991).

The constant capacitance model is a special case of the diffuse-layer model for solutions of high ionic strength and surfaces of low potential. In such systems, equation (5.18) can be approximated by

$$T_{\sigma o} \cong C_{cap}\psi_o \tag{5.19}$$

where $C_{cap}$ is a constant capacitance term. Equation (5.19) is used to evaluate equation (5.16) for the constant capacitance model. Although the models are similar in implementation, the capacitance term $C_{cap}$ is often treated as a fitting parameter rather than as a measured characteristic of the system and the constant capacitance model can be applied to systems of all ionic strengths. Outside the range of ionic strength where the approximation of equation (5.19) is valid, the constant capacitance and diffuse-layer models are not the same.

As mentioned, the assignment of specifically adsorbed species to the o-plane, the mass action equations, and the charge balance equations for the constant capacitance and diffuse-layer models are the same. Figure 5.1 shows a conceptual structure of an oxide surface as represented by either of these two models. The discussion of surface reactions that follows applies to either model.

Surface reactions are represented by mass action expressions with Boltzmann factors represented as components, see equation (5.15). Stoichiometries of those components are included in the definition of surface reactions provided. Following are some examples of such reactions and their corresponding mass action expressions to illustrate the use of Boltzmann factors.

For the protonation reaction

$$SOH + H_s^+ \longleftrightarrow SOH_2^+ \tag{5.20}$$

where $H_s^+$ denotes a hydronium ion near the surface. The corresponding mass action expression is

$$K = \{SOH_2^+\} / \{SOH\}\{H_s^+\} \qquad (5.21)$$

As mentioned previously, the surface species are presumed to have activity coefficients equal to unity and the terms $\{SOH_2^+\}$ and $\{SOH\}$ need no further conversion; however, the activity of the surface hydronium ions must be corrected for the energy expended in moving them to the charged surface where the reaction occurs. This is accomplished by expressing $\{H_s^+\}$ in terms of the bulk solution hydronium ion activity $\{H^+\}$. In this case, $Z = 1$ and equation (5.15) is written

$$\{H_s^+\} = \{H^+\} e^{-\psi_o F/RT} \qquad (5.22)$$

The mass action expression used in the calculation is obtained by substituting this expression into equation (5.21).

$$K = \{SOH_2^+\} / \{SOH\}\{H^+\} e^{-\psi_o F/RT} \qquad (5.23)$$

With the Boltzmann factor incorporated as a component, the stoichiometry for this reaction in MINTEQA2 corresponds to:

$$SOH + H^+ + e^{-\psi_o F/RT} \longleftrightarrow SOH_2^+ \qquad (5.24)$$

For the corresponding de-protonation reaction

$$SOH - H_s^+ \longleftrightarrow SO^- \qquad (5.25)$$

and its mass action expression

$$K = \{SO^-\}\{H^+\}[e^{-\psi_o F/RT}] / \{SOH\} \qquad (5.26)$$

The stoichiometry in MINTEQA2 corresponds to:

$$SOH - H^+ - e^{-\psi_o F/RT} \longleftrightarrow SO^- \qquad (5.27)$$

For multivalent species, both charge and stoichiometry of the adsorbing ion must be considered in writing the mass action expression.

For the surface reaction involving the divalent cation $M^{2+}$

$$SOH + M_s^{2+} - H_s^+ \longleftrightarrow SO{\cdot}M^+ \tag{5.28}$$

The corresponding mass action expression is

$$\begin{aligned} K &= \{SO{\cdot}M^+\}\,\{H_s^+\} \,/\, \{SOH\}\,\{M_s^{2+}\} \\ &= \{SO{\cdot}M^+\}\,\{H^+\}\,[e^{-\psi_o F/RT}] \,/\, \{SOH\}\,\{M^{2+}\}\,[e^{-\psi_o F/RT}]^2 \\ &= \{SOH_2^+\} / \{SOH\}\,\{H^+\} e^{-\psi_o F/RT} \end{aligned} \tag{5.29}$$

In this case, the Boltzmann factor in the numerator can be canceled and the stoichiometry in MINTEQA2 corresponds to:

$$SOH + M^{2+} - H^+ + e^{-\psi_o F/RT} \longleftrightarrow SO{\cdot}M^+ \tag{5.30}$$

Mass action expressions for other surface reactions are formulated in a similar manner. In addition to the surface reactions with their equilibrium constants and the parameters of equation (5.17), the constant capacitance model requires an input value for the capacitance, ($C_{cap}$). This is the capacitance (Farads/m$^2$) between the o-plane and the diffuse layer of counter-ions (Allison et al 1991).

### 5.3.3 Triple-Layer Model

The triple-layer model is generally more complex than the constant capacitance and diffuse-layer models. In the MINTEQA2 (Allison et al 1991) implementation of the triple-layer model, only protonation and deprotonation of surface sites are assigned to the o-plane. Other specifically adsorbed ions are assigned to the β-plane and determine the charge $\sigma_\beta$ and potential $\psi_\beta$ in that zone. Non-specifically adsorbed ions are envisioned as residing in the diffuse layer or "d" plane and are influenced by $\psi_d$ potentials. The capacitance between the o-plane and the β-plane is denoted $C_{cap1}$ and between the β-plane and d-plane, $C_{cap2}$. The potential gradients in the inner and outer zones are linear, but potentials decay exponentially in the diffuse layer zone. A schematic diagram of the triple layer model surface is shown in Figure 5.2.

Total charges associated with the triple-layer model o-, β-, and d- planes are related to the potential differences between planes.

$$T_{\sigma o} = C_{cap1} ( \psi_o - \psi_\beta ) \tag{5.31}$$

$$T_{\sigma\beta} = C_{cap1} (\psi_\beta - \psi_o) + C_{cap2} (\psi_\beta - \psi_d) \tag{5.32}$$

$$T_{\sigma d} = C_{cap2} (\psi_d - \psi_\beta ) \tag{5.33}$$

Where:

| | |
|---|---|
| $T_{\sigma o}$ , $T_{\sigma\beta}$ , and $T_{\sigma d}$: | total charges associated with the o-, β -, and d-planes |
| $C_{cap1}$ and $C_{cap2}$: | capacitances associated with the zones between the o- and β-planes and d-planes, respectively |
| $\psi_o$, $\psi_\beta$ , and $\psi_d$ : | electrostatic potentials at the o-, β -, and d-planes |

The total charge on the o- and β- planes are used in equation (5.16) along with the summation of species that are specifically adsorbed on each plane and have non-zero stoichiometry in the appropriate electrostatic component.

Recalling that the d-plane has no specifically adsorbed ions and thus has zero stoichiometry in all species, equation (5.16) for this plane only is replaced with

$$Y_{\sigma d} = \sigma_d - T_{\sigma d} \tag{5.34}$$

where the diffuse layer charge ($\sigma_d$) for a monovalent symmetric electrolyte is given by the Gouy-Chapman relationship:

$$\sigma_d = - (\varepsilon\varepsilon_o RIT)^{1/2} \sinh(F\psi_d/2RT) \tag{5.35}$$

Where:

$\varepsilon$ : dielectric constant
$\varepsilon_o$: permittivity in free space (8.85 x $10^{-12}$ (coulombs)$^2$/joule-m
I : ionic strength

Surface reactions in the triple layer model are represented in a manner similar to the other two electrostatic models except that mass action expressions must have the proper stoichiometry for the electrostatic component representing the $\beta$-plane as well as the o-plane. No stoichiometry is needed for the d-plane because no specific adsorption occurs on that plane.

The following surface reactions and mass action expressions illustrate the determination of stoichiometric coefficients for those components.

For the monovalent metal ion $M^+$

$$SOH - H_s^+ + M_s^+ \longleftrightarrow (SO\bullet M) \qquad (5.36)$$

With the substitution for $H_s^+$

$$\{H_s^+\} = \{H^+\}e^{-\psi_o F/RT} \qquad (5.37)$$

as in equation (5.15), and a similar substitution for the metal ion near the surface (except the effective potential refers to the $\beta$-plane because that is where $M^+$ is specifically adsorbed).

$$\{M_s^+\} = \{M^+\}e^{-\psi_\beta F/RT} \qquad (5.38)$$

The mass action expression is

$$K = \{SO\bullet M\}\ \{H^+\}\ [e^{-\psi_o F/RT}] \ / \ \{SOH\}\ \{M^+\}\ [e^{-\psi_\beta F/RT}] \qquad (5.39)$$

The reaction written in terms of MINTEQA2 components and including the electrostatic components is

$$SOH - H^+ - e^{-\psi_o F/RT} + M^+ + e^{-\psi_\beta F/RT} \longleftrightarrow SO{\cdot}M \qquad (5.40)$$

For a surface reaction involving a divalent metal, $M^{2+}$

$$SOH - H_s^+ + M_s^{2+} \longleftrightarrow (SO{\cdot}M)^+ \qquad (5.41)$$

The substitution of equation (5.37) together with

$$\{M_s^{2+}\} = \{M^{2+}\}\ [e^{-\psi_\beta F/RT}]^2 \qquad (5.42)$$

provides the mass action expression

$$K = \{SO{\cdot}M^+\}\ \{H^+\}\ [e^{-\psi_o F/RT}] /\ \{SOH\}\ \{M^{2+}\}\ [e^{-\psi_\beta F/RT}]^2 \qquad (5.43)$$

The corresponding reaction in MINTEQA2 is

$$SOH - H^+ - e^{-\psi_o F/RT} + M^{2+} + 2\ e^{-\psi_\beta F/RT} \longleftrightarrow SO{\cdot}M^+ \qquad (5.44)$$

The combined hydrolysis/sorption reaction for an $M^{2+}$ ion is expressed

$$SOH + M_s^{2+} + H_2O - 2H_s^+ \longleftrightarrow SO{\cdot}MOH \qquad (5.45)$$

and the corresponding mass action expression is written

$$K = \{SO{\cdot}MOH\}\ \{H^+\}^2\ [e^{-\psi_o F/RT}]^2 / \{SOH\}\ \{M^{2+}\}\ \{H_2O\}\ [e^{-\psi_\beta F/RT}]^2 \qquad (5.46)$$

The corresponding MINTEQA2 reaction is

$$SOH + M^{2+} + 2\ e^{-\psi_\beta F/RT} + H_2O - 2H^+ - e^{-\psi_o F/RT} \longleftrightarrow SO{\cdot}M^+ \qquad (5.47)$$

For the reaction of a monovalent anion ($A^-$), a neutral surface species can result

$$SOH + A_s^- + H_s^+ \longleftrightarrow SOH_2{\cdot}A \qquad (5.48)$$

With the substitution,

$$\{A_s^-\} = \{A^-\}\ [e^{-\psi_\beta F/RT}]^{-1} \qquad (5.49)$$

the mass action expression is

$$K = \{SOH_2{\cdot}A\}\ [e^{-\psi_\beta F/RT}] / \{SOH\}\ \{A^-\}\ \{H^+\}\ [e^{-\psi_o F/RT}] \qquad (5.50)$$

and the reaction in MINTEQA2 is written

$$SOH + A^{-} - e^{-\psi_{\beta}F/RT} + H^{+} + e^{-\psi_{o}F/RT} \longleftrightarrow SOH_2{\cdot}A \qquad (5.51)$$

Finally, for a divalent anion,

$$SOH + A_s^{2-} + H_s^{+} \longleftrightarrow SOH_2{\cdot}A^{-} \qquad (5.52)$$

the mass action expression is

$$K = \{SOH_2{\cdot}A^{-}\}\,[e^{-\psi_{\beta}F/RT}]^2 / \{SOH\}\,\{A^{2-}\}\,\{H^{+}\}\,[e^{-\psi_{o}F/RT}] \qquad (5.53)$$

The reaction in MINTEQA2 is written

$$SOH + A^{2-} - 2\,e^{-\psi_{\beta}F/RT} + H^{+} + e^{-\psi_{o}F/RT} \longleftrightarrow SOH_2{\cdot}A^{-} \qquad (5.54)$$

After the adsorption reactions, in terms of MINTEQA2 components being defined, the appropriate electrostatic components at the correct stoichiometry would be added automatically.

The triple layer model was adopted to investigate mercury behaviour within the wetland.

## 5.4 Parametric Study

The design of constructed wetlands can consider local material availability but also can incorporate those materials that will optimise metal removal from water. Variability of soil structure can promote the adsorption of particular mercury forms and/or can have more bioavailable forms for natural uptake by plants. In this context a parametric study was performed to investigate four different types of soil structure representing: kaolinite, glokonite, bentonite and natural soil.

The uptake of mercury by plants and mercury distribution and transport are affected by the mass of solid material suspended in the water column. Consequently, the study included the presence of some suspended materials in the water column.

Initial Hg concentration, pH of the solution, and the concentration of the adsorbent medium (soil) in solution can also affect the characteristics of mercury sorption on soil surfaces. In this part, the effect of each of these parameters will be analysed while all other factors pertaining to the soil and equilibrium solution remain constant throughout the model runs.

The philosophy adopted in formulating a model to represent all different factors mentioned above, could be summarised as follows:

1. Three different adsorbent concentrations (suspension, sediments, and lighter sediments) were considered for the first soil type (kaolinite representing the lowest SSA).
2. For each of the resulting three cases, the effect of three values of pH (5.35 to 8.0) was then investigated.
3. For the same three cases (resulting from step 1), the effect of five initial mercury concentrations (1E-7 to 1E-3 moles) was then studied.

Similar procedures were followed to create the required input files for natural soil (representing almost twice the SSA of kaolinite), glokonite (representing five times higher SSA than kaolinite), and bentonite (representing 17 times higher SSA than kaolinite) resulting in a grand total of 96 input files. A comprehensive layout of the scenarios investigated is represented below (tables 5.1 through 5.4).

Table 5.1: Effect of pH Variation on Mercury Sorption for Different Adsorbent Concentrations, Soil Types, and Initial Mercury Concentration in Solution.

| | **Adsorbent Concentration (mg/L)** | **Soil type represented by specific surface area ($m^2/g$)** | **Initial mercury concentration (moles)** |
|---|---|---|---|
| Effect of pH variation on mercury sorption | 10000 (Sediments) | Kaolinite (80) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Natural Soil (129) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Glokonite (400) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Bentonite (1350) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | 8174 (Light sediments) | Kaolinite (80) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Natural Soil (129) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Glokonite (400) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Bentonite (1350) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | 10 (Suspended material) | Kaolinite (80) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Natural Soil (129) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Glokonite (400) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Bentonite (1350) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |

Table 5.2: Effect of Initial Mercury Concentration on Mercury Sorption for Different Adsorbent Concentration, Soil Type, and Solution's pH Values.

| | **Adsorbent Concentration (mg/L)** | **Soil type represented by specific surface area ($m^2/g$)** | **pH values** |
|---|---|---|---|
| Effect of initial mercury concentration on mercury sorption | 10000 (Sediments) | Kaolinite (80) | 5.36, 6.5, and 8.0 |
| | | Natural Soil (129) | 5.36, 6.5, and 8.0 |
| | | Glokonite (400) | 5.36, 6.5, and 8.0 |
| | | Bentonite (1350) | 5.36, 6.5, and 8.0 |
| | 8174 (Light sediments) | Kaolinite (80) | 5.36, 6.5, and 8.0 |
| | | Natural Soil (129) | 5.36, 6.5, and 8.0 |
| | | Glokonite (400) | 5.36, 6.5, and 8.0 |
| | | Bentonite (1350) | 5.36, 6.5, and 8.0 |
| | 10 (Suspended material) | Kaolinite (80) | 5.36, 6.5, and 8.0 |
| | | Natural Soil (129) | 5.36, 6.5, and 8.0 |
| | | Glokonite (400) | 5.36, 6.5, and 8.0 |
| | | Bentonite (1350) | 5.36, 6.5, and 8.0 |

Table 5.3: Effect of Soil Type (Represented by Specific Surface Area) on Mercury Sorption for Different Adsorbent Concentration, Solution's pH Values, and Initial Mercury Concentration.

| | **Adsorbent Concentration (mg/L)** | **pH of the solution** | **Initial mercury concentration (moles)** |
|---|---|---|---|
| Effect of soil type represented by specific surface area on mercury sorption | 10000 (Sediments) | 5.36 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | 6.5 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | 8.0 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | 8174 (Light sediments) | 5.36 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | 6.5 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | 8.0 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | 10 (Suspended material) | 5.36 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | 6.5 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | 8.0 | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |

Table 5.4: Effect of Adsorbent Medium Concentration on Mercury Sorption for Different Solution's pH Values, Soil Type, and Initial Mercury Concentration.

| | **pH of the solution** | **Soil type represented by specific surface area ($m^2/g$)** | **Initial mercury concentration (moles)** |
|---|---|---|---|
| Effect of adsorbent medium concentration on mercury sorption | 5.36 | Kaolinite (80) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Natural Soil (129) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Glokonite (400) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Bentonite (1350) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | 6.5 | Kaolinite (80) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Natural Soil (129) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Glokonite (400) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Bentonite (1350) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | 8.0 | Kaolinite (80) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Natural Soil (129) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Glokonite (400) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |
| | | Bentonite (1350) | 1E-3 ,1E-4, 1E-5, 1E-6, and 1E-7 |

The input files were then processed by MINTEQA2 using the Triple Layer Model described in section 5.3.3. The following are the four major species that were considered in the output:

- $=1SO^-$, concentration of the negative sorbing sites still available on the soil surface (moles).
- $=1SOH_2^+$, concentration of the positive sorbing sites still available on the soil surface (moles).

- =1SOHG, concentration of the sorbing sites adsorbing mercury (moles).
- =1SOH$_2$Cl, concentration of the sorbing sites adsorbing chloride (moles).

Influences of each suggested factor on mercury sorption on soils are discussed in the following sections.

### 5.4.1 Effect of pH Variation on Mercury Sorption

The pH values of the equilibrium solution usually affect the sorption process and amount of sorbed material. In a following section the effect of pH on sorption will be studied and discussed. The values of pH chosen for this analysis are: 5.36, 6.5, and 8, the same values used in chapter 4 to perform the analysis of mercury speciation in the water column. The value 5.36 represents the actual pH of mercury solution used in the experimental solution. The range of the values chosen in the analysis ensures that the plants can survive and the environment does not inhibit the growing process.

Three values for the adsorbent medium concentrations were considered: a) 10,000 mg/L representing sediments, b) 8,174 mg/L representing light sediments, and c) 10 mg/L representing solid material suspended in the water column. These values were applied to investigate the effect of pH variation for four different soils: a) kaolinite (Specific Surface Area: 80 m$^2$/g), b) natural soil (SSA: 129 m$^2$/g), c) glokonite (SSA: 400 m$^2$/g), and d) bentonite (SSA: 1350 m$^2$/g). The initial mercury concentration in solution varied from 1E-3 to 1E-7 moles, all other factors remain unchanged.

The results obtained show the relationship between mercury sorption on soil surface as a function of pH for different adsorbent medium concentration, the specified range of initial mercury concentration in solution, and different Specific Surface Areas (soils), (Table 5.5).

As pH increased from 5.36 to 8.00 -in the case of kaolinite, sediment, and initial mercury concentration of 1E-3 moles- the concentration of =1SOHG have increased from 2.91 E-8 to 1.9E-6 moles. The rate of increase was however different. As the pH changes from 5.36 to 6.5, the rate of increase in the adsorbed amount is 1.57 E-7 moles per pH unit, while the increase of pH from 6.5 to 8 causes a rate of increase of 1.13 E-6 moles per pH unit suggesting that a slightly basic solution increases the sorption on the soil surface by almost one fold, (Figure 5.3). For the lowest initial mercury concentration of 1E-7 moles, as pH increased from 5.36 to 8.00, the concentration of =1SOHG have increased from 2.24 E-10 to 1.86 E-8 moles. As the pH changes from 5.36 to 6.5, the rate of increase in the adsorbed amount is 1.21 E-9 moles per pH unit, while the increase of pH from 6.5 to 8 causes a rate of increase of1.13 E-8 moles per pH unit suggesting that a slightly basic solution increases the sorption on the soil surface by almost one fold at the lowest initial mercury concentration used, (Figure 5.4). The behaviour of kaolinite sediments for the intermediate initial mercury concentrations are shown in Figures 1 through 3, appendix B.

For natural soil (Figures 5.5, 5.6, and Figures 4, 5, 6 appendix B), glokonite (Figures 5.7, 5.8, and Figures 7, 8, 9 appendix B), and bentonite (Figures 5.9, 5.10 and Figures 10, 11, 12 appendix B) similar trends, but different rates were observed.

Table 5.5: Effect of pH on Mercury Sorption

| **Adsorbent concentration (mg/L)** | **Initial concentration (moles)** | **Type of sediment** | **Concentration of =1SOHG min/max pH (moles)** | **Rate of increase (moles / pH unit)** | |
|---|---|---|---|---|---|
| | | | | **5.36-6.5** | **6.5-8** |
| 10,000 | $1E10^{-3}$ | K | 2.91E-8 / 1.96E-6 | 1.57E-7 | 1.13E-6 |
| | | N | 3.58E-8 / 2.06E-6 | 2.00E-7 | 1.20E-6 |
| | | G | 4.18E-8 / 2.46E-6 | 3.11E-7 | 1.37E-6 |
| | | B | 4.05E-8 / 2.73E-6 | 3.67E-7 | 1.51E-6 |
| | $1E10^{-4}$ | K | 7.55E-9 / 6.09E-7 | 4.07E-8 | 3.70E-7 |
| | | N | 9.66E-9 / 6.57E-7 | 5.24E-8 | 3.91E-7 |
| | | G | 1.32E-8 / 7.89E-7 | 8.87E-8 | 4.5E-7 |
| | | B | 1.34E-8 / 8.99E-7 | 1.17E-7 | 5.01E-7 |
| | $1E10^{-5}$ | K | 2.26E-9 / 1.93E-7 | 1.22E-8 | 1.18E-7 |
| | | N | 2.91E-9 / 2.07E-7 | 1.57E-8 | 1.24E-7 |
| | | G | 4.13E-9 / 2.49E-7 | 2.7E-8 | 1.43E-7 |
| | | B | 4.26E-9 / 2.85E-7 | 3.67E-8 | 1.59E-7 |
| | $1E10^{-6}$ | K | 7.10E-10 / 6.07E-8 | 3.83E-9 | 3.71E-8 |
| | | N | 9.14E-10 / 6.51E-8 | 4.92E-9 | 3.90E-8 |
| | | G | 1.30E-9 / 7.78E-8 | 8.47E-9 | 4.45E-8 |
| | | B | 1.35E-9 / 8.88E-8 | 1.16E-8 | 4.95E-8 |
| | $1E10^{-7}$ | K | 2.24E-10 / 1.86E-8 | 1.21E-9 | 1.13E-8 |
| | | N | 2.89E-10 / 1.99E-8 | 1.55E-9 | 1.19E-8 |
| | | G | 4.11E-10 / 2.36E-8 | 2.66E-9 | 1.34E-8 |
| | | B | 4.26E-10 / 2.68E-8 | 3.63E-9 | 1.48E-8 |
| 8,174 | $1E10^{-3}$ | K | 2.62E-8 / 1.83E-6 | 1.41E-7 | 1.10E-6 |
| | | N | 3.31E-8 / 1.99E-6 | 1.81E-7 | 1.17E-6 |
| | | G | 4.18E-8 / 2.39E-6 | 2.93E-7 | 1.35E-6 |
| | | B | 4.07E-8 / 2.70E-6 | 3.62E-7 | 1.50E-6 |
| | $1E10^{-4}$ | K | 6.73 E-9 / 5.92E-7 | 3.67 E-8 | 3.62E-7 |
| | | N | 8.75E-9 / 6.36E-7 | 4.71E-8 | 3.82E-7 |
| | | G | 1.29E-8 / 7.65E-7 | 8.19E-8 | 4.39E-7 |
| | | B | 1.34E-8 / 8.85E-7 | 1.14E-7 | 4.94E-7 |
| | $1E10^{-5}$ | K | 2.01E-9 / 1.88 E-7 | 1.10E-8 | 1.16E-7 |
| | | N | 2.63E-9 / 2.01E-7 | 1.41E-8 | 1.22E-7 |
| | | G | 4.00E-9 / 2.41E-7 | 2.48E-8 | 1.39E-7 |
| | | B | 4.27E-9 / 2.80E-7 | 3.57E-8 | 1.57E-8 |
| | $1E10^{-6}$ | K | 6.32E-10 / 5.92 E-8 | 3.46E-9 | 3.64E-8 |
| | | N | 8.25E-10 / 6.31E-8 | 4.43E-9 | 3.82E-8 |
| | | G | 1.26E-9 / 7.55E-8 | 7.80E-9 | 4.35E-8 |
| | | B | 1.35E-9 / 8.74E-8 | 1.12E-8 | 4.89E-8 |
| | $1E10^{-7}$ | K | 2.00E-10 / 1.81E-8 | 1.09E-9 | 1.11E-8 |
| | | N | 2.61E-10 / 1.93 E-8 | 1.39E-9 | 1.16E-8 |
| | | G | 3.99E-10 / 2.29E-8 | 2.45E-9 | 1.31E-8 |
| | | B | 4.27E-10 / 2.64E-8 | 3.52E-9 | 1.46E-8 |

| Adsorbent concentration (mg/L) | Initial concentration (moles) | Type of sediment | Concentration of =1SOHG min/max pH (moles) | Rate of increase (moles / pH unit) | |
|---|---|---|---|---|---|
| | | | | 5.36-6.5 | 6.5-8 |
| 10 | $1E10^{-3}$ | K | 5.49E-9 / 3.79E-7 | 4.01E-8 | 2.18E-7 |
| | | N | 5.55E-9 / 4..93E-7 | 4.30E-8 | 2.92E-7 |
| | | G | 5.69E-9 / 8.18E-7 | 4.73E-8 | 5.05E-7 |
| | | B | 5.03E-8 / 7.24E-7 | 5.03E-8 | 7.24E-7 |
| | $1E10^{-4}$ | K | 1.66E-9 / 2.20E-7 | 1.42E-8 | 1.35E-7 |
| | | N | 1.67E-9 / 2.68 E-7 | 1.45E-8 | 1.67E-7 |
| | | G | 1.70E-9 / 3.76E-7 | 1.51E-8 | 2.38E-7 |
| | | B | 1.78E-9 / 4.51E-7 | 1.56E-8 | 2.88E-7 |
| | $1E10^{-5}$ | K | 5.20E-10 / 1.07E-7 | 4.66E-9 | 6.74E-8 |
| | | N | 5.21E-10 / 1.21E-7 | 4.71E-9 | 7.65E-8 |
| | | G | 5.28E-10 / 1.44E-7 | 4.78E-9 | 9.17E-8 |
| | | B | 5.52E-10 / 1.55E-7 | 4.90E-9 | 9.91E-8 |
| | $1E10^{-6}$ | K | 1.64E-10 / 4.29E-8 | 1.50E-9 | 2.73E-8 |
| | | N | 1.65E-10 / 4.53E-8 | 1.50E-9 | 2.90E-8 |
| | | G | 1.67E-10 / 4.86E-8 | 1.52E-9 | 3.11E-8 |
| | | B | 1.74E-10 / 5.00E-8 | 1.55E-9 | 3.20E-8 |
| | $1E10^{-7}$ | K | 5.19E-11 / 1.47 E-8 | 4.75E-10 | 9.4E-9 |
| | | N | 5.21E-11 / 1.50E-8 | 4.76E-10 | 9.60E-9 |
| | | G | 5.27E-11 / 1.53 E-8 | 4.79 E-10 | 9.83E-9 |
| | | B | 5.51E-11 / 1.55E-8 | 4.89E-10 | 9.93E-9 |

K: Kaolinite, N: Natural Soil, G: Glokonite, B: Bentonite
Adsorbent Concentration: Concentration of adsorbent medium
Initial concentration: Initial mercury concentration in solution
Concentration of =1SOHG: concentration of mercury sorbed on soil surface
5.36-6.5, 6.5-8: range of pH change

Similar behaviour was observed for kaolinite (Figures 5.11, 5.12, and Figures 13, 14, 15 appendix B), natural soil (Figures 5.13, 5.14, and Figures 16, 17, 18 appendix B), glokonite (Figures 5.15, 5.16, and Figures 19, 20, 21 appendix B), and bentonite (Figures 5.17, 5.18, and Figures 22, 23, 24 appendix B) when they were used to build light sediments (adsorbent medium concentration 8174 mg/L)

The results obtained for suspended solids in the water column (adsorbent medium concentration 10 mg/L) continued to show similar trends but different rates of adsorption for kaolinite (Figures 5.19, 5.20, and Figures 25, 26, 27 appendix B), natural soil (Figures

5.21, 5.22, and Figures 28, 29, 30 appendix B), glokonite (Figures 5.23, 5.24, and Figures 31, 32, 33 appendix B), and bentonite (Figures 5.25, 5.26, and Figures 34, 35, 36 appendix B).

The following conclusions arise from studying the effect of pH variation on mercury sorption:

- Mercury sorption increased by two folds as the pH increased from 5.36 to 8.00 for all soils tested.
- The rate of increase of mercury sorption (moles/pH unit) was one fold higher in the case of pH change from 6.5 to 8.0 than the change from 5.36 to 6.5.
- For high solid mass density (10 g/L), the slight increase of pH (from 5.36 to 6.5) demonstrates the higher dependence of the adsorption rate on water quality. This dependence is especially visible for lower initial concentration of mercury.
- For the high specific surface area (1350 $m^2/g$), the amount of adsorbed mercury has increased for all initial mercury concentration as the pH increased from 5.36 to 8.0. Amounts of mercury adsorbed were higher as the adsorbent mass increased:
  a) For initial mercury concentration of 1E-3 moles amount of mercury sorbed increased from 6.05 E-9 moles to 1.15E-6 moles for 10 mg/L and from 4.05 E-8 moles to 2.73 E-6 moles for 10 g/L.
  b) For initial concentration of 1 E-7 moles amount of mercury sorbed increased from 5.51 E-11 moles to 1.55 E-8 moles for 10 mg/L and from 4.26 E-10 moles to 2.68 E-8 moles for 10 g/L.

- It was also observed that lower initial mercury concentration has higher adsorption rate and lower mass concentration is more sensitive to pH changes.
- Higher pH, lower initial mercury concentration in the water column or pore water results in less amount of bioavailable mercury for plants.

### 5.4.2. Effect of Initial Mercury Concentration on Mercury Sorption

Mercury concentration in solution is sought to influence the sorption on soil surface. Five different values were chosen to study this effect. It ranged from a relatively low value (1 E –7 moles) to a high value of 1 E-3 moles. Three intermediate value were considered namely: 1E-6, 1E-5, and 1E-4 moles. Those values were carefully chosen to study how will the change in concentration of mercury would impact the sorption process.

The analysis were conducted for three adsorbent medium concentrations levels (10000 , 8174, and 10 mg/L) and applied to investigate the effect of initial mercury concentration on mercury sorption for kaolinite, natural soil, glokonite, and bentonite. The pH values varied from 5.36 to 8.00, all other factors remain unchanged.

The results obtained show the relationship between mercury sorption on soil surface as a function of initial mercury concentration for different adsorbent medium concentration, Specific Surface Areas (soils), and different pH values (table 5.6).

As the initial mercury concentration increased from 1 E-7 to 1 E-3 –in the case of kaolinite sediment, and pH 5.36 - the concentration of =1SOHG have increased from 2.24 E-10 to 2.91 E-8 moles. The rate of increase was however different. As the initial Hg concentration in solution changed from 1 E-7 to 1 E-6, the rate of increase in the adsorbed amount is 5.39 E-4 moles per one fold increase in the initial concentration. Further increases in the initial Hg concentration (one fold at a time) resulted in more mercury sorbed to the soil surface, however, the rate of increase presented lower values.

The corresponding values of the rate of increase in the sorbed Hg are: 1.72 E-4, 5.87 E-5, and 2.39 E-5 moles per one fold increase in the initial concentration, (Figure 5.27). At the highest pH value (pH 8), as the initial mercury concentration increased from 1 E-7 to 1 E-3, the concentration of =1SOHG have increased from 1.86 E-8 to 1.9 E-6 moles.

Table 5.6: Effect of Initial Mercury Concentration on Mercury Sorption

| **Adsorbent concentration (mg/L)** | **Type of sediment** | **pH** | **Concentration of =1SOHG min/max initial concentration values (moles)** | **Rate of increase (moles / one fold increase)** | | | |
|---|---|---|---|---|---|---|---|
| | | | | **E-7/-6** | **E-6/-5** | **E-5/-4** | **E-4/-3** |
| 10,000 | K | 5.36 | 2.24E-10 / 2.91E-8 | 5.39E-4 | 1.72E-4 | 5.87E-5 | 2.39E-5 |
| | | 6.5 | 1.60E-9 / 2.08E-7 | 3.87E-3 | 1.23E-3 | 4.20E-4 | 1.71E-4 |
| | | 8.0 | 1.86E-8 / 1.90E-6 | 4.68E-2 | 1.47E-2 | 4.62E-3 | 1.43E-3 |
| | N | 5.36 | 2.89E-10 / 3.58E-8 | 6.95E-4 | 2.22E-4 | 7.50E-5 | 2.91E-5 |
| | | 6.5 | 2.06E-9 / 2.64E-7 | 4.97E-3 | 1.58E-3 | 5.40E-4 | 2.16E-4 |
| | | 8.0 | 1.99E-8 / 2.06E-6 | 5.02E-2 | 1.58E-2 | 4.99E-3 | 1.56E-3 |
| | G | 5.36 | 4.11E-10 / 4.18E-8 | 9.90E-4 | 3.14E-4 | 1.01E-4 | 3.17E-5 |
| | | 6.5 | 3.45E-9 / 3.96 E-7 | 8.35E-3 | 2.66E-3 | 8.82E-4 | 3.13E-4 |
| | | 8.0 | 2.36E-8 / 2.46 E-6 | 6.02E-2 | 1.90E-2 | 6.00E-3 | 1.85E-3 |
| | B | 5.36 | 4.26E-10 / 4.05 E-8 | 1.02E-3 | 3.24E-4 | 1.02E-4 | 3.01E-5 |
| | | 6.5 | 4.56E-9 / 4.59E-7 | 1.11E-2 | 3.51E-3 | 1.12E-3 | 3.47E-4 |
| | | 8.0 | 2.68E-8 / 2.73E-6 | 6.90E-2 | 2.18E-2 | 6.82E-3 | 2.03E-3 |
| 8,174 | K | 5.36 | 2.00E-10 / 2.62E-8 | 4.80E-4 | 1.53E-4 | 5.24E-5 | 2.16E-5 |
| | | 6.5 | 1.44E-9 / 1.87E-7 | 3.48E-3 | 1.11E-3 | 3.78E-4 | 1.54E-4 |
| | | 8.0 | 1.81E-8 / 1.83E-6 | 4.56E-2 | 1.43E-2 | 4.49E-3 | 1.38E-3 |
| | N | 5.36 | 2.61E-10 / 3.31 E-8 | 6.27E-4 | 2.00E-4 | 6.80E-5 | 2.71E-5 |
| | | 6.5 | 1.85E-9 / 2.40E-7 | 4.47E-3 | 1.43E-3 | 4.86E-4 | 1.97E-4 |
| | | 8.0 | 1.93E-8 / 1.99E-6 | 4.87E-2 | 1.53E-2 | 4.83E-3 | 1.51E-3 |
| | G | 5.36 | 3.99E-10 / 4.18E-8 | 9.59E-4 | 3.05E-4 | 9.89E-5 | 3.21E-5 |
| | | 6.5 | 3.19E-9 / 3.76 E-7 | 7.73E-3 | 2.46E-3 | 8.22E-4 | 3.00E-4 |
| | | 8.0 | 2.29E-8 / 2.39E-6 | 5.84E-2 | 1.84E-2 | 5.82E-3 | 1.81E-3 |
| | B | 5.36 | 4.27E-10 / 4.07E-8 | 1.03E-3 | 3.24E-4 | 1.02E-4 | 3.03E-5 |
| | | 6.5 | 4.44E-9 / 4.54E-7 | 1.08E-2 | 3.42E-3 | 1.10E-3 | 3.45E-4 |
| | | 8.0 | 2.64E-8 / 2.70E-6 | 6.79E-2 | 2.14E-2 | 6.72E-3 | 2.01E-3 |

| Adsorbent concentration (mg/L) | Type of sediment | pH | Concentration of =1SOHG min/max initial concentration values (moles) | Rate of increase (moles / one fold increase) | | | |
|---|---|---|---|---|---|---|---|
| | | | | E-7/-6 | E-6/-5 | E-5/-4 | E-4/-3 |
| 10 | K | 5.36 | 5.19E-11 / 5.49 E-9 | 1.25E-4 | 3.95E-5 | 1.27E-5 | 4.25E-6 |
| | | 6.5 | 5.94E-10 / 5.12E-8 | 1.42E-3 | 4.41E-4 | 1.33E-4 | 3.71E-5 |
| | | 8.0 | 1.47E-8 / 3.79E-6 | 3.13E-2 | 7.11E-3 | 1.26E-3 | 1.74E-4 |
| | N | 5.36 | 5.21E-11 / 5.55E-9 | 1.25E-4 | 3.96E-5 | 1.25E-5 | 4.31E-6 |
| | | 6.5 | 5.95E-10 / 5.46E-8 | 1.42E-3 | 4.46E-4 | 1.37E-4 | 4.03E-5 |
| | | 8.0 | 1.50E-8 / 4.93E-7 | 3.37E-2 | 8.37E-3 | 1.64E-3 | 2.49E-4 |
| | G | 5.36 | 5.27E-11 / 5.569E-9 | 1.27E-4 | 4.02E-5 | 1.30E-5 | 4.44E-6 |
| | | 6.5 | 5.99E-10 / 5.96E-8 | 1.44E-3 | 4.54E-4 | 1.43E-4 | 4.52E-5 |
| | | 8.0 | 1.53E-8 / 8.18E-7 | 3.69E-2 | 1.05E-2 | 2.58E-3 | 4.91E-4 |
| | B | 5.36 | 5.51E-11 / 6.05E-9 | 1.32E-4 | 4.20E-5 | 1.36E-5 | 4.75E-6 |
| | | 6.5 | 6.13E-10 / 6.34E-8 | 1.47E-3 | 4.66E-4 | 1.49E-4 | 4.88E-5 |
| | | 8.0 | 1.55E-8 / 1.15E-6 | 3.83E-2 | 1.16E-2 | 3.29E-3 | 7.77E-4 |

K: Kaolinite, N: Natural Soil, G: Glokonite, B: Bentonite
Adsorbent Concentration: Concentration of adsorbent medium
Concentration of =1SOHG: concentration of mercury sorbed on soil surface
E-7/-6, E-6/-5, E-5/-4, E-4/-3: range of initial mercury concentration change

As the initial Hg concentration in solution changes from 1 E-7 to 1 E-6, the rate of increase in the adsorbed amount is 4.68 E-2 moles per one fold increase in the initial concentration. Further increases in the initial Hg concentration (one fold at a time) resulted in more mercury sorbed to the soil surface, however, the rate of increase is decreasing. The corresponding values of the rate of increase in the sorbed Hg are: 1.47 E-2, 4.62 E-3, and 1.43 E-3 moles per one fold increase in the initial concentration, (Figure 5.28). The behaviour of kaolinite sediments for the neutral pH value (pH 6.50) is shown in Figure 37, appendix B.

For natural soil (Figures 5.29, 5.30, and Figure 38 appendix B), glokonite (Figures 5.31, 5.32, and Figure 39 appendix B), and bentonite (Figures 5.33, 5.34 and Figure 40 appendix B) similar trends, but different rates, were observed.

Similar sorption was observed when light sediments (adsorbent medium concentration 8174 mg/L) for kaolinite (Figures 5.35, 5.36, and Figure 41 appendix B), natural soil (Figures 5.37, 5.38, and Figure 42 appendix B), glokonite (Figures 5.39, 5.40, and Figure 43 appendix B), and bentonite (Figures 5.41, 5.42, and Figure 44 appendix B) was used.

The results obtained for suspended solids in the water column (adsorbent medium concentration 10 mg/L) continued to show similar trends but different rates of adsorption for kaolinite (Figures 5.43, 5.44, and Figure 45 appendix B), natural soil (Figures 5.45, 5.46, and Figure 46 appendix B), glokonite (Figures 5.47, 5.48, and Figure 47 appendix B), and bentonite (Figures 5.49, 5.50, and Figure 48 appendix B).

The following conclusions arise from studying the effect of initial mercury concentration variation on mercury sorption:

- For soils with low specific area (e.g. 80 $m^2/g$) at pH (5.36), mercury has higher adsorption rate for higher mass concentration as well as for lower initial concentrations (Figures 5.27, 5.43). For low specific area of sediments, the increase of pH up to 8 increases the rate of sorption for all initial concentrations, however for lower initial concentrations E-7 moles it is the highest one resulting in an increase in adsorption by 3 times (Figures 5.28 and 5.44).
- At pH (8) where initial mercury concentration is low (1E-7 moles), the adsorption rate did not increase as mass concentration increased (Figures 5.56, 5.68). The increase of adsorption was observed when initial concentrations increased (1E-3 moles) (Figures 5.55, 5.67). When the concentration of soil

mass was high (10 g/L) the adsorption rate increased as specific surface area increased for all tested pH. The difference of this adsorption rate, among different types of soil, was more visible for lower initial concentration of mercury (Figures 5.51, 5.52). At pH (5.36), the mass adsorbent concentration influences adsorption rate for all initial concentrations of mercury (Figures 5.51, 5.52, 5.63, 5.64).

- For soil with high specific surface area (1350 $m^2/g$) at pH (5.36), 1000 times lower mass of sediment can adsorb 1 fold less mercury for low initial mercury concentration (1E-7 moles). For higher initial mercury concentration (1E-3 moles), the difference of adsorption capacity between higher and lower adsorbent mass concentration seems smaller.
- Lower initial concentrations lead to higher adsorption rate for both higher and lower mass concentrations (Figures 5.34, 5.50).

### 5.4.3. Effect of the Specific Surface Area on Mercury Sorption

Specific Surface Area ($m^2/g$) is one of the most significant factors that differentiate between different soil types. It can vary from very small to considerably high values depending on the soil type. Four values of the Specific Surface Area were considered in this comparison to represent four different soils: 80, 129, 400, and 1350 $m^2/g$ representing: kaolinite, natural soil, glokonite, and bentonite respectively. The values were chosen to cover a range of values of soil materials, which are expected to sorb Hg when utilised in constructed wetlands.

The analysis were conducted for three adsorbent medium concentrations levels (10000, 8174, and 10 mg/L) and were applied to investigate the effect of specific surface area (soils) on mercury sorption for initial mercury concentrations ranging from 1E-7 to 1E-3 moles. The pH values varied from 5.36 to 8.00, all other factors remain unchanged.

The results obtained show the relationship between mercury sorption on soil surface as a function of specific surface area for different adsorbent medium concentration, initial mercury concentration, and different pH values (Table 5.7).

As the Particle's Specific Surface Area increased from 80 to 1350 $m^2/g$ - in the case of sediment, pH 5.36, and initial mercury concentration of 1E-3 moles - the concentration of =1SOHG have increased from 2.91 E-8 to 4.05 E-8 moles. The rate of increase was however different. As the Specific Surface Area changes from 80 to 129 $m^2/g$, the rate of increase in the adsorbed amount is 1.38 E-10 moles per unit ($m^2/g$) increase in the Specific Surface Area. Increasing the Specific Surface Area from 129 to 400 $m^2/g$, resulted in a rate of increase in the adsorbed amount of 2.19 E-11 moles per unit ($m^2/g$) increase in the Specific Surface Area.

Further increases in the Specific Surface Area did not increase significantly the amount of mercury sorbed to the soil surface (Figure 5.51).

For the lowest initial mercury concentration of 1E-7 moles, as the Particle's Specific Surface Area increased from 80 to 1350 $m^2/g$, the concentration of =1SOHG have increased from 2.24 E-10 to 4.26 E-10 moles.

Table 5.7: Effect of the Specific Surface Area on Mercury Sorption

| **Adsorbent concentration (mg/L)** | **Initial concentration (moles)** | **pH** | **Concentration of =1SOHG min/max SSA (moles)** | **Rate of increase (moles/($m^2$/g))** | | |
|---|---|---|---|---|---|---|
| | | | | **80-129** | **129-400** | **400-1350** |
| 10,000 | 1E-3 | 5.36 | 2.91E-8 / 4.05E-8 | 1.38E-10 | 2.19E-11 | - |
| | | 6.5 | 2.08E-7 / 4.59E-7 | 1.14E-9 | 4.86E-10 | 6.69E-11 |
| | | 8.0 | 1.90E-6 / 2.73E-6 | 3.37E-9 | 1.46E-9 | 2.85E-10 |
| | 1E-4 | 5.36 | 7.55E-9 / 1.34E-8 | 4.31E-11 | 1.30E-11 | 2.21E-13 |
| | | 6.5 | 5.40E-8 / 1.47E-7 | 3.14E-10 | 1.66E-10 | 3.42E-11 |
| | | 8.0 | 6.09E-7 / 8.99 E-7 | 9.65E-10 | 4.88E-10 | 1.16E-10 |
| | 1E-5 | 5.36 | 2.26E-9 / 4.29E-9 | 1.33E-11 | 4.49E-12 | 1.45E-13 |
| | | 6.5 | 1.62E-8 / 4.61E-8 | 9.41E-11 | 5.20E-11 | 1.18E-11 |
| | | 8.0 | 1.93E-7 / 2.85E-7 | 2.90E-10 | 1.52E-10 | 3.79E-11 |
| | 1E-6 | 5.36 | 7.10E-10 / 1.35E-9 | 4.18E-12 | 1.43E-12 | 4.84E-14 |
| | | 6.5 | 5.08E-9 / 1.45E-8 | 2.95E-11 | 1.64E-11 | 3.77E-12 |
| | | 8.0 | 6.07E-8 / 8.88E-8 | 8.90E-11 | 4.68E-11 | 1.17E-11 |
| | 1E-7 | 5.36 | 2.24E-10 / 4.26E-10 | 1.32E-12 | 4.52E-13 | 1.56E-14 |
| | | 6.5 | 1.60E-9 / 4.56E-9 | 9.27E-12 | 5.13E-12 | 1.17E-12 |
| | | 8.0 | 1.86E-8 / 2.68E-8 | 2.61E-11 | 1.37E-11 | 3.36E-12 |
| 8,174 | 1E-3 | 5.36 | 2.62E-8 / 4.07E-8 | 1.42E-10 | 3.18E-11 | - |
| | | 6.5 | 1.87E-7 / 4.54E-7 | 1.07E-9 | 5.05E-10 | 8.17E-11 |
| | | 8.0 | 1.83E-6 / 2.70E-6 | 3.20E-9 | 1.49E-9 | 3.2E-10 |
| | 1E-4 | 5.36 | 6.73E-9 / 1.34E-8 | 4.13E-11 | 1.53E-11 | 5.58E-13 |
| | | 6.5 | 4.86E-8 / 1.44E-7 | 2.83E-10 | 1.62E-10 | 3.92E-11 |
| | | 8.0 | 5.92E-7 / 8.85E-7 | 8.84E-10 | 4.79E-10 | 1.26E-10 |
| | 1E-5 | 5.36 | 2.01E-9 / 4.27E-9 | 1.26E-11 | 5.08E-12 | 2.79E-13 |
| | | 6.5 | 1.46E-8 / 4.49E-8 | 8.43E-11 | 5.01E-11 | 1.33E-11 |
| | | 8.0 | 1.88E-7 / 2.80E-7 | 2.63E-10 | 1.48E-10 | 4.09E-11 |
| | 1E-6 | 5.36 | 6.32E-10 / 1.35E-9 | 3.95E-12 | 1.61E-12 | 9.26E-14 |
| | | 6.5 | 4.58E-9 / 1.42E-8 | 2.64E-11 | 1.58E-11 | 4.21E-12 |
| | | 8.0 | 5.92E-8 / 8.74E-8 | 8.06E-11 | 4.56E-11 | 1.26E-11 |
| | 1E-7 | 5.36 | 2.00E-10 / 4.27E-10 | 1.25E-12 | 5.10E-13 | 2.93E-14 |
| | | 6.5 | 1.44E-9 / 4.44E-9 | 8.29E-12 | 4.94E-12 | 1.32E-12 |
| | | 8.0 | 1.81E-8 / 2.64E-8 | 2.37E-11 | 1.33E-11 | 3.63E-12 |
| 10 | 1E-3 | 5.36 | 5.49E-9 / 6.05E-9 | 1.16E-12 | 5.24E-13 | 3.79E-13 |
| | | 6.5 | 5.12E-8 / 6.34E-8 | 6.92E-11 | 1.86E-11 | 4.03E-12 |
| | | 8.0 | 3.79E-7 / 1.15E-6 | 2.32E-9 | 1.20E-9 | 3.50E-10 |
| | 1E-4 | 5.36 | 1.66E-9 / 1.78E-9 | 1.63E-13 | 9.96E-14 | 8.63E-14 |
| | | 6.5 | 1.78E-8 / 1.95 E-8 | 9.18E-12 | 2.36E-12 | 6.84E-13 |
| | | 8.0 | 2.20E-7 / 4.51E-7 | 9.86E-10 | 3.97E-10 | 7.89E-11 |
| | 1E-5 | 5.36 | 5.20E-10 / 5.52E-10 | 3.27E-14 | 2.62E-14 | 2.52E-14 |
| | | 6.5 | 5.84E-9 / 6.14E-9 | 1.10E-12 | 3.39E-13 | 1.62E-13 |
| | | 8.0 | 1.07E-7 / 1.55E-7 | 2.80E-10 | 8.45E-11 | 1.19E-11 |

| Adsorbent concentration (mg/L) | Initial concentration (moles) | pH | Concentration of =1SOHG min/max SSA (moles) | Rate of increase (moles/$(m^2/g)$) | | |
|---|---|---|---|---|---|---|
| | | | | 80-129 | 129-400 | 400-1350 |
| | 1E-6 | 5.36 | 1.64E-10 / 1.74E-10 | 8.16E-15 | 7.75E-15 | 7.89E-15 |
| | | 6.5 | 1.87E-9 / 1.94E-9 | 1.43E-13 | 6.64E-14 | 4.63E-14 |
| | | 8.0 | 4.29E-8 / 5.00E-8 | 4.98E-11 | 1.20E-11 | 1.46E-12 |
| | 1E-7 | 5.36 | 5.19E-11 / 5.51E-11 | 2.45E-15 | 2.47E-15 | 2.49E-15 |
| | | 6.5 | 5.94E-10 / 6.13E-10 | 2.45E-14 | 1.62E-14 | 1.43E-14 |
| | | 8.0 | 1.47E-8 / 1.55E-8 | 5.92E-12 | 1.29E-12 | 1.79E-13 |

K: Kaolinite, N: Natural Soil, G: Glokonite, B: Bentonite
Adsorbent Concentration: Concentration of adsorbent medium
Initial concentration: initial mercury concentration is solution
Concentration of =1SOHG: concentration of mercury sorbed on soil surface
80-129, 129-400, 400-1350: range of specific surface area change

As the Specific Surface Area changes from 80 to 129 $m^2/g$, the rate of increase in the adsorbed amount is 1.32 E-12 moles per unit ($m^2/g$) increase in the Specific Surface Area. Further increases in the Specific Surface Area resulted in more mercury sorbed to the soil surface, however, the rate of increase was observed to be decreasing. The corresponding values of the rate of increase in the sorbed Hg are: 4.52 E-13, and 1.56 E-14 moles per unit ($m^2/g$) increase in the Specific Surface Area (Figure 5.52). The behaviour of sediments at pH 5.36 for the intermediate initial mercury concentrations are shown in Figures 49 through 51, appendix B.

For close to neutral pH value (pH 6.50), (Figures 5.53, 5.54, and Figures 52, 53, 54 appendix B), and slightly basic pH (pH 8.00), (Figures 5.55, 5.56, and Figures 55, 56, 57 appendix B) similar trends, but different rates were observed.

Similar behaviour was observed when using light sediments (adsorbent medium concentration 8174 mg/L) at pH 5.36 (Figures 5.57, 5.58, and Figures 58, 59, 60 appendix B), at pH 6.5 (Figures 5.59, 5.60, and Figures 61, 62, 63 appendix B), and at pH 8 (Figures 5.61, 5.62, and Figures 64, 65, 66 appendix B).

The results obtained for suspended solids in the water column (adsorbent medium concentration 10 mg/L) continued to show similar trends, different rates of adsorption at pH 5.36 (Figures 5.63, 5.64, and Figures 67, 68, 69 appendix B), pH 6.50 (Figures 5.65, 5.66, and Figures 70, 71, 72 appendix B), and pH 8.00 (Figures 5.67, 5.68, and Figures 73, 74, 75 appendix B).

The following conclusions arise from studying the effect of specific surface area variation on mercury sorption:

- The type of soil influences the level of mercury adsorption only for high initial concentration of mercury at the highest pH value of 8 (Figures 5.77 – 5.80).
- It is evident that adsorption rate increases as specific surface area increases. It was observed that the available mercury (in water) for plants decreases in proportional way to pH increase for low solid mass concentration for all types of soils (i.e. increase of pH by one unit increases adsorption and decreases available mercury in water by 1 fold).
- The soil with specific surface area of 129 $m^2/g$ (representing natural soil) - at the mass concentration of 10 g/L - seems to have an excellent adsorption rate (at low and high pH) for all tested concentrations (Figures 5.29, 5.30). The adsorption rate of this type of soils is higher than kaolinite and only slightly lower than bentonite particles.
- Sediments with high specific area at pH (8) with higher level of mass concentration have higher adsorption capacity. For very fine uniform sediment particle (e.g. bentonite) upper and bottom layers of sediments have a similar behaviour regarding adsorption of mercury at low pH (Figures 5.33, 5.49).

### 5.4.4. Effect of Adsorbent Medium (Soil) Concentration in Solution on Mercury Sorption

The concentration of the adsorbent medium represents the solids' concentration (mg/L). The higher the values of the concentration, the higher the density of the solids in the water. Sediment concentrations up to 10000 mg/L were reported (Thoumann 1986). In the water column of a lake, the solids' concentrations were found to be 10 mg/L (Thoumann 1986). In this current study, the following three values were chosen: a) 10 mg/L referring to suspension, b) 8174 referring to a light type of sediments, c) 10000 mg/L) referring to sediments.

The analysis were conducted for three pH levels (5.36, 6.50, and 8.00) and were applied to investigate the effect of adsorbent medium concentration on mercury sorption for kaolinite, natural soil, glokonite, and bentonite. The initial mercury concentrations range from 1E-7 to 1E-3 moles.

The obtained results show the relationship between mercury sorption on soil surface as a function of adsorbent medium concentration for different initial mercury concentration, specific surface area (soils), and different pH values (Table 5.8).

As the Adsorbent Medium Concentration (AMC) increased from 10 to 10,000 mg/L – in the case of kaolinite, pH 5.35, initial mercury concentration of 1E-3 moles - the concentration of =1SOHG have increased from 5.49 E-9 to 2.91 E-8 moles. As the Adsorbent Medium Concentration changes from 10 to 8174 mg/L, the rate of increase in the adsorbed amount is 2.53 E-12 moles per AMC unit increase (mg/L).

As Adsorbent Medium Concentration increased from 8174 to 10000 mg/L, the rate of increase in the adsorbed Hg amount has decreased to 1.61 E-12 moles per AMC unit increase (mg/L) (Figure 5.69).

For the lowest initial mercury concentration of 1E-7 moles, as the Adsorbent Medium Concentration increased from 10 to 10000 mg/L, the concentration of =1SOHG have increased from 5.19 E-11 to 2.24 E-10 moles. As the Adsorbent Medium Concentration changes from 10 to 8,174 mg/L, the rate of increase in the adsorbed amount is 1.81 E-14 moles per AMC unit (mg/L) increase. As Adsorbent Medium Concentration increased from 8174 to 10000 mg/L, the rate of increase in the adsorbed Hg amount has decreased to 1.34 E-14 moles per AMC unit (mg/L) increase (Figure 5.69). The behaviour of kaolinite for the intermediate initial mercury concentrations is shown in Figure 5.69.

For natural soil (Figure 5.70), glokonite (Figure 5.71), and bentonite (Figure 5.72) similar trends, but different rates were observed.

Similar behaviour was observed when using the close to neutral pH (pH 6.5) for kaolinite (Figure 5.73), natural soil (Figure 5.74), glokonite (Figure 5.75), and bentonite (Figure 5.76).

The results obtained for the slightly basic pH (pH 8.00) continued to show similar trends, different rates of adsorption for kaolinite (Figure 5.77), natural soil (Figure 5.78), glokonite (Figure 5.79), and bentonite (Figure 5.80).

Table 5.8: Effect of Adsorbent Medium Concentration in Solution on Mercury Sorption

| **Initial concentration (moles)** | **Type of sediment** | **pH** | **Concentration of =1SOHG min/max medium concentration (moles)** | **Rate of increase (moles/(mg/L))** | |
|---|---|---|---|---|---|
| | | | | **10-8174** | **8174-10000** |
| 1E-3 | K | 5.36 | 5.49E-9 / 2.91 E-8 | 2.53 E-12 | 1.61E-12 |
| | | 6.5 | 5.12E-8 / 2.08E-7 | 1.66E-11 | 1.14E-11 |
| | | 8.0 | 3.79E-7 / 1.90E-6 | 1.78E-10 | 3.50E-11 |
| | N | 5.36 | 5.55E-9 / 3.58E-8 | 3.38E-12 | 1.48E-12 |
| | | 6.5 | 5.46E-8 / 2.64E-7 | 2.27E-11 | 1.35E-11 |
| | | 8.0 | 4.93E-7 / 2.06E-6 | 1.84E-10 | 3.94E-11 |
| | G | 5.36 | 5.69E-9 / 4.18 E-8 | 4.42E-12 | 5.48E-15 |
| | | 6.5 | 5.96E-8 / 3.96E-7 | 3.88E-11 | 1.07E-11 |
| | | 8.0 | 8.18E-7 / 2.46E-6 | 1.93E-10 | 3.50E-11 |
| | B | 5.36 | 6.05E-9 / 4.05E-8 | 4.24E-12 | - |
| | | 6.5 | 6.34E-8 / 4.59E-7 | 4.78E-11 | 3.01E-12 |
| | | 8.0 | 1.15E-6 / 2.73E-6 | 1.9E-10 | 1.70E-11 |
| 1E-4 | K | 5.36 | 1.66E-9 / 7.55E-9 | 6.21E-13 | 4.47E-13 |
| | | 6.5 | 1.78E-8 / 5.40E-8 | 3.77E-12 | 2.95E-12 |
| | | 8.0 | 2.20E-7 / 6.09E-7 | 4.56E-11 | 9.31E-12 |
| | N | 5.36 | 1.67E-9 / 9.66E-9 | 8.67E-13 | 4.97E-13 |
| | | 6.5 | 1.83E-8 / 6.94 E-8 | 5.41E-12 | 3.79E-12 |
| | | 8.0 | 2.68E-7 / 6.57E-7 | 4.50E-11 | 1.15E-11 |
| | G | 5.36 | 1.70E-9 / 1.32 E-8 | 1.37E-12 | 1.59E-13 |
| | | 6.5 | 1.89E-8 / 1.14E-7 | 1.07E-11 | 4.38E-12 |
| | | 8.0 | 3.76E-7 / 7.89E-7 | 4.77E-11 | 1.28E-11 |
| | B | 5.36 | 1.78E-9 / 1.34E-8 | 1.43E-12 | - |
| | | 6.5 | 1.95E-8 / 1.47 E-7 | 1.52E-11 | 1.81E-12 |
| | | 8.0 | 4.51E-7 / 8.99E-7 | 5.32E-11 | 7.50E-12 |
| 1E-5 | K | 5.36 | 5.20E-10 / 2.26E-9 | 1.83E-13 | 1.35E-13 |
| | | 6.5 | 5.84E-9 / 1.62E-8 | 1.07E-12 | 8.76E-13 |
| | | 8.0 | 1.07E-7 / 1.93E-7 | 9.96E-12 | 2.74E-12 |
| | N | 5.36 | 5.21E-10 / 2.91E-9 | 2.58E-13 | 1.54E-13 |
| | | 6.5 | 5.89E-9 / 2.08E-8 | 1.57E-12 | 1.14E-12 |
| | | 8.0 | 1.21E-7 / 2.07E-7 | 9.86E-12 | 3.45E-12 |
| | G | 5.36 | 5.28E-10 / 4.13E-9 | 4.26E-13 | 6.68E-14 |
| | | 6.5 | 5.98E-9 / 3.49E-8 | 3.22E-12 | 1.41E-12 |
| | | 8.0 | 1.44E-7 / 2.49E-7 | 1.20E-11 | 4.11E-12 |
| | B | 5.36 | 5.52E-10 / 4.26E-9 | 4.55E-13 | - |
| | | 6.5 | 6.14E-9 / 4.61E-8 | 4.75E-12 | 6.57E-13 |
| | | 8.0 | 1.55E-7 / 2.85E-7 | 1.53E-11 | 2.52E-12 |

| Initial concentration (moles) | Type of sediment | pH | Concentration of =1SOHG min/max medium concentration (moles) | Rate of increase (moles/(mg/L)) | |
|---|---|---|---|---|---|
| | | | | 10-8174 | 8174-10000 |
| 1E-6 | K | 5.36 | 1.64E-10 / 7.10E-10 | 5.73E-14 | 4.24E-14 |
| | | 6.5 | 1.87E-9 / 5.08E-9 | 3.32E-13 | 2.74E-13 |
| | | 8.0 | 4.29E-8 / 6.07E-8 | 2.00E-12 | 8.49E-13 |
| | N | 5.36 | 1.65E-10 / 9.14E-10 | 8.09E-14 | 4.87E-14 |
| | | 6.5 | 1.88E-9 / 6.53E-9 | 4.89E-13 | 3.58E-13 |
| | | 8.0 | 4.53E-8 / 6.51E-8 | 2.18E-12 | 1.07E-12 |
| | G | 5.36 | 1.67E-10 / 1.30E-9 | 1.34E-13 | 2.19E-14 |
| | | 6.5 | 1.90E-9 / 1.10E-8 | 1.01E-12 | 4.44E-13 |
| | | 8.0 | 4.86E-8 / 7.78E-8 | 3.29E-12 | 1.26E-12 |
| | B | 5.36 | 1.74E-10 / 1.35E-9 | 1.44E-13 | - |
| | | 6.5 | 1.94E-9 / 1.45E-8 | 1.50E-12 | 2.14E-13 |
| | | 8.0 | 5.00E-8 / 8.88E-8 | 4.59E-12 | 7.72E-13 |
| 1E-7 | K | 5.36 | 5.19E-11 / 2.24E-10 | 1.81E-14 | 1.34E-14 |
| | | 6.5 | 5.94E-10 / 1.60E-9 | 1.04E-13 | 8.60E-14 |
| | | 8.0 | 1.47E-8 / 1.86E-8 | 4.21E-13 | 2.52E-13 |
| | N | 5.36 | 5.21E-11 / 2.89E-10 | 2.56E-14 | 1.54E-14 |
| | | 6.5 | 5.95E-10 / 2.06E-9 | 1.54E-13 | 1.12E-13 |
| | | 8.0 | 1.50E-8 / 1.99E-8 | 5.28E-13 | 3.18E-13 |
| | G | 5.36 | 5.27E-11 / 4.11E-10 | 4.24E-14 | 6.79E-15 |
| | | 6.5 | 5.99E-10 / 3.45E-9 | 3.17E-13 | 1.40E-13 |
| | | 8.0 | 1.53E-8 / 2.36E-8 | 9.27E-13 | 3.67E-13 |
| | B | 5.36 | 5.51E-11 / 4.26E-10 | 4.55E-14 | - |
| | | 6.5 | 6.13E-10 / 4.56E-9 | 4.69E-13 | 6.57E-14 |
| | | 8.0 | 1.55E-8 / 2.68E-8 | 1.33E-12 | 2.25E-13 |

K: Kaolinite, N: Natural Soil, G: Glokonite, B: Bentonite
Initial concentration: initial mercury concentration is solution
Concentration of =1SOHG: concentration of mercury sorbed on soil surface
10-8174, 8174-10000: range of adsorbent medium concentration change

The following conclusions arise from studying the effect of adsorbent medium concentration variation on mercury sorption:

- No significant difference in adsorption was observed among various mass concentrations tested for soils with low specific surface area at pH 8, and low initial mercury concentration (1E-7 moles) (Figure 5.28, 5.44). At pH 5.36

only slightly higher adsorption is observed by mass with higher concentrations.

- No difference in adsorption is observed for most types of soils at low solid mass concentration when other conditions remain the same (Figures 5.60, 5.63, 5.68). The exception was observed for highest concentration of mercury (1E-3 moles) at pH 8 (Figure 5.67). The type of soil used for sediments does not have considerable effect on rate of adsorption at pH 5.36 (Figures 5.69 - 5.72) and does not change it dramatically at pH 8 (Figures 5.77 – 5.80) for low initial concentration of mercury (1E-7).
- The soil with specific surface area 129 $m^2/g$, at the mass concentration of 10 mg/L, has a similar behaviour (regarding the rate of adsorption) than that of kaolinite. This type of sediments, if stratified due to various densities, would have different adsorption rate at each layer, especially for lower pH. This soil has an interesting adsorption conditions for lower initial concentrations of mercury (actual mercury concentration used in experiment), higher pH, for high and low adsorbent mass.

### 5.5 Conclusion

The general conclusions arise from the investigation conducted in this chapter could be summarised as follows:

- Higher pH, lower initial mercury concentration in the water column or pore water results in less amount of bioavailable mercury for plants.
- At the normal conditions of lower mercury level concentration in water (e.g. those tested in the lab experiment) the amount of available mercury for plants does not

depend heavily on the type of soil, nor their densities. It mostly depends on the pH of wastewater discharged.

- Natural soil could be employed in constructing the wetland instead of the expensive bentonite material. As the study indicates, the adsorption rate of this type of soils is higher than kaolinite and only slightly lower than bentonite particles.
- Effluents from the constructed wetland should pass through a trap system to capture mercury sorbed on the surfaces of the colloid material suspended in the water column.
- The rate of adsorption does not increase linearly as initial mercury concentration increase for all tested concentrations of the adsorbent mass. For higher mercury initial concentrations, higher adsorption rate is observed for higher specific surface area.
- The results showed that, in natural conditions (at pH above 7) around 10% of initial mercury concentration would be available for plants. Considering a removal rate by wetland plants at 95% (Chapter 3) of available part of mercury, only 0.5% of mercury will escape removal by natural system within the wetlands.
- High sorptive materials were considered in this analysis. In other situations where coarse materials (such as sand) are present, mercury adsorption is expected to be less than indicated in this study resulting in higher amount of bioavailable mercury.
- The process of mercury adsorption is speculated to take place before the formation of the biofilm on the solid phase, which limits the possibility of mercury methylation within the system. However, periodical monitoring should be maintained to reduce the possibility of mercury methylation as the system becomes older.

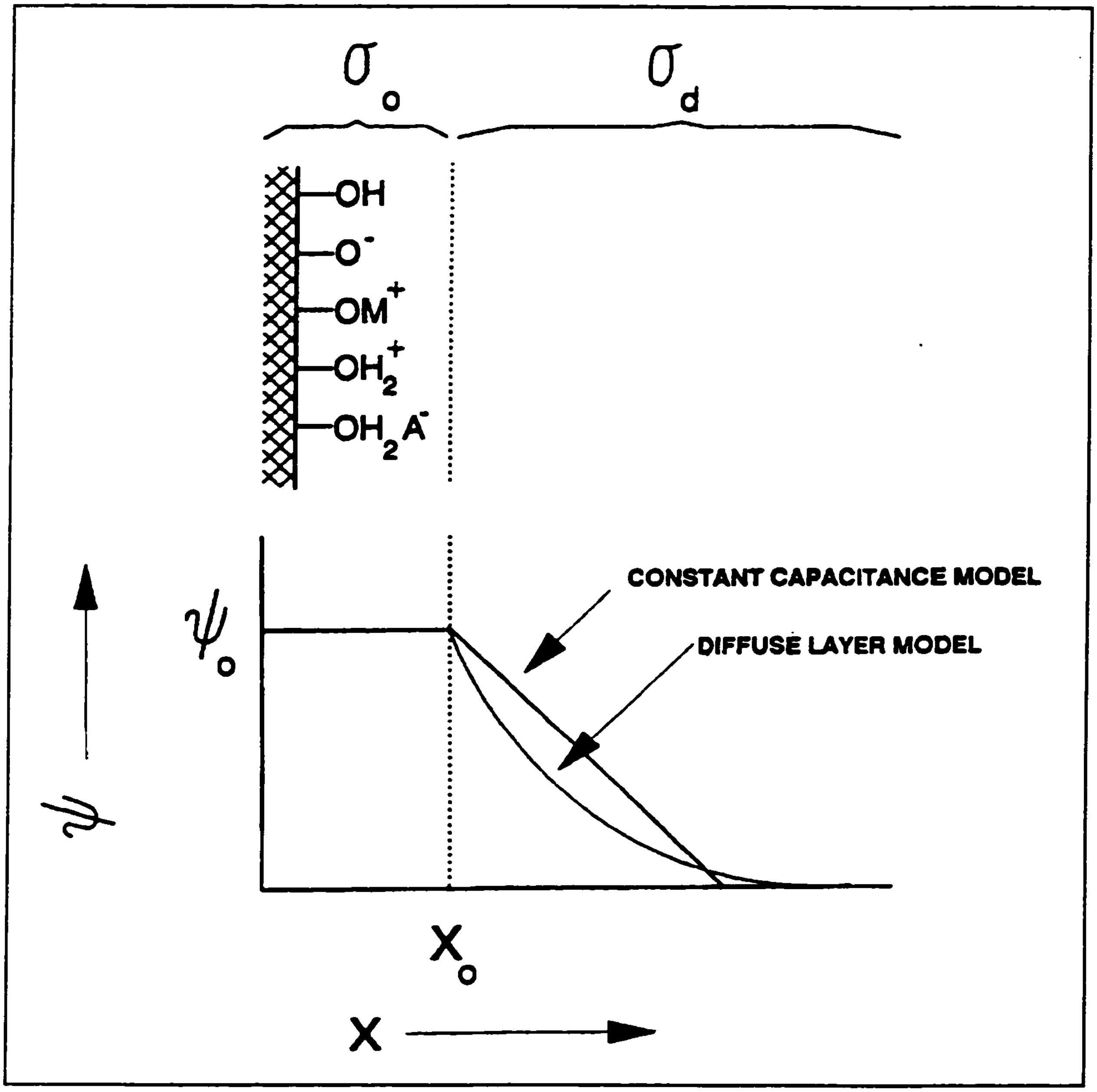


Figure 5.1 Schematic diagram of the Constant Capacitance and Diffuse Layer models (after Allison et. al. 1991).

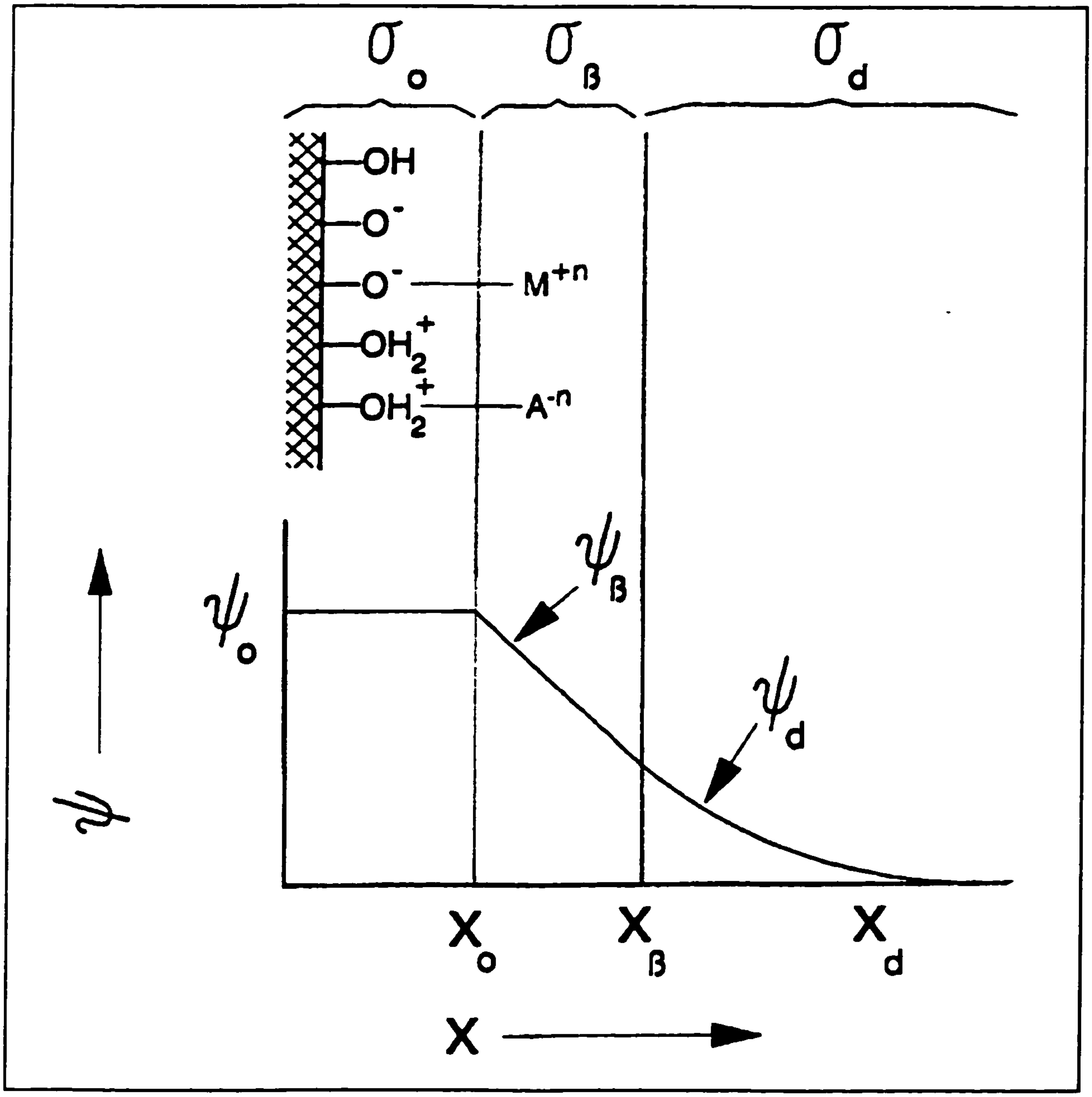


Figure 5.2 Schematic diagram of the triple layer model (after Allison et. al. 1991).

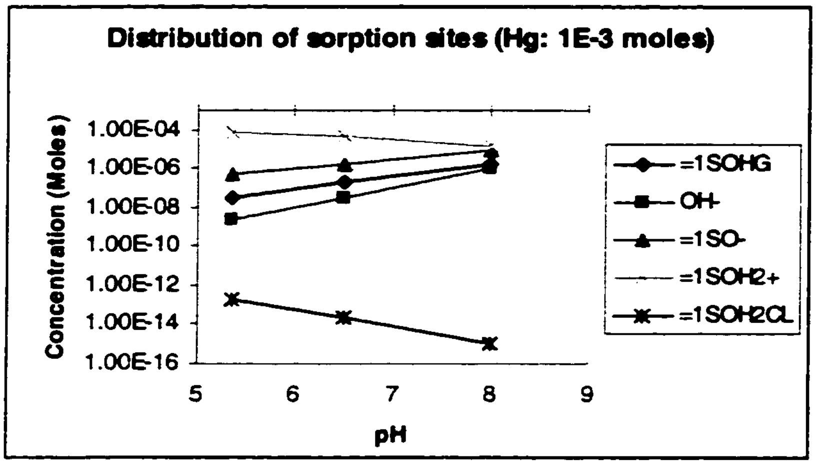


Figure 5.3 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 10 g/L.

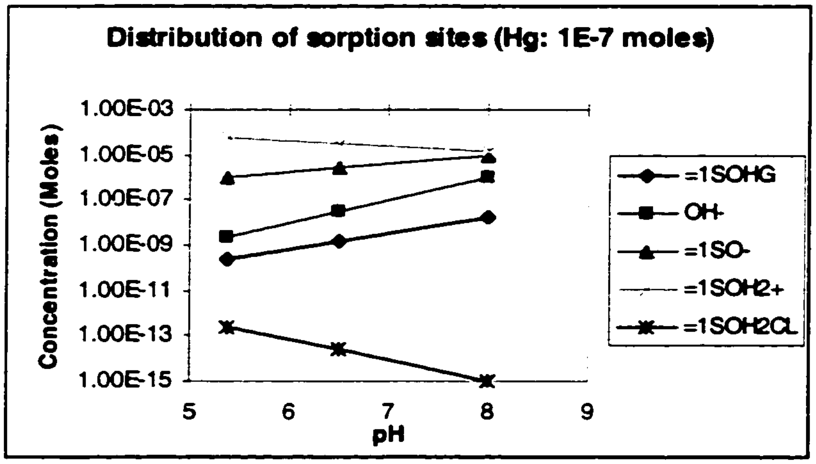


Figure 5.4 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 10 g/L.

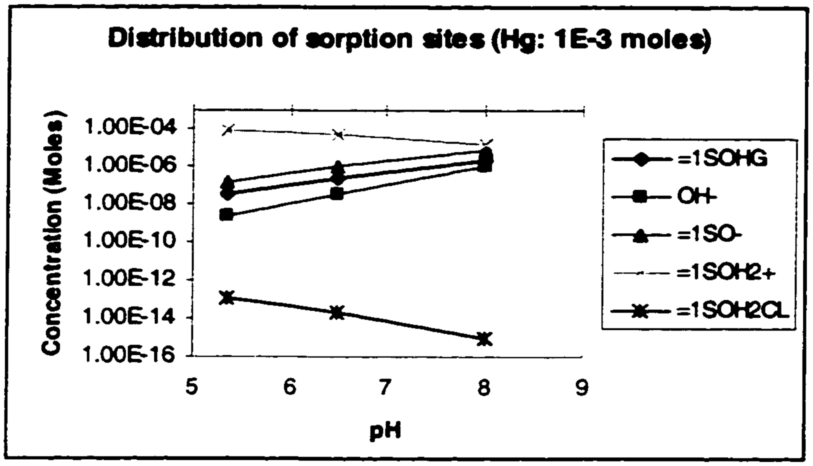


Figure 5.5 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 10 g/L.

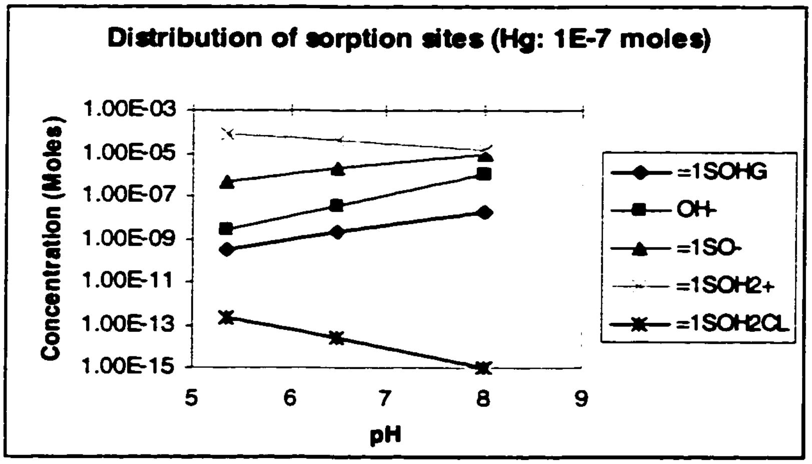


Figure 5.6 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 10 g/L.

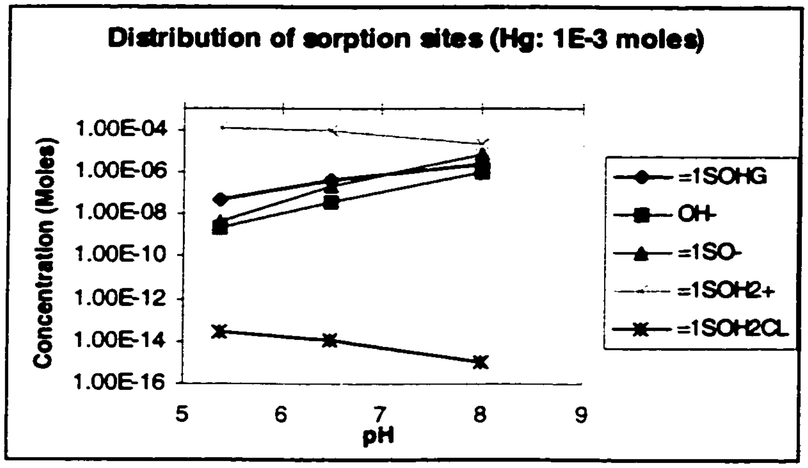


Figure 5.7 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 10 g/L.

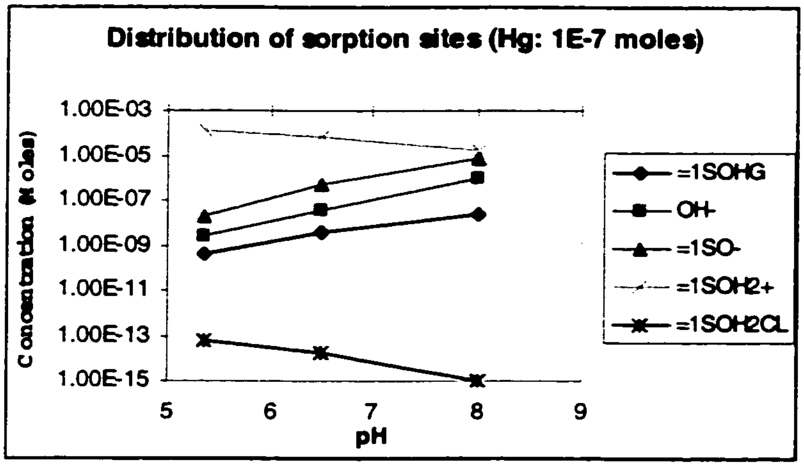


Figure 5.8 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 10 g/L.

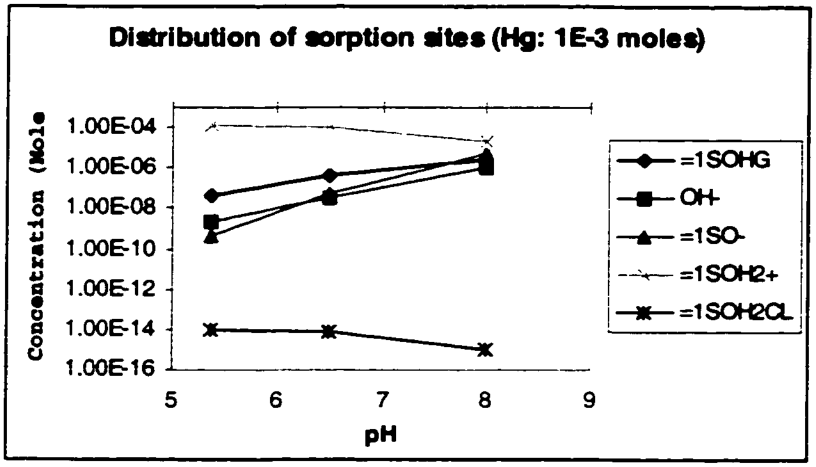


Figure 5.9 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 10 g/L.

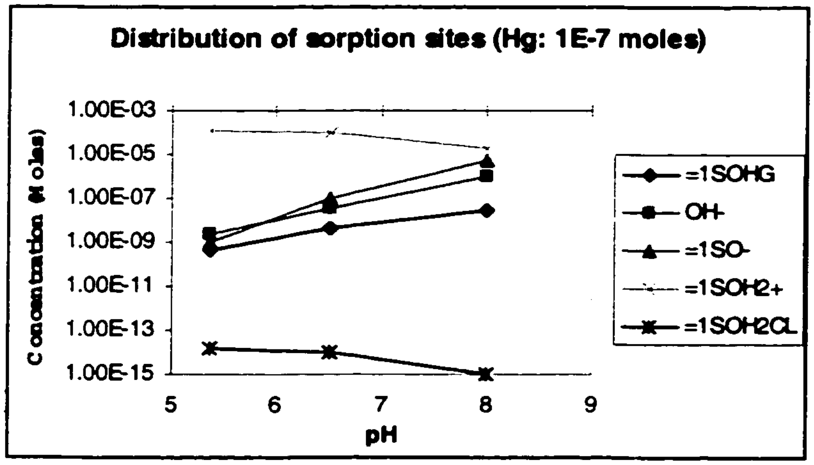


Figure 5.10 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 10 g/L.

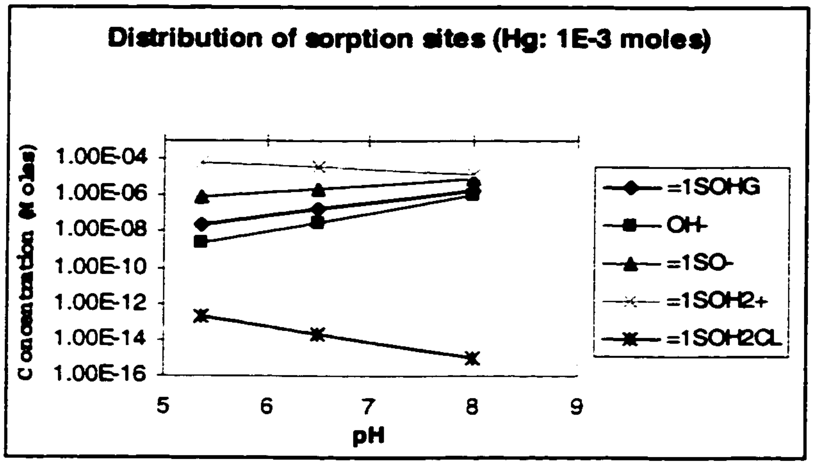


Figure 5.11 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 8.174 g/L.

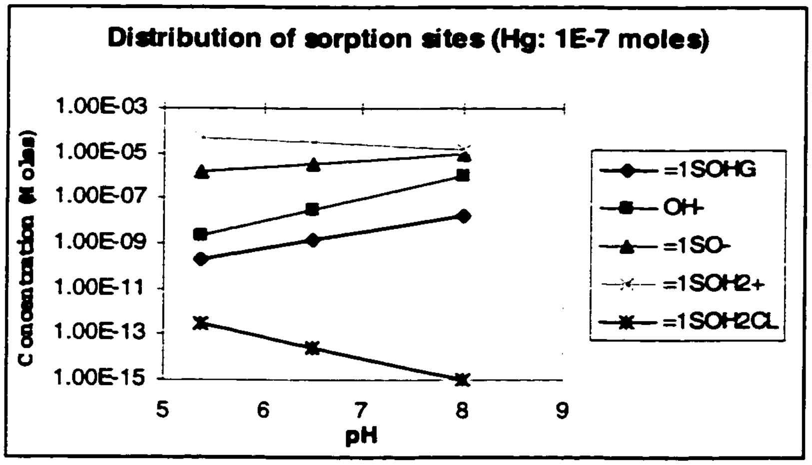


Figure 5.12 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 8.174 g/L.

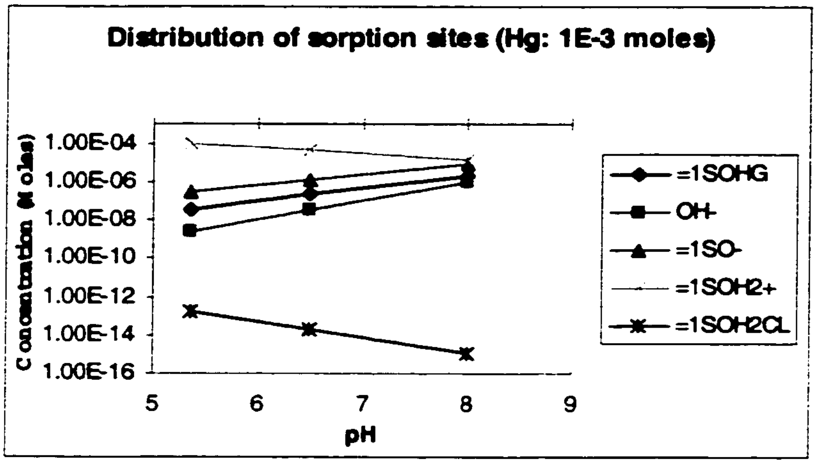


Figure 5.13 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 8.174 g/L.

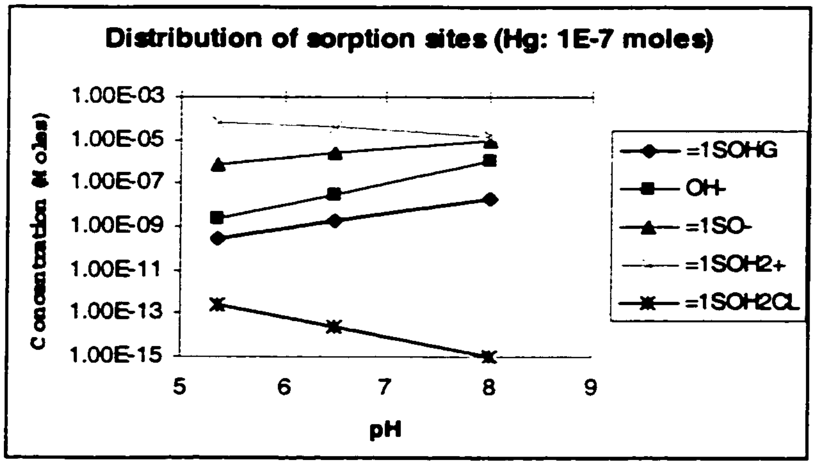


Figure 5.14 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 8.174 g/L.

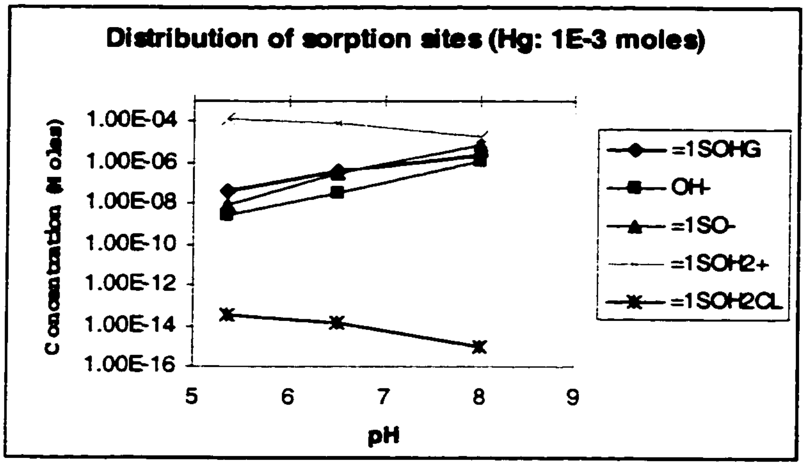


Figure 5.15 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface .(specific surface area: 400 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 8.174 g/L

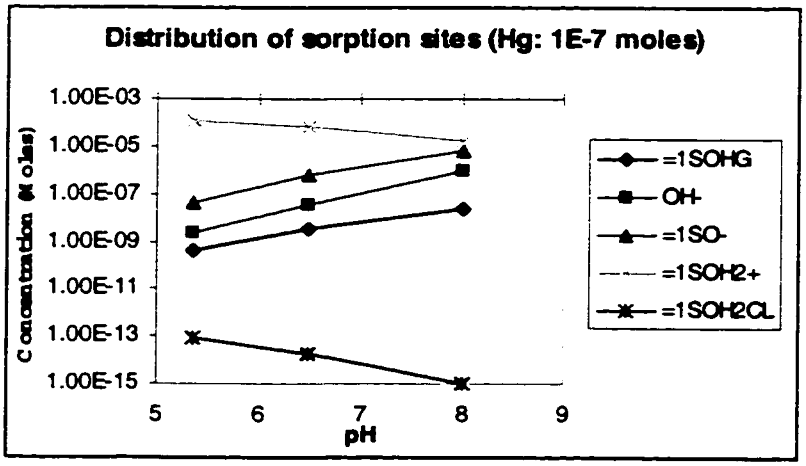


Figure 5.16 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 8.174 g/L.

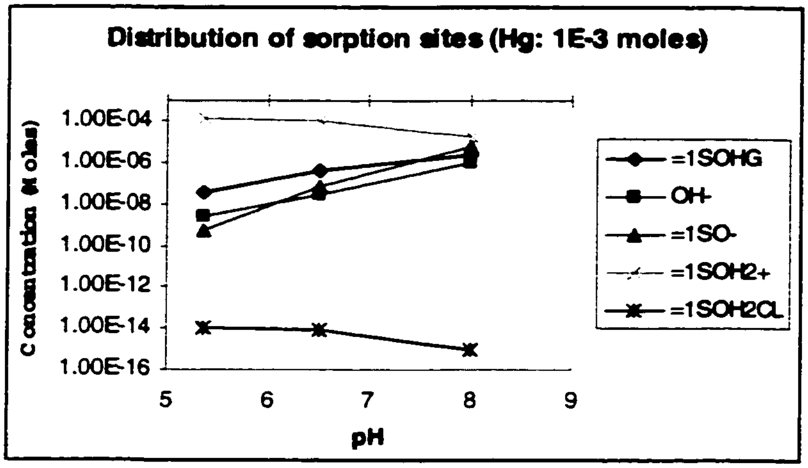


Figure 5.17 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 8.174 g/L.

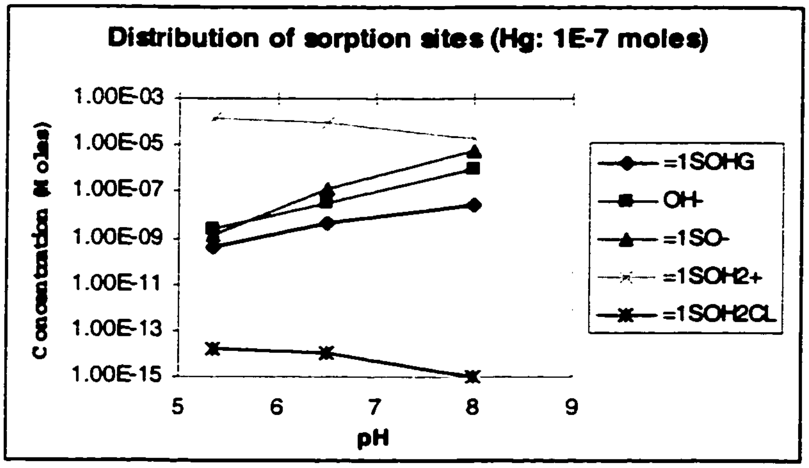


Figure 5.18 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 8.174 g/L.

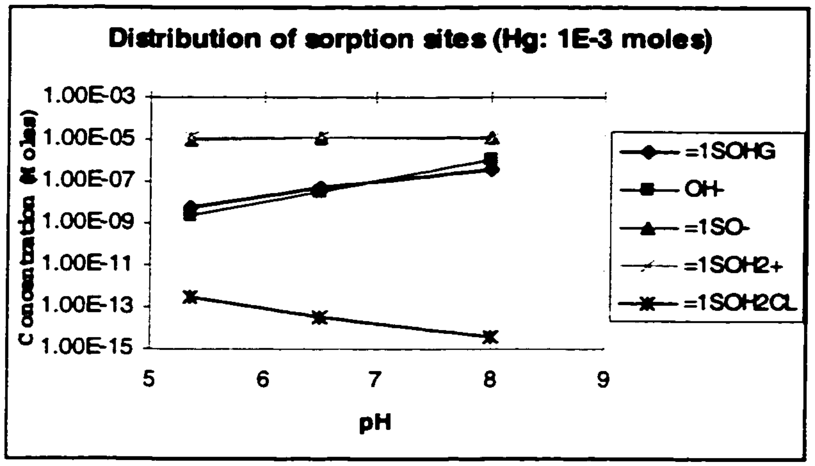


Figure 5.19 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 10 mg/L.

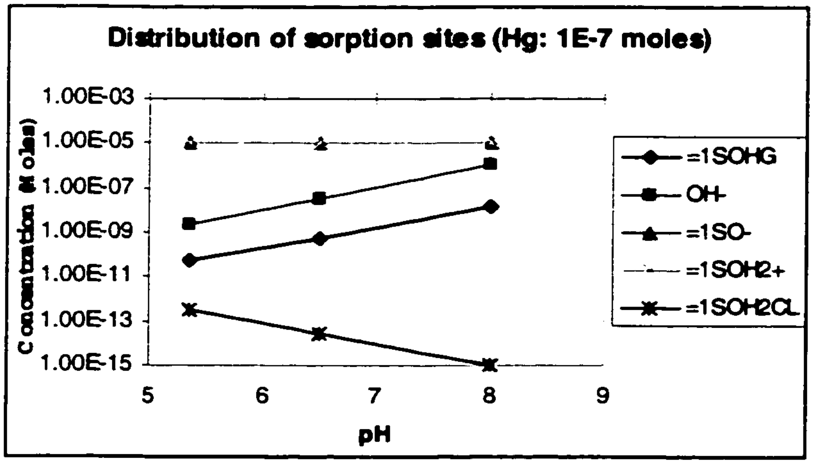


Figure 5.20 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 10 mg/L.

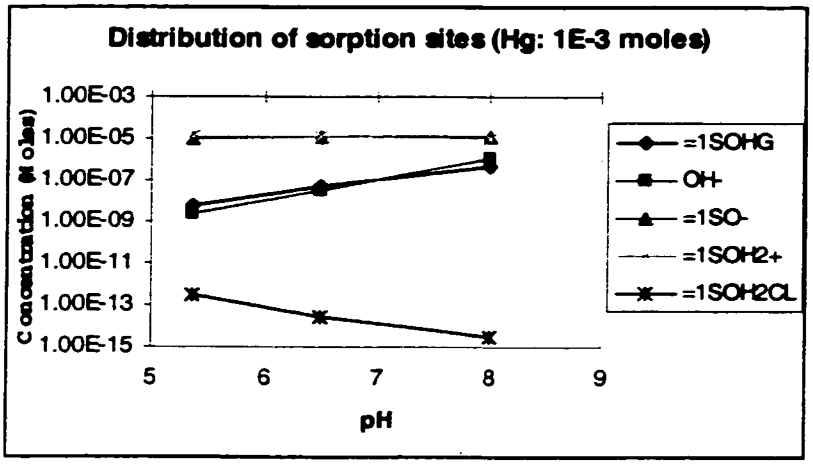


Figure 5.21 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 10 mg/L.

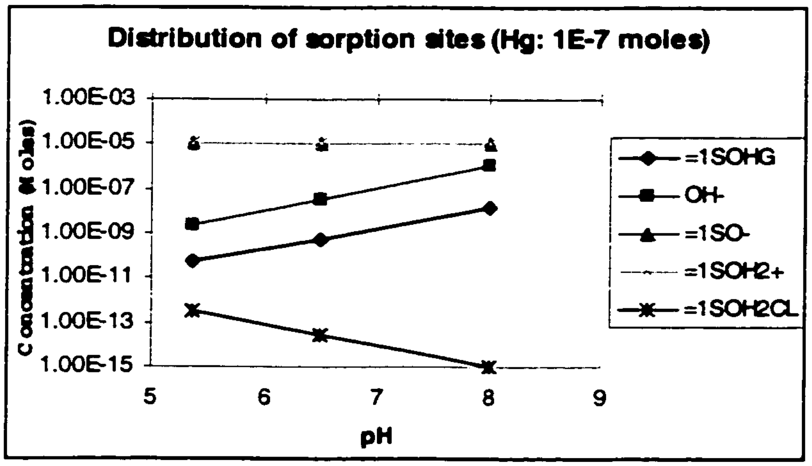


Figure 5.22 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 10 mg/L.

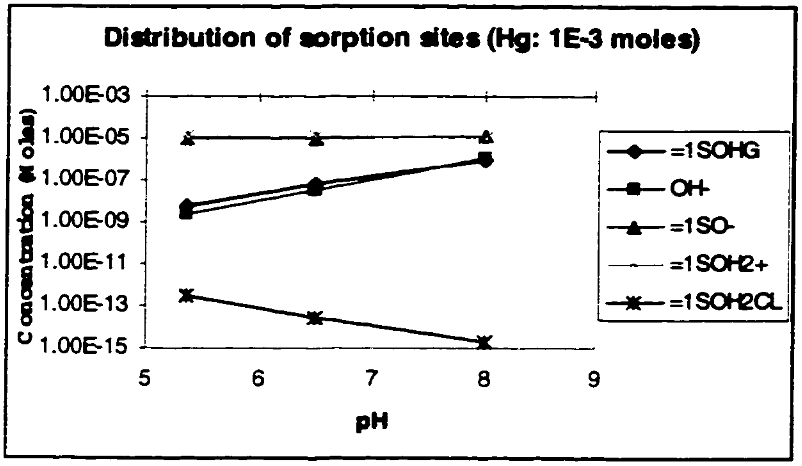
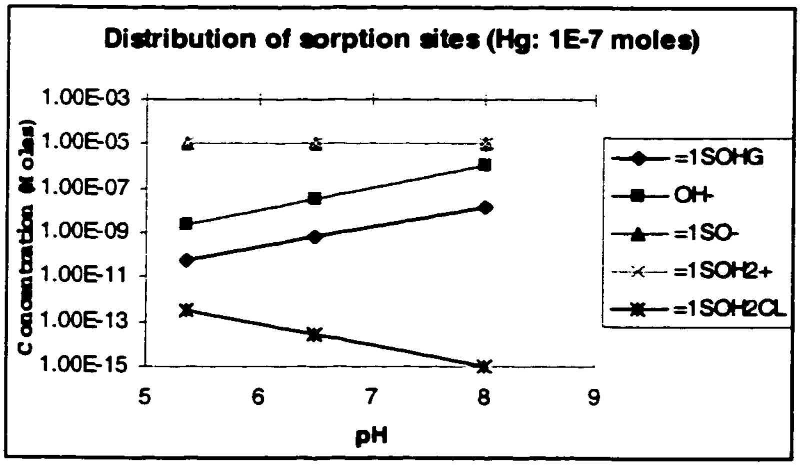


Figure 5.23 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 10 mg/L.



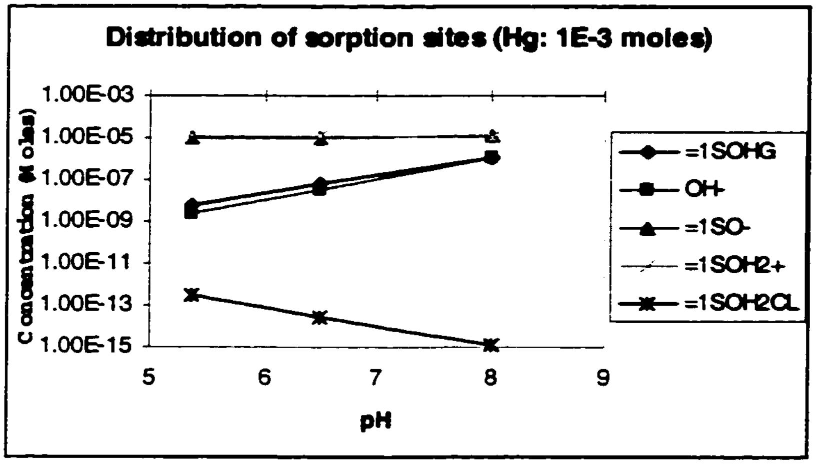


Figure 5.25 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) for Hg concentration 1E-3 moles and adsorbent concentration 10 mg/L.

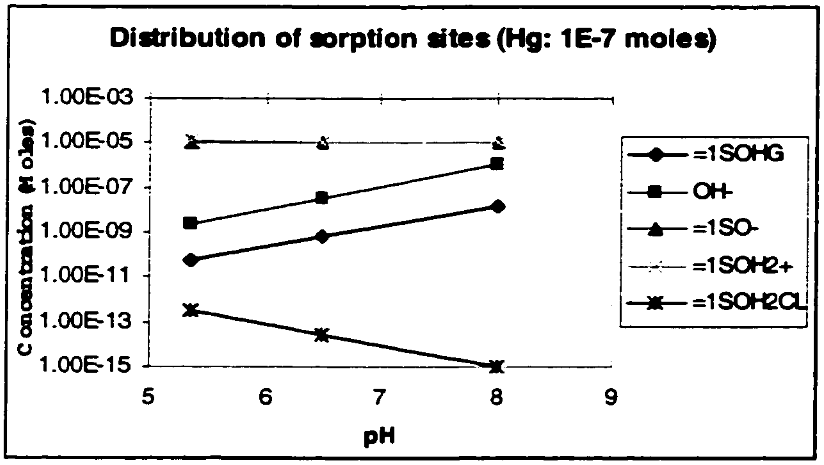


Figure 5.26 Effect of pH variation (from 5.36 to 8.0) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) for Hg concentration 1E-7 moles and adsorbent concentration 10 mg/L.

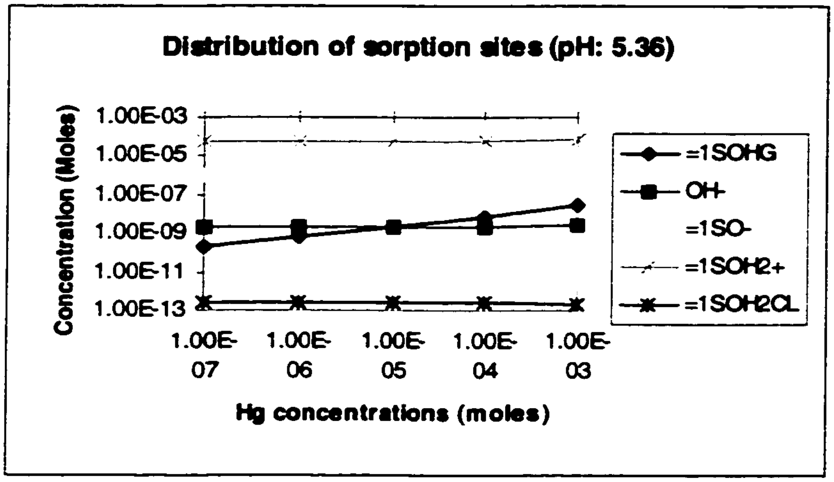


Figure 5.27 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 80 m$^2$/g) at pH 5.36 and adsorbent concentration 10 g/L.

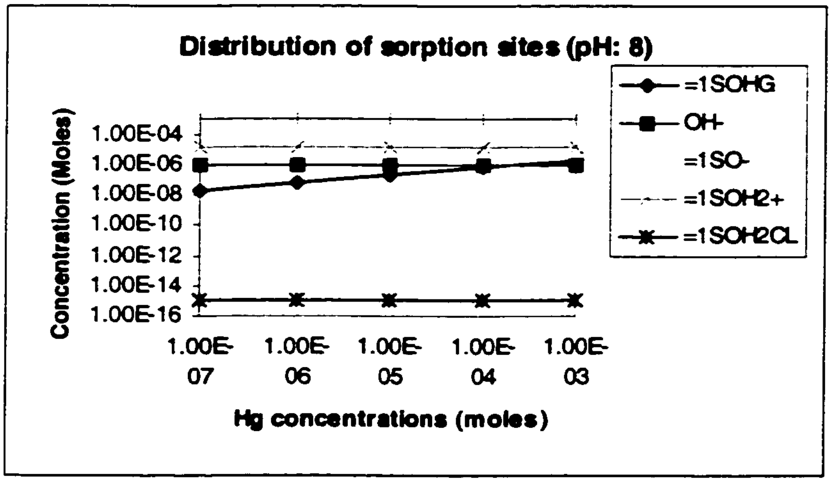


Figure 5.28 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 80 m$^2$/g) at pH 8 and adsorbent concentration 10 g/L.

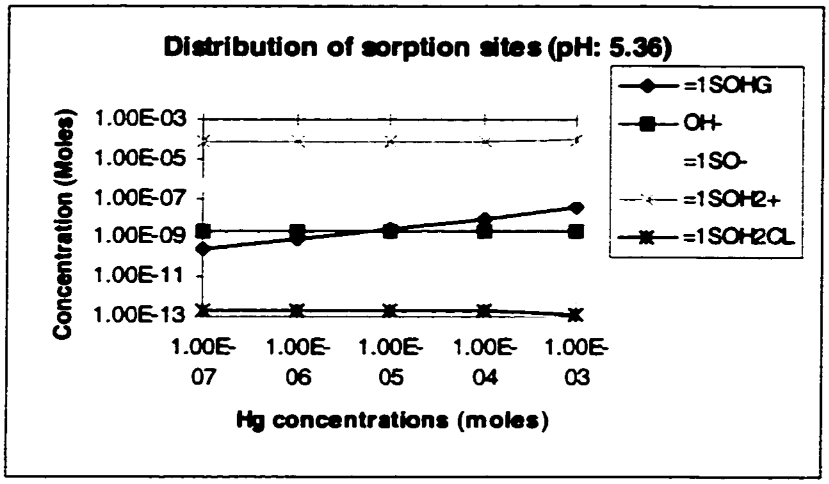


Figure 5.29 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) at pH 5.36 and adsorbent concentration 10 g/L.

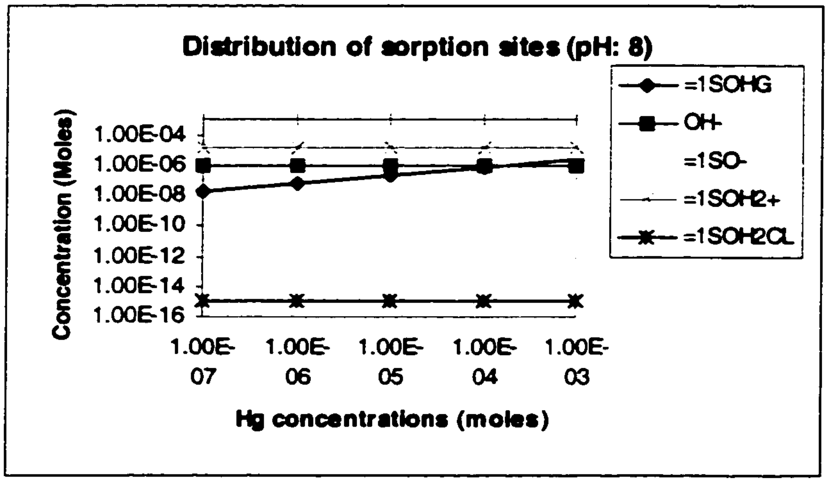


Figure 5.30 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) at pH 8 and adsorbent concentration 10 g/L.

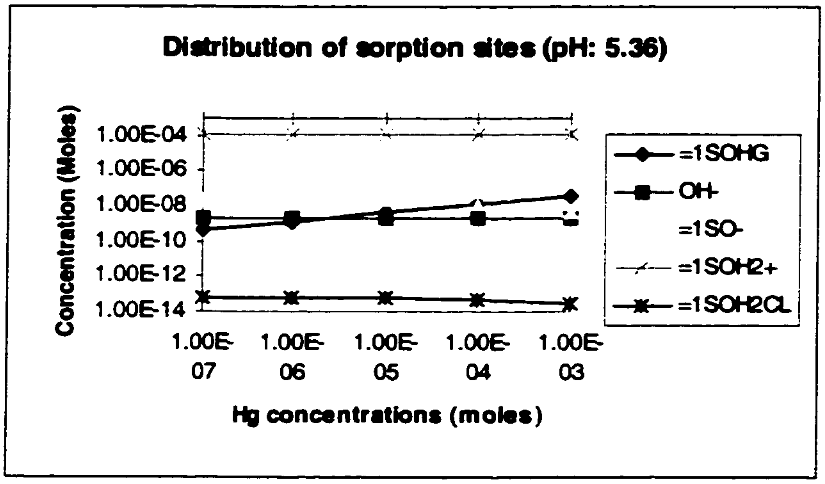


Figure 5.31 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) at pH 5.36 and adsorbent concentration 10 g/L.

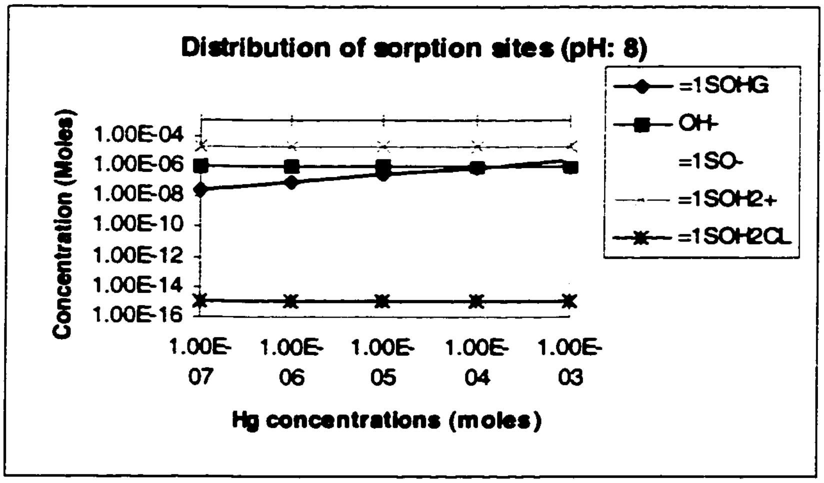


Figure 5.32 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) at pH 8 and adsorbent concentration 10 g/L.

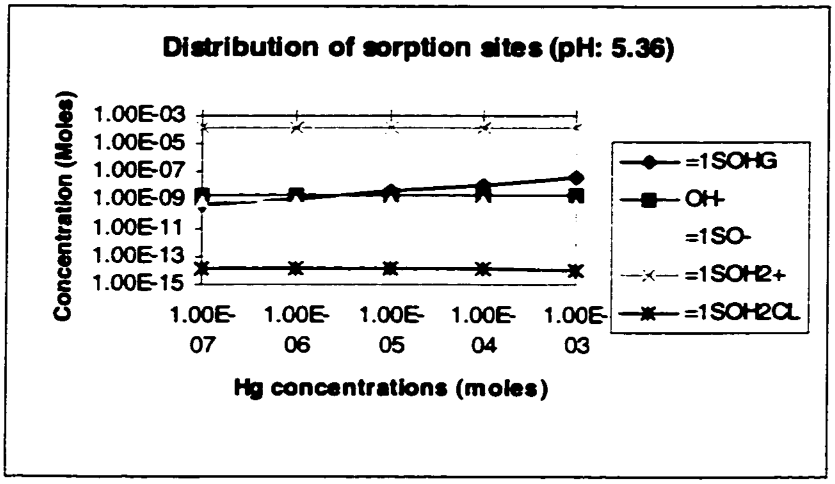


Figure 5.33 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) at pH 5.36 and adsorbent concentration 10 g/L.

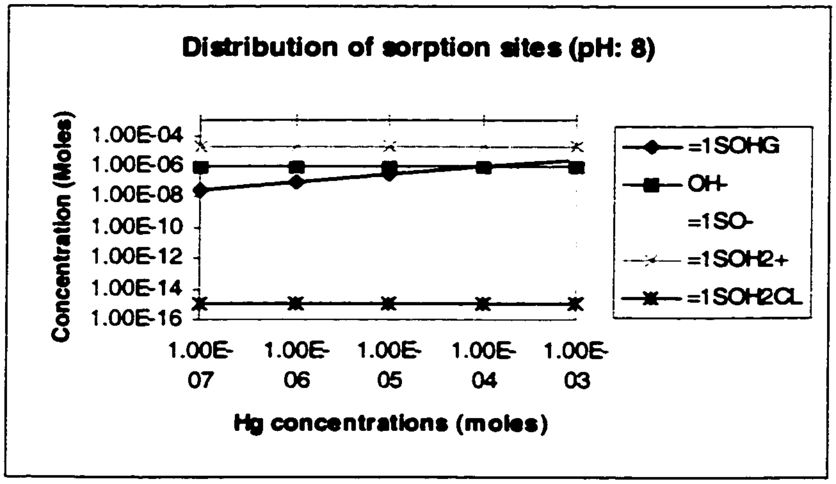


Figure 5.34 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) at pH 8 and adsorbent concentration 10 g/L.

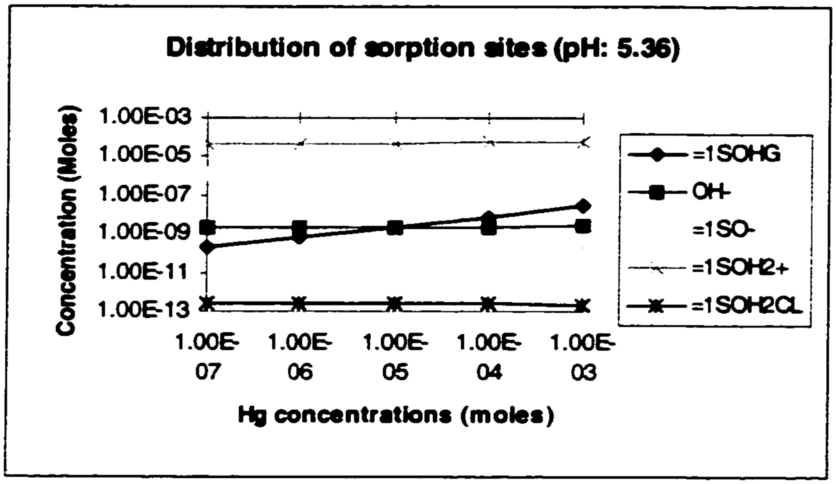


Figure 5.35 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) at pH 5.36 and adsorbent concentration 8.174 g/L.

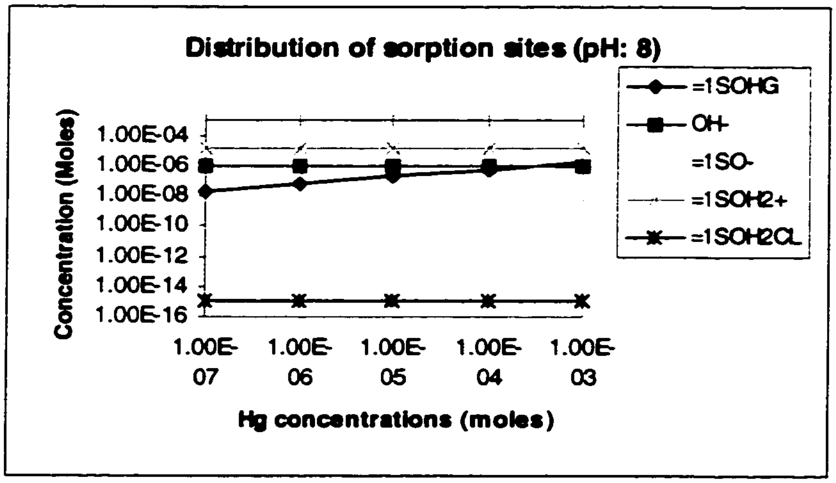


Figure 5.36 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) at pH 8 and adsorbent concentration 8.174 g/L.

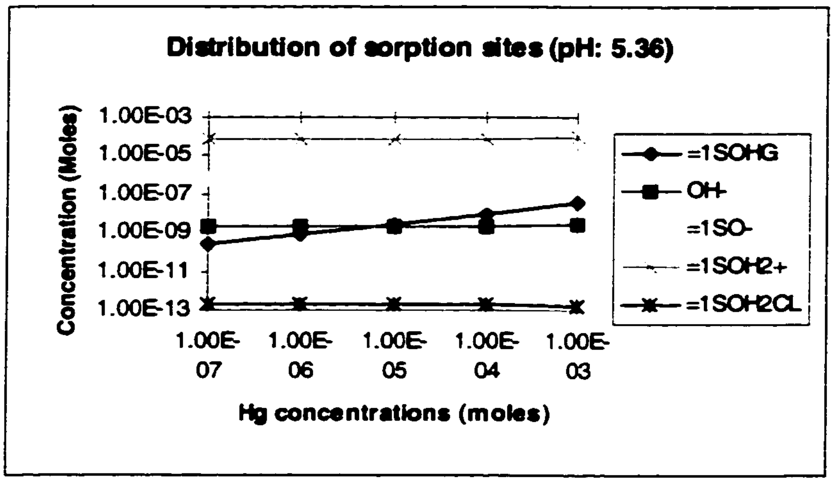


Figure 5.37 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 129 m$^2$/g) at pH 5.36 and adsorbent concentration 8.174 g/L.

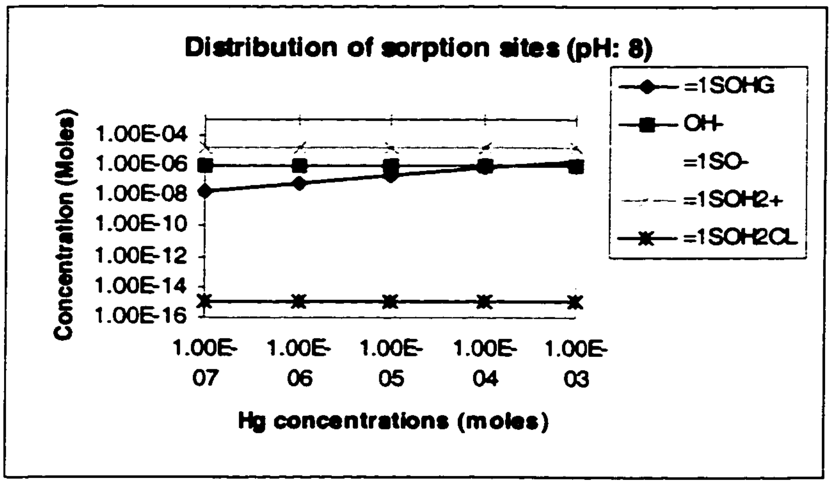


Figure 5.38 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 129 m$^2$/g) at pH 8 and adsorbent concentration 8.174 g/L.

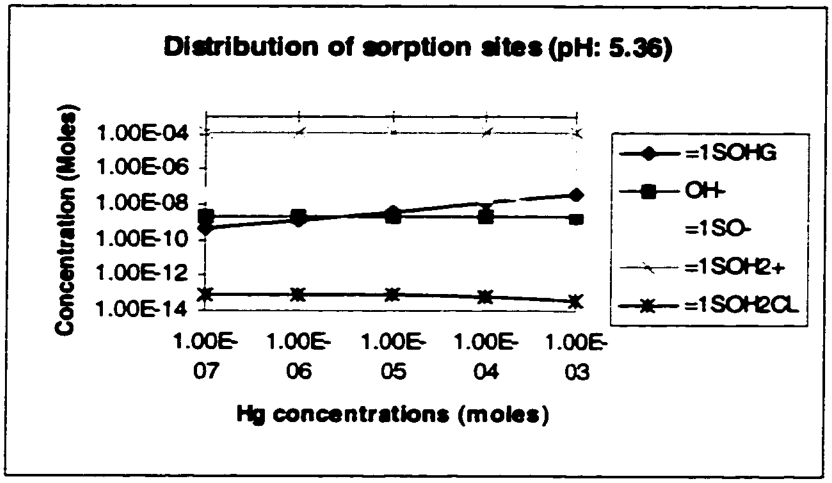


Figure 5.39 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) at pH 5.36 and adsorbent concentration 8.174 g/L.

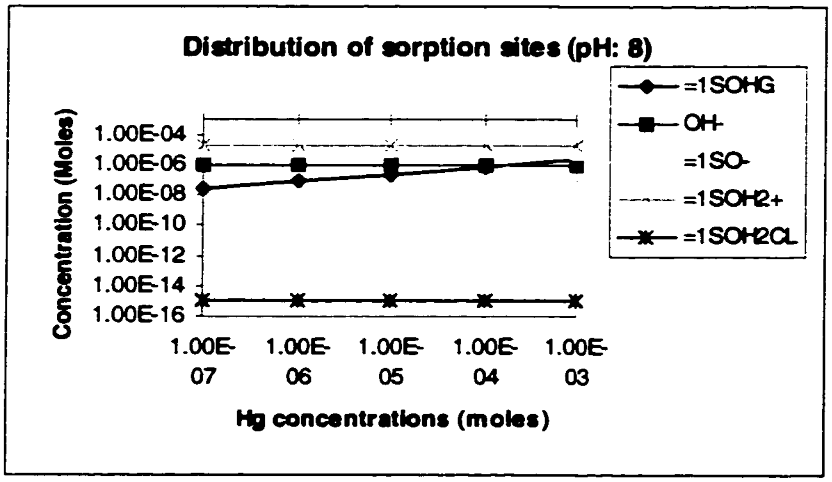


Figure 5.40 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) at pH 8 and adsorbent concentration 8.174 g/L.

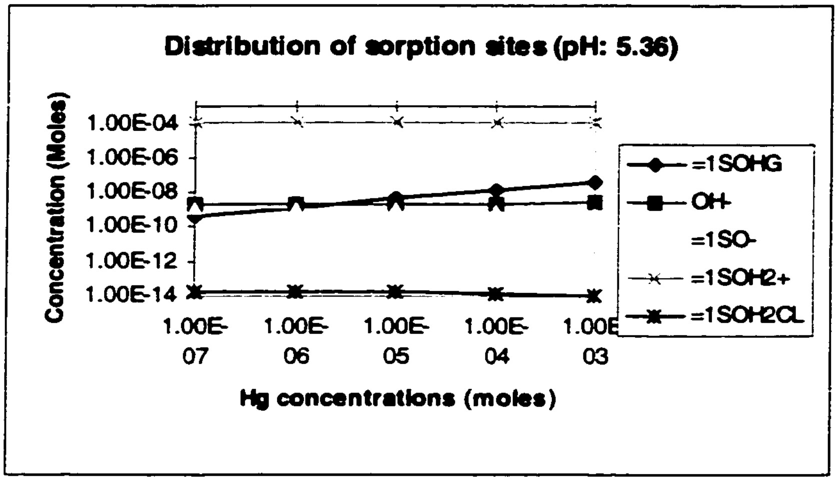


Figure 5.41 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) at pH 5.36 and adsorbent concentration 8.174 g/L.

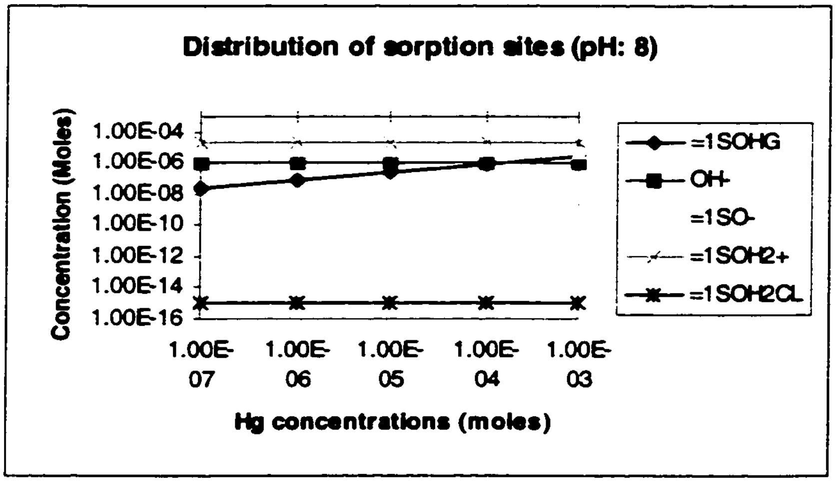


Figure 5.42 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) at pH 8 and adsorbent concentration 8.174 g/L.

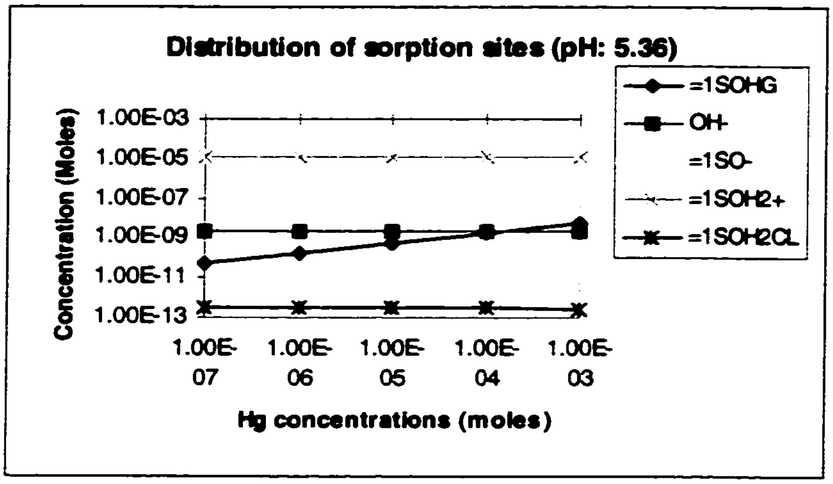


Figure 5.43 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) at pH 5.36 and adsorbent concentration 10 mg/L.

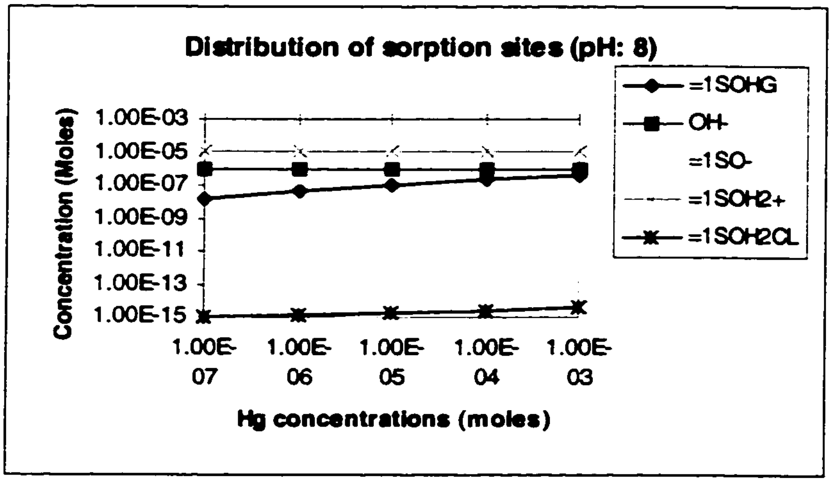


Figure 5.44 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 80 $m^2/g$) at pH 8 and adsorbent concentration 10 mg/L.

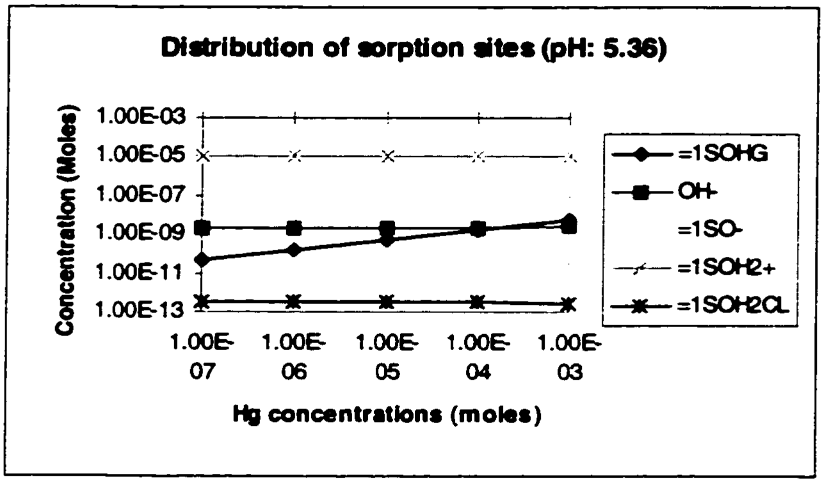


Figure 5.45 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) at pH 5.36 and adsorbent concentration 10 mg/L.

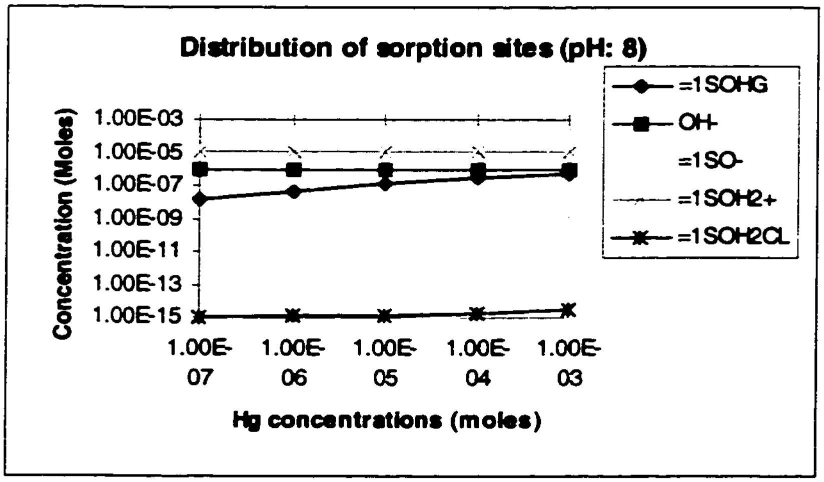


Figure 5.46 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 129 $m^2/g$) at pH 8 and adsorbent concentration 10 mg/L.

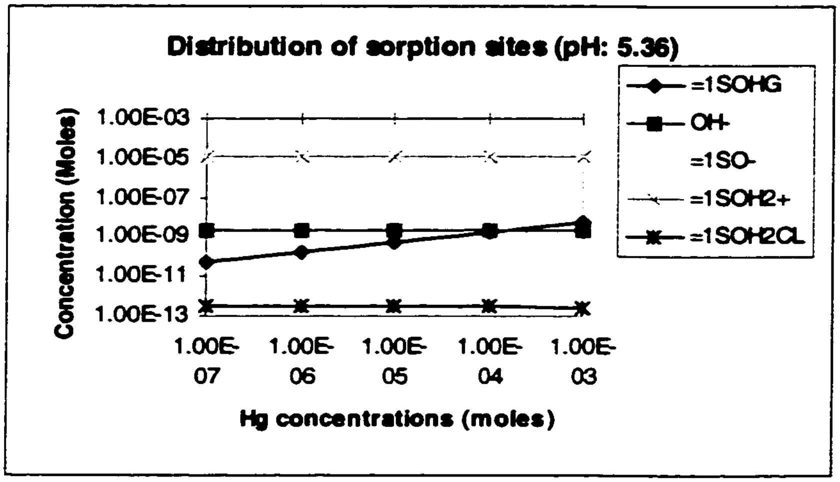


Figure 5.47 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) at pH 5.36 and adsorbent concentration 10 mg/L.

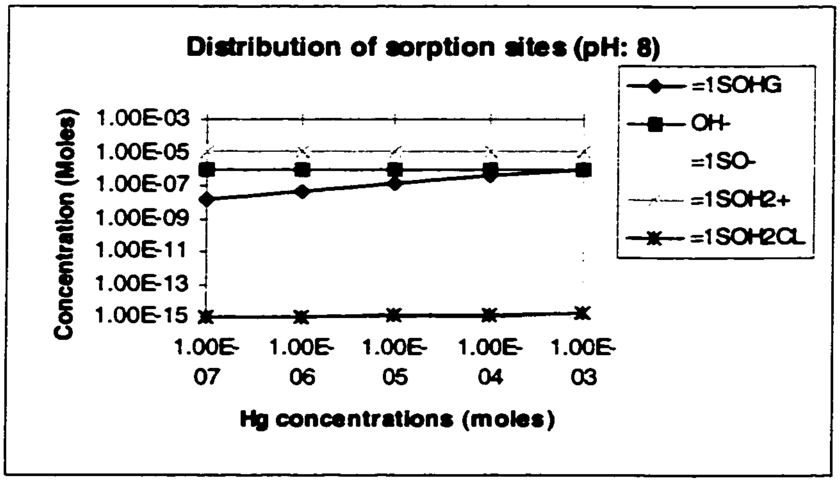


Figure 5.48 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 400 $m^2/g$) at pH 8 and adsorbent concentration 10 mg/L.

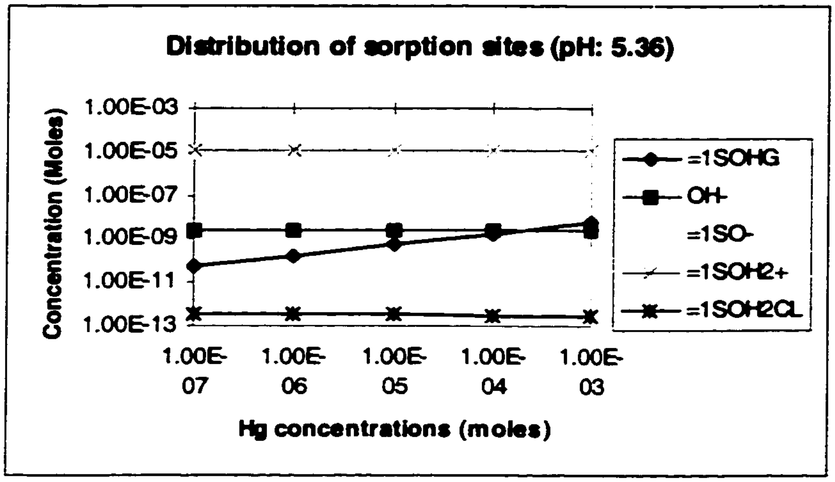


Figure 5.49 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) at pH 5.36 and adsorbent concentration 10 mg/L.

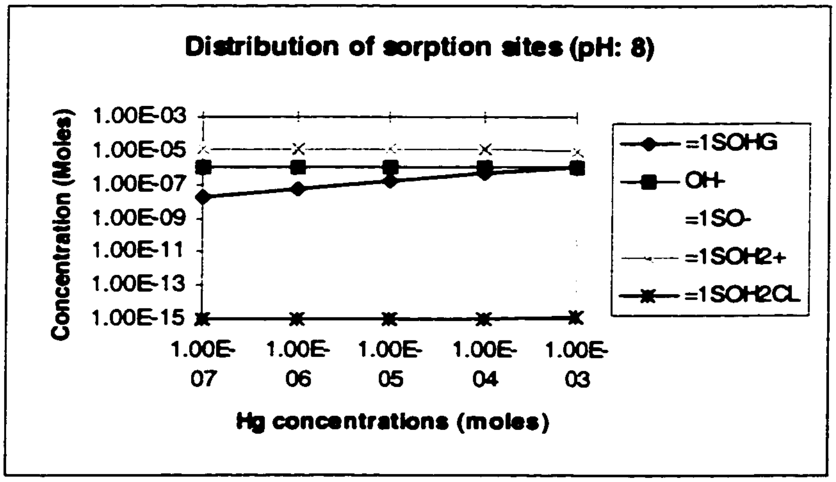


Figure 5.50 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorption on particles' surface (specific surface area: 1350 $m^2/g$) at pH 8 and adsorbent concentration 10 mg/L.

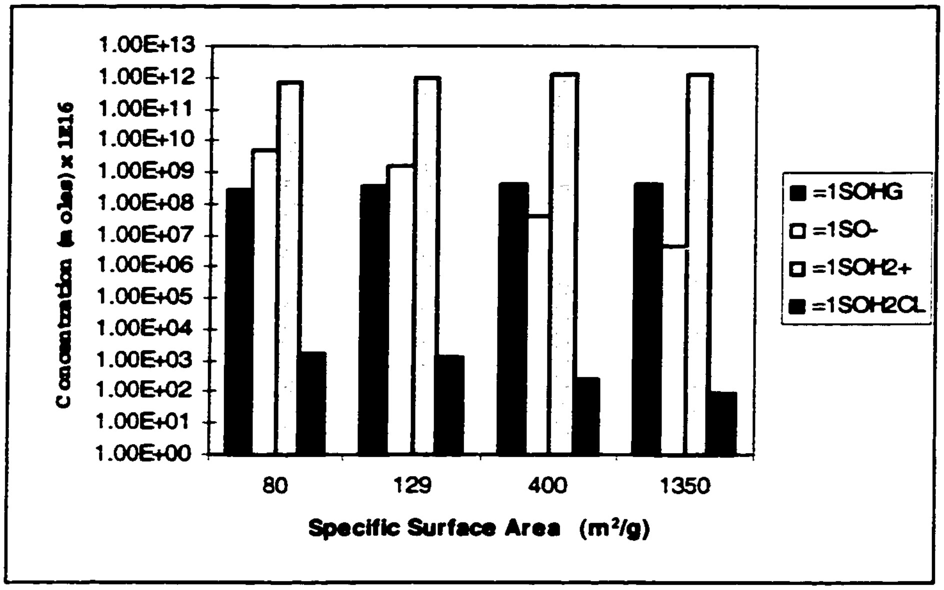


Figure 5.51 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 5.36, adsorbent concentration 10 g/L and initial mercury concentration of 1 E-3 moles.

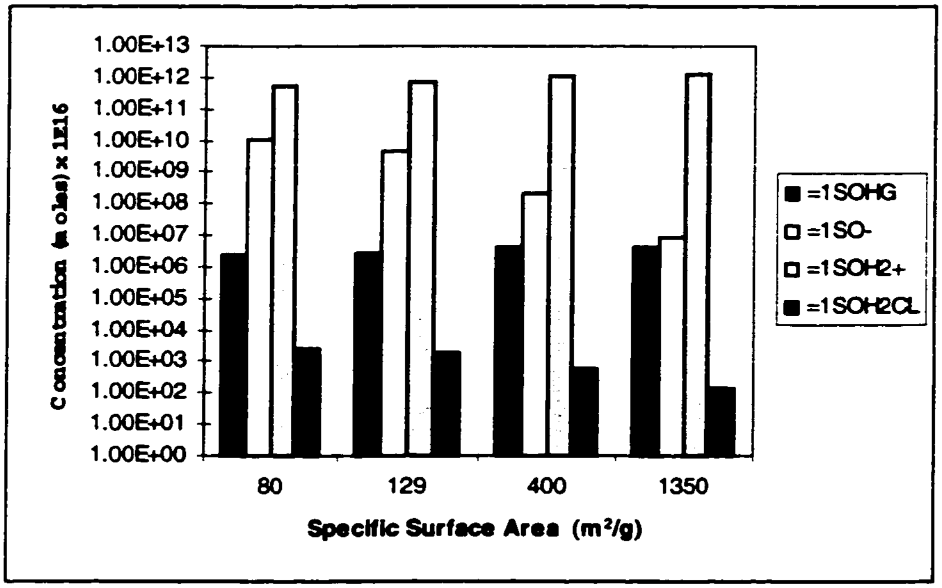


Figure 5.52 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 5.36, adsorbent concentration 10 g/L and initial mercury concentration of 1 E-7 moles.

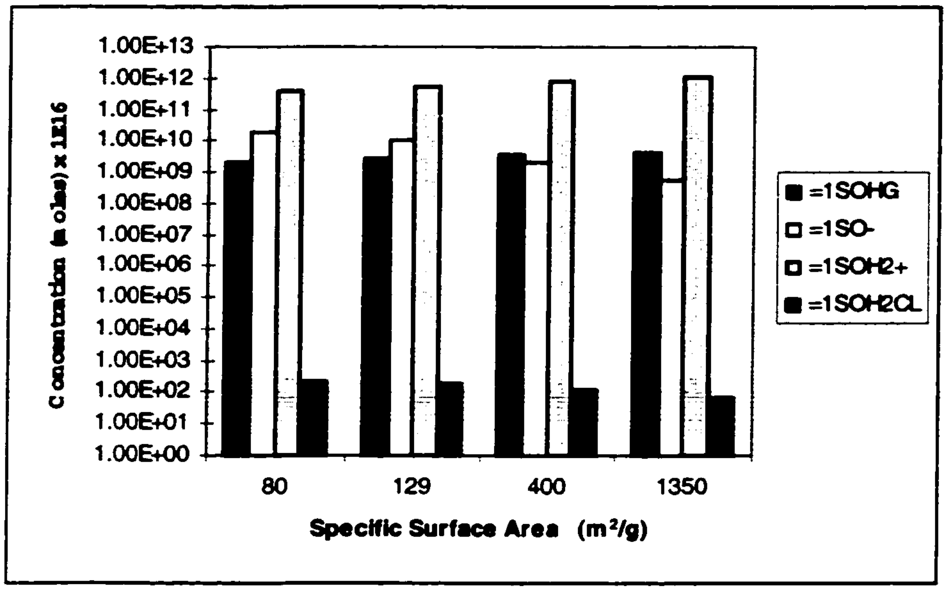


Figure 5.53 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 6.5, adsorbent concentration 10 g/L and initial mercury concentration of 1 E-3 moles.

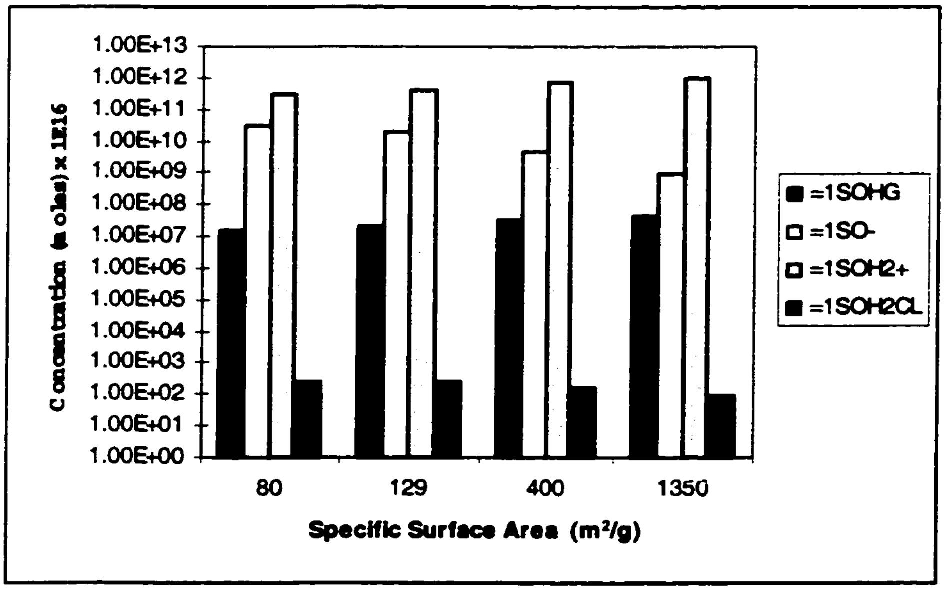


Figure 5.54 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 6.5, adsorbent concentration 10 g/L and initial mercury concentration of 1 E-7 moles.

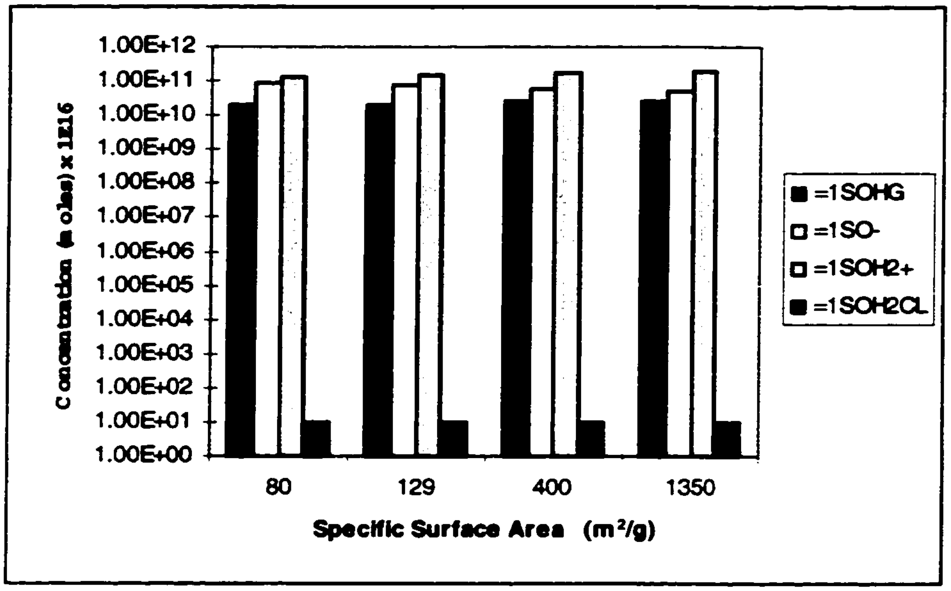


Figure 5.55 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 8, adsorbent concentration 10 g/L and initial mercury concentration of 1 E-3 moles.

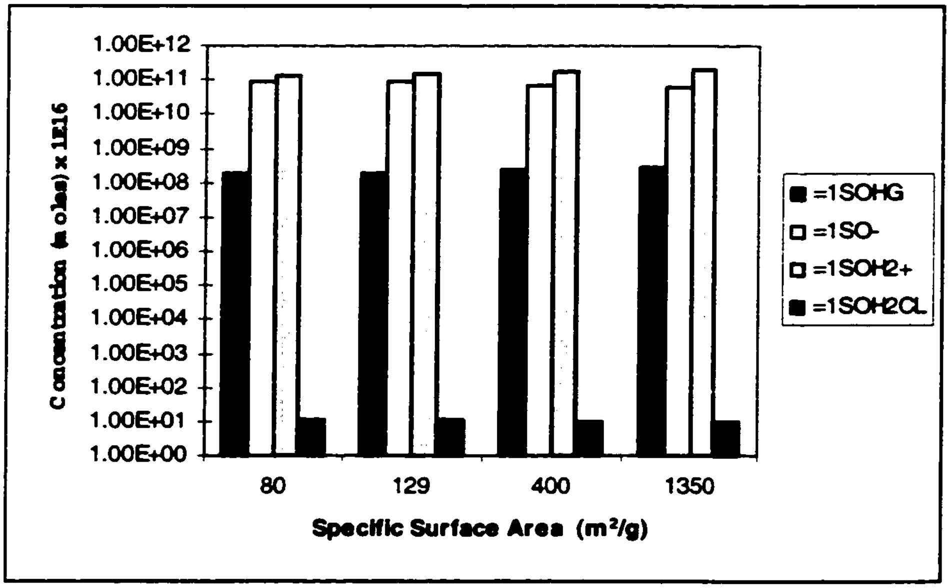


Figure 5.56 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 8, adsorbent concentration 10 g/L and initial mercury concentration of 1 E-7 moles.

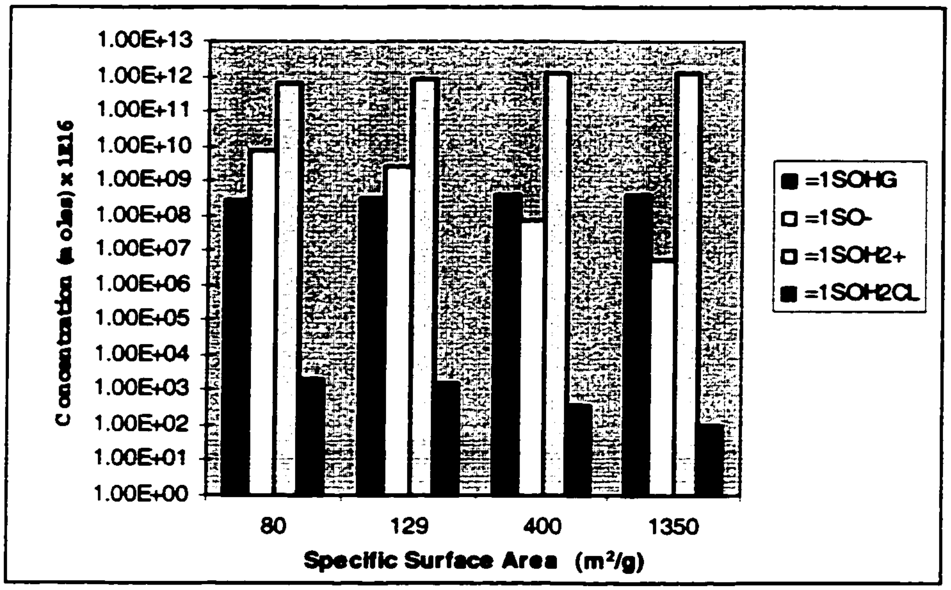


Figure 5.57 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g) on mercury sorption on particles' surface at pH 5.36, adsorbent concentration 8.174 g/L and initial mercury concentration of 1 E-3 moles.

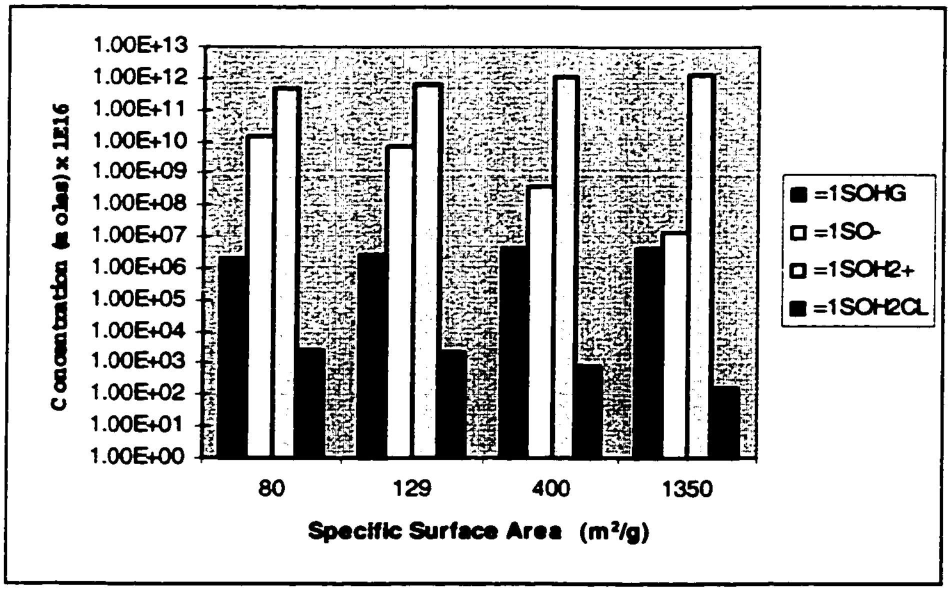


Figure 5.58 Effect of different soil's specific surface areas (80 to 1350 m2/g) on mercury sorption on particles' surface at pH 5.36, adsorbent concentration 8.174 g/L and initial mercury concentration of 1 E-7 moles.

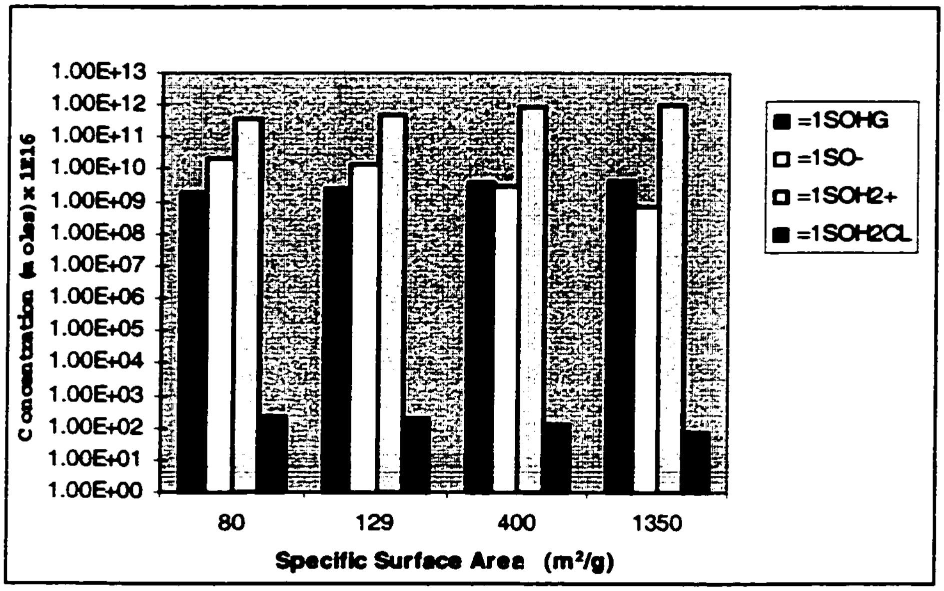


Figure 5.59 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g) on mercury sorption on particles' surface at pH 6.5, adsorbent concentration 8.174 g/L and initial mercury concentration of 1 E-3 moles.

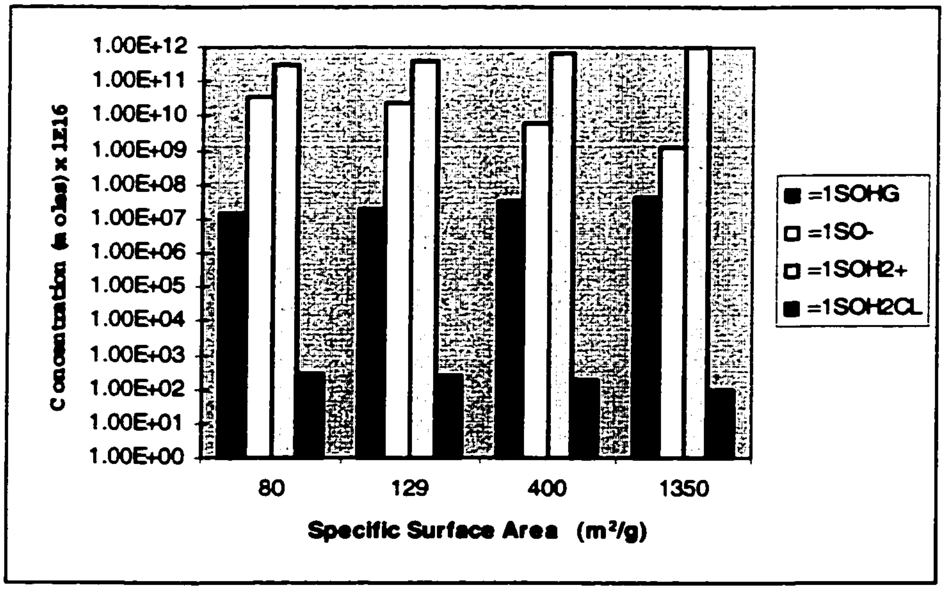


Figure 5.60 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g) on mercury sorption on particles' surface at pH 6.5, adsorbent concentration 8.174 g/L and initial mercury concentration of 1 E-7 moles.

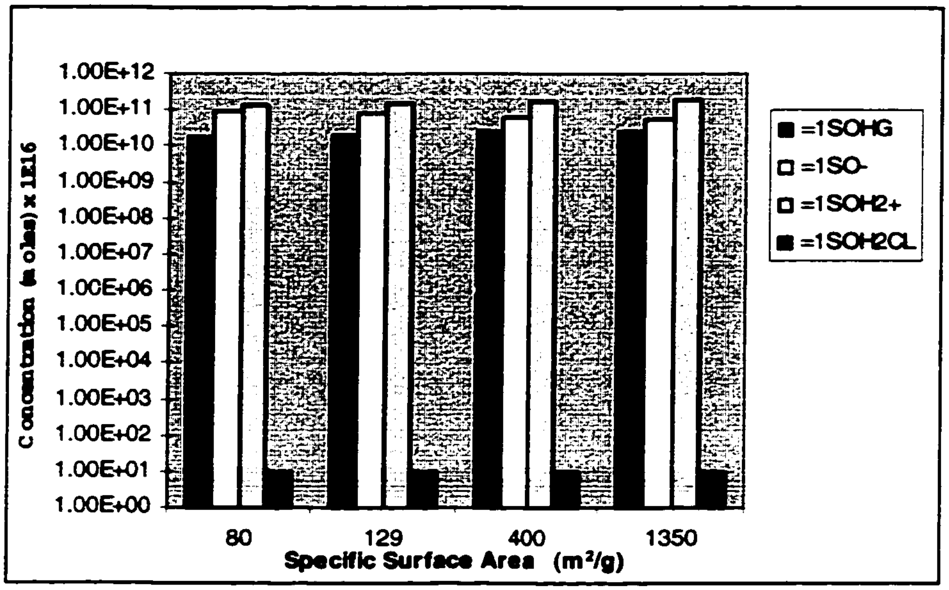


Figure 5.61 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 8, adsorbent concentration 8.174 g/L and initial mercury concentration of 1 E-3 moles.

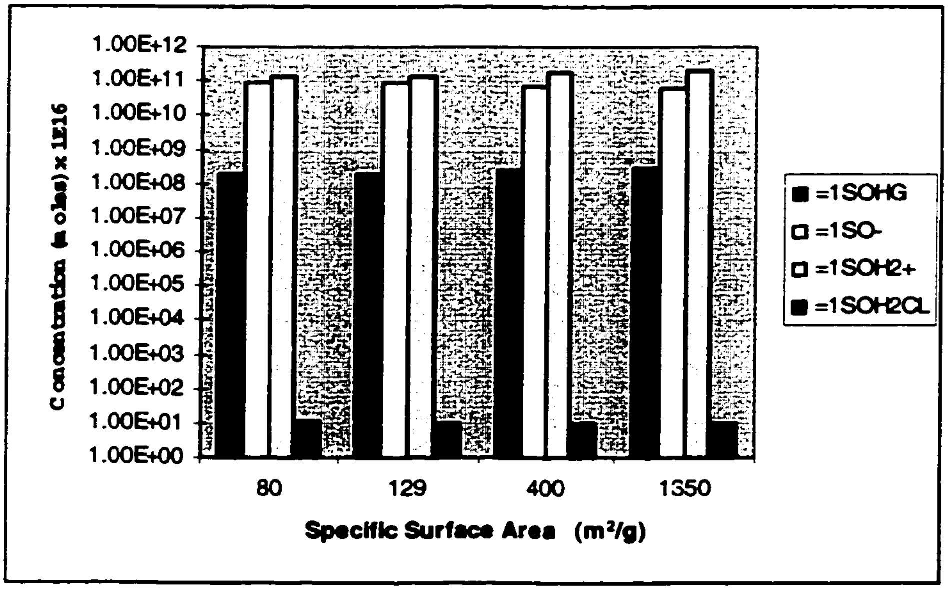


Figure 5.62 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 8, adsorbent concentration 8.174 g/L and initial mercury concentration of 1 E-7 moles.

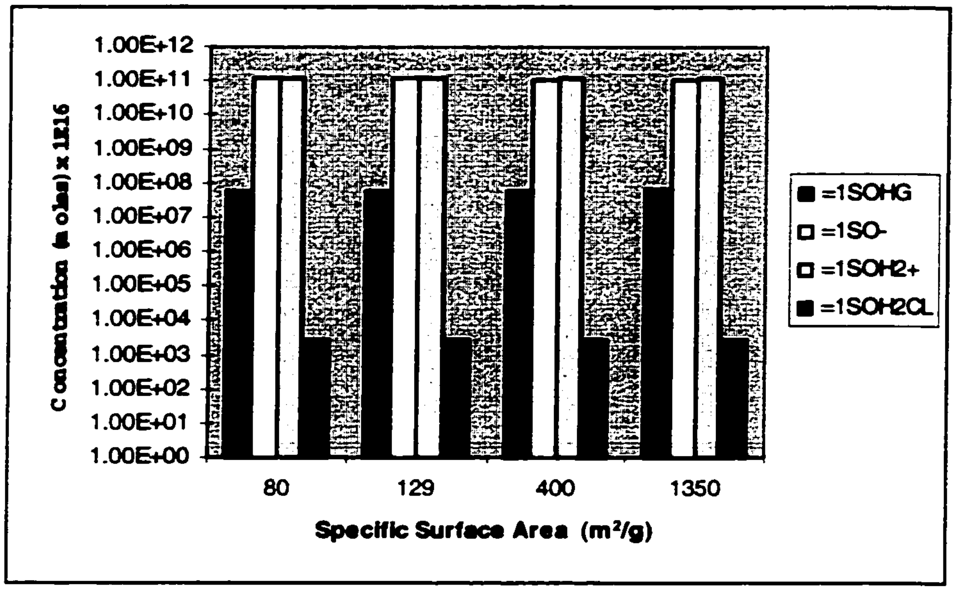


Figure 5.63 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 5.36, adsorbent concentration 10 mg/L and initial mercury concentration of 1 E-3 moles.

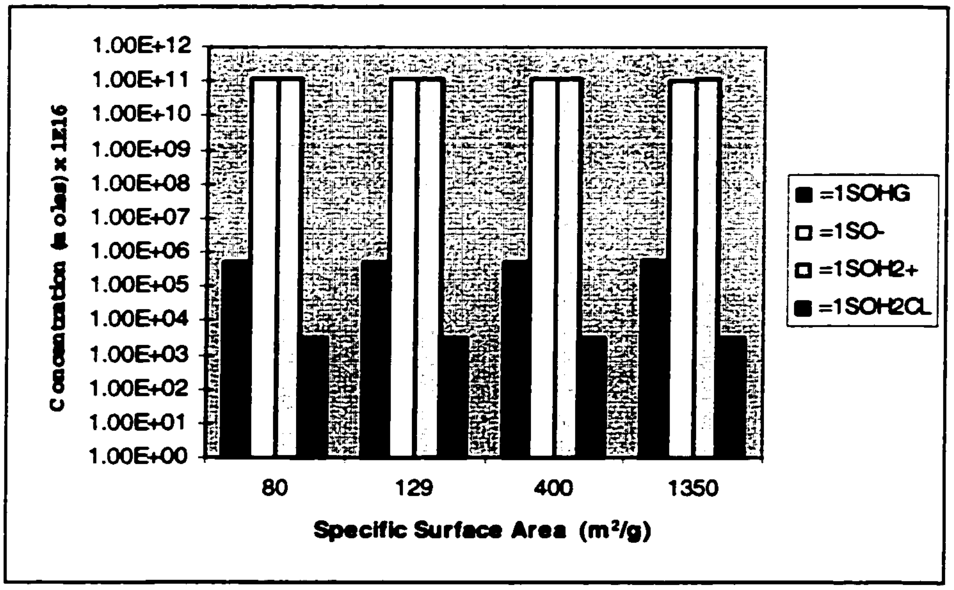


Figure 5.64 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 5.36, adsorbent concentration 10 mg/L and initial mercury concentration of 1 E-7 moles.

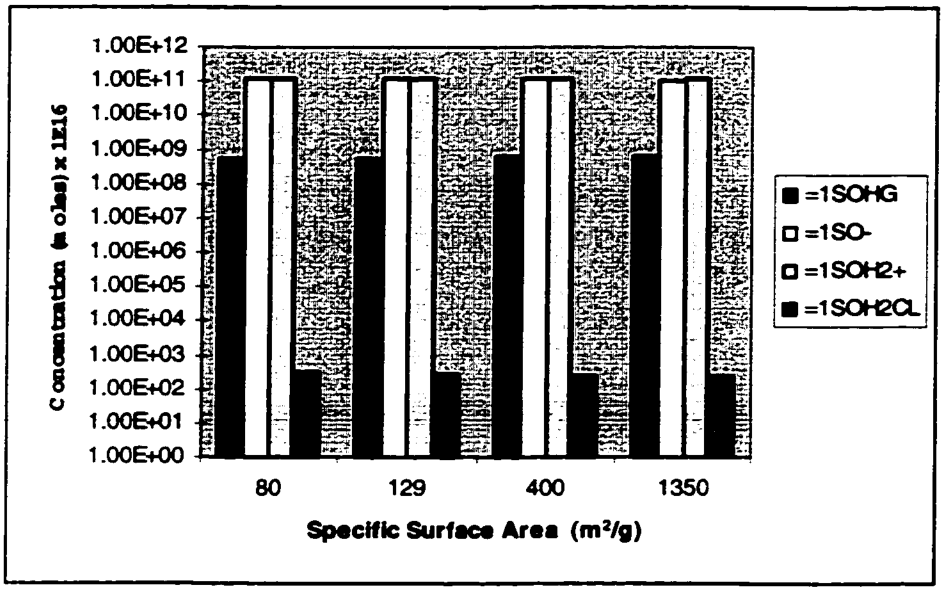


Figure 5.65 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 6.5, adsorbent concentration 10 mg/L and initial mercury concentration of 1 E-3 moles.

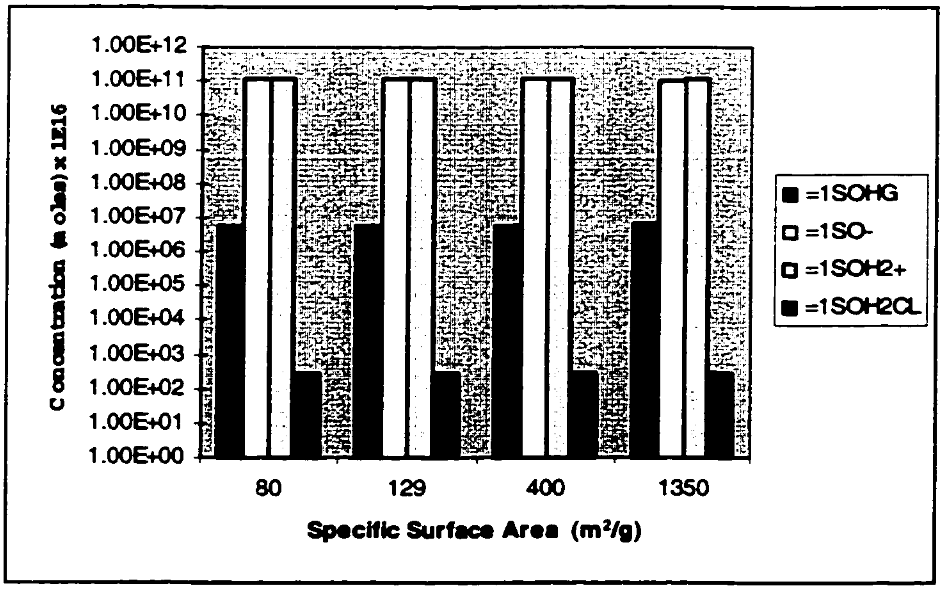


Figure 5.66 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 6.5, adsorbent concentration 10 mg/L and initial mercury concentration of 1 E-7 moles.

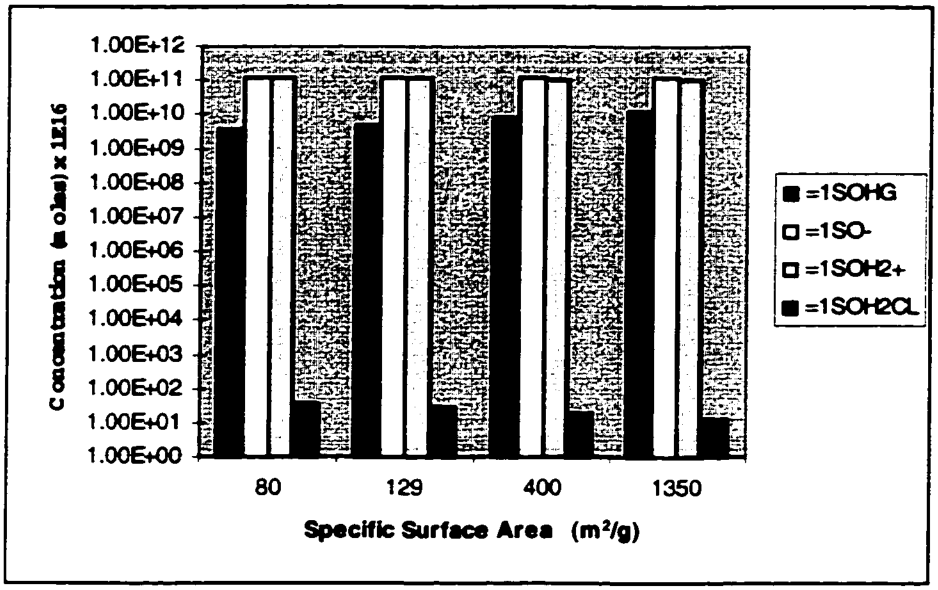


Figure 5.67 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 8, adsorbent concentration 10 mg/L and initial mercury concentration of 1 E-3 moles.

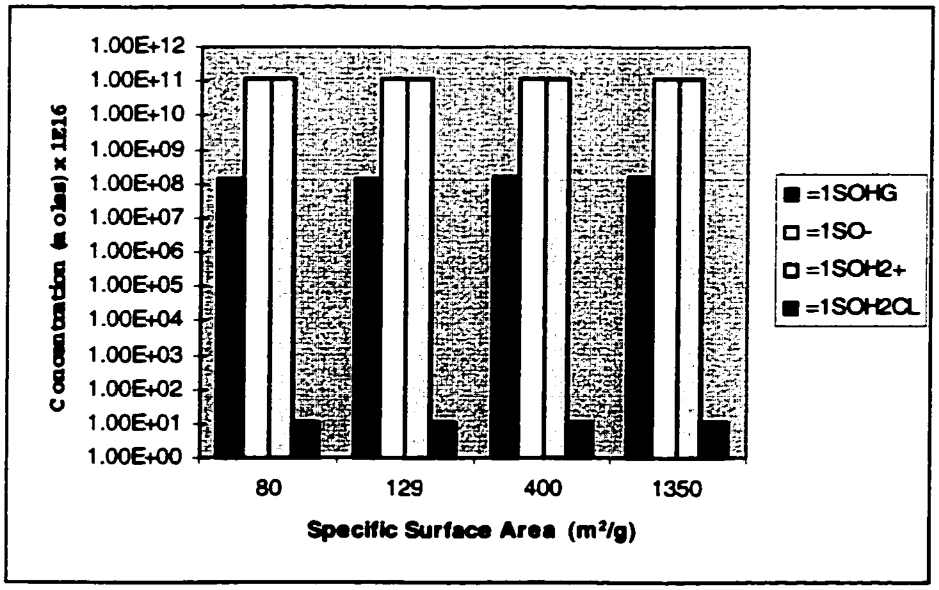


Figure 5.68 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$) on mercury sorption on particles' surface at pH 8, adsorbent concentration 10 mg/L and initial mercury concentration of 1 E-7 moles.

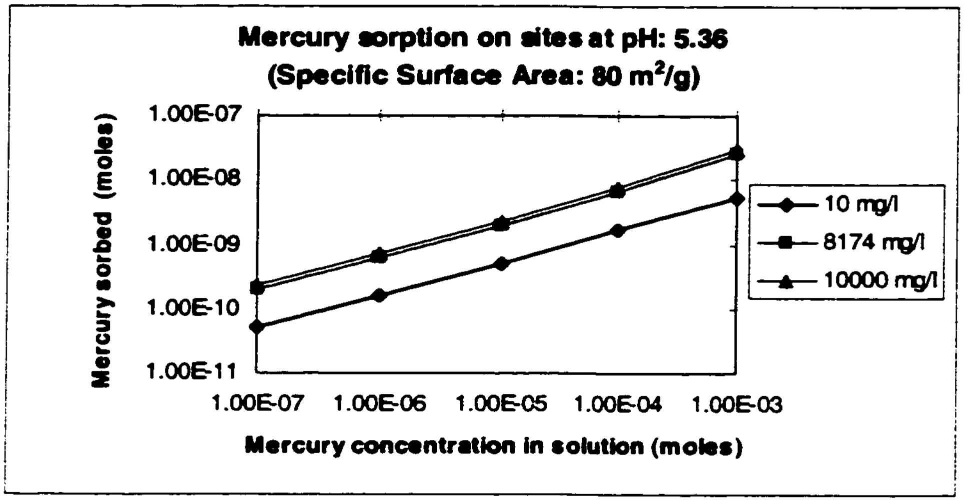


Figure 5.69 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 80 $m^2/g$) at pH 5.36, and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

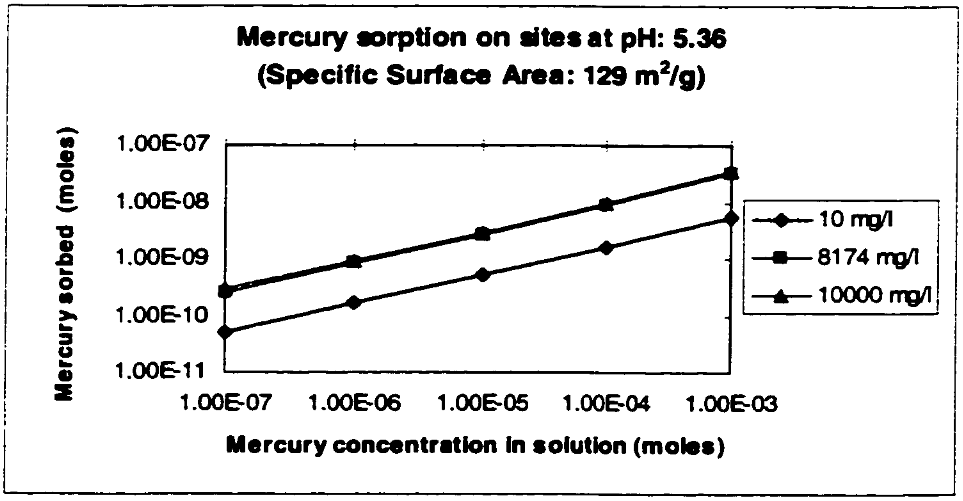


Figure 5.70 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 129 $m^2/g$) at pH 5.36 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

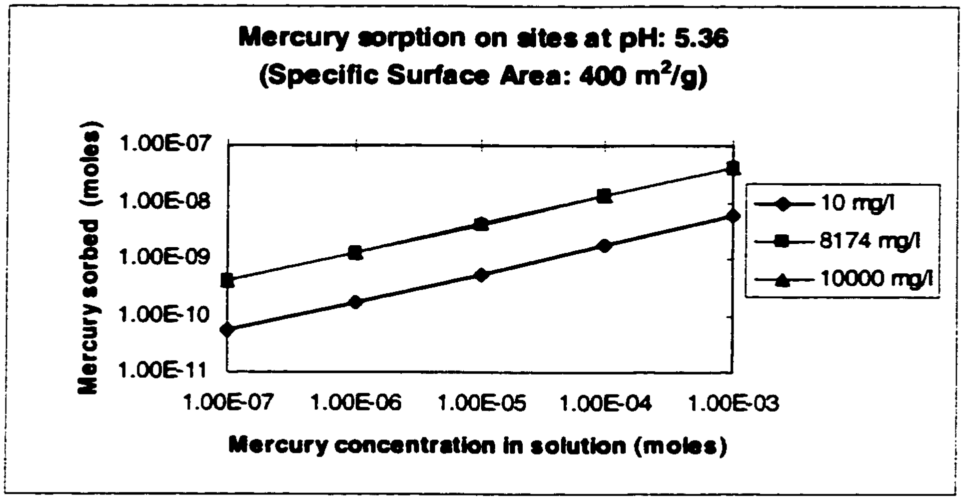


Figure 5.71 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 400 $m^2/g$) at pH 5.36 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

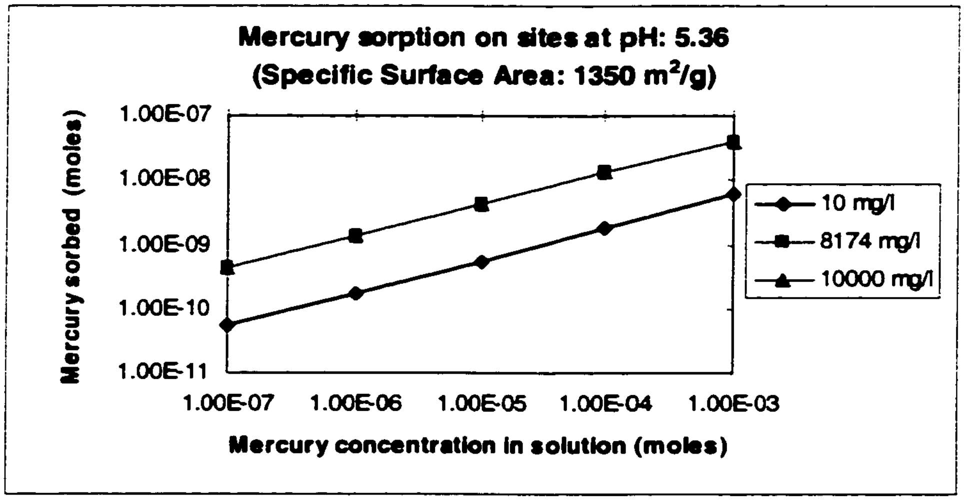


Figure 5.72 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 1350 $m^2/g$) at pH 5.36 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

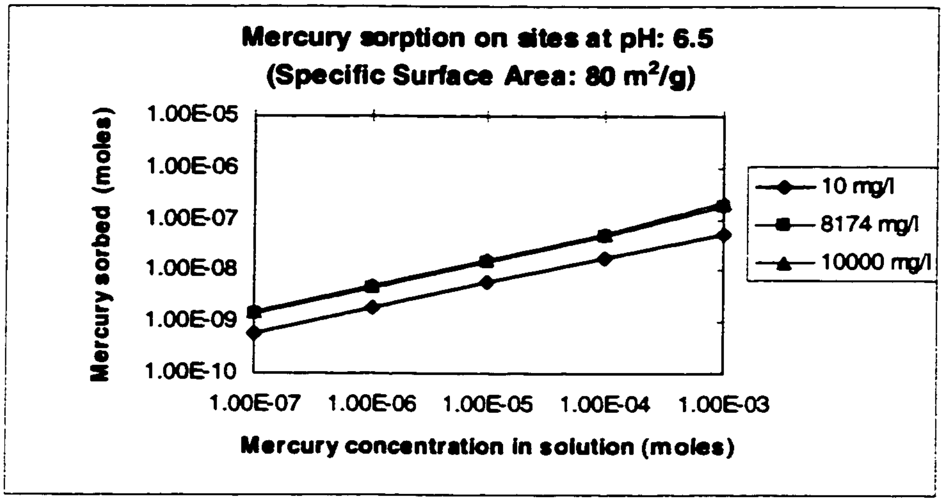


Figure 5.73 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 80 $m^2/g$) at pH 6.5 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

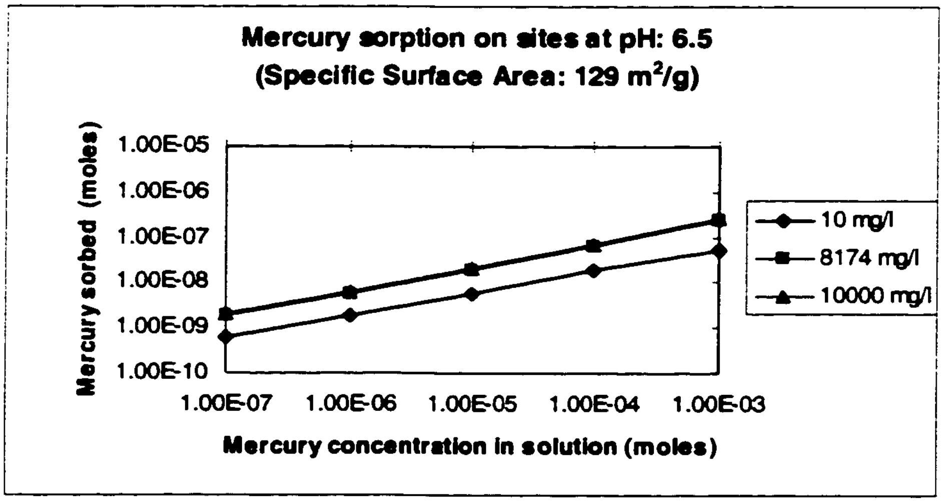


Figure 5.74 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 129 $m^2/g$) at pH 6.5 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

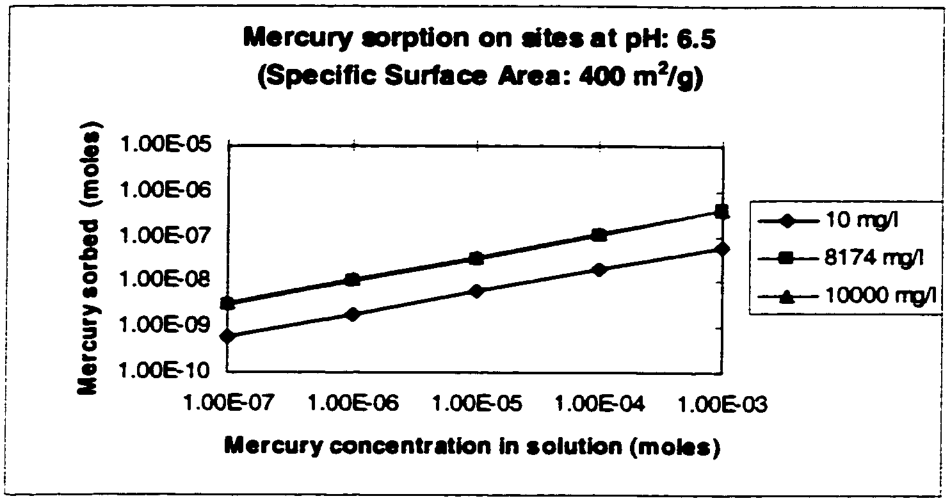


Figure 5.75 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 400 m$^2$/g) at pH 6.5 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

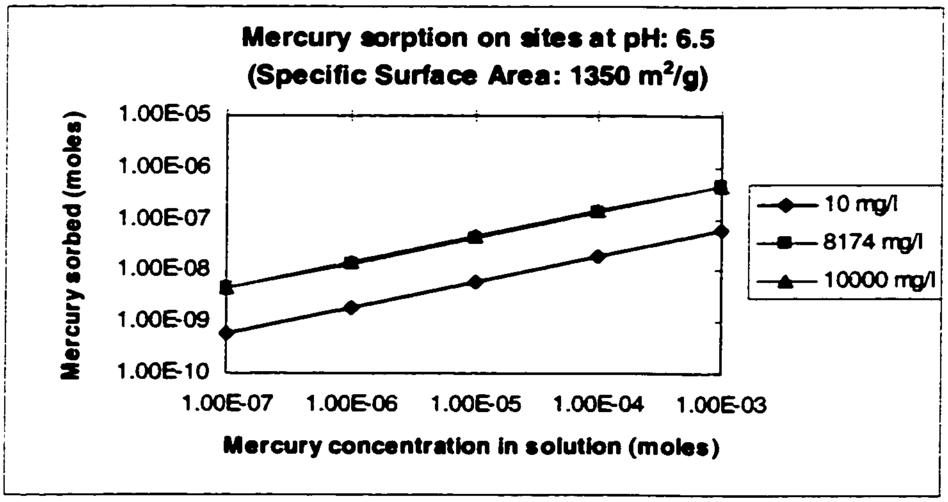


Figure 5.76 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 1350 m$^2$/g) at pH 6.5 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

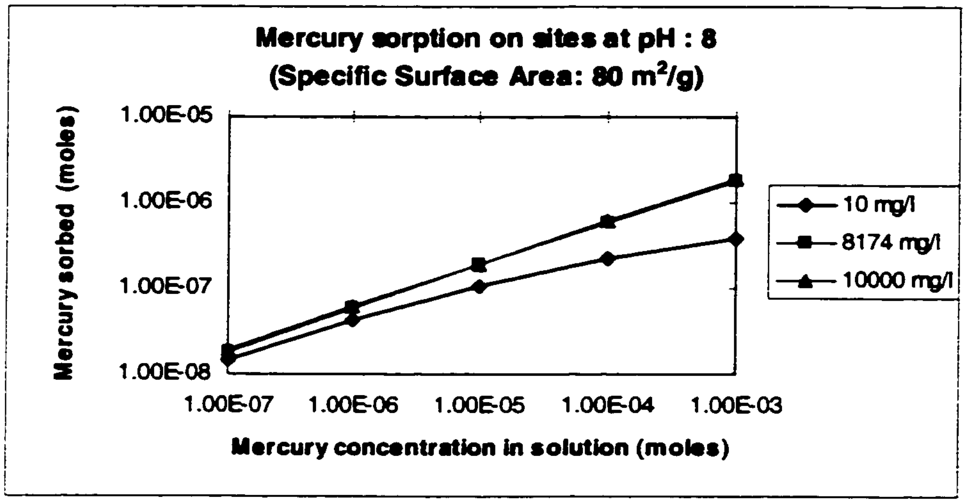


Figure 5.77 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 80 $m^2/g$) at pH 8 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

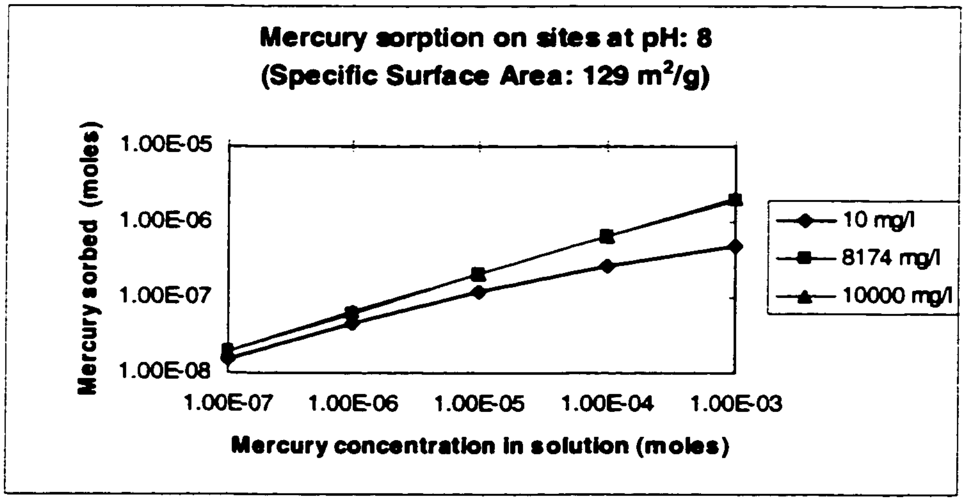


Figure 5.78 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 129 $m^2/g$) at pH 8 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

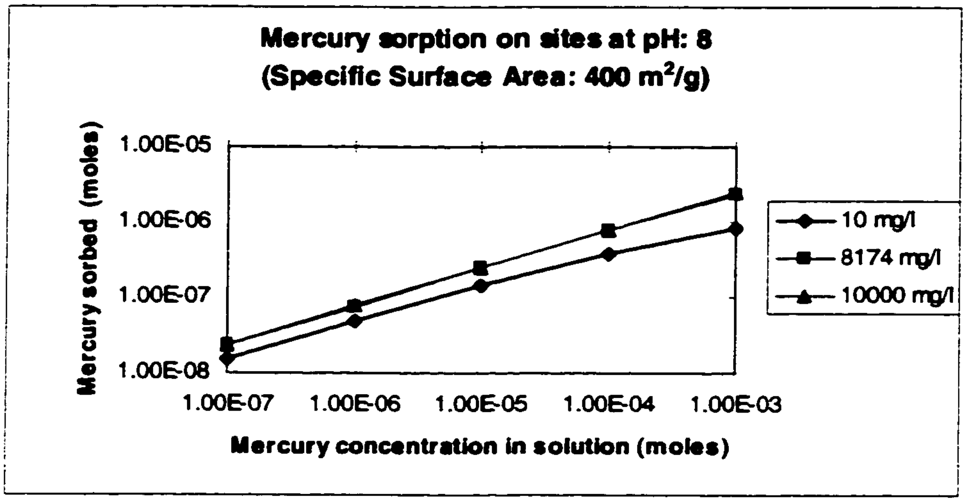


Figure 5.79 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 400 m$^2$/g) at pH 8 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

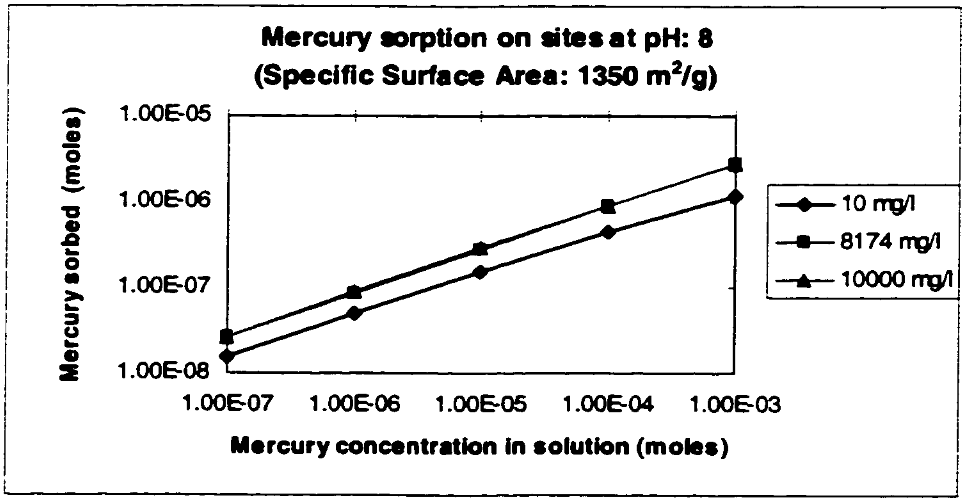


Figure 5.80 Effect of different adsorbent concentrations (10 to 10,000 mg/L) on mercury sorption on particles' surface (specific surface area 1350 m$^2$/g) at pH 8 and initial mercury concentration range: 1 E-7 to 1 E-3 moles.

# CHAPTER 6

# CONCLUSION AND RECOMMENDATIONS

In this study, the ability of constructed wetlands to remove mercury from contaminated waters has been investigated. Series of experimental investigations were conducted on two types of wetland's plants: floating and rooted. The study has also employed MINTEQA2, a geochemical computer model to study various forms of mercury in aquatic environment and sorption characteristics on different types of clayey sediments under different environmental factors, consequently quantifying their effects on mercury sorption. Constructed wetlands appear to be effective in removing mercury from contaminated water, as they have already treated other types of wastewater, by offering a reliable efficiency in removing the contaminant from the wastewater at competitive cost. However, a detailed and careful design procedure should be adopted. The findings of this current investigation were then incorporated in suggesting a method for designing constructed wetlands to treat mercury-contaminated wastewater.

The conclusions of this study could be summarised as follows:

1. Constructed wetlands are an effective technology to remove mercury from contaminated water and no by-products chemicals are produced as a result of the removal process.
2. Water Hyacinth (*Eichhornia crassipes*) - floating wetland plants - were able to remove mercury from experimental solution with the following efficiencies: 94%,

94%, and 95 % for the initial concentrations of 5, 50, and 150 ppb respectively, after 72 hours.

3. Reeds (*Phragmites communis*) - rooted wetland plants - were able to reduce mercury content in the experimental solutions by 92%, and 97 % for the initial concentrations of 50, and 150 ppb respectively, after 72 hours.
4. The highest mercury uptake was observed for higher initial mercury concentration in solution. Assuming that total mercury uptake is by roots, mercury contents in the roots of Water Hyacinth (*Eichhornia crassipes*) increased from 11.11 to 484.46 µg/g (dry weight) for 5 and 150 ppb initial mercury concentrations after 72 hours from the first exposure. The results obtained for Reeds (*Phragmites communis*) are: 39.5 and 114.7 µg/g (dry weight) corresponding to an increase in the initial mercury concentration from 50 to 150 ppb after a 72 hours exposure period.
5. In terms of dry root material, Water Hyacinths achieved much higher mercury accumulation per gram of dry root than those of Reeds for the same initial concentrations. The main reason is that the natural composition of Water Hyacinth is 90 ~ 95 % water and higher surface area of the roots.
6. Removal kinetic studies of Water Hyacinths and Reeds reveals that the removal process occurs during two distinctive phases: The first phase, a rapid and short lasted phase where most of the mercury removed in the first 3 hours followed by much slower phase of mercury removal.
7. The speciation analysis suggests that mercury species in the aquatic environment are distributed as follows: the least concentration present in the equilibrium solution are $HgCl_4^{-2}$, $HgCl_3^{-1}$, and $Hg(OH)_3^{-1}$. The following mean species are present in water

column: $HgCl_2$ (aq), $HgCl^{+1}$, HgClOH (aq), $Hg^{+2}$, $HgOH^{+1}$ in an increasing order. The ionic form: $Hg_2^{+2}$ is the most dominant form available for living organisms.

8. As the chloride concentration increased in the solution 4 folds, various behaviours of mercury speciations were specified. Forms such as $Hg(OH)_2$, $HgOH^{+1}$, $Hg(OH)_3^{-1}$, and $Hg^{+2}$ had less concentration as the chloride increased, while $HgCl^{+1}$, $HgCl_2$ (aq), $HgCl_3^{-1}$, $HgCl_4^{-1}$, and HgClOH (aq) had more concentration at solution. At the high values of chloride concentration (1 E-5, and 1 E-4 moles), the solid Calomel ($Hg_2Cl_2$) has appeared in precipitated form.
9. As the solution temperature increased from 15 °C to 35 °C at pH 5.36, all mercury species had increased their concentrations in solution except $Hg^{+2}$, and HgClOH (aq). Different behaviour of these species was observed as the pH value increased to reach 8.0.
10. Less amounts of mercury compounds were found in solution as the pH increased from 5.36 to 8.0 at an initial mercury concentration of 1 E-3 moles solution Except $Hg(OH)_3^{-1}$, $Hg(OH)_2$, and $Hg_2(OH)_2$,. This decrease was offset by an increase in the three mentioned compounds.
11. Mercury would precipitate in solution at various combinations of pH values and initial mercury concentration in solution. For example, $Hg_2(OH)_2$ was not present at the low initial mercury concentrations of 1 E-6 and 1E-7 moles at the pH of 5.36. The compound appears when an initial mercury concentration of 1 E-5 and higher was used.
12. As the pH values increase from 5.36 to 8.0, mercury sorption on soil surface increased for all soils considered in the study at all initial mercury concentrations. As an

example, the increase of mercury sorbed on the soil surface in the case of kalonite sediment, mercury concentration of lE-3 moles, ranged from 2.91 E-8 to 1.9E-6 moles as the pH increased from 5.36 to 8.0.

13. As the initial mercury concentration increase from 1 E -7 moles to a high value of 1 E-3 moles, the amount of mercury sorbed on the soil surface increase for all soils considered in the study at all pH values considered in the study. As an example, the increase of mercury sorbed on the soil surface in the case of kalonite sediment at pH 5.36, ranged from 2.24 E-10 to 2.91 E-8 moles as the initial mercury concentration increased from 1 E-7 to 1 E-3 moles.
14. The type of soil used for sediments does not have considerable effect on the rate of adsorption at pH 5.36 and does not change dramatically this rate at the higher pH levels (pH: 8) for low initial concentration of mercury (lE-7). The type of soil influences the level of mercury adsorption only for high initial concentration of mercury at the highest pH value (pH: 8).
15. At the normal conditions of lower mercury level concentration in water (e.g. those tested in the lab experiment) the amount of available mercury for plants does not depend heavily on the type of soil, or their densities. It mostly depends on the pH of wastewater discharged.
16. The rate of adsorption does not increase linearly as initial mercury concentration increase for all tested concentrations of the adsorbent mass. For higher mercury initial concentrations, higher adsorption rate is observed for higher specific surface area.

17. As the adsorbent medium (soil) concentration in solution increased from 10 to 10000 mg/L, the amount of mercury sorbed on soil particles increased from 5.49 E-9 to 2.91 E-8 moles on kalonite at pH 5.36 for high initial mercury concentration (1 E-3 moles).
18. Higher adsorbent mass concentration, higher pH, and lower initial mercury content decrease the amount of available mercury (in water column or in pore water) for plants.
19. In natural conditions (at pH above 7) around 10% of initial mercury concentration would be available for plants. Considering a removal rate by wetland plants at 95% of available part of mercury, only 0.5% of mercury will escape removal by natural system within the wetlands.
20. Due to their ability to bioaccumulate mercury in their tissues (roots), Water Hyacinths and Reeds could be employed as Bio-indicators of mercury presence in their surrounding environments for the purpose of Environmental Risk Assessment studies.
21. The study provided the necessary control values for the design of constructed wetlands such as the recommend plants and sediments types, characteristics of contaminated water discharged to the system. It has also provided the extent of mercury removal by the system.
22. The results obtained through this research could form the first nuclei of establishing a computerised artificial intelligence system such as "Neural Network" to explore much needed issues in this scientific field.
23. As an integral and complementary part to this study, a pilot scale physical model should be tested under the specific field conditions to verify the performances

obtained in the laboratory experimental investigations. The final design should be adjusted accordingly.

24. Although wetlands systems appear to be a promising technique to treat mercury contaminated water, still some other properties have to be verified. Among them is mercury methylation in the anaerobic environment of the wetlands. More research and data are required to quantify the methylation process and to specify its rates of occurrence and the effects of different environmental factors. As the knowledge of mercury transformations is still developing and their interaction with the biological activities within the wetland's environment, any new addition by a researcher from any scientific field will definitely add to improving and further optimise the design of wetlands in the context of mercury removal systems.
25. The study in its current format could be also introduced as a comprehensive work plan for future investigations aiming to designing constructed wetlands for treating other contaminants including metals or contaminants of organic nature.

The main recommendations for future work could be summarised as follows:

1. As the investigations were carried out in controlled environment inside the lab, the results have to be verified in real conditions. A pilot field study should be undertaken to provide additional parameters for the design of constructed wetlands.
2. In hot countries where Water Hyacinths are looked at as a major problem (due to the high water consumption), a beneficial use of the plant has been introduced in the study. The plant could be employed in wetland removal systems protecting the surrounding environment.

3. Developing a computer software - ncorporating the findings of the current research work and the modifications from field testing - for designing constructed wetlands systems for mercury removal.
4. Investigating if the plants would release mercury after sorbing it, and if so, in which form and how long it would take to transfer their previously sorbed load.
5. Investigating the plants response if more than one contaminant exists at the same time of exposure.
6. Unfortunately, precise causes for mercury contamination problem are poorly understood. To adequately understand this phenomena, it is required to conduct an interdisciplinary approach covering many aspects of the problem such as: a) Mercury impact on aquatic biota, wild life, and human health, b) Mercury biogeochemistry and cycling, c) The source - transport mechanics, etc.

# REFERENCES

Ailstock, M.S.,(1989). *Utilization and treatment of thermal discharge by the establishment of a wetland plant nursery, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural*, Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI

Allison, J. D., D. S. Brown, and K. J. Novo-Gradac., (1991). *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0 user's manual*, Computer Sciences Corporation, Environmental Research Laboratory, Athens, GA.

Andersson, A., (1979). *Mercury in soil* p. 79-112. In J.O. Nriagu (ed.) *The biogeochemistry of mercury in the environment.* Elsevier, North Holland Biomedical Press, Amsterdam, the Netherlands.

Ashton, G. (ed.), (1986). *River and Lake Ice Engineering*, Water Resources Publications, Littleton, CO.

ASIWPCA, (1984). *America's clean water, the states evaluation of progress 1978-1982.* Association of State and Interstate Water Pollution Control Administrator, Washington, D.C.

Barnett, M., Tschantz, B., and Lessman, G., (1991). *Reuse of an industrial waste water at saturn, in Environmental Engineering*: proceedings of the 1991 specialty Conference, Krenkel, P.A. (ed.), Published by the American society of Civil Engineers, NY.

Beauford , W., J. Barber, and A.R. Barringer, (1977). *Physiol Plant* 39: 261-265,

Bisogni, J.and Lawrence A., (1975. Kinetics of mercury methylation in aerobic and anaerobic aquatic environments. *J. Wat. Poll. Cont. Fed.* 47: 135-152

Bjorklund, I., Borg, H., and Johansson K., (1984). *Ambio.*, (139)118

Bloom, N.S., (1992). On the chemical form of mercury in edible fish and marine invertebrate tissue, *Can.J. Fish. Aquat. Sci*, 46:1131-1140

Bloom, N.S. and Watras, C.J. in J.P. Vernet (Ed.), (1989). *Heavy Metals in the environment*, Vol.2, CEP consultants, Edinburgh, p. 349

Bloom,N.S., and Crecelius, E.A., (1983). *Mar. Chem.*, 14, 49

Bodek, I., Lyman, W.J., Reehl, W.F., and Rosenblatt, D.H., (1988). *Environmental Inorganic Chemistry: Properties, Processes, and Estimation Methods.* A special Publication of SETAC. Pergamon Press, U.S.A.

Brix, H., and Schierup, H., (1989). *Danish experience with sewage treatment in constructed wetlands, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural,* Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Brodie, G.A., Hammer, D.A., and Tomljanovich, D.A., (1989). *Constructed wetlands for treatment of Ash Pond seepage, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural,* Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Brosset, C., (1983). *Water Sci. Technol.,* 15,59

Christensen , T. H., (1989). *Water, Air, Soil pollution* 44:71-82

Cole, H., Hitchcock, A., and Collins, R., (1992). *Mercury Warning: the fish you catch may be unsafe to eat.* Clean water fund/Clean Water Action Washington D.C.

Costello, C.J.,(1989). *Wetlands Treatment of dairy Animal Wastes in Irish Drumlin Landscape, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural,* Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Cotton, F. A. and Wilkinson G., (1972). *Advanced Inorganic Chemistry.* A Comprehensive Text (3rd Edittion), Wiley, New York

Craig P.J. in Craig, P.J.(Ed.), (1986). *Organometallic compounds in the environment,* Wiley, New York, pp 65-110

Craig,P.J., and Bartlett,P.D., (1978). *Nature* (London), 275, 635.

D'itri P.A. and D'itri F.M., (1977). *Mercury contamination: A Human Tragedy,* John Wiley & Sons, Inc., USA, pp.311

Dalziel, J. and Yeats, P.A., (1985). *Mar. Chem.,* 15, 357

Damluhi, S.F. and Tikriti,S., (1972). Mercury poisoning from wheat, *Brit. Med. J.,* 1:804

Dukes, P., Lowry, D., and Walker, W.W., (1989). *Design of wet detention basins and constructed wetlands for treatment of storm water run-off from a regional shopping mall in Massachusetts, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural,* Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Davies, T.H., and Cottingham, P.D., (1994). The use of constructed wetlands for treating industrial effluent (Textile Dyes), *Water Science and Technology*, V:29, N:4, p.227

De Simmone, R.E., (1972). *Chem. Commun.*, 13, 780

Di Toro D. M., J.D. Mahony, R.R. Kirchgraber, A.L. O'Byrne, L. R. Pasquale, and D. C. Piccirilli, (1986). *Environmental Science & Technology* 20:55-61

Doku, I.A. and G.W. Heinke, (1995). Potential for greater use of wetlands for wastewater treatment in Northern Canada, *Journal of Cold Regions Engineering*, Vol 9, n:2

Environment Canada, September (1993). *St-Lawrence Technologies data sheets, contaminated soil, Demonstration of a pilot unit to treat Mercury-contaminated soil.*

Environment Canada, Environmental Protection series, November (1994). *Compliance with Chlor-Alkali Mercury Regulations, 1986-1989: Status Report*, EPS 1/HA/2

Fagerstrom T.and Jernelov A., (1972). Some aspects of the quantitative ecology of mercury. *Wat. Res.* 6: 1193-1202

Fang S.C., (1978). *Enviromental Science &Technology* 12:285-288.

Ferrara, R. Petrosino, A. Maserti, E., Seritti, A. and Barghigiani, C., (1982). The biogeochemical cycle of mercury in the Mediterranean. II Mercury in the atmosphere, aerosol and in rain water of a northern Tyrrhenian area. *Environ. Technol. Lett.*, 3: 449-456

Fitzgerald, W.F. and Watras, (1989). C.J. *Sci. Total Environ.*, 87,88 232.

Frayer,W.E., Monahan,T.J., Bowden, d.C., and Graybill, F.A., (1983). *Status and trends of wetlands and deep water habitat in the coterminous United States, 1950s to 1970s.* Dept. of Forest and Wood Sciences, Colorado State University, Fort Collins, 32 P.

Gambrell, R.P., Khalid, R.A., and Patrick, W.H., (1987). Capacity of a swamp forest to assimilate the TOC loading from a sugar refinery waste water stream, *Journal of water pollution control Federation*, v:59, p. 897

Gardener, D., (1975). *Marine Pollution bulletin*, 6, 43-46

Gazette officielle du Quebec, Q-2, r.4.1, (1993). *"Reglement sur l'eau potable"* a jour au 2 fevrier (1993.

Gebhart, E. and Rossman, T.G., (1991). *Mutagenicity, Carcinogenicity, Teratogenicity in Metals and Their Compounds in the Environment: Occurrence, Analysis, and Biological relevance.* Meriam, E. (ed.), Published jointly by VCH Weinleim, Germany and VCH Publishers, Inc., New York

Gersberg, R. M., Elkins B.V., Lyon S.R., and Goldman, C.R., (1986). Role of aquatic plants in waste water treatment by artificial wetlands, *Water res.* 20:363-368

Gill, G.A., and Bruland, K., (1990). *Environ. Sci. Technol.*, 24, 1392

Gracy H. I., and J. W. B. Stewart, (1974). *In Proceding of International Conf on Land Water Management*, 97 – 103. Ottawa, Ontario, Canada.

Grieb, T.M., Driscoll C.T., Gloss S.P., Schofield, C.L., Bowie,G.L., and Porcella, D.B.,(1990). Factors affecting mercury accumulation in fish in the upper Michigan Peninsula, *Environ. Toxocol. Chem.*, 9:919-930

Guida,V.G., and Kugelman, I.J., (1989). *Experiments in waste water polishing in constructed tidal marshes: does it work? Are the results predictable?, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural,* Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Hammer, D.A. (Ed.),(1989). *Constructed wetlands for waste water treatment: Municipal, Industrial, and, Agricultural.* Lewis Publishers, Inc., Chelsea, Michigan.,

Hammer, D.A., Pullin, B.P., McCaskey, T.A., Eason, J., and Payne, V.W.E, (1993). *Treating Livestock waste waters with constructed wetlands, in Constructed wetlands for water quality improvement*, Moshiri G.A. (ed.), Lewis Publishers, Chelsea, MI

Herskowitz, J., (1986). *Listowel artificial marsh project. External Research Projects, Part B, Water Quality Research.* Technology Transfer Conference: Proceedings. Toronto, Ontario.

Higgins, M.J., Rock, C.A., Bouchard, R., and Wengrezynek, B., (1993). *Controlling Agricultural Runoff by use of Constructed wetlands, in Constructed wetlands for water quality improvement*, Moshiri G.A. (ed.), Lewis Publishers, Chelsea, MI

Hochster, R.M. and Quastel, J.H. (eds.), (1963). *Metabolic Inhibitors*, Academic Press, New York, USA

Hogg, T.J., W.B. Stewart, and J.R. Bettany, (1978). *Jounal of Environmental Quality* 7: 445-450

Horan N.J., (1990). *Biological Wastewater Treatment Systems / Theory and Operation.* John Wiley & Sons

Howard, E.A., Emerick, J.C., and Wildeman,, T.R., (1989). *Design and Construction of a research site for Passive Mine Drainage Treatment in Idaho Springs, Colorado, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural*, Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Hudson, R.J.M., Gherini, S.A., Watras, C.J., and Porcella D.B., (1994). *Modelling the biogeochemical cycle of mercury in lakes: the mercury cycling model (MCM) and its application to the MTL study lakes, In: Mercury Pollution: Integration and synthesis*, Watras, C.J. and Huckabbe, J.W., Eds., Lewis Publishers, Chelsea, MI.

Jackson, J., (1989). *Man-Made wetlands for waste water treatment : Two case studies, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural*, Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI

Jemelov A., (1970). Release of methylmercury from sediments with layers containing inorganic mercury at different depths. *Limnol. Oceanogr.* 15: 958-960

Kelly, D.P., Norris, P.R., and Brierly, C.L., (1979). *Microbiological methods for extraction and recovery of metals in microbial technology: Current state, future prospects*, Bull, A.T., Ellwood, C., and Ratledge C. (eds.), New York, Cambridge University Press.

Knight, R., R. Kadlec, and S. Reed, Sep. (1993). *Database: North American Wetlands for Water Quality Treatment,* U.S. Environmental Protection Agency, Risk Reduction Environmental Laboratory, Cincinanati, OH.

Kolbash, R.L., and Romanoski, T.L.,(1989). *Windsor Coal company wetland: An overview, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural*, Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Langley D.G., (1973). Mercury methylation in an aquatic environment *J. Wat. Poll. Cont.* Fed. 45:44-51

Lenka M., K.K. Panda, and B.B. Panda, (1990. ) *Environmental Pollution* 66:89-99

Lindqvist, O. (Ed.), (1991). *Mercury in the Swedish environment, Recent Research on Causes, Consequences and corrective methods,* Kluwer, Dordrecht.

Lindqvist, O., Jemelov,A.,Johansson,K., Rodhe, H., (1984). *Mercury in the Swedish environment. Global and local sources*, solna, National Swedish Environment Protection Board, pp 105

Litchfield, D.K., and Schatz,D.D, (1989). *Constructed wetlands for waste water treatment at Amoco Oil Company's Mandan, North dakota Refinery, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural*, Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Mason, R.P. and Fitzgerlad, W.F.,(1990. ) alkylmercury species in the equatorial Pacific, *Nature*,347:457-459

Michigan Mercury Pollution Prevention Task Force. (1996). "*Mercury Pollution Prevention in Michigan: Summary of Current Efforts and Recommendations for Future Activities*"

Miller D.R.and Agaki H., (1979). pH affects mercury distribution, not methylation. *Ecotox. Environ. Safety* 3: 36-38.

Miller, G., (1989). *Use of artificial cattail Marshes to treat sewage in Northern Ontario, Canada, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural*, Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Ministere de l' Environment, Gouvernement du Quebec, Direction des substances dangereuses. (1988). " *Politique de Rehabilitation des Terranins Contamines*", Sainte-Foy, Fevrier 1988.

Mitra S., (1986). *Mercury in The Ecosystem*, Trans Tech Publications Ltd., Switzerland

Morel, F.M.M., (1983). *Principles of Aquatic Chemistry.* John Wiley and Sons, New York, NY

Nagase H., Ose Y., Sato T., and Ishikawa, (1982). Methylation of mercury by humic substances in an aquatic environment. *Sci. Tot. Environ.* 24: 133-142

National Wetlands Working Group, (1988). *Wetlands of Canada.* Canada Committee on Ecological Land Classification. Environment Canada, Ottawa, ON.

O'Neill, P., (1993). *Environmental Chemistry*, 2nd edition, Chapman & Hall

Olsson, B.H., Barkay, T. and Colwell R., (1979). Role of plasmids in mercury transformation by bacteria isolated from the aquatic environment. *Apl. Environ. Microbiol.* 38: 478-485.

Organization for Economic Co-Operation and Development (OECD). (1974). "*Mercury and the Environment*". Paris (1974

Patty, F.A., (1981). Mercury, Hg in Clayton, S. and Clayton, F. (eds.) *Patty's industrial Hygiene and toxicology*, Vol 2A , pp. 1769-1792, John Wiley & Sons, New York

Perkin Elmer, (1978). *MHS-10Mercury / Hydride System. Operator's manual.* West Germany.

Porcella, D. B., (1994). *Mercury in the Environment: Biogeochemistry, In: Mercury Pollution: Integration and synthesis*, Watras, C.J. and Huckabbe, J.W., Eds., Lewis Publishers, Chelsea, MI.

Pries, J., (1994). *Waste water and Stormwater Applications of wetlands in Canada*, Ottawa, Ontario: North American Wetlands Conservation Council (Canada).

Reed S. C., R.W. Crites, and E.J. Middlebrooks, (1995). *Natural Systems for waste management and treatment*, second eddition, McGraw Hill, Inc.

Reed,S.C., Middlebrooks, E.J., and Crites,R.W., (1988). *Natural systems for waste water management and treatment*, McGraw-Hill, Inc., New York, New York.

Ridley, W.P., Dizikes, L.J., and Wood, J.M., (1977). Biomethylation of toxic elements in the environment. *Science* 197: 329-332

Rogers, R.D., (1978). *Volatility of mercury from soils amended with various mercury compounds*. EPA 600/3-78-046. Office of research and development U.S.EPA

Rudd, J.W.M., Turner, M.A., Furutani, A., Swick A., and Townsend B.E., (1983). A synthesis of recent research with a view towards mercury amelioration. *Can. J. Fish. Aquat. Sci.* 40:2218-2227

Sanders, F., J. Rahe, and D. Pastor, and R. Anderson, (1999). *Civil Engineering*, American Society of Civil Engineers, January 1999:53-55

Semu , E., B.R. Singh, and A.R. Selmer-Olsen, (1987). *Water, Air, Soil Pollution* 32:1-10

Sheehy, Greg., (1993). *Conserving Wetlands in Managed Forests. Sustaining Wetlands* Issues Paper, No. 1993 - 2. Ottawa, Ontario: North American Wetlands Conservation Council (Canada).

Sherwood, R., Tchobanoglous, G., Colt, J., and Knight, A., (1979). *The use of aquatic plants and animals for the treatment of waste water.* Departments of Civil Engineering and Land, Air, and Water Resources, University of California, Davis, California

Shumate, S.E., and Strandberg, G.W., (1985). *Accumulation of metals by microbial cells in comprehensive biotechnology*, Robinson,C.W. and Howell, J.A. (eds.), Oxford, Pergamon Press, Inc., p.235

Skerfving, S., Hanson, K., Mangs, C., Lindsten, J., and Tyman, N., (1974). Methylmercury Induced Chromosome Damage in Man. *Environ. Res.* 7, 83 -98.

Slemr, F., Seiler, W., and Schuster, G., (1981). *Journal of Geophysical research*, 86, 1159-1166

Smith, R. G., (1980). *Development of a rational basis for the design and operation of the overland flow process, In Proceedings National Seminar on Overland Flow Technology for Municipal wastewater*, Dallas, TX.

Spry, D.J., and j.G. Wiener, (1991). Metal bioavailability and toxicity to fish in low-alkalinity lakes: a critical review, *Environ. Pollut.*, 71:243-304

Staubitz, W.W., Surface, J.M., Steenhuis, T.S., Peverly,J.H., Lavine, N.C., Weeks, N.C., Sanford, W.E., and kopka, R.J., (1989). *Potential use of constructed wetlands to treat landfill leachate, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural,* Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI

Stock,A. and Cucuel,F., (1934). *Naturwissenschaften*, 22, 390-3

Stumm, W. and Morgam, J.J., (1981). *Aquatic Chemistry, 2nd ed.*, John Wiley& Sons, New York

Tchobanoglous, G., F. L. Burton, (1991). *Wastewater Engineering: Treatment, Disposal, and Reuse*. Metcalf & Eddy, Inc.

Tettleton,R.P., Howell, F.G., and Reaves, R.P.,(1993). *Performance of a constructed marsh in the tertiary treatment of bleach kraft pulp mill effluent: results of a two year Pilot project, in Constructed wetlands for water quality improvement*, Moshiri G.A. (ed.), Lewis Publishers, Chelsea, MI

Thomann, R. V., and J. A. Mueller, (1987). *Principles of surface water quality modeling and control*, Harper & Row , New York.

Thut, R.N.,(1993). *Feasibility of treating pulp mill effluent with a constructed wetland, in Constructed wetlands for water quality improvement*, Moshiri G.A. (ed.), Lewis Publishers, Chelsea, MI

U.S. Environmental Protection Agency. (1988). *Constructed wetlands and aquatic plant systems for municipal waste water treatment.* EPA/625/1-88/022, Cincinnati,Ohio.

UK Department of the Environment, (1976). *Mercury in the Environment.*

USEPA. (1984). *National water Quality Inventory: 1984 Report to Congress.* EPA 440/4-85-029. Washington, D.C.

Wallace, A.and E. M. Romney, (1977). In H. Drucker and R.E. Wildung, eds. *Biological implications off metals in the environment*, 370-379. CONF-750929. NTIS, Springfield, VA.

Water Pollution Control Federation. (1990. ) *Natural Systems for Waste Water Treatment*, Manual of practice FD-16, WPCF, Alexandria, Virginia.

Watras, C.J. and Bloom, N.S., (1984). *Limnol Oceanogr*, 37, 1313

Weast, R.C., (1978). *Handbook of chemistry and Physics*, 59 th Ed. 1978-1979. The Chemical rubber Co., Publisher, West Palm Peach, Florida.

Westall, J.C. and H. Hohl., (1980). A Comparison of Electrostatic Models for the Oxide/Solution Interface. *Adv. Coll. Inter. Sci.* 12:265-294.

WHO, (1971). *International Standards for Drinking Water*, World Health Organization, Geneva.

WHO, (1976). *Environmental Health Criteria: Mercury*, World Health Organization, Geneva.

Wiener, J.G., Fitzgerald, W.F., Watras, C.J., and Rader R.G.,(1990). *Environ. Toxicol. Chem.*, 909

Wilkinson, J.F., (1957). Extracellular Bacterial Polysaccharides, *Bacterial. Rev.* 22:46-72

Wood, A., and Hensman, L.C., (1989). *Research to develop engineering guide lines for implementation of Constructed wetlands for waste water treatment in Southern Africa, in Constructed wetlands for waste water treatment: Municipal, Industrial, and agricultural*, Hammer D.H. (ed.), Lewis Publishers, Chelsea, MI.

Wood, J.M., (1979). Environmental pollution by mercury. *Environ. Sci. TEchnol.* 2:39-56

Wright D.R.and Hamilton R.D., (1982). Release of methylmercury from sediments: Effects of mercury concentration and nutrient addition. *Can. J. Fish. Equate. Sci.* 39: 1459-1466

Yong, R.N., A.M.O. Mohamed and B.P. Warkentin, (1992). *Principles of Contaminant Transport in Soils.* Developments in Geotechnical Engineering, 73. Elsevier

Yujun Yin, H.E. Allen, C.P. Huang, and P.F. Sanders, (1997). *Soil Science* vol 162 no 1:35-45

Zvonaric T., Horvat M. and Stegnar, P., (1987). in *Heavy Metals in the environment*, Vol.2, CEP consultants, Edinburgh, p. 461

# APPENDIX A

## A.1 Principle of Operation of MHS 10

The MHS 10 requires a supply of inert gas (argon or nitrogen) at an inlet pressure of 250 kPa (2.5 bar). The inert purge gas has two functions: to purge air from the system; and to purge mercury from the system after the determination. The instrument incorporates a pressure reducer that is that is set at 1.5 kPa. A pneumatic diagram of the MHS 10 system is shown (Figure 1).

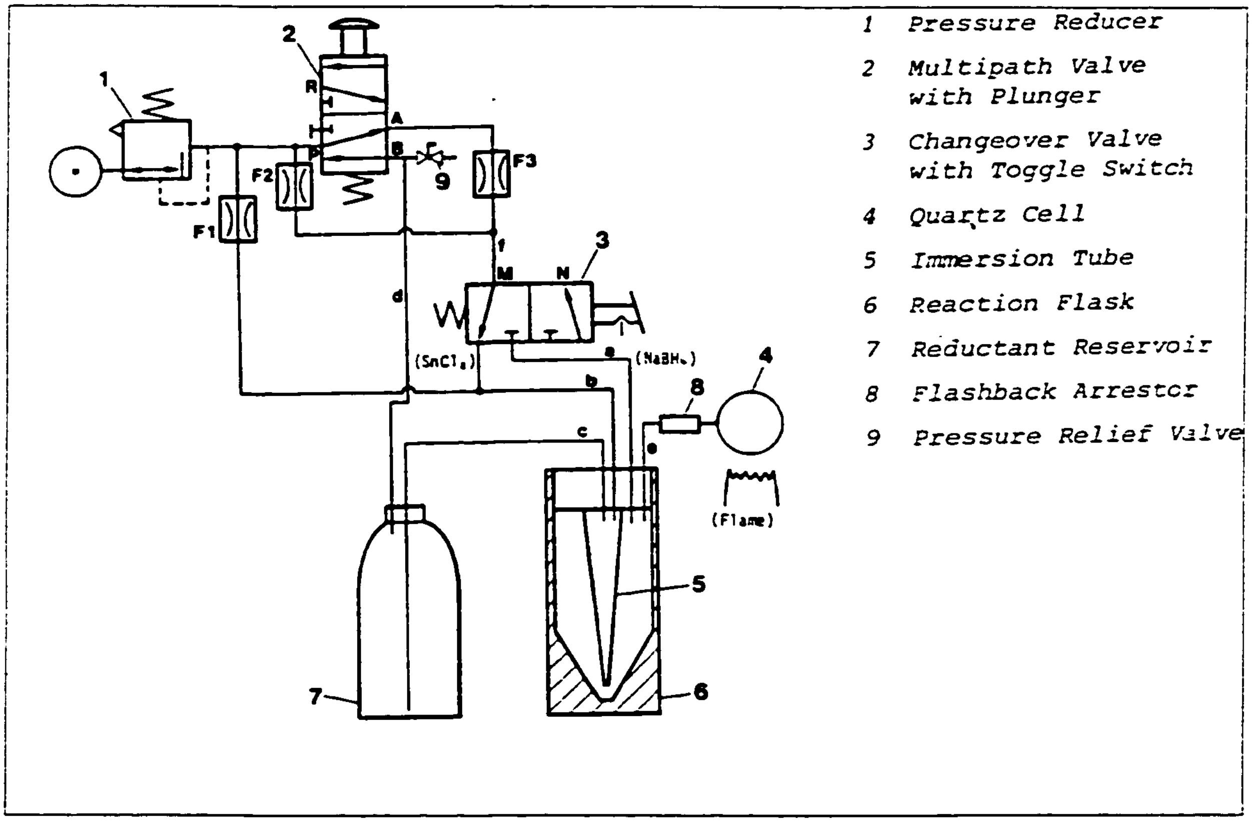


Figure 1. Pneumatic diagram for the MHS 10 System (after Bodenseewerk 1987)

A continuous stream of inert gas flows from the pressure reducer through flow restrictor $F_1$ (nominal flow rate 25 ml/min) and line b, through flow restrictor $F_2$ (nominal flow rate 400 ml/min) and line f, and also through multipath valve (2).

When the multi valve is in the standby position (not depressed), inert gas streams continuously inlet P to outlet A and then through flow restrictor $F_3$ (nominal flow rate 600 ml/min.) to line f, the inert gas is routed through the change over valve (3) according to the position of the toggle switch.

When using $SnCl_2$ as a reductant, inert gas streams from inlet M through line b to the immersion tube, combined with the conical form of the reaction flask, provides excellent mixing of the solution. At the end of reductant addition, this gas stream also blows the immersion tube free of reductant solution. The combined gas stream through $F_1$ and $F_2$ and line b drives metallic mercury vapour from solution and transport it to the quartz cell where the atomic absorption of the metal is measured.

To perform a determination the plunger is depressed and held. The gas stream through $F_3$ is shut off. Pressure is applied from outlet B of the valve via line D to the reductant reservoir. Reductant is forced through line C to the immersion tube and from there into the sample solution.

When the tracing on the recorder indicates that the maximum signal has been attained and the signal starts to decrease, the plunger is released. The flow of reductant stops immediately and the purge gas stream via $F_3$ is resumed. The reaction proceeds rapidly to completion, after which the reaction flask can be removed and the next sample prepared.

A pressure relief valve fitted to outlet B opens if the pressure in the reductant reservoir exceeds 4 kPa. This safety feature is provided to prevent excessive pressure build-up in the system should the sample transfer hose or flash back arresstor become obstructed for any reason. It is now generally accepted that because of its simplicity, atomic absorption spectroscopy, together with appropriate sample handling accessories (e.g. the MHS 10); best meet the requirements for the economic determination of traces of mercury.

## A.2 Specifications

| | |
|---|---|
| Absorption cell: | Quartz cell, 165 mm long, 12 mm diameter |
| Cell heating: | Up to approx. 1000 °C in the spectrophotometer's air/acetylene flame |
| Reaction flask: | Polypropylene, with special internal conical form connection to the analyser assembly via bayonet flange with gasket. |
| Sample volume: | Max. prepared volume 50 ml |
| Reducing agent: | Tin (II) chloride ($SnCl_2$) |
| Inert gas: | Nitrogen |
| Required inlet pressure: | 250 kPa (2.5 bar; 36 - 37 psig) |
| Gas consumption: | Approx. 1100 ml/min. |

The MHS 10 Mercury Hydride system is a manually operated accessory that permits high sensitivity determination of mercury and metallic hydride forming elements by Atomic Absorption Spectrophotometry. The MHS 10 comprises an Analyser Assembly and a Quartz Cell Assembly.

The Analyser assembly is free standing and is placed adjacent to the sample compartment of the AA spectrophotometer. This assembly includes a reaction flask, a reservoir for the reducing agent, and all pneumatic components for control of the carrier gas and transport of mercury vapour to the quartz cell.

The cell assembly consists of a quartz cell and a mount. The mount installs on any Perkin-Elmer 10 cm standard burner head, thus permitting the quartz cell to be heated in the flame in the spectrophotometer. The quartz cell is positioned in the sample light beam of the spectrophotometer, and alignment is provided by the instrument's burner adjust controls. A swivel on the mount permits the quartz cell to be tilted out of the flame. The cell is 165 mm long and 12 mm in diameter. It has a central inlet and is open at both ends. It is connected to the Analyser assembly by a silicon rubber hose. The cell can be heated to about 1000°C in the air/acetylene flame. Graphite cooling rings at the cell ends prevent ignition of the hydrogen liberated during the determination. In the unlikely event that hydrogen should ignite, a flashback arrestor in the transfer hose prevents a flashback into the reaction flask.

### A.3 Chemical Principle

Tin (II) chloride solution is used as the reducing agent (reductant) in the experiment. The reaction mechanisms involved in the reduction of metal ions are complicated and almost certainly take place via the formation of intermediate radicals. Mercury determinations were performed using the cold vapour technique. The sample solution was first treated so that mercury is present in ionic form in acid solution. Reductant is dispensed into the sample solution and mercury is reduced to the metallic state. Since mercury has an appreciable volatility even at ambient temperature, metallic mercury vapour is driven out of the sample solution and transported to the quartz cell where its absorption is measured. The cell is not generally heated for mercury determinations.

## A.4 System Set-up Procedures

### A.4.1 Cell Alignment Procedures

The system was set up for analytical operation as follows:

1. Mercury Elctrodeless Discharge Lamp (EDL) was installed in the lamp compartment (EDL lamps provide greater light output than the corresponding hollow cathode lamps).
2. The Spectrophotometer was switched ON
3. With the quartz cell tilted out of the light beam, the lamp alignment procedures were carried out as described in the Operator's Manual for the Spectrophotometer.
4. The quartz cell was tilted back into the light beam.
5. A piece of matt white paper was held at the end of the quartz cell and the adjustments with the burner's Vertical, Horizontal, and rotational controls were carried out until the light beam passes through the cell.

After completion of this coarse alignment procedure, the fine alignment and preliminary preparations were performed as follows:

1. After the installation of the mercury EDL, the instrument was allowed to warm up (Mercury Electrodeless Discharge Lamp requires 30 -45 minutes to achieve operational stability).
2. The quartz cell was tilted out of the light beam.

3. Lamp alignment and wavelength adjustment were performed as described in the Operator's Manual of the Spectrophotometer. For Mercury the values for the wavelength and slit setting (Spectral bandwidth) are 253.7 nm and 0.7 nm respectively.
4. The operating mode on the Spectrophotometer was set to suit the MHS 10 operation. The MHS 10 generates time-dependent, peak shaped signals. Print out of the readings was obtained.
5. The display on the spectrophotometer was adjusted to zero.
6. The quartz cell was tilted back into the light beam.
7. Increment adjustments to the burner's vertical, Horizontal, and Rotational controls were made to obtain minimum absorbance readings on the display

The sensitivity of measurements was 4.68 ng Hg / 1% Absorption (relative sensitivity 0.000468 mg/ml 1 % for 10 ml calibration volume).

## A.5 Performing Determinations

A cleaning solution (5% $HNO_3$ and 5% $H_2SO_4$: A300-225, 95 %ACS Certified, Fisher Chemicals) was prepared for the purpose of washing the reaction flask and the central dispenser each time after performing a determination. The general procedure could be summarised as follows:

1. The reaction flask was rinsed three times by washing down the walls with a small amount of $HNO_3/H_2SO_4$ mixture.
2. Analyte solution (blank or standard or sample) was dispensed into the reaction flask (10 ml), then the flask was mounted on the MHS 10.

3. The plunger was actuated almost immediately (generally 15 seconds should be allowed to purge the system out of air, but in case of mercury, a loss in sensitivity has been observed when the delay time between installation of the reaction flask and actuation of plunger is too long. For this reason the plunger should be actuated immediately after installation of the flask).
4. The READ button on the Analyst 100 Spectrophotometer should be pressed.
5. The plunger should be pushed down and held for about 15 seconds to dispense the tin (II) chloride into the sample solution.
6. After 55 seconds (the integration time chosen for mercury determination to ensure that the maximum peak signal is reliably detected), the READ light should go OFF, then the flask could be removed and the contents disposed in the appropriate hazardous waste container.
7. The previous steps were repeated for each determination performed.

# APPENDIX B

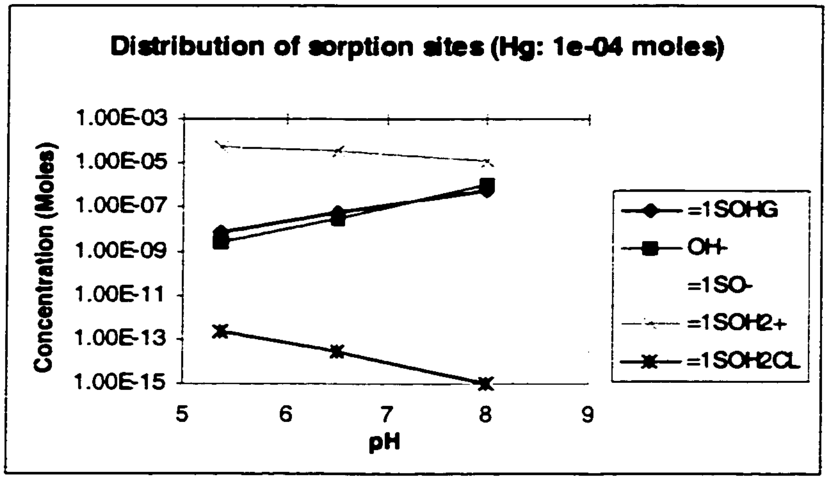


Figure 1 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04moles and adsorbent concentration 10.0 g/l and specific surface area : 80.00 $m^2/g$

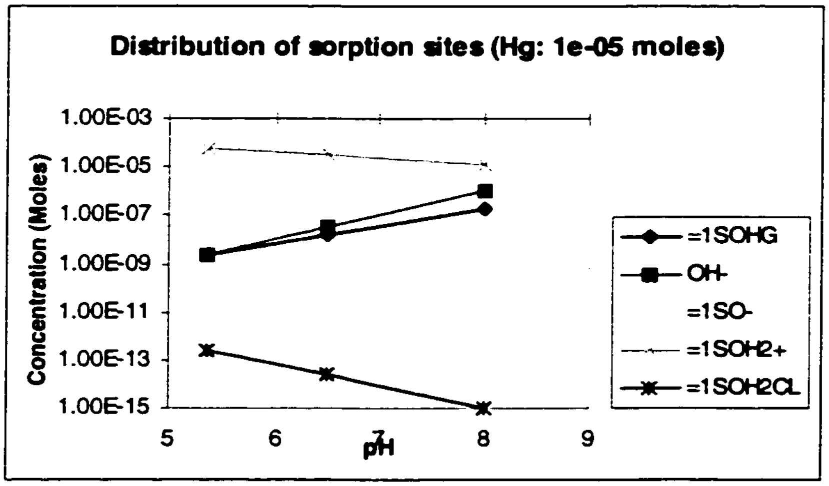


Figure 2 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 10.0 g/l and specific surface area : 80.00 $m^2/g$

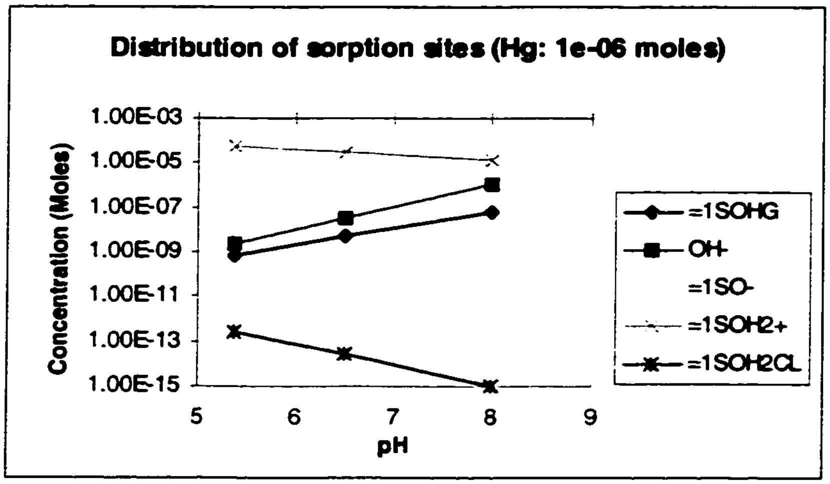


Figure 3 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 10.0 g/l and specific surface area : 80.00 $m^2/g$

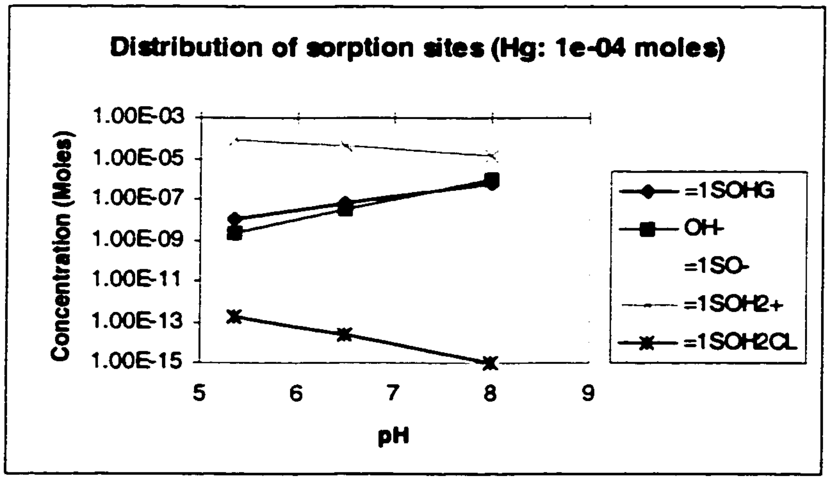


Figure 4 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 10.0 g/l and specific surface area : 129.00 $m^2/g$

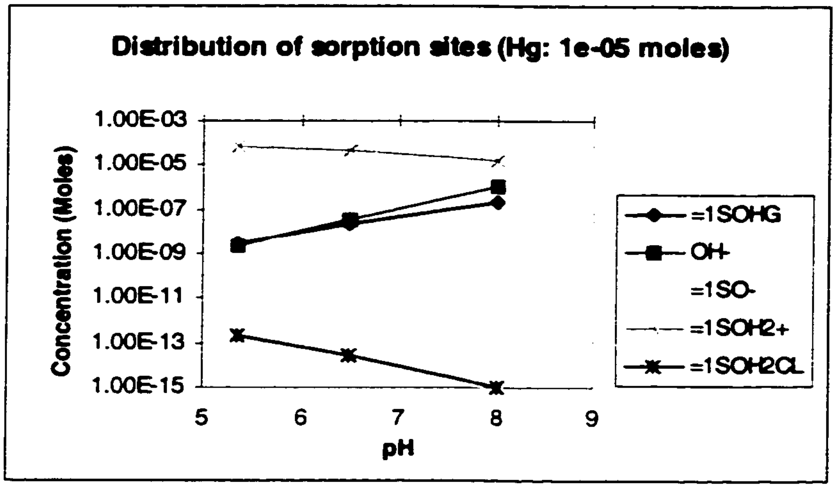


Figure 5 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 10.0 g/l and specific surface area : 129.00 m2/g

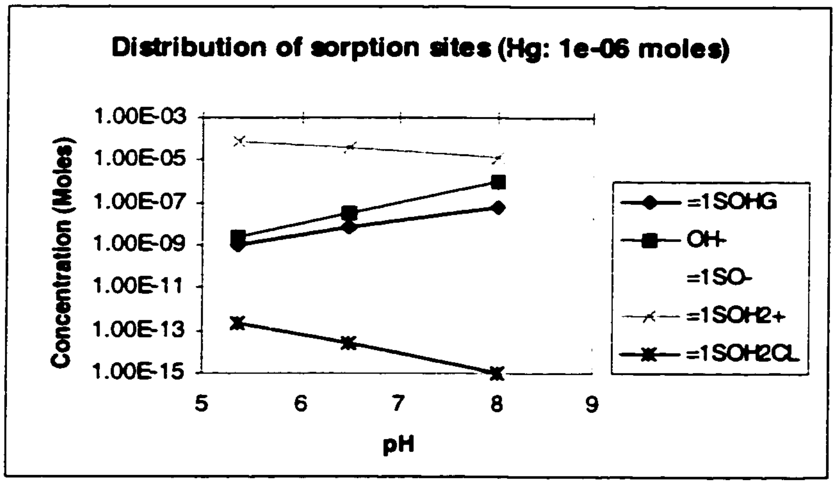


Figure 6 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 10.0 g/l and specific surface area : 129.00 $m^2/g$

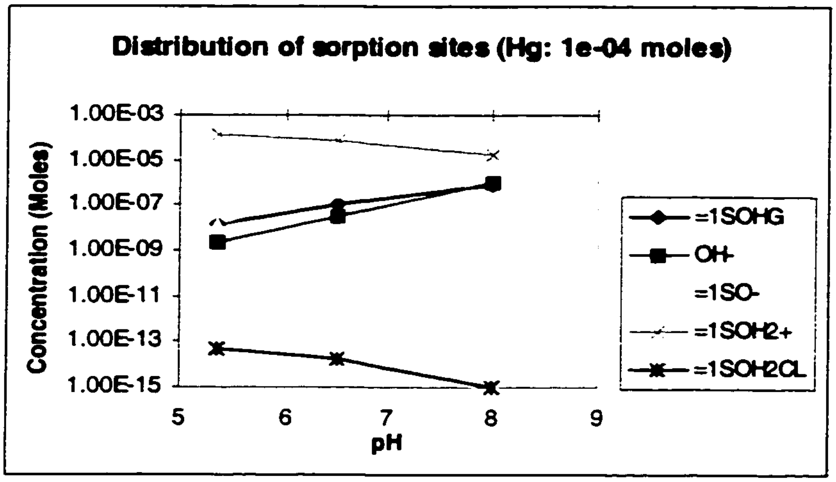


Figure 7 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration le-04 moles and adsorbent concentration 10.0 g/l and specific surface area : 400.00 $m^2/g$

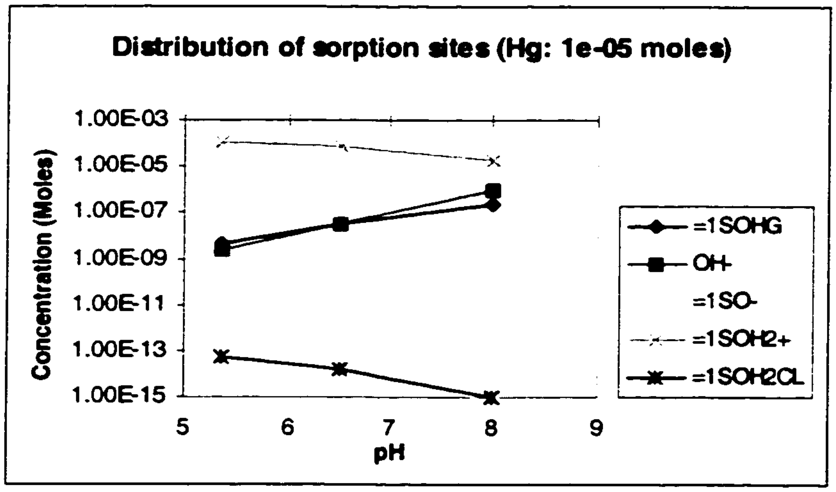


Figure 8 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration le-05 moles and adsorbent concentration 10.0 g/l and specific surface area : 400.00 $m^2/g$

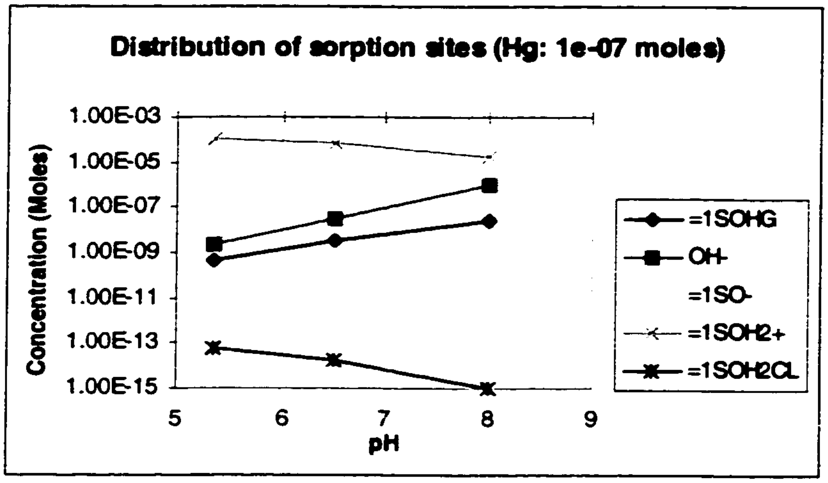


Figure 9 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 10.0 g/l and specific surface area : 400.00 $m^2/g$

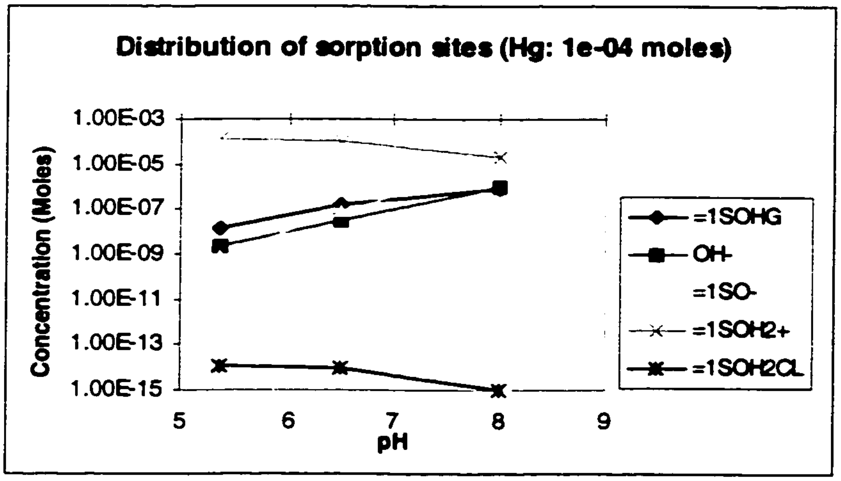


Figure 10 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 10.0 g/l and specific surface area : 1350.00 $m^2/g$

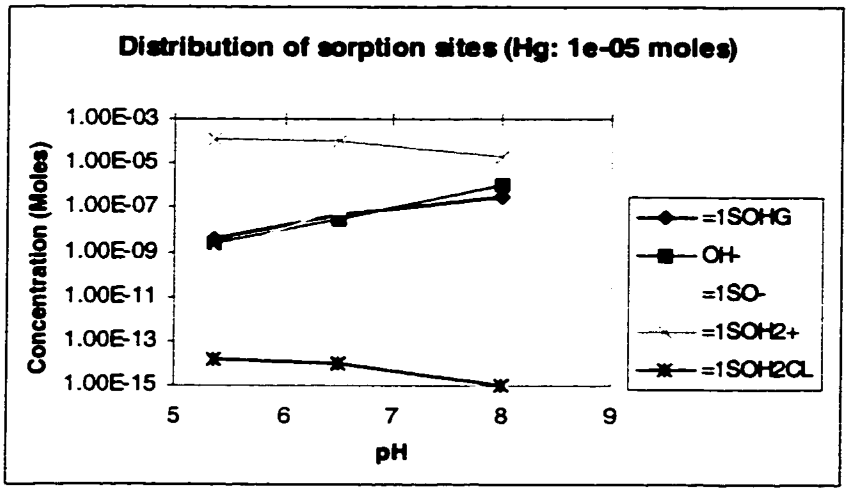


Figure 11 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 10.0 g/l and specific surface area : 1350.00 m$^2$/g

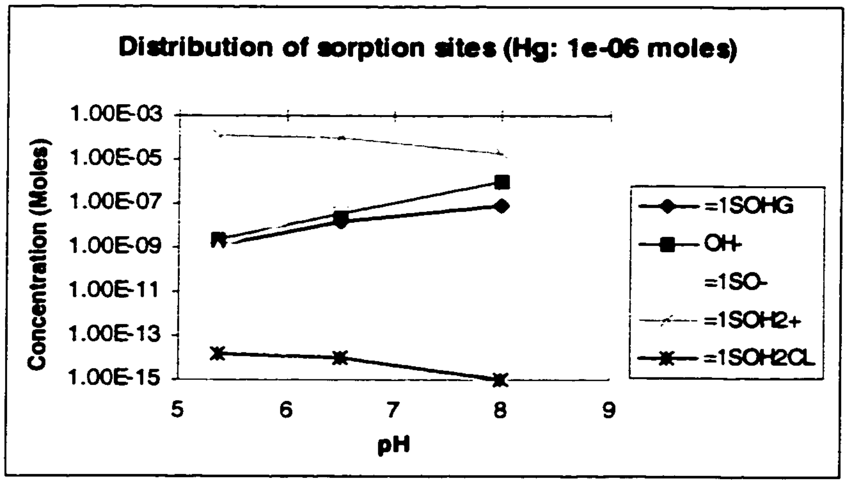


Figure 12 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 10.0 g/l and specific surface area : 1350.00 m$^2$/g

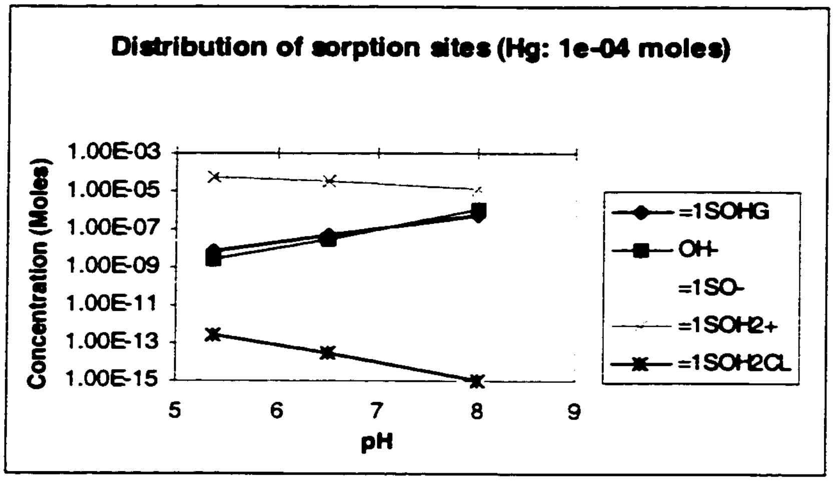


Figure 13 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 8.174 g/l and specific surface area : 80.00 $m^2/g$

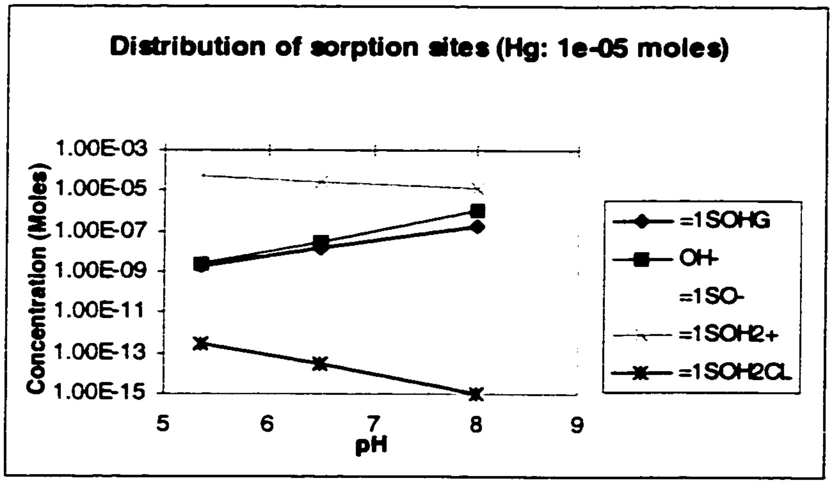


Figure 14 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 8.174 g/l and specific surface area : 80.00 $m^2/g$

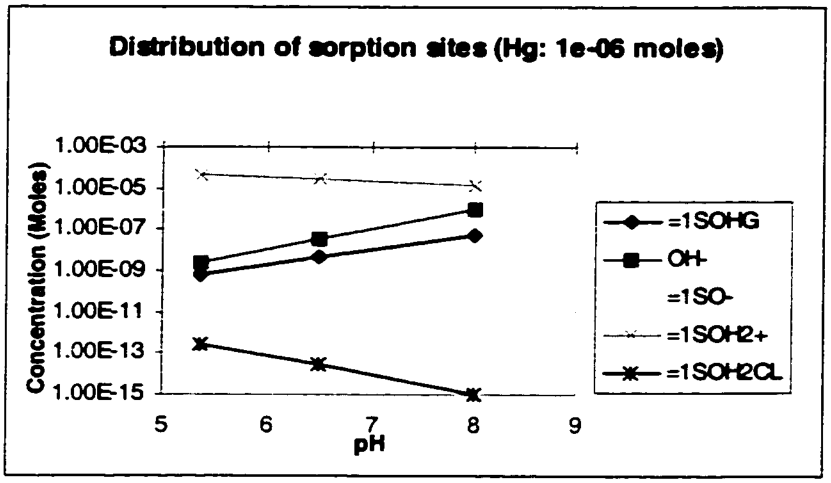


Figure 15 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 8.174 g/l and specific surface area : 80.00 $m^2/g$

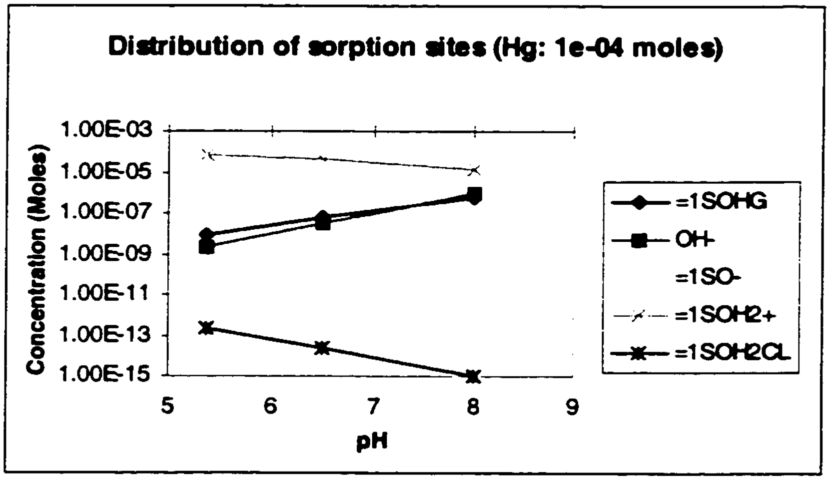


Figure 16 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 8.174 g/l and specific surface area : 129.00 $m^2/g$

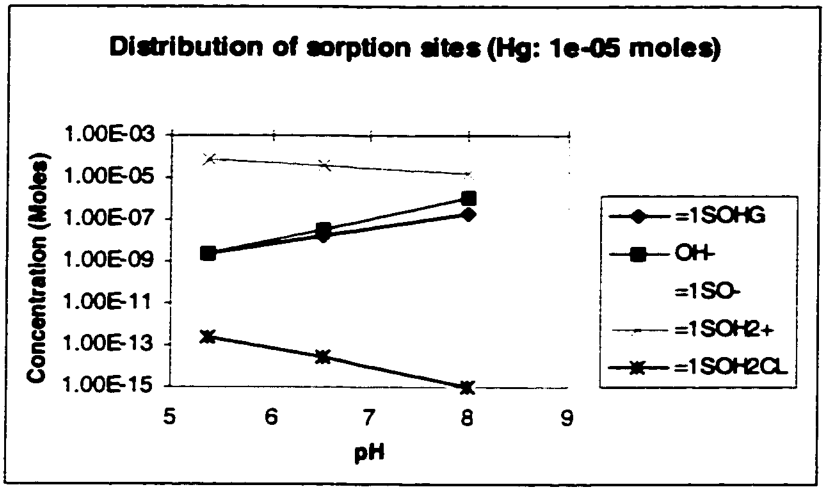


Figure 17 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 8.174 g/l and specific surface area : 129.00 m$^2$/g

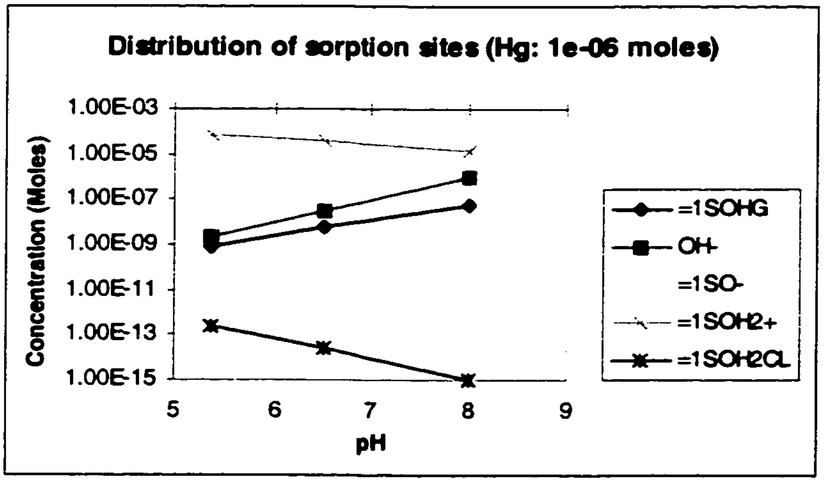


Figure 18 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 8.174 g/l and specific surface area : 129.00 m$^2$/g

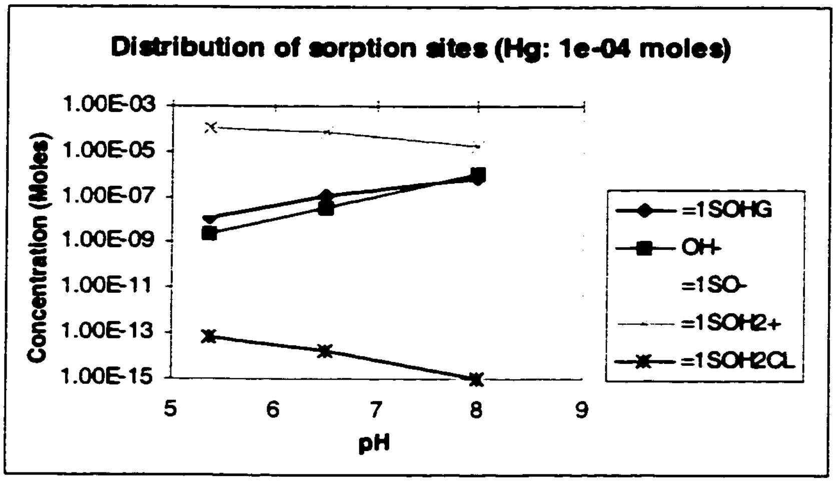


Figure 19 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 8.174 g/l and specific surface area : 400.00 $m^2/g$

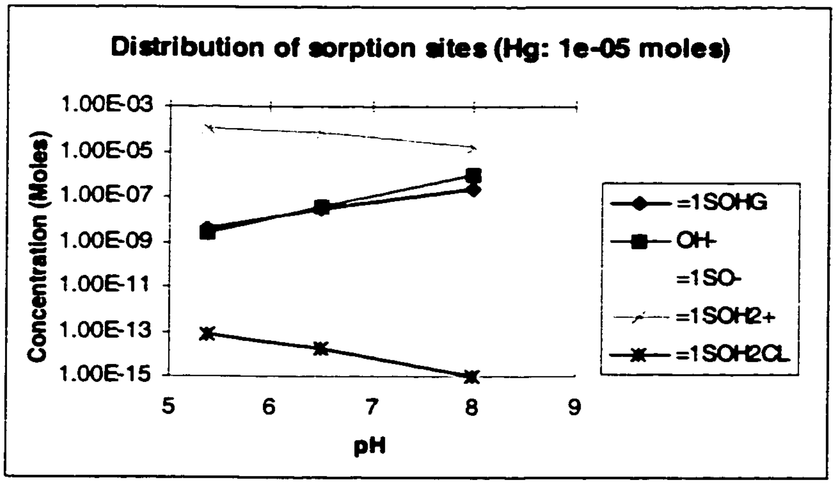


Figure 20 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 8.174 g/l and specific surface area : 400.00 $m^2/g$

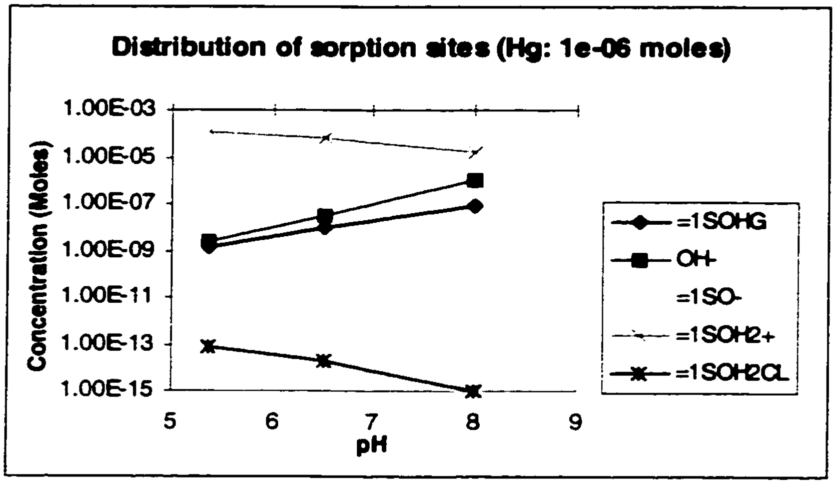


Figure 21 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 8.174 g/l and specific surface area : 400.00 $m^2/g$

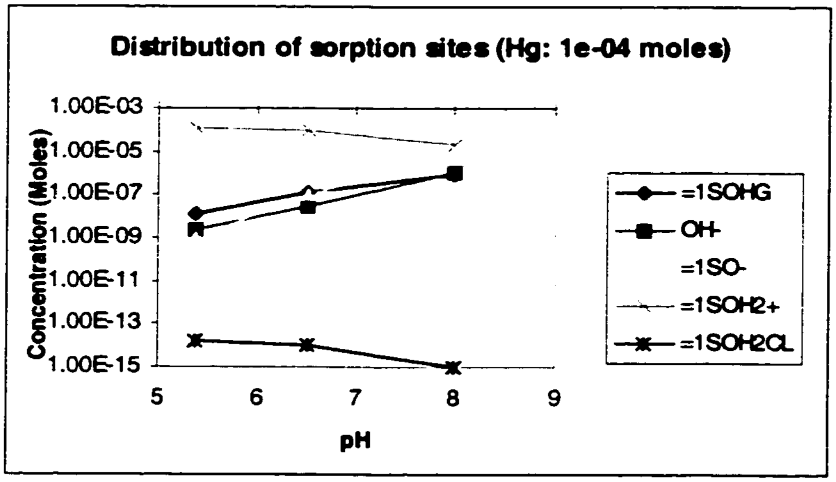


Figure 22 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 8.174 g/l and specific surface area : 1350.00 $m^2/g$

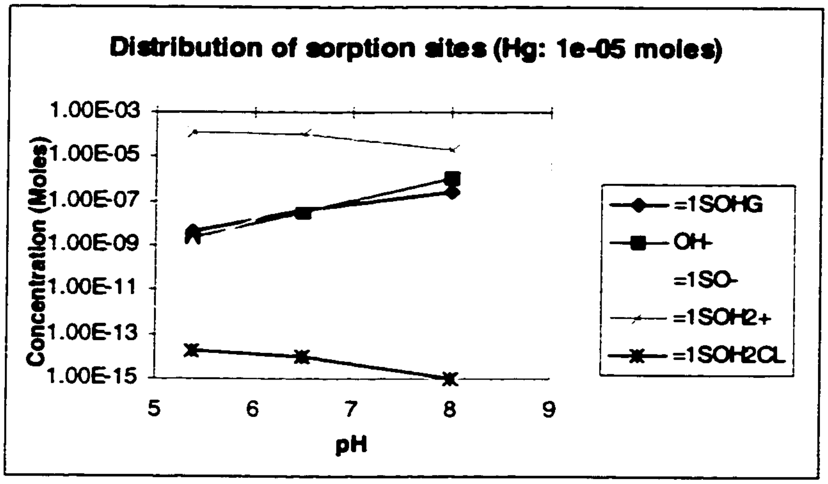


Figure 23 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 8.174 g/l and specific surface area : 1350.00 $m^2/g$

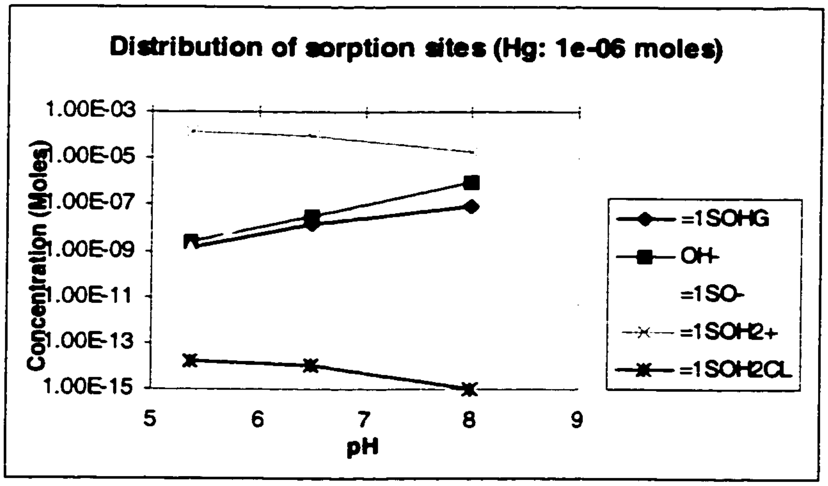


Figure 24 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 8.174 g/l and specific surface area : 1350.00 $m^2/g$

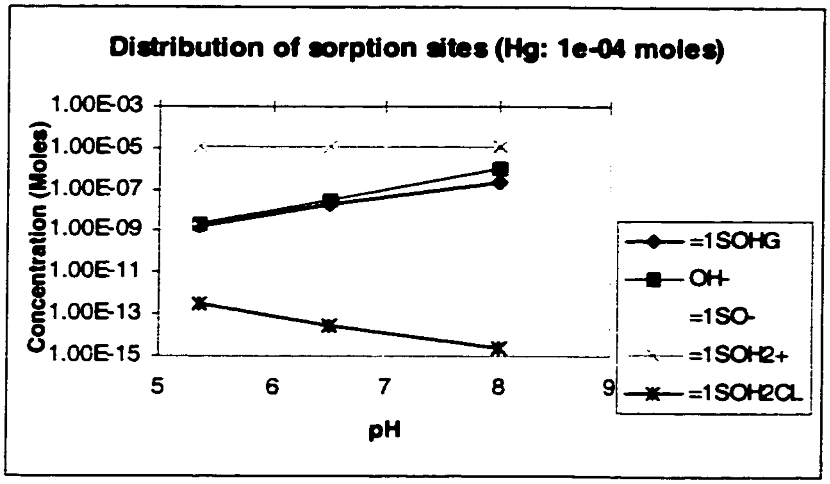


Figure 25 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 10 mg/l and specific surface area : 80.00 $m^2/g$

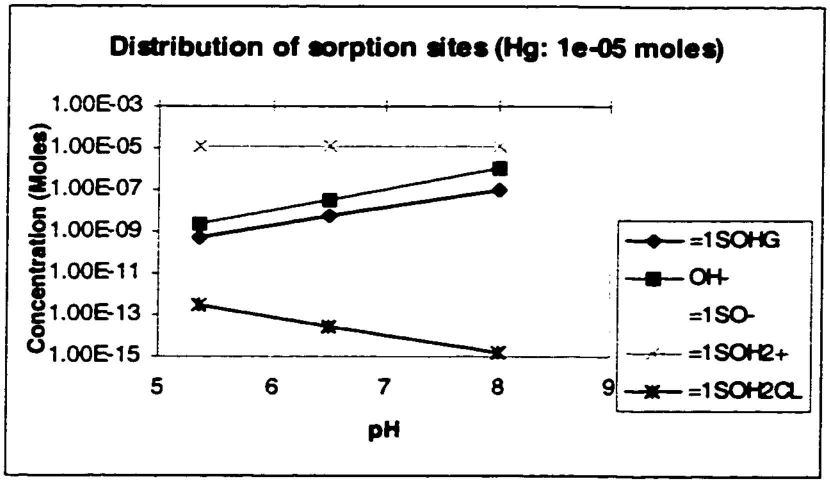


Figure 26 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 10 mg/l and specific surface area : 80.00 $m^2/g$

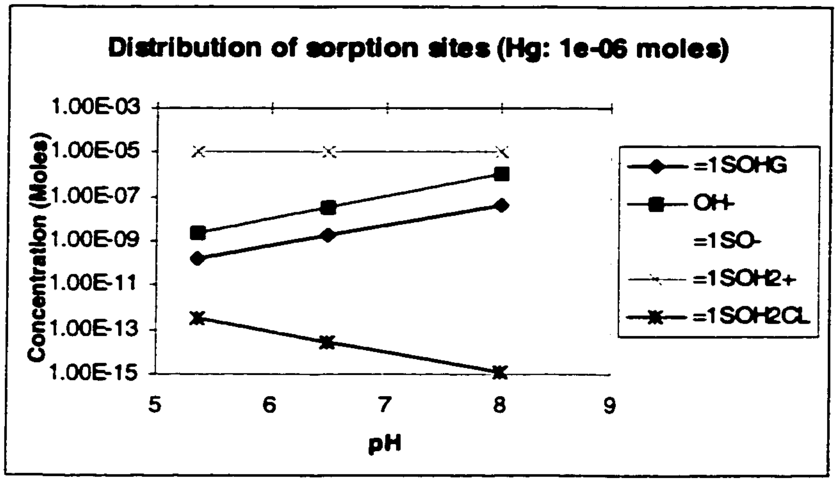


Figure 27 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 10 mg/l and specific surface area : 80.00 $m^2/g$

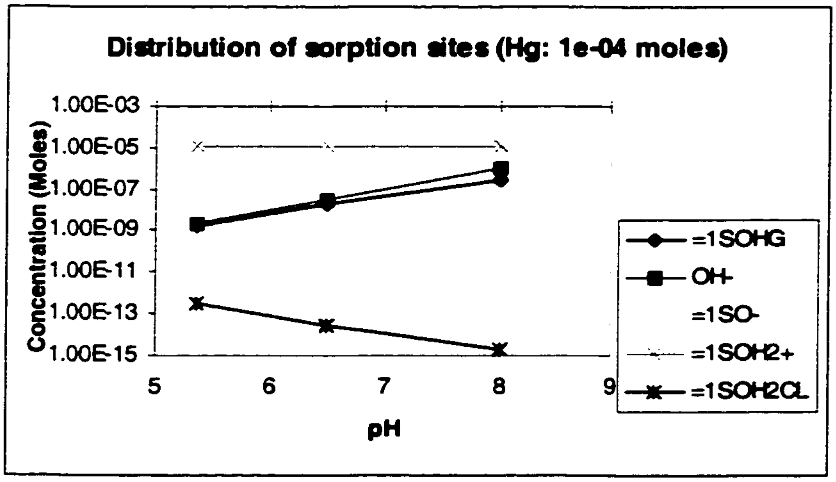


Figure 28 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 10 mg/l and specific surface area : 129.00 $m^2/g$

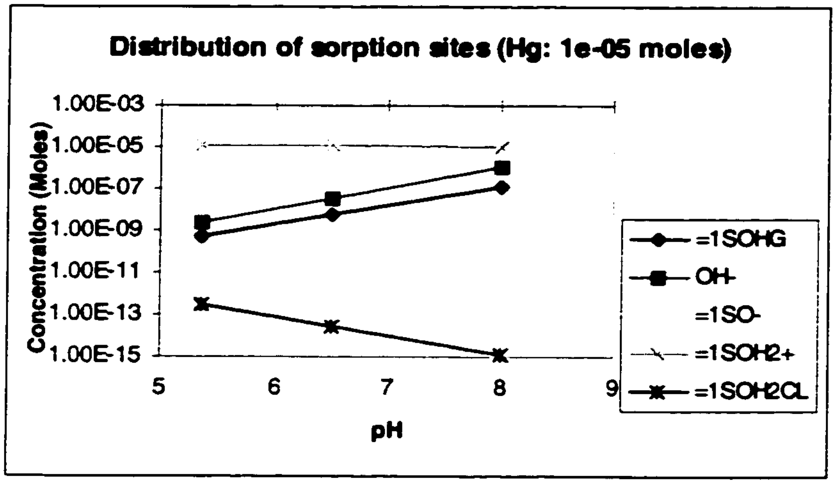


Figure 29 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 10 mg/l and specific surface area : 129.00 $m^2/g$

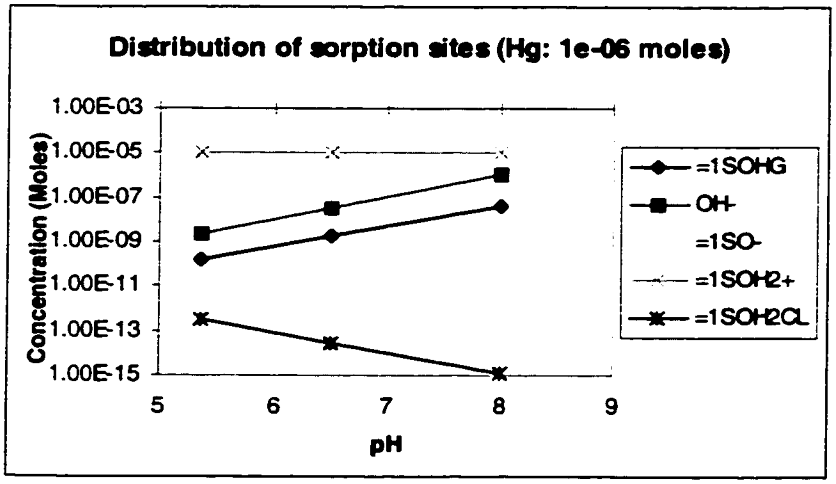


Figure 30 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 10 mg/l and specific surface area : 129.00 $m^2/g$

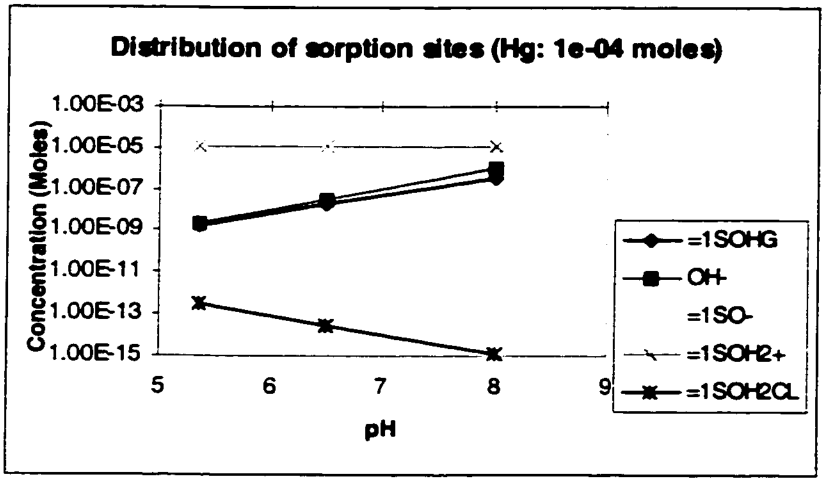


Figure 31 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 10 mg/l and specific surface area : 400.00 $m^2/g$

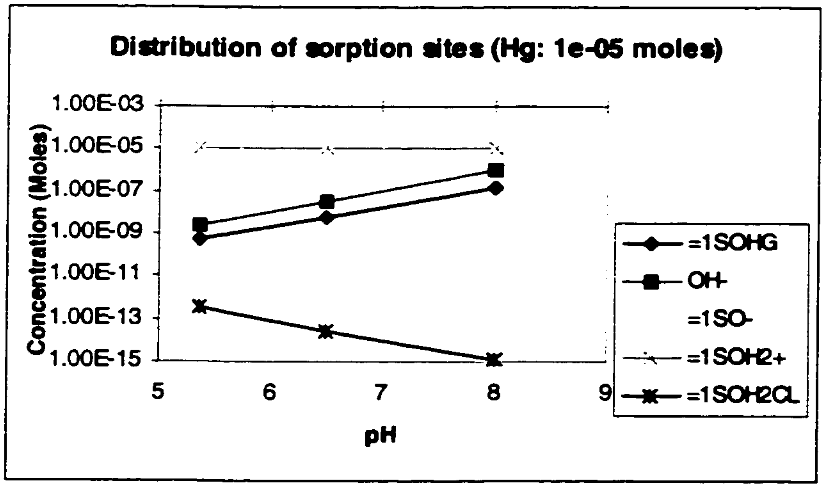


Figure 32 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 10 mg/l and specific surface area : 400.00 $m^2/g$

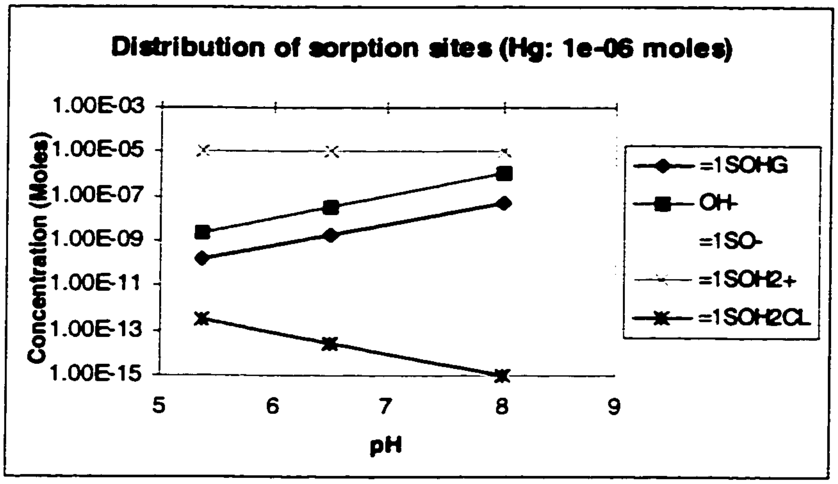


Figure 33 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 10 mg/l and specific surface area : 400.00 $m^2/g$

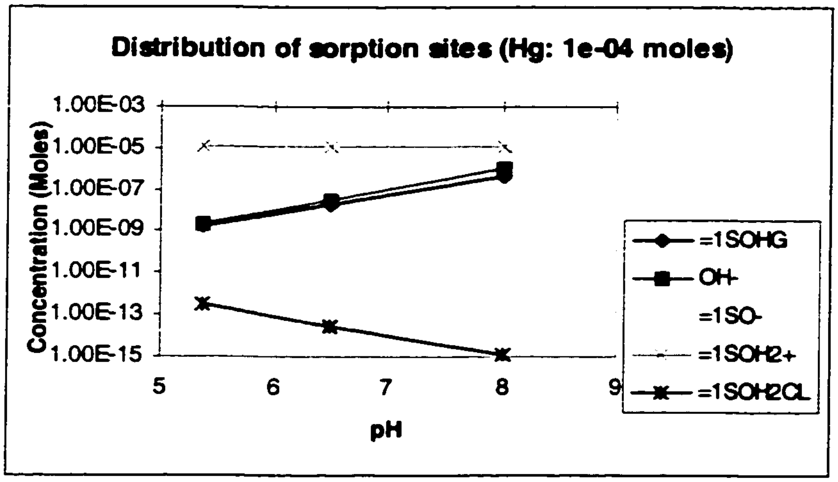


Figure 34 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-04 moles and adsorbent concentration 10 mg/l and specific surface area : 1350.00 $m^2/g$

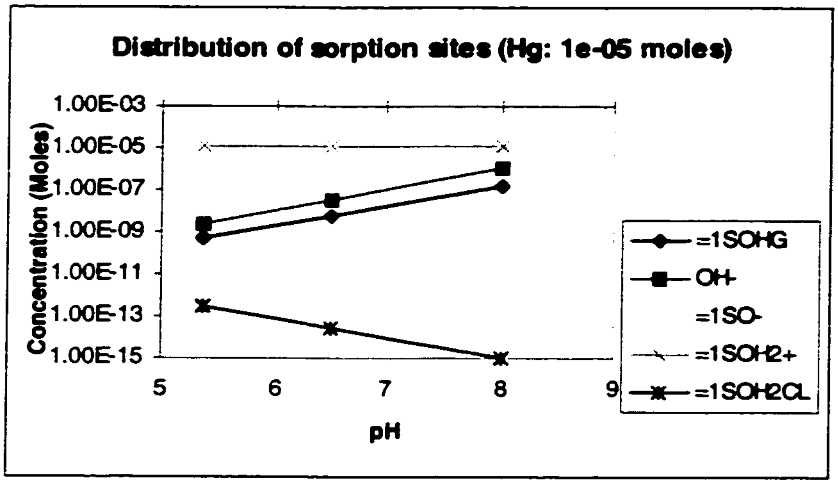


Figure 35 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-05 moles and adsorbent concentration 10 mg/l and specific surface area : 1350.00 $m^2/g$

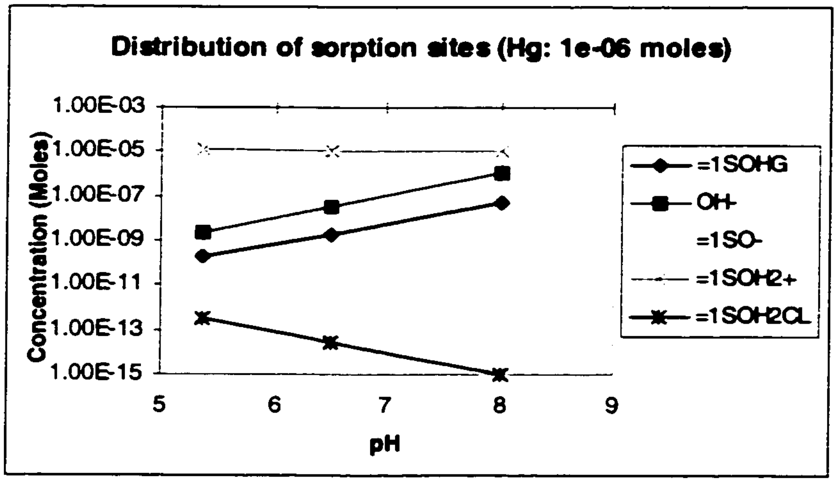


Figure 36 Effect of pH variation (from 5.36 to 8.0) on mercury sorbed on particle's surface for Hg concentration 1e-06 moles and adsorbent concentration 10 mg/l and specific surface area : 1350.00 $m^2/g$

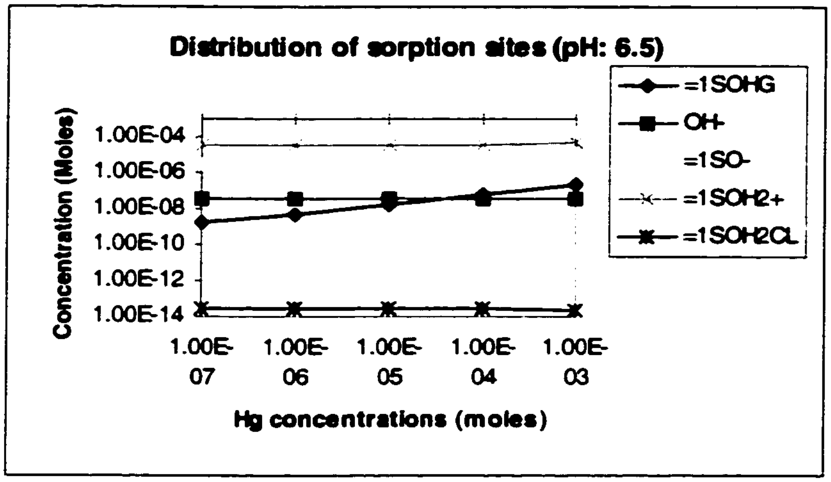


Figure 37 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 g/l and specific surface area : 80.00 $m^2/g$

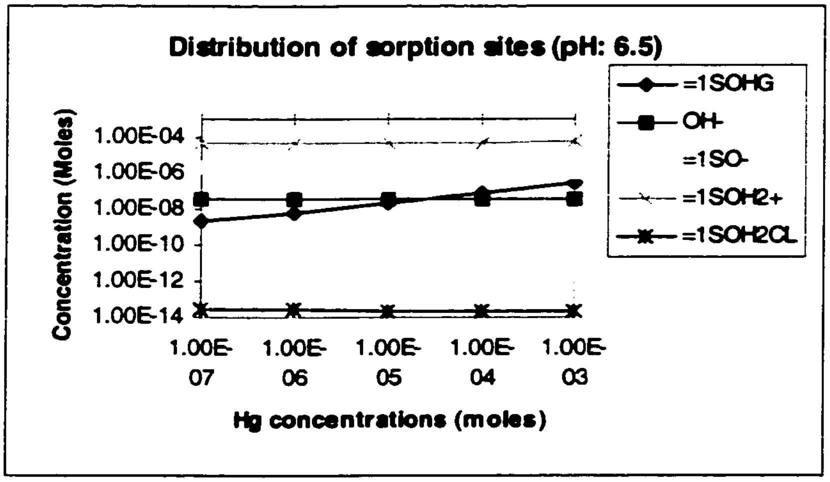


Figure 38 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 g/l and specific surface area : 129.00 $m^2/g$

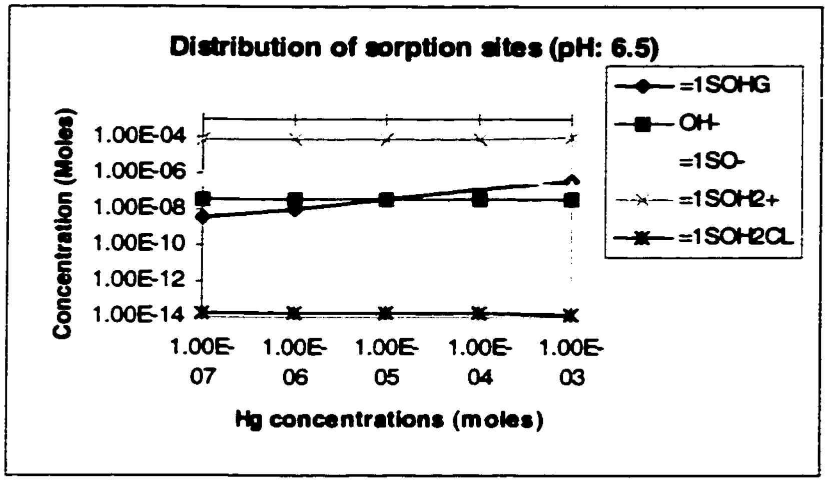


Figure 39 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 g/l and specific surface area : 400.00 $m^2/g$

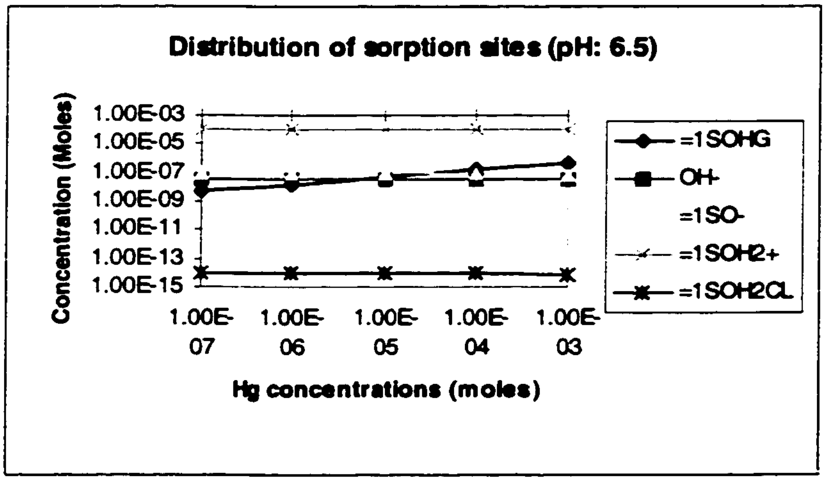


Figure 40Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 g/l and specific surface area : 1350.00 $m^2/g$

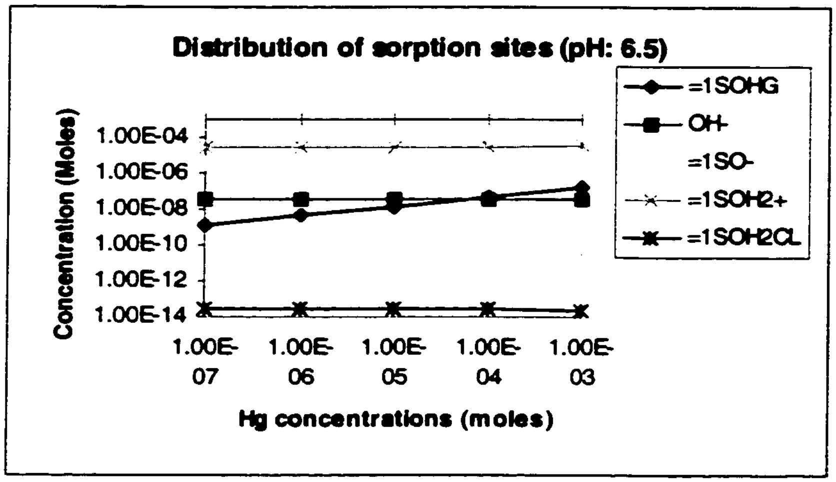


Figure 41 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 8.174 g/l and specific surface area : 80.00 $m^2/g$

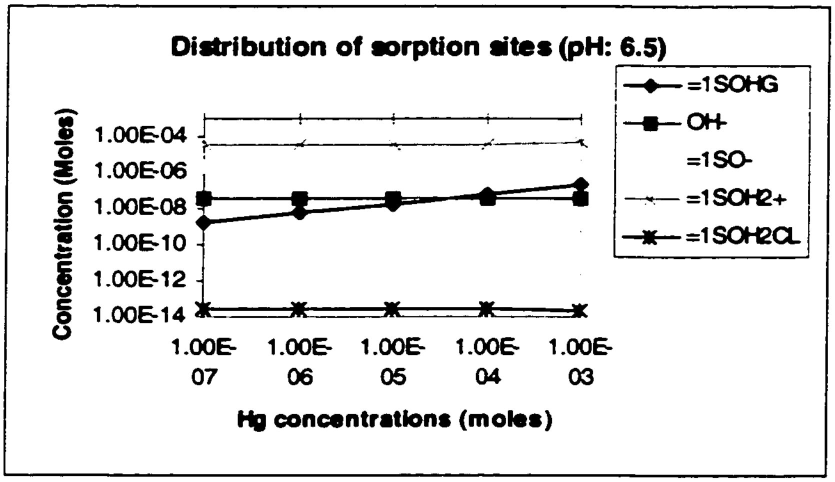


Figure 42 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 8.174 g/l and specific surface area : 129.00 $m^2/g$

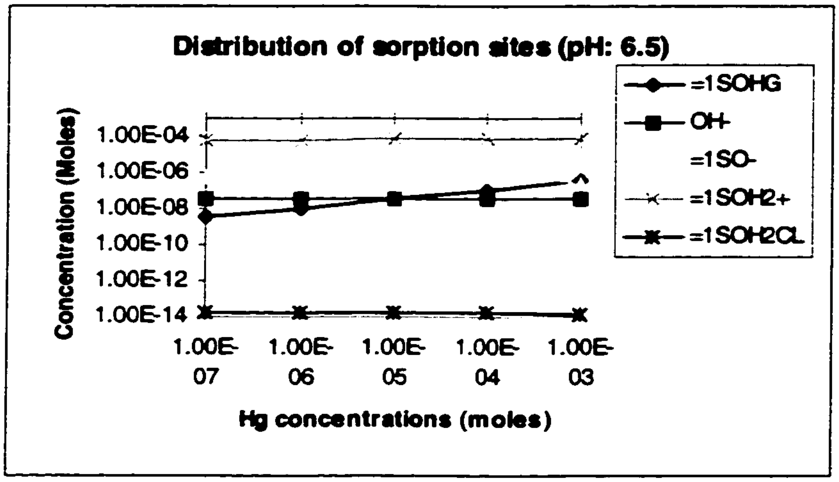


Figure 43 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 8.174 g/l and specific surface area : 400.00 $m^2/g$

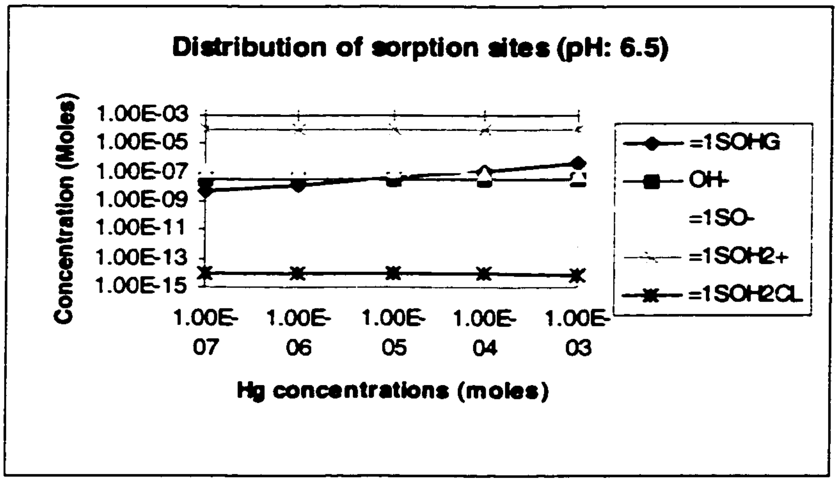


Figure 44 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 8.174 g/l and specific surface area : 1350.00 $m^2/g$

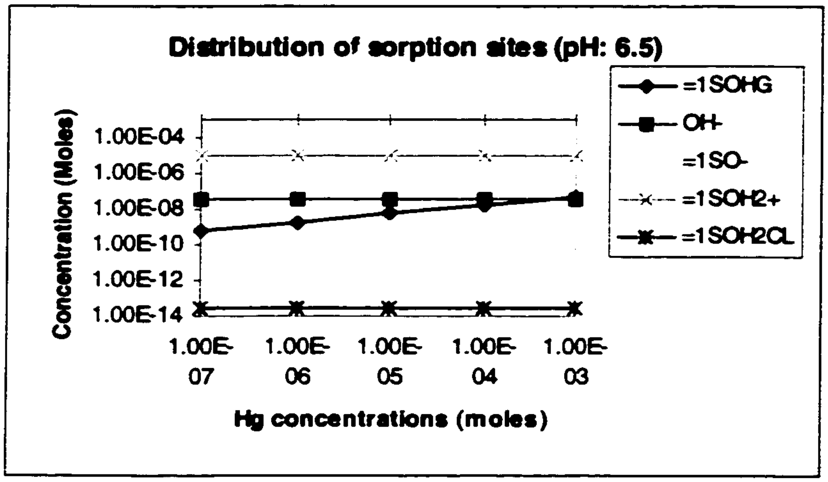


Figure 45 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 mg/l and specific surface area : 80.00 m$^2$/g

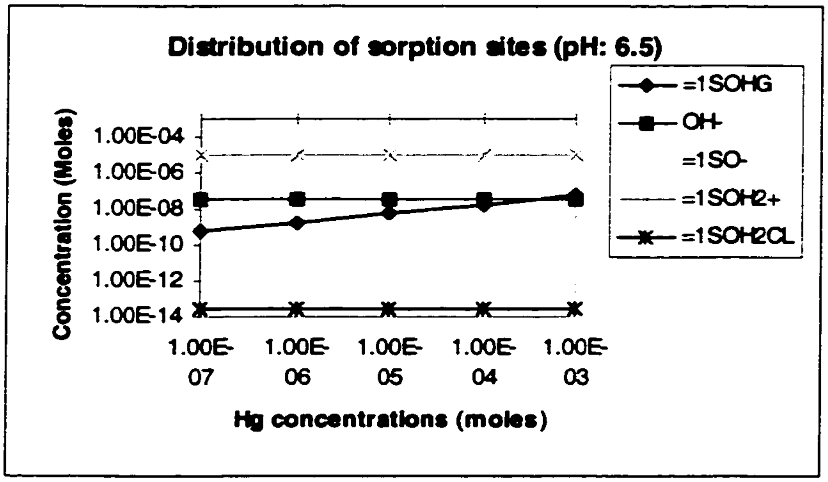


Figure 46 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 mg/l and specific surface area : 129.00 m$^2$/g

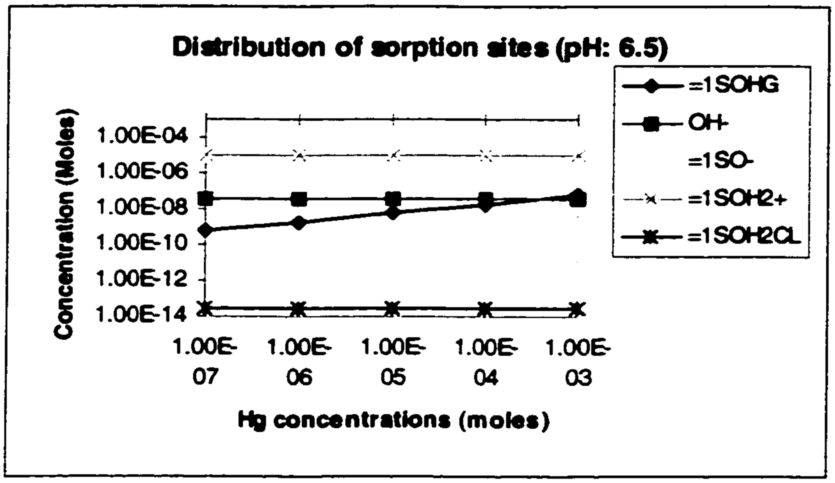


Figure 47 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 mg/l and specific surface area : 400.00 $m^2/g$

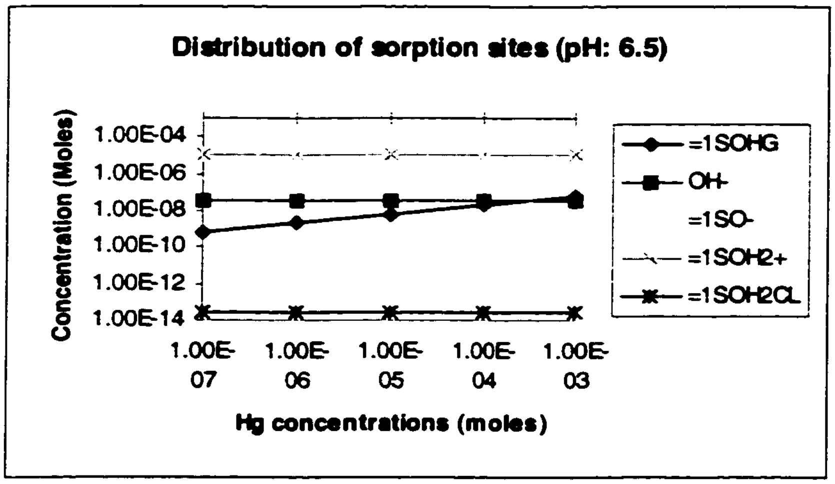


Figure 48 Effect of different initial mercury concentrations (1 E-7 to 1 E-3 moles) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 mg/l and specific surface area : 1350.00 $m^2/g$

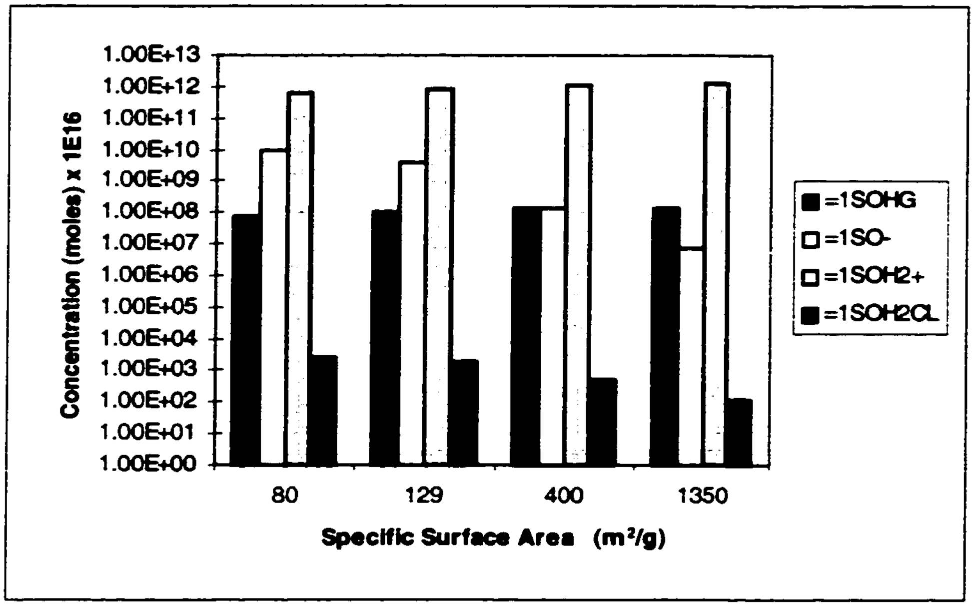


Figure 49 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-4 moles

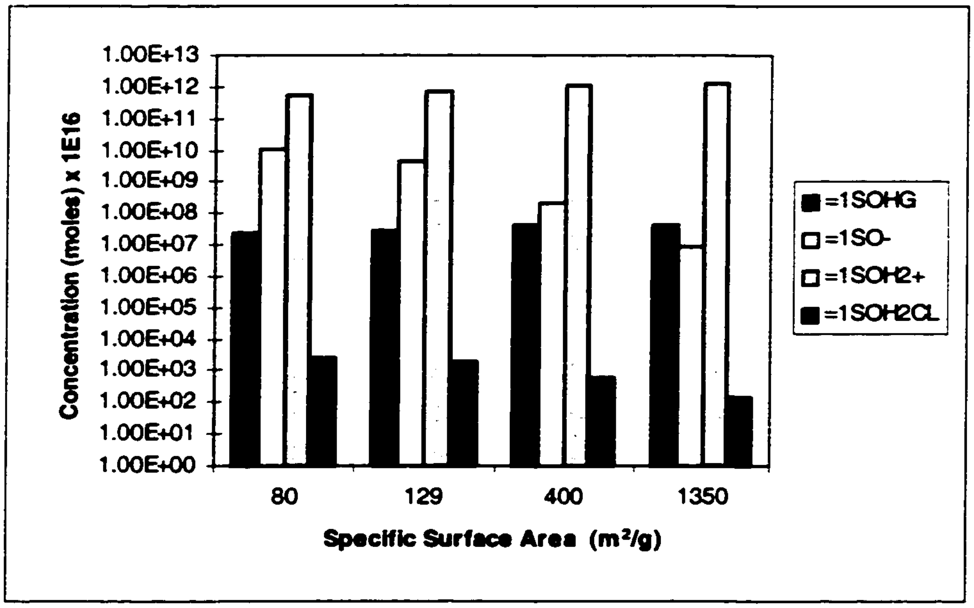


Figure 50 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-5 moles

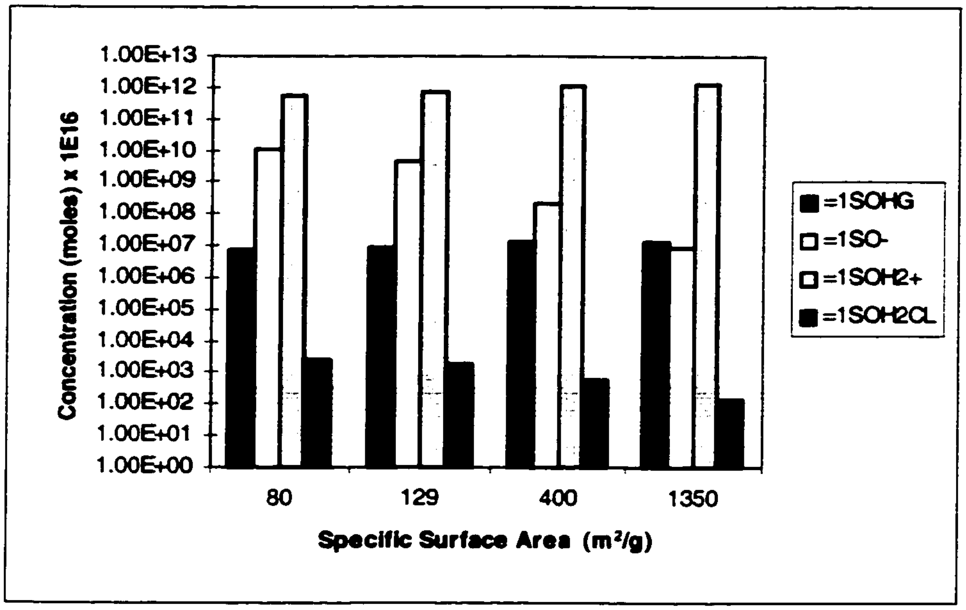


Figure 51 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-6 moles

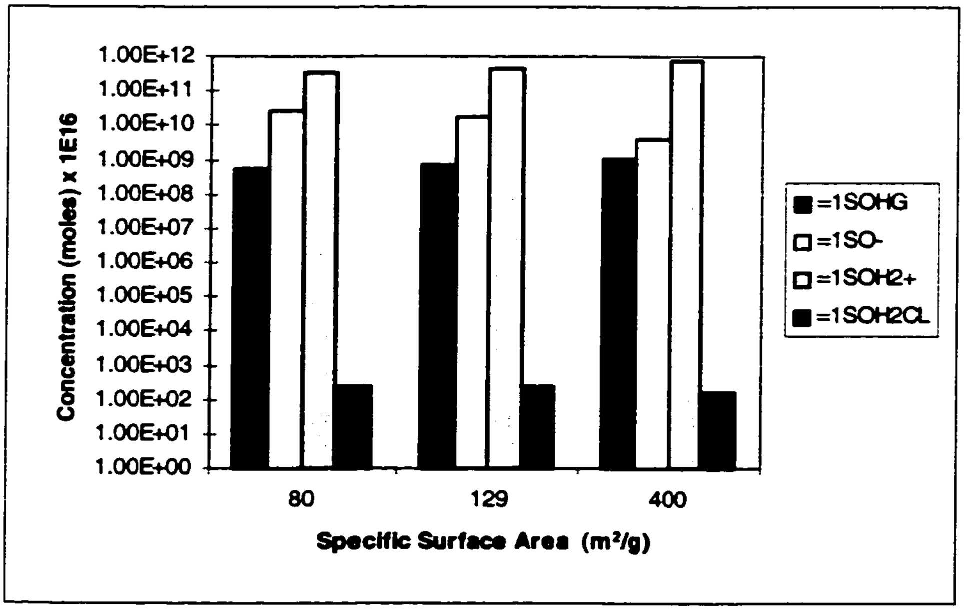


Figure 52 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-4 moles

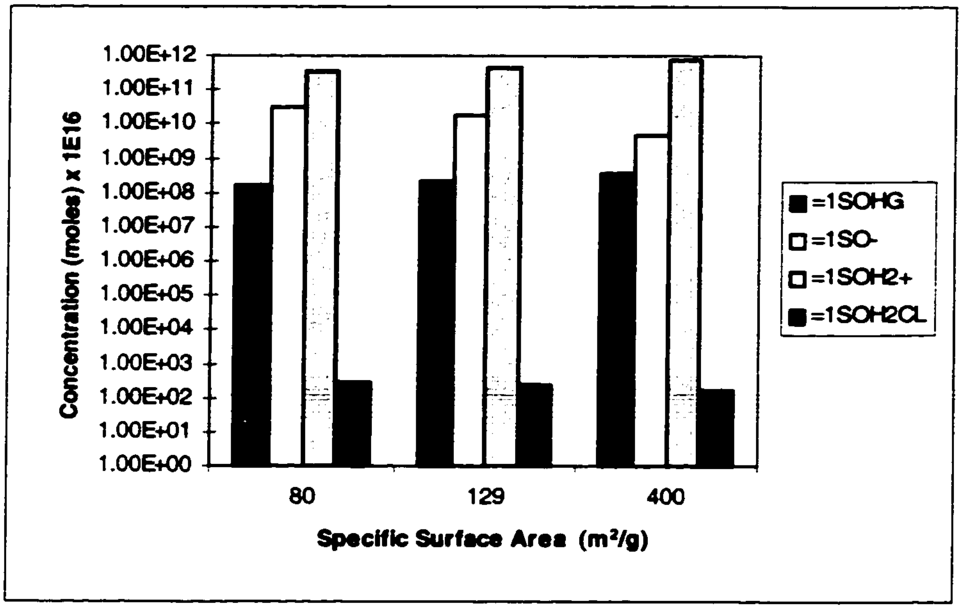


Figure 53 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-5 moles

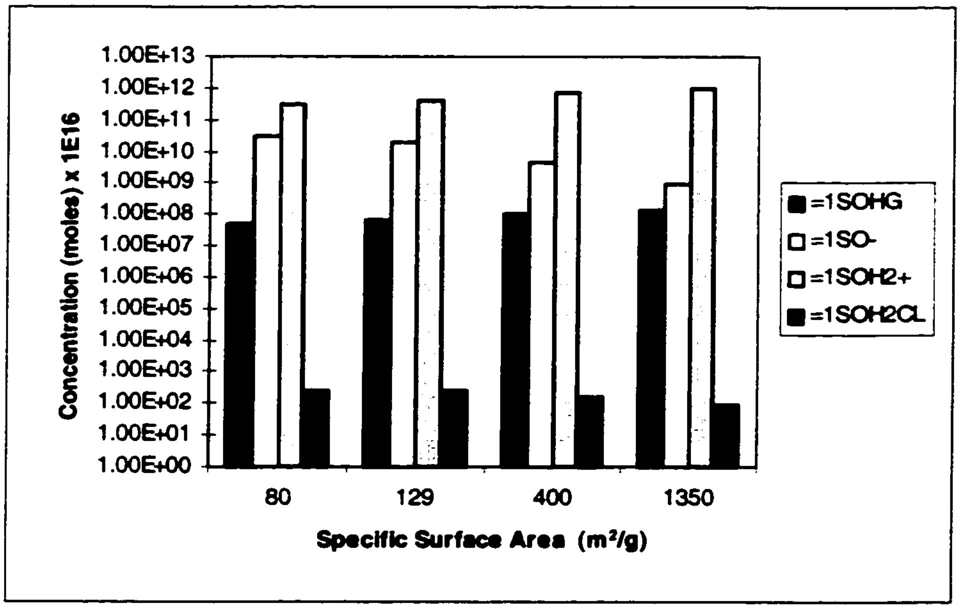


Figure 54 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-6 moles

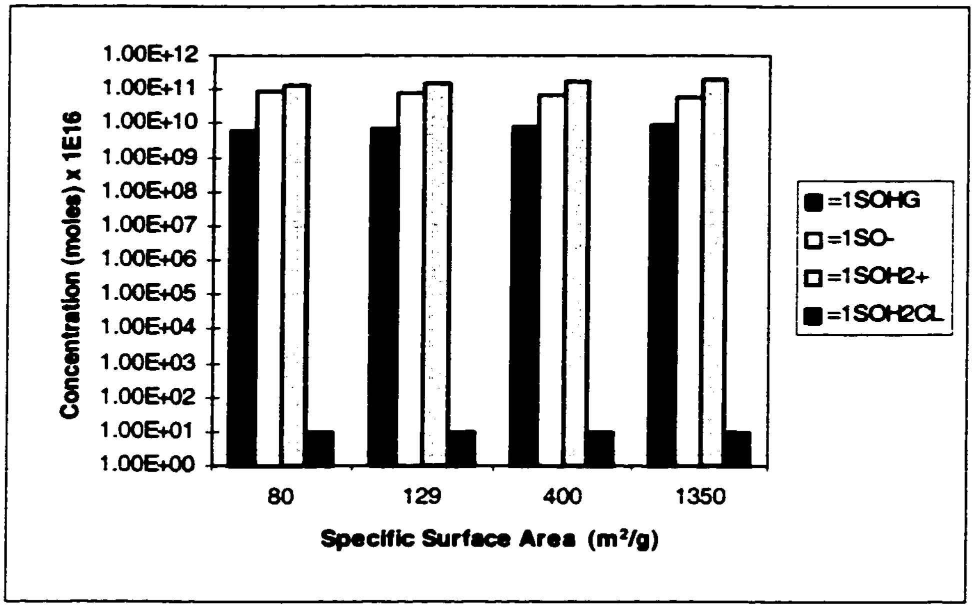


Figure 55 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-4 moles

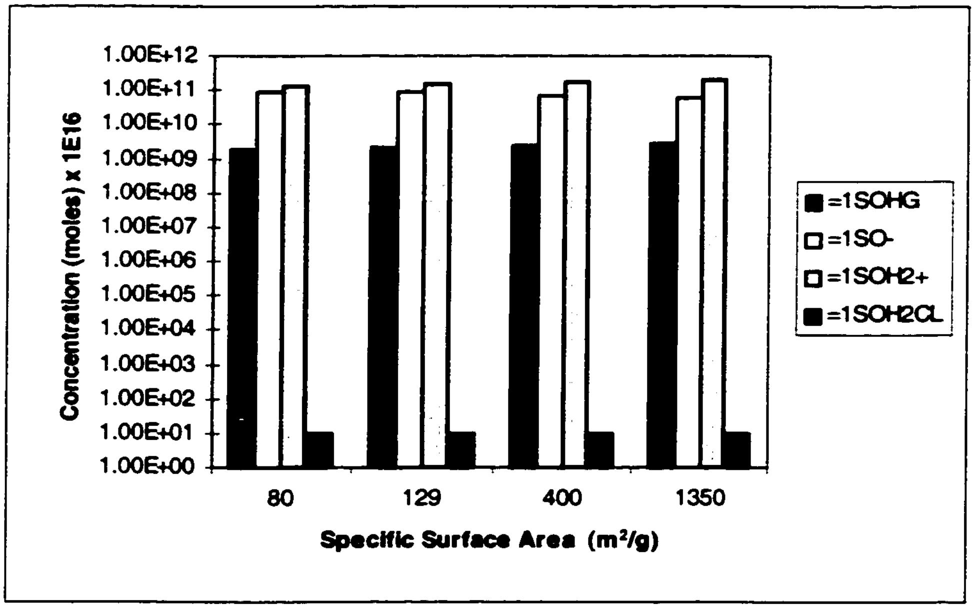


Figure 56 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-5 moles

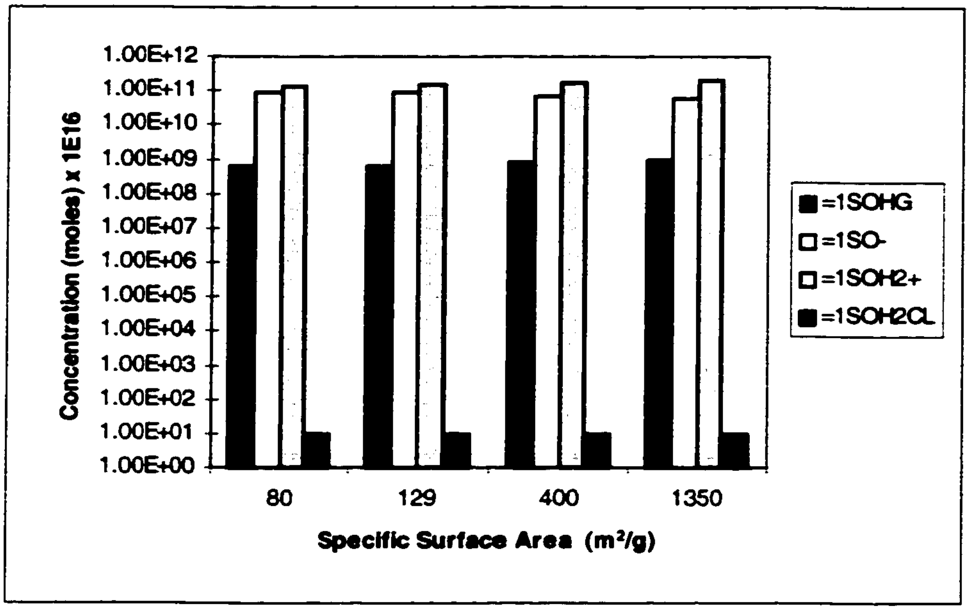


Figure 57 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 10 g/l and initial mercury concentration of 1 E-6 moles

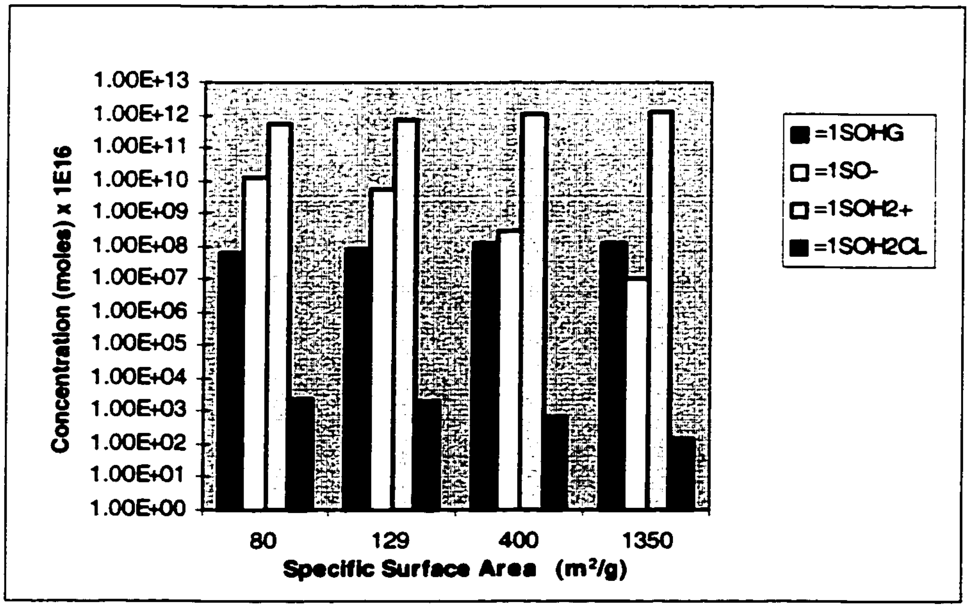


Figure 58 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-4 moles

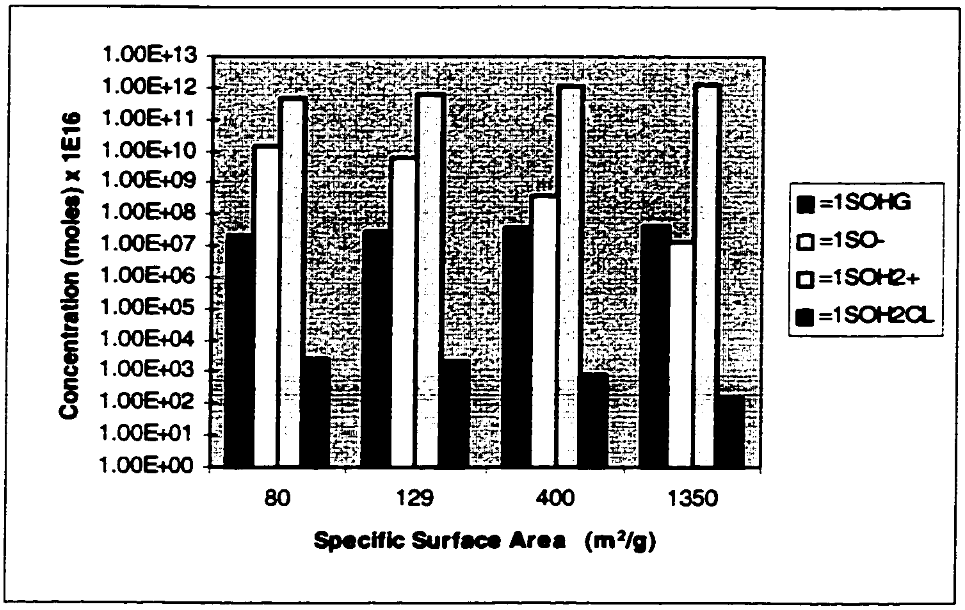


Figure 59 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-5 moles

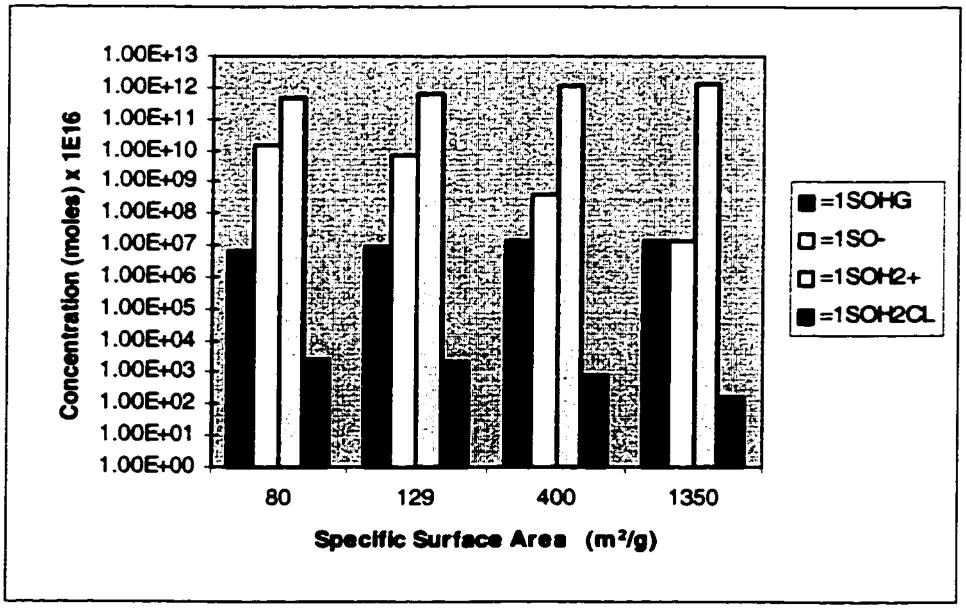


Figure 60 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-6 moles

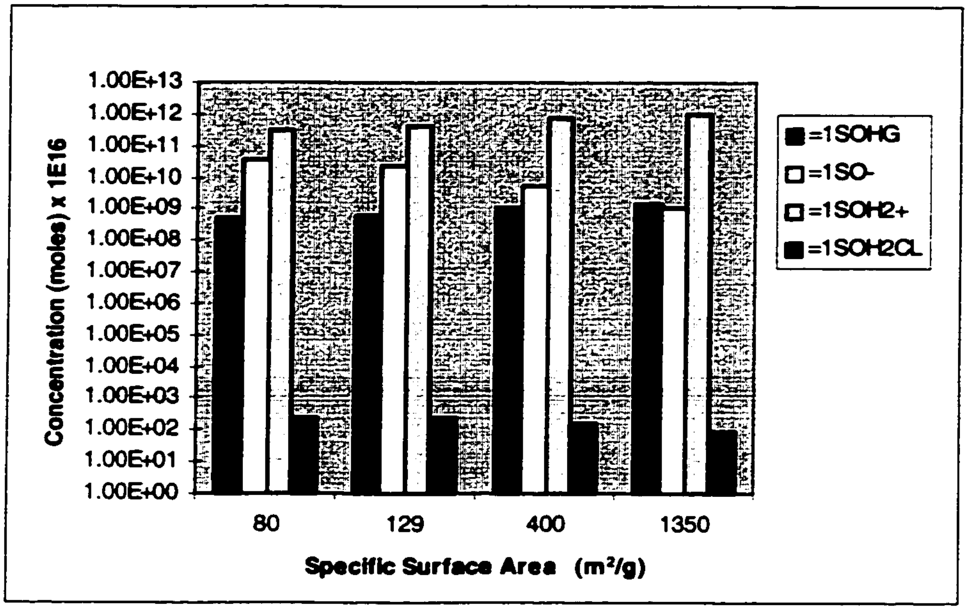


Figure 61 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-4 moles

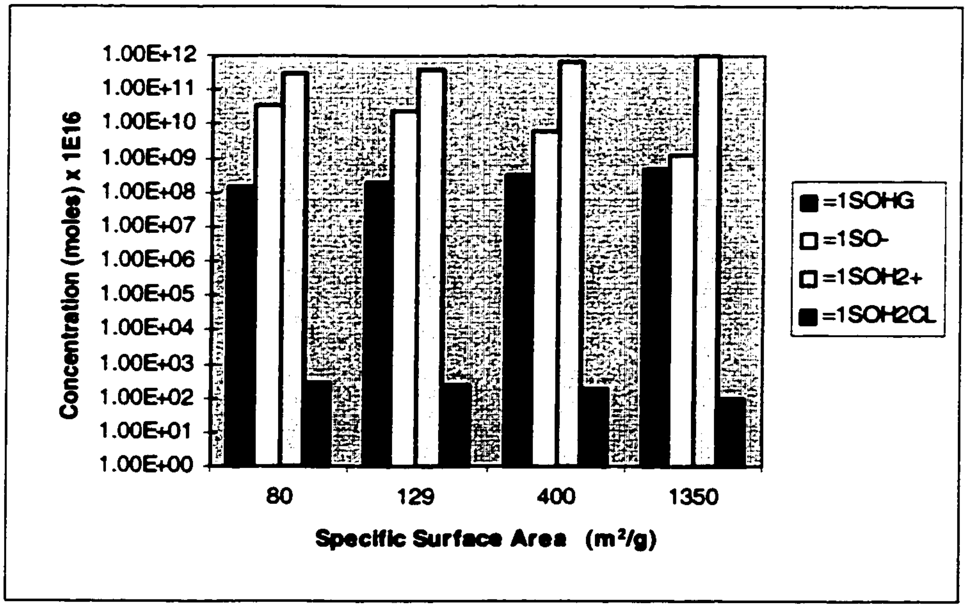


Figure 62 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-5 moles

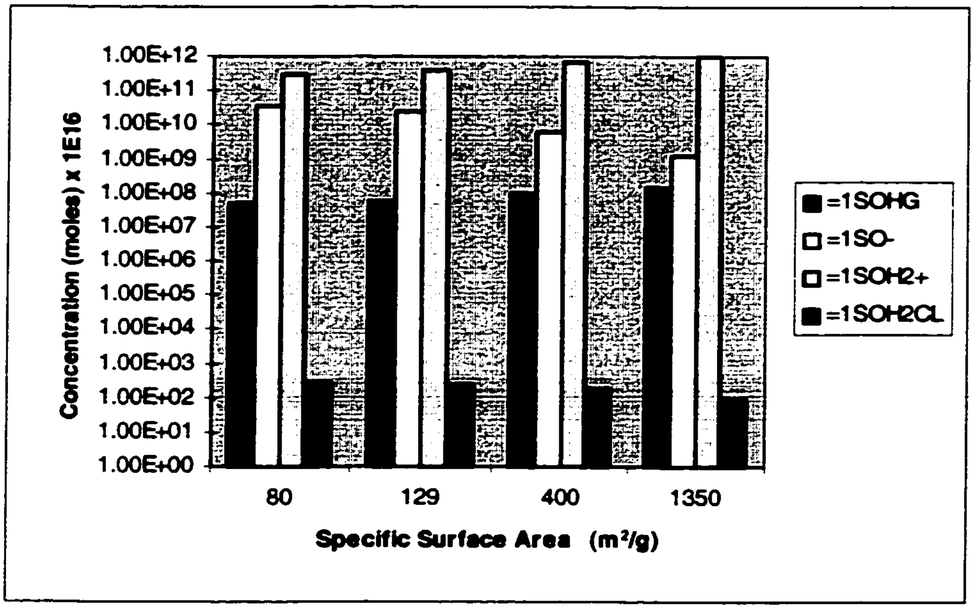


Figure 63 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-6 moles

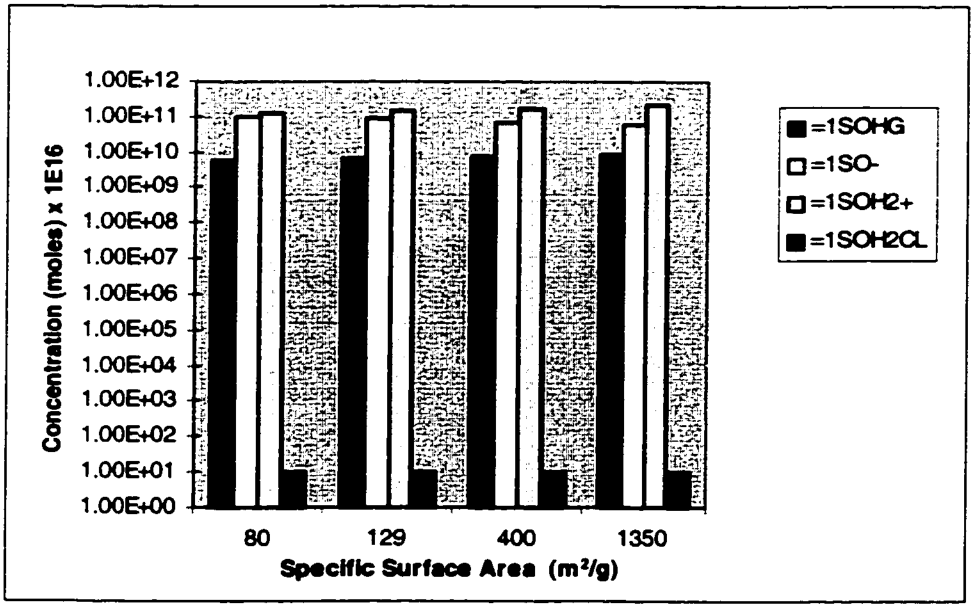


Figure 64 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-4 moles

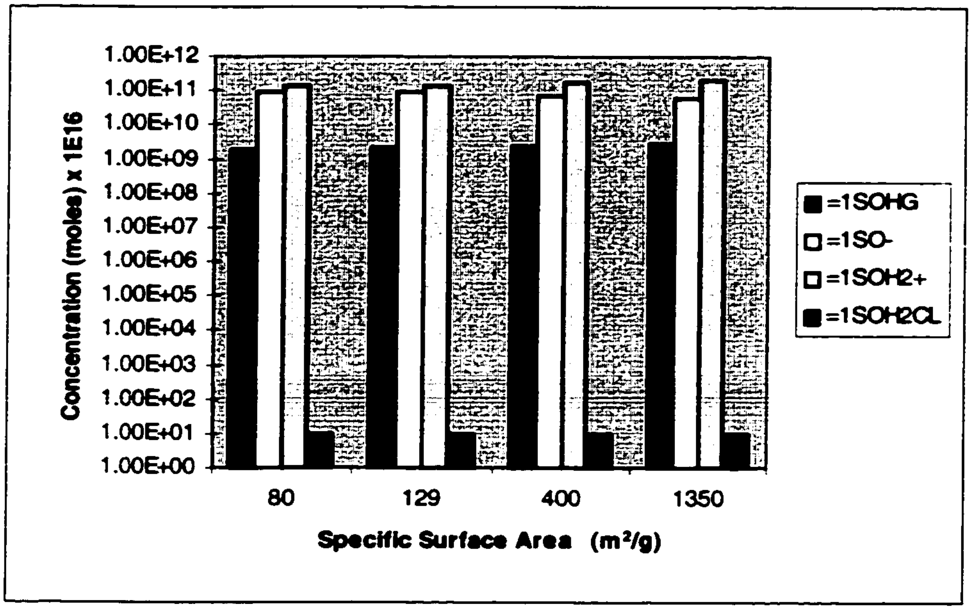


Figure 65 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-5 moles

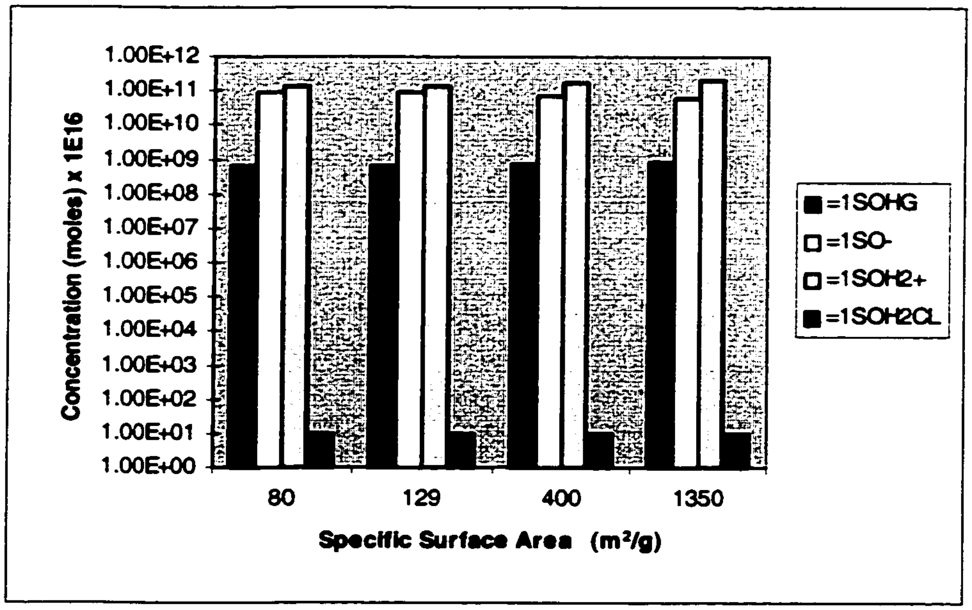


Figure 66 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 8.174 g/l and initial mercury concentration of 1 E-6 moles

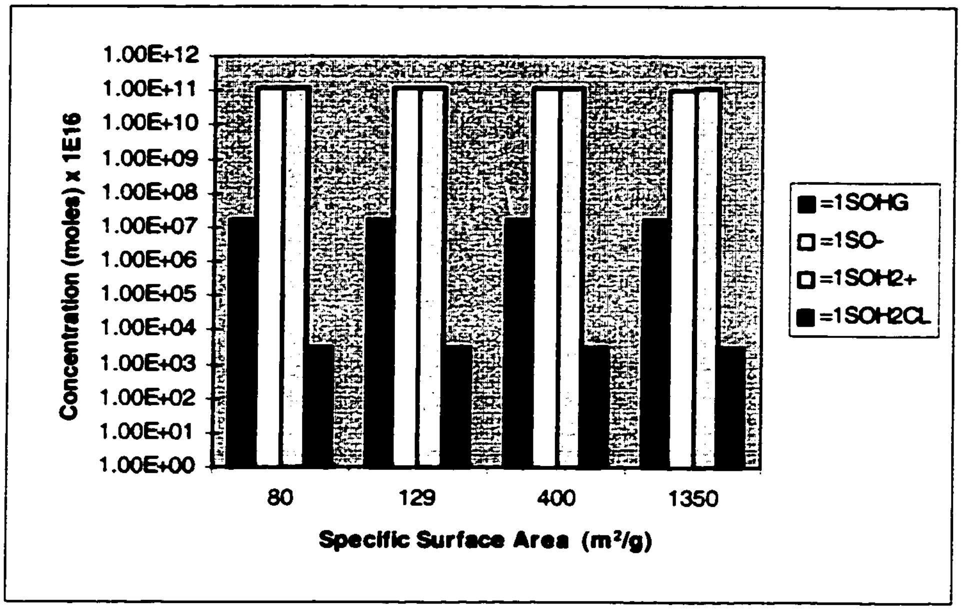


Figure 67 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-4 moles

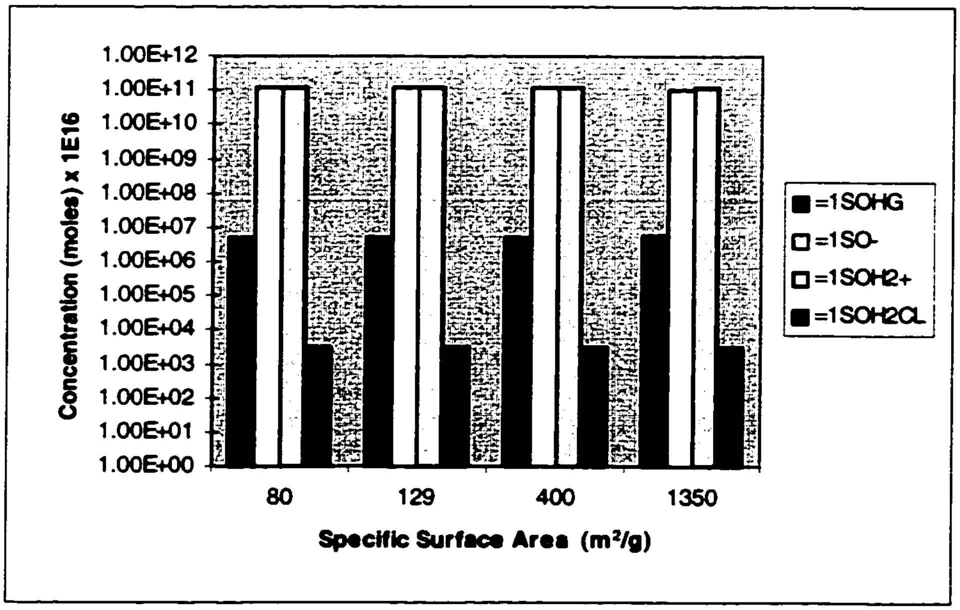


Figure 68 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-5 moles

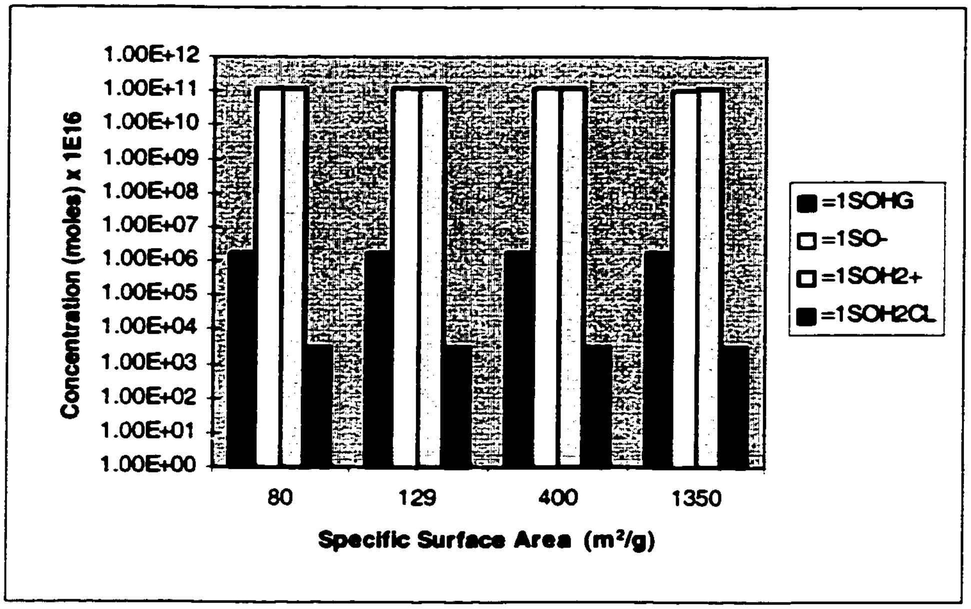


Figure 69 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 5.36 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-6 moles

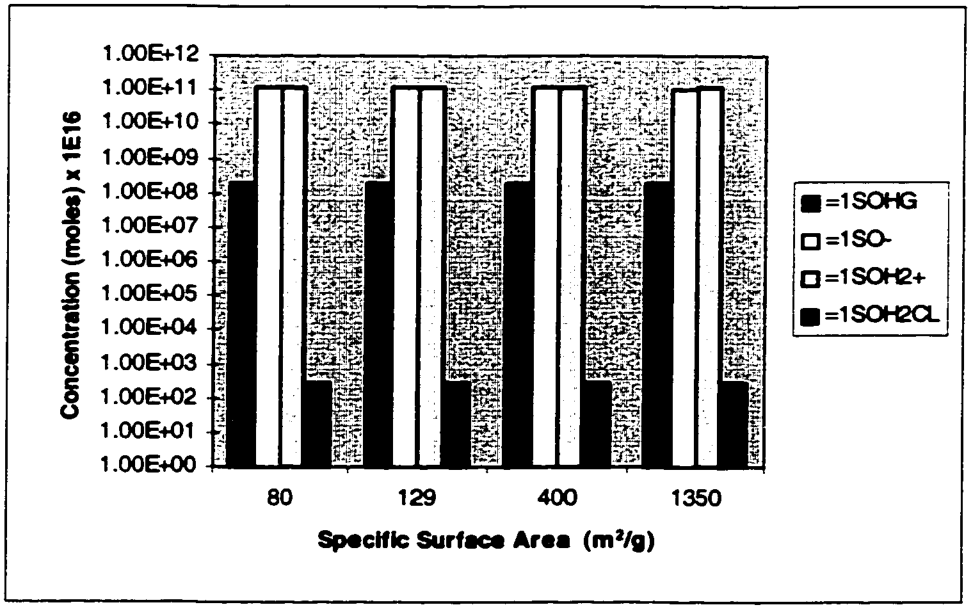


Figure 70 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-4 moles

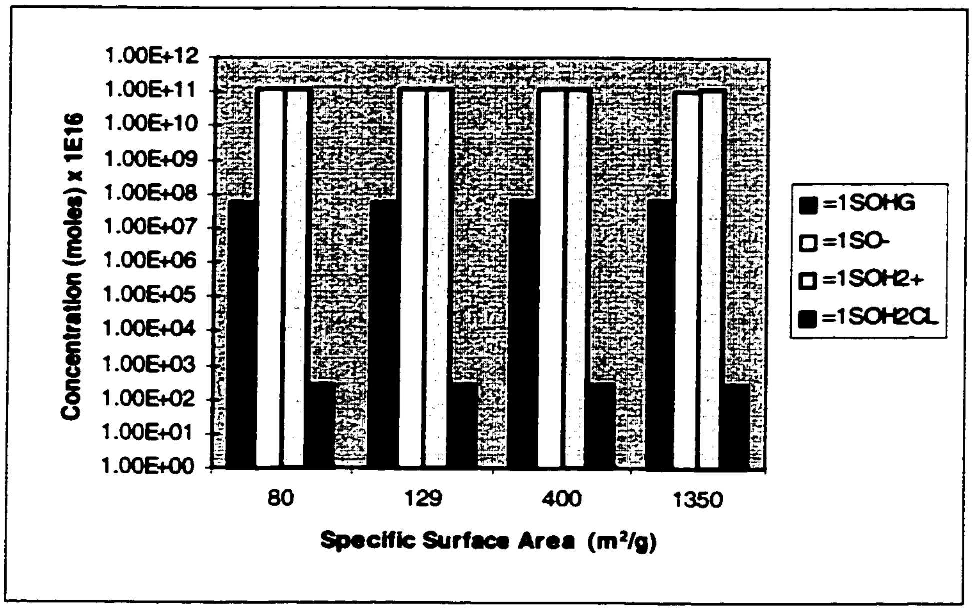


Figure 71 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-5 moles

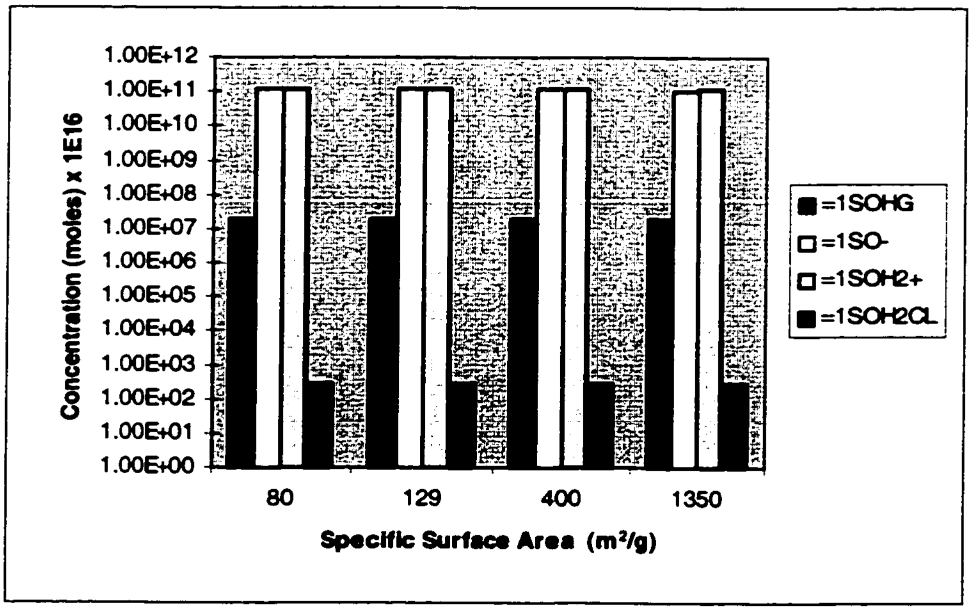


Figure 72 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 6.5 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-6 moles

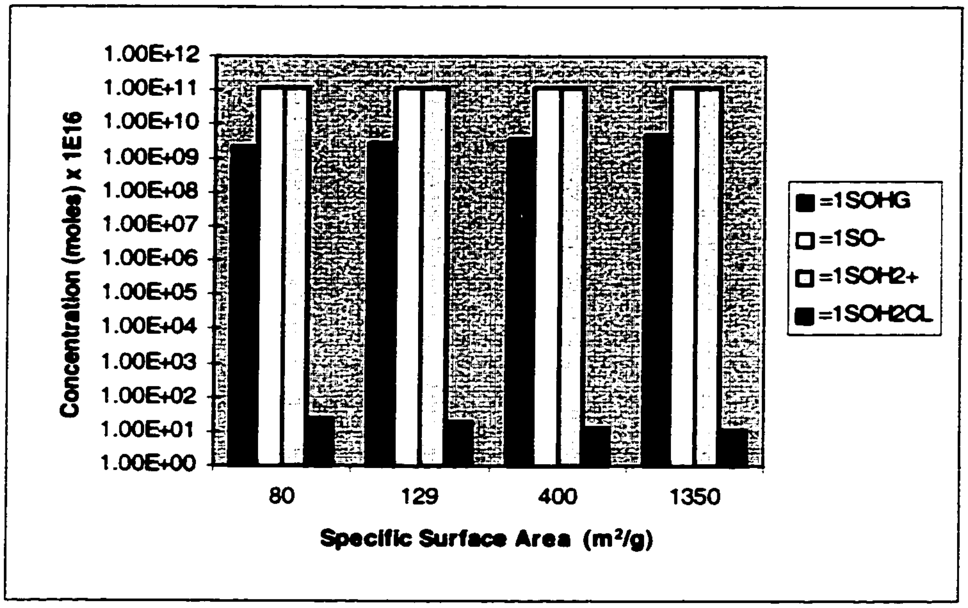


Figure 73 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-4 moles

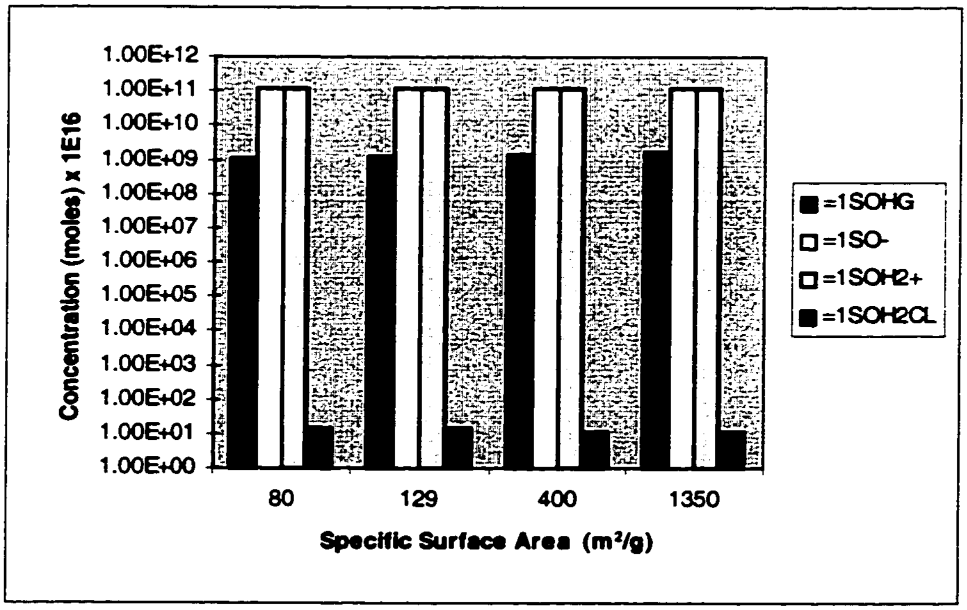


Figure 74 Effect of different soil's specific surface areas (80 to 1350 m$^2$/g ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-5 moles

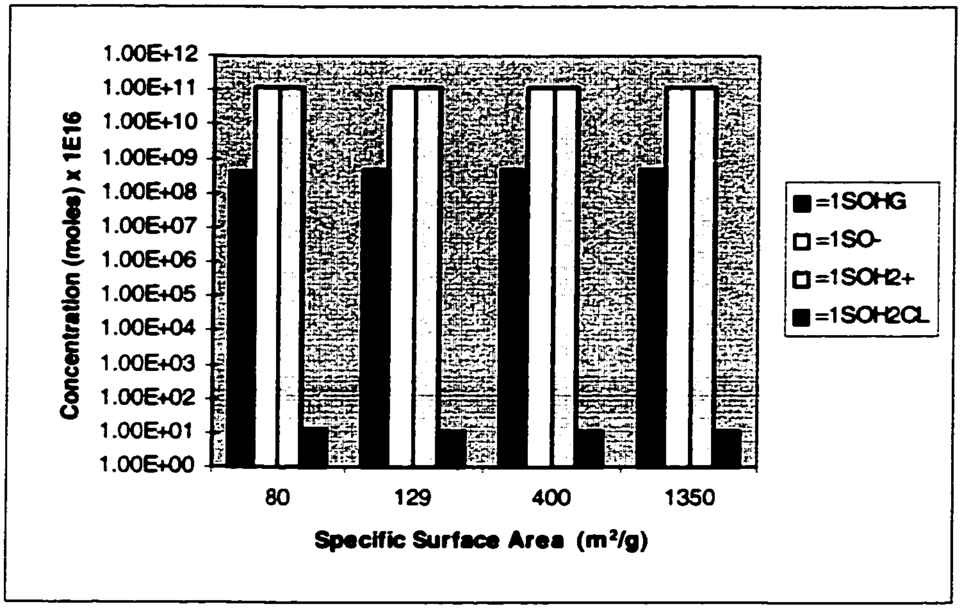


Figure 75 Effect of different soil's specific surface areas (80 to 1350 $m^2/g$ ) on mercury sorbed on particle's surface at pH 8 and adsorbent concentration 10 mg/l and initial mercury concentration of 1 E-6 moles