Adsorption of Metallic Ions onto Chitosan: Equilibrium and Kinetic Studies

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Licentiate Thesis

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To my family
Equilibrium isotherms and the adsorption kinetics of heavy metals onto chitosan were studied experimentally. Chitosan, a biopolymer produced from crustacean shells, has applications in various areas, particularly in drinking water and wastewater treatment due to its ability to remove metallic ions from solutions. The adsorption capacity of chitosan depends on a number of parameters: deacetylation degree, molecular weight, particle size and crystallinity. The purpose of this work was to study the adsorption of copper, zinc, mercury, and arsenic on chitosan produced from shrimp shells at a laboratory level.

The experimental work involved the determination of the adsorption isotherms for each metallic ion in a batch system. The resulting isotherms were fitted using the Langmuir model and the parameters of the equation were determined. Kinetic studies of adsorption for different metallic ions at different concentrations and with different particle sizes were performed in batch and column systems. Simplified models such as pseudo-first-order, pseudo-second-order, and intra-particle diffusion equations were used to determine the rate-controlling step. Some preliminary studies were carried out to address the application of chitosan as an adsorbent in the removal of heavy metals or other metallic ions from natural water and wastewater. The regeneration of chitosan was also studied.

The results showed that the adsorption capacity depends strongly on pH and on the species of metallic ions in the solution. The optimum pH value for the metallic cation adsorption was between 4 and 6, whereas for arsenic adsorption it was about 3. When the pH is not controlled, the adsorption capacity is independent of the initial pH with the solution reaching a final pH of about 7. It was also found that the Langmuir equation described very well the experimental adsorption data for each metallic ion. The adsorption capacity for the metals on chitosan follows the sequence Hg>Cu>Zn>As.

The study of the adsorption kinetics of these metallic ions shows that the particle size has a significant influence on the metal uptake rate for copper; but that it has only a slight influence on the adsorption rate of zinc and mercury in the range studied. Arsenic adsorption exhibited an interesting behaviour which depends strongly on the pH of the solution; the uptake increased at short adsorption times and then decreased at long times. The analysis of kinetic models showed that the pseudo-second-order adsorption mechanism is predominant, and the overall rate of the metallic ion adsorption process is therefore controlled by adsorption reactions and not by mass transfer for the range of particle sizes examined in this study.

With regard to the regeneration of chitosan, it was found that sodium hydroxide is a good agent for zinc and arsenic desorption, whereas ammonium sulphate and sodium chloride were the most suitable for copper and mercury desorption, respectively. The ability of chitosan to remove arsenic from natural water, and copper and zinc from mining waste water was verified. The use of these results for designing purposes is a subject for future work.

Keywords: Adsorption; biosorption; chitin; heavy metals; isotherm; kinetic models; mining; speciation; water treatment.
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And finally, thanks to my family: my mother, Lilliam, my daughters, Lilliam and Marling, and my lover, Marlon, for his continuous support, patience and love even in times when I was in Sweden.
LIST OF PAPERS

This thesis is based on the following papers referred to by roman numerals I to III:


These papers are appended at the end of this thesis.

Author’s contribution

Paper 1. Principal author, planning of the experiments, design of the experimental set-up, chemical speciation, and part of the experimental work.

Paper 2. Principal author, planning of the experiments, and an important part of the experimental work.

Paper 3. Principal author, planning of the experiments, design of the experimental set-up, chemical speciation, and part of the experimental work.
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1 INTRODUCTION

1.1 Background

Pollution by heavy metals is a serious threat to aquatic ecosystems because some of these metals are potentially toxic, even at very low concentrations. Additionally, heavy metals are not biodegradable and tend to accumulate in living organisms, and they can cause severe problems to both human health and wildlife (Crini, 2005).

Natural processes and human activities have polluted and reduced the quality of water resources in Nicaragua. Groundwater and superficial water have been contaminated in various ways; e.g. by mining wastes including cyanide and toxic heavy metals, by agricultural chemicals, by industrial and domestic sewage that is sometimes discharged without treatment into waterways and by natural trace elements (e.g. arsenic).

Since it is important to eliminate or reduce the concentration of heavy metals in the aquatic ecosystems, various methods and technologies are commonly applied in the treatment of mining and refining industry effluents before they are discharged to receiving water. These methods include precipitation, ion exchange, and membrane processes. However, the application of some of these methods may be impractical due to economic constraints or may be insufficient to meet strict regulatory requirements. Furthermore, they may generate hazardous products or products which are difficult to treat (Gavrilescu, 2004; Reddad et al., 2002).

The traditional coagulation and flocculation processes use inorganic coagulants such as aluminium hydroxides in drinking water treatment. Metal coagulants can be used to partially remove heavy metal from wastewater (Eilbeck and Mattock, 1987), but, the use of metal coagulants is not 100% effective for removing metal cations from water at pH 7 (Bell and Saunders, 2005).

The high cost of adsorbents such as activated carbon and some ion-exchange resins used for the treatment of water and wastewater have conducted to new more effective and cheaper adsorbents. Bailey et al. (1999) mentioned that natural materials that are available in large quantities or industrial waste products can also be used as adsorbents.

Chitin and its deacetylated form, chitosan, are two biopolymers that come from crustacean shells and have the ability to fix a great variety of heavy metals (Muzzarelli, 1977). The strong affinity of metal ions for these sorbents is explained by the relatively high proportion of nitrogen sites.

Currently, Nicaragua produces about 5.5 thousand tons of shrimp per year and the residual shells, the raw material for chitin, constitute about 20% of the production volume. The fishery factories are located on the Pacific and Atlantic coasts and the production of large volumes of solid waste may become an environmental menace. The use of these biopolymers can be a low cost alternative for the removal of contaminants from industrial effluents and from the natural water supply.
The metal sorption capacity of chitosan varies with crystallinity, affinity for water, deacetylation degree and amino group content. Kinetic studies have demonstrated that the rate of metallic ion sorption onto chitosan differs depending on the raw material (shrimp, crab or lobster shells), preparation method, chemical modification, and chitosan particle shape. Wu (2000) evaluated the sorption capacities and rates for Cu(II) onto flakes and bead forms of chitosan prepared from fishery wastes. They found that the bead type of chitosan exhibited a greater sorption rate than the flake type. On the other hand, Wan Ngah et al. (2004) performed kinetic studies of Cu(II) sorption on chitosan beads and chitosan/PVA beads, and reported that the pseudo-second-order rate constant of chitosan beads was higher than the rate constant of chitosan/PVA beads.

The sorption process also depends on the physicochemical characteristics of the aqueous solutions, such as pH, pE, temperature, metallic ion concentration and the form of the main species in the solution (Guibal, 2004). For example, it is observed that the uptake of As(V) is greater than As(III) onto chitosan (Boddu et al., 2007), and that it depends greatly on the pH and redox conditions (Dambies et al., 2002) and on the temperature (Gerente et al., 2005).

The design of a chitosan filter for the removal of metallic ions from contaminated effluents requires equilibrium and kinetics data for the system. Numerous studies have demonstrated that chitosan posses a great sorption capacity and favourable kinetics for most metals. Reviews have been presented by Guibal (2004) and by Gerente et al. (2007). Simplified kinetic models have been used to determine the sorption mechanisms and potential rate-controlling steps, such as external and intra-particle mass transfer as well as adsorption of copper and zinc onto chitosan. These models included the pseudo-first-order, pseudo-second-order, and intra-particle diffusion equations.

1.2 Objectives

The objective of the present work has been to study the removal of Cu, Zn, Hg, and As from aqueous solution using chitosan. Equilibrium and kinetic experiments at different metallic ion concentrations and with different particle sizes have been performed. The experimental data have been tested with the Langmuir equation, and simplified kinetic models have been applied to determine the rate-controlling mechanisms for the adsorption process. In addition, desorption studies and the studies of application of chitosan for the removal of heavy metals from natural water and mining effluents have been carried out. To accomplish this, the biosorbent has been produced on a laboratory scale from residual shrimp shells.

1.3 Outline

Chapter 2 presents the main characteristics of chitosan, and the interaction mechanisms of adsorption and its applications. Chapter 3 shows the principles of adsorption, adsorption equilibria and the sorption mechanisms applied to this study. Chapter 4 describes the experimental work, and the results and discussion are present in Chapter 5. Finally, Chapter 6 presents the conclusions drawn from this work.
2 CHITIN AND CHITOSAN

Chitin and chitosan are nitrogenous polysaccharides that are made up of acetylglucosamine and glucosamine units. In fact, these two polymers have exactly the same basic chemical structure: \((1\rightarrow4)-2\text{-acetamido-2-deoxy-}\beta\text{-D-glucan}\) and \((1\rightarrow4)-2\text{-amino-2-deoxy-}\beta\text{-D-glucan}\), respectively (Figure 2.1). The difference between them is the deacetylation degree (DD) and their respective solubility in dilute acidic media. Sorlier et al. (2001) considered that chitosan is the only derivative to be soluble at a DD above 40%.

![Figure 2.1 Scheme of chemical deacetylation of chitin to produce chitosan](image)

Chitin is the second most abundant polymer in nature. Chitin occurs in nature as ordered crystalline microfibrils forming structural components in the exoskeleton of arthropods (Rinaudo, 2006), its major source being the seafood crustacean (crab, shrimp, prawn, and lobster shells) that are usually disposed as waste material. Depending on its source, three different crystalline polymorphic forms of chitin have been identified: \(\alpha\)-chitin (shrimp and crab shells), \(\beta\)-chitin (squid pen), and \(\gamma\)-chitin (stomach cuticles of cephalopoda) (Jang et al., 2004).

Chitin is a white, hard, inelastic, and inert solid. It is highly hydrophobic and is insoluble in water and most organic solvents. It is soluble in hexafluoroisopropanol, hexafluoroacetone, and chloroalcohols in conjugation with aqueous solutions of mineral acids (Ravi Kumar, 2000). When the deacetylation degree of chitin drops to about 50%, it becomes soluble in aqueous acidic media and is called chitosan (Rinaudo, 2006).

The production of chitin involves chemical or enzymatic desproteinization and acid treatment to dissolve calcium carbonate. In addition, a decolouration step is often added to remove residual pigments. Chitosan is produced at an industrial level by chemical deacetylation of chitin using sodium hydroxide (see Figure 2.1), but chitosan can also be produced by enzymatic deacetylation of chitin using lysozyme, snailase, neutral protease, and chitin deacetylase (Cai et al., 2006).

Due to the free amino groups in chitosan, this polymer chelates five to six times greater amounts of metals that chitin (Bailey et al., 1999). Muzzarrelli (1977) found that chitosan is selective with regard to the sorption of metal ions. It does not take up alkali and alkali earth metal ions but it collects transition and post-transition metal ions from the aqueous solution. These sorption properties have been used for environmental purposes (uptake of heavy metals), separation processes (recovery of valuable metals), and analytical purposes. However, chitosan has not found any practical applications on an industrial scale because of the cost of material, the variability in the characteristics of the material, and the availability of the resource (Guibal, 2004).
2.1 Characteristics of Chitosan

Chitosan is a semicrystalline polymer in the solid state (Rinaudo, 2006). Chitosan has been shown to be biologically renewable, biodegradable, biocompatible, non-antigenic, non-toxic and biofunctional (Malafaya et al., 2007). The main parameters for its characterization are the deacetylation degree (DD), the crystallinity, and the polymer molecular weight (Guibal, 2004). These parameters may affect its conformation in solution, and its physico-chemical and biological properties (Sorlier et al., 2001). The deacetylation degree controls the fraction of free amino groups that will be available for interactions with metals ions. Infra-red spectroscopy and NMR analysis are the most common methods to evaluate the deacetylation degree. Infrared spectra of chitosan are usually obtained with a frequency range of 4000–400 cm\(^{-1}\) and the degree of deacetylation (DD) is given by equation (Domszy and Roberts, 1985),

\[
DD = 100 - \left[ \frac{A_{1654}}{A_{1450}} \times 100 / 1.33 \right]
\]  

(2.1)

In contrast, Guibal (2004) asserted that rather than the deacetylation degree it is better to consider the total number of free amino groups accessible to metal uptake, since some amino groups can be involved in hydrogen bonds. This can be controlled by the residual crystallinity, which can be influenced by the experimental preparation procedure and the origin of the raw material. Methods used to decrease the crystallinity involve the dissolution of chitosan (in acid solution) followed by a coagulation process and direct freeze-drying of the polymer solution. The crystallinity of this polymer can be measured by X-ray diffraction.

The polymer weight may control the solubility of chitosan. Solubilisation occurs by protonation of the \(-\text{NH}_2\) group on the C-2 position of the D-glucosamine repeated unit (Rinaudo, 2006). This biomaterial is soluble in most mineral and organic acids; it is relatively stable in sulphuric acid solutions, and it is insoluble at higher pH levels. This fact should be taken into account when designing experiments, the chemical modification of the polymer, and the metal desorption (Guibal, 2004). A simple method to determine the chitosan molecular weigh is viscometry (Ravi Kumar, 2000). The polymer molecular weigh may be found by applying the Mark-Houwink equation:

\[
[\eta] = KM^\alpha
\]

(2.2)

where \([\eta]\) is the intrinsic viscosity and \(M\) is the molecular weight. \(\alpha\) and \(K\) are experimental values which can be determined in several solvents. In 0.1 M acetic acid and 0.2 M sodium chloride solution, the expression for the intrinsic viscosity is:

\[
[\eta] = 1.81 \times 10^{-3} M^{0.93}
\]

(2.3)

2.2 Modified Chitosan

Chitosan can be modified by chemical or physical processes in order to control the reactivity of the polymer or enhance the sorption kinetics depending on the field of application (Guibal, 2004).
2.2.1 Physical Modification

Various techniques have been used to physically modify chitosan, obtaining conditioned polymer forms such as powders, nanoparticles, and gels (beads, membranes, sponge, honeycomb, fibres or hollow fibres).

Several studies have demonstrated that the particle size plays an important role in the uptake of metallic ions. Ng et al. (2003) found that the uptake of Pb ions depends on the inverse of the particle sizes. Chitosan nanoparticles (between 40 and 110 nm) produced by ionic chelation of sorbent were used to remove lead from aqueous solution. A decrease in the particle size of the chitosan improved the adsorption capacity for lead ions. In addition, a decrease in the crystallinity of sorbent was observed (Qi and Xu, 2004).

Guibal (2004) mentioned that, due to the resistance of intra-particle mass transfer, the use of small particles is necessary. However, these can be inappropriate for a column system because they can lead to hydrodynamic limitations. To improve diffusion properties and hydrodynamic behaviour, chitosan gel beads can be used. However, the adsorption capacity for metallic ions usually decreases. Chen and Chung (2006) reported a low uptake for As(III) and As(V) using gel beads compared with other studies using chitosan.

Spherical gel beads of different sizes and porosities, membranes, and fibres can be prepared using neutralization methods. Gel beads are obtained by adding an acetic acid-chitosan solution dropwise to a 1M NaOH solution with a microsyringe (Krajewska, 2005). Chitosan membranes can be also prepared from chitosan solutions in acetic acid. The solution is poured into a Petri dish and, after the solvent has evaporated, the membrane is neutralized with sodium hydroxide (Guibal, 2004).

Furthermore, porous three-dimensional sponges can be prepared by freeze-drying, where chitosan solutions or gels are frozen followed by lyophilisation. The porosity and morphology of the material produced depends on the chitosan molecular weight and on the composition and concentration of the starting solution, and most importantly on the freezing temperature and freezing rate (Krajewska, 2005).

2.2.2 Chemical Modification

Chemical modification of chitosan has two main aims: (a) to improve the metal adsorption properties, and (b) to change the solubility properties of chitosan in water or acidic medium. This includes substitution reactions, chain elongation (cross-linking, graft copolymerization, and polymer networks), and depolymerisation (chemical, physical, and enzymatic) (Harish Prashanth and Tharanathan, 2007).

The insertion of functional groups in the chitosan may involve the –NH₂ group at the C-2 position (specific reactions) or –OH groups at the C-3 and C-6 positions (non specific reactions) (Rinaudo, 2006). In fact, the preparation of water-soluble chitosan derivatives was carried out by simple N,O–acetylation using AcCl and Ac₂O in MeSO₃H, where the degree of substitution of the NHAc group was 0.15–0.29 and that of the OAc group was around 1.0 (Hitoshi et al., 2002).
The modification of chitosan to produce Schiff bases may improve its capacity to interact with metallic ions. These Schiff bases can be obtained via a reaction with aldehydes and ketones (Muzzarelli et al., 1985), with aromatic aldehydes in acetic acid (Tirkistani, 1998), and with salicylaldehyde and five derivatives: 5–brome, 5–chlorine, 5–nitro, 5–methyl, and 5–methoxy (Dos Santos et al., 2005).

Other chitosan derivatives produced by substitution reactions are O– and N–carboximethyl chitosan, an amphoteric polymer; chitosan 6–O–sulphate, an anticoagulant; N–methylene phosphonic chitosan, an anionic derivative; and trimethylchitosan ammonium, a cationic derivative (Rinaudo, 2006). An important chitosan derivative for the effective uptake of As(III) and As(V) from aqueous solution is molybdate-impregnated chitosan beads (Dambies et al., 2002). This derivative can be prepared by the molybdate adsorption and coagulation methods.

The possibility of extending the uptake of metallic ions from acidic medium has motivated the production of crosslinked chitosan. The cross-linking method improves the acidic stability of chitosan. However, this process may cause a decrease in the adsorption capacity of the sorbent, especially in the case of chemical reactions involving amino groups (Guibal, 2004). These derivatives can be obtained by reaction of chitosan with different di/polyfunctional reagents such as tripolyphosphate (Lee et al., 2001), formaldehyde (Desai, 2005), gluteraldehyde (Jeon and Höll, 2003), ethylene glycol diglycidyl ether (Li and Bai, 2006), hexamethylene disocyanate (Arrascue et al., 2003) or cross-linked N-carboximethyl chitosan (Muzzarelli et al., 1989).

Chitosan derivates have also been obtained by grafting new functional groups: (a) to increase the density of sorption sites, (b) to change the pH range for metal sorption, (c) to change the sorption sites with the purpose of increasing sorption selectivity for the target metal (Guibal, 2004).

The feasibility of grafting poly(methyl acrylate) and poly[1-(methoxycarbonyl) ethylene] onto chitosan, poly-β(1→4)-2-amino-2-deoxy-d-glucose, has also been investigated. The grafting reaction was carried out in aqueous solution using ferrous ammonium sulphate (FAS) in combination with H₂O₂ as redox initiator. The grafted chitosan was found to be insoluble in solvents, which normally dissolve chitosan. The results showed that the graft copolymer was thermally more stable than pure chitosan (Yazdani-Pedram et al., 1995). Additionally, the grafting of phosphate or phosphonic groups onto chitosan promoted the uptake of some alkaline and alkaline-earth metals (e.g. calcium and sodium) (Guibal, 2004).

The degradation products of chitosan, such as low molecular weight chitosan (LMWC), chitooligosaccharides (CO₃), and monomers, were found useful for biomedical applications. Chemical, physical or enzymatic depolymerisation has been used to produce these products (Harish Prashanth and Tharanathan, 2007).
2.3 Applications of Chitosan

Chitosan has a wide range of applications which depend on its physical, chemical, and biological properties. The principal areas are agriculture, drinking water and wastewater treatment, food and beverages, cosmetics and toiletries, biomedics and pharmaceutics, fibres and textiles, and paper technology (Rinaudo, 2006; Ravi Kumar, 2000). A summary of the main applications are presented in Table 2.1.

Table 2.1 Applications of chitosan and its derivatives

<table>
<thead>
<tr>
<th>Areas</th>
<th>Application</th>
<th>Reference:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agricultural</td>
<td>Coating of fertilizers, pesticides, herbicides, nematocides and insecticides for their controlled release to soil. Coating of seeds and leaves to prevent microbial infections.</td>
<td>Krajewska (2005)</td>
</tr>
<tr>
<td>Biomedical and</td>
<td>The tissue engineering and drug delivery fields, ranging from skin, bone, cartilage, and vascular graft. For the lowering of serum cholesterol, its application in enzyme and cell immobilizations, as material for the production of contact lenses or eye bandages.</td>
<td>Bodnar et al. (2007); Malafaya et al. (2007); Synowiecki (1986); Sandford (1989);</td>
</tr>
<tr>
<td>Pharmaceutical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cosmetic</td>
<td>Component of toothpaste, hand and body creams, shampoos, cosmetics and toiletries.</td>
<td>Synowiecki (1986)</td>
</tr>
<tr>
<td>Environmental</td>
<td>In drinking water and wastewater treatment. Chitosan is used as flocculating and chelating agents, for the removal of heavy metals and dyes, as an ecological polymer (eliminates synthetic polymers and reduces odours).</td>
<td>Gerente et al. (2007); Guibal (2004); Rinaudo (2006); Wan et al. (2004); Wu et al. (2000);</td>
</tr>
<tr>
<td>Food Industries</td>
<td>Clarification of juices, production of biodegradable packaging films, antimicrobial agents, beverage clarification additives, flavour extenders and colour and texture stabilizers.</td>
<td>Krajewska (2005); Mayer et al. (1989);</td>
</tr>
<tr>
<td>Pulp and Paper Industry</td>
<td>As a carbonless copy paper, as a processing additive for surface treatment applications, and for incorporation into photographic papers.</td>
<td>Gerente et al. (2007)</td>
</tr>
<tr>
<td>Textile Industry</td>
<td>Inclusion of chitosan into mixtures, blends, and coatings, of other textiles such as silk, wool, viscose, cotton, and others are based on chitosan’s properties to repel water.</td>
<td>Gerente et al. (2007)</td>
</tr>
</tbody>
</table>
2.4 Effects of Heavy Metals

A heavy metal can be defined as a chemical element with metallic properties at room temperature. They are toxic or poisonous at low concentrations. Although heavy metals are natural components of the Earth's crust, their concentrations in an aquatic environments have increased due to mining and industrial activities and geochemical processes. Heavy metals are common in industrial applications such as the manufacture of pesticides, batteries, mining operations, alloys, metal plating facilities, textile dyes, tanneries, etc. (CIS, 1999).

Living organisms require trace amounts of some heavy metals, e.g., iron, copper, and zinc, as they are essential to maintain the metabolism of the human body, but, at higher concentrations these metals can lead to poisoning and other hazards because they cannot be degraded or destroyed, and tend to bioaccumulate (Crini, 2005). They can enter a water source by:

- direct discharge of industrial and consumer waste,
- percolation of contaminated soil,
- leaching of wastes from landfills,
- naturally, since for some heavy metals, toxic levels can be just above the background concentrations found in nature,
- acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Table 2.2 shows the main effects of some heavy metals in the environment and human health. Heavy metals can enter the bodies of humans via the food chain, drinking water, air or absorption through the skin (see Figure 2.2) (CIS, 1999).

![Figure 2.2 Scheme of heavy metal cycle. The heavy metals are moving from the environment (pollution) to the human body through the food chain.](image-url)
Table 2.2 Effects of Copper, Zinc, Mercury, and Arsenic on the environment and human health (CIS, 1999).

<table>
<thead>
<tr>
<th>Element</th>
<th>Metal in the environment</th>
<th>Health effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. Anthropogenic examples are mining, metal production, wood production and phosphate fertilizer production.</td>
<td>At high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk of health effects from over-exposure to copper.</td>
</tr>
<tr>
<td>Zinc</td>
<td>Mainly emitted by mining and metal production. Large quantities of zinc can be found in soils, which can be adsorbed by both animals and plants. They can take up concentrations that are damaging to their health.</td>
<td>It can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders.</td>
</tr>
<tr>
<td>Mercury</td>
<td>Used in various products, such as batteries and electronics. It is also used in silver and gold mining.</td>
<td>Inorganic mercury poisoning is associated with tremors, gingivitis, psychological changes, spontaneous abortion and congenital malformation. In addition, the organic compound monomethyl-mercury causes damage to the brain and the central nervous system.</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Mainly emitted by the copper-producing industries, but also during lead and zinc production and in agriculture.</td>
<td>A very high exposure to inorganic arsenic can cause infertility and miscarriages in women, and it can cause skin disturbances, declined resistance to infections, heart disruption and brain damage. Inorganic arsenic can damage DNA.</td>
</tr>
</tbody>
</table>

2.5 Interaction Mechanisms in Metal Sorption

It is widely known that chitosan can build complexes with certain metal ions. Amino sites are the main reactive groups for metals ions, although hydroxyl groups (especially in the C3 position) may contribute to sorption (Guibal, 2004). Adsorption, ion exchange, and chelation have been discussed as the mechanisms responsible for complex formation. The type of interaction depends on the composition of the solution, the pH of the solution, and the speciation of metal ions (Vold et al., 2003).

The affinity of chitosan for cations adsorbed on film presents selectivity in the following order: Cu$^{2+}$>>Hg$^{2+}$>Zn$^{2+}$>Cd$^{2+}$>Ni$^{2+}$>Co$^{2+}$~Ca$^{2+}$, and Eu$^{3+}$>Nd$^{3+}$>Cr$^{3+}$~Pr$^{3+}$ (Rinaudo, 2006).
2.5.1 Chelation

Most studies of the chelation mechanism have been focused on the adsorption of copper. Two coordination models have been proposed for chitosan-metal complexes. Based on an X-ray study of chitosan complexes with Cd(II), Zn(II), and Cu(II) Ogawa and Oka (1993) proposed the “Pendant Model” in which the metal ion is attached to an amino group of the chitosan chain like a pendant. This model was supported by Domard (1986). He suggested that \([\text{Cu NH}_2 (\text{OH})_2]^0\) is the only structure, where the complex is uncharged and has two OH\(^-\) and one NH\(_2\) as ligands, and the fourth site could be occupied by an H\(_2\)O molecule or the OH on (C3) (Figure 2.3).

![Figure 2.3 Coordination models of Cu(II)-Chitosan complex: (a) Pendant model and (b) Bridge model. (Schlick, 1985)](image)

The “bridge model” proposed by Schlick (1985) suggests that a metal ion such as cupric ion is coordinated with four nitrogen atoms of intra- and inter-chitosan chains forming a square-planar structure.

![Figure 2.4 Proposed structures of Cu-Chitosan complex (a) at pH between 5.3 and 5.8 and (b) at pH > 5.8. (Rhazi et al., 2002)](image)

On the other hand, Rhazi et al. (2002) proposed two types of complex for Cu(II)-chitosan which depend on the pH of the solution. At pH between 5.3–5.8, the complex \([\text{Cu(–NH}_2\text{)}_2]^2+, \text{2OH}, \text{H}_2\text{O})\) is suggested; whereas at pH>5.8, the complex \([\text{Cu(–NH}_2\text{)}_2]^2+, \text{2OH})\) is considered (see Figure 2.4)
2.5.2 Ion Exchange/Electrostatic Attraction

Chitosan is a weak base and its dissociation equilibrium is described by

\[
\text{Chitosan–NH}_3^+ + H_2O \rightleftharpoons \text{Chitosan–NH}_2 + H_3O^+ \quad \text{(2.4)}
\]

with a dissociation equilibrium constant,

\[
K_a = \frac{[\text{Chitosan} - NH_2][H_3O^+]}{[\text{Chitosan} - NH_3^+]} \quad \text{(2.5)}
\]

The pKₐ of chitosan controls the protonation of amine functions in acid solutions and it is controlled by the deacetylation degree of the chitosan and its charge density (Guibal, 2004). Sorlier et al. (2001) found that the pKₐ varies directly with the deacetylation degree between 6.3 and 7.2 at complete dissociation. This property is very important for an understanding of the electrostatic interactions of chitosan with cations and anions.

Eq. 2.4 takes into account the influence of pH in the formation of –NH₃⁺ groups. At low pH, the protonation of amino groups is high and the efficiency to uptake metal anions is elevated. The optimum pH is frequently found around 2 – 4. This electrostatic attraction may occur by direct interaction with free metal anions. This property has been used for gelation of chitosan. At neutral pH, about 50% of the total amino groups remain protonated (Guibal, 2004). As the pH increases, the total number of protonated amino groups decreases, and they become available for the uptake of metallic cations.

2.5.3 Uptake by Formation of Ternary Complexes

Although chitosan is not effective for the adsorption of alkaline and alkaline-earth ions, Piron and Domard (1998) demonstrated that adsorption of Sr²⁺ and Ba²⁺ by chitosan is possible due to the formation of ternary complexes. The proposed mechanism requires the existence of a moderate interaction involving chitosan, carbonate ions, and cations. They concluded that the interactions chitosan–CO₃²⁻–Sr²⁺ are not of an electrostatic nature since the ion-pair Sr²⁺–CO₃²⁻ is first formed, and it is then complexed with an amino group of chitosan. The proposed model is shown in Figure 2.5.

---

**Figure 2.5** Representation of the ternary complex. (Piron and Domard, 1998)
3 ADSORPTION

Adsorption is a process where one or more components (adsorbates) are attracted and bonded to the surface of a solid (adsorbent) with which they are in contact. The exact nature of the bonding (ionic, covalent, or metallic) depends on the properties of the species involved, but the adsorbed material is generally classified as exhibiting physisorption, chemisorption or electrostatic sorption.

Some features which are useful in recognizing physisorption and chemisorption are presented in Table 3.1 (Ruthven, 1984)

<table>
<thead>
<tr>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Low heat of adsorption (&lt;2 or 3 times the latent heat of evaporation.)</td>
<td>- High heat of adsorption (&gt;2 or 3 times the latent heat of evaporation.)</td>
</tr>
<tr>
<td>- Relatively low temperature, always under the critical temperature of the adsorbate</td>
<td>- High temperatures.</td>
</tr>
<tr>
<td>- Non-specific</td>
<td>- Type of interaction: strong; covalent bond between adsorbate and surface.</td>
</tr>
<tr>
<td>- Adsorption takes place in monolayer or multilayer</td>
<td>- Adsorption takes place only in a monolayer.</td>
</tr>
<tr>
<td>- No dissociation of adsorbed species.</td>
<td>- High activation energy</td>
</tr>
<tr>
<td>- Rapid, non-activated, reversible.</td>
<td>- Increase in electron density in the adsorbent-adsorbate interface.</td>
</tr>
<tr>
<td>- Low activation energy.</td>
<td>- Reversible only at high temperature.</td>
</tr>
<tr>
<td>- No electrons transfer although polarization of sorbate may occur.</td>
<td></td>
</tr>
</tbody>
</table>

Adsorption phenomena are increasingly being utilised to perform a desired bulk separation or purification. Adsorption separation processes are used at an industrial level. However, for an adsorption process to be implemented on a commercial scale, a suitable adsorbent must be available in tonnage quantities at a low economic cost (Ruthven, 1984).

A proper understanding of the adsorption process and design of adsorption equipment demands knowledge of equilibrium isotherms and adsorption kinetics. The first determines the adsorption capacity, and the second determines the adsorption velocity.

3.1 Adsorption Equilibrium

Adsorption is usually described by isotherms which show how much solute can be adsorbed by the adsorbent at a given temperature. An adsorption isotherm relates the concentration of solute on the surface of the adsorbent to the concentration of the solute in the fluid with which the adsorbent is in contact. These values are usually determined experimentally, but there are also models to predict them, both for single metal adsorption and multicomponent adsorption.

Although the Langmuir and the Freundlich adsorption isotherms are the two well established types of adsorption isotherms for single metal adsorption, there are other equations which model adsorption equilibrium. Table 3.2 shows the main equations.
Table 3.2 Equations of Isotherm Models for Adsorption Equilibrium. In each case, $q_e$ is the adsorption capacity and $C_{eq}$ is the equilibrium solution concentration of the adsorbed species.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>$q_e = a_F C_{eq}^{b_F}$</td>
<td>$a_F$ and $b_F$ are empirical parameters. $b_F$ is usually $&lt; 1$ (Gerente et al., 2007).</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_e = \frac{q_{e,\text{max}} b C_{eq}}{1 + b C_{eq}}$</td>
<td>$q_{e,\text{max}}$ is the maximum adsorption capacity and $b$ is a constant (Gerente et al., 2007).</td>
</tr>
<tr>
<td>BET</td>
<td>$q_e = \frac{q_{e,\text{max}} K_b C_{eq}}{(C_s - C_{eq}) \left[ 1 + (K_b - 1) \frac{C_{eq}}{C_s} \right]}$</td>
<td>$q_{e,\text{max}}$ is the maximum adsorption capacity, $K_b$ is a dimensionless constant; $C_s$ is the concentration at which all sites are saturated. This model is valid for multiply layers on a homogeneous surface (Do, 1998).</td>
</tr>
<tr>
<td>Redlich–Peterson</td>
<td>$q_e = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{b_R}}$</td>
<td>$K_R$ and $a_R$ are constants. The exponent $b_R$ lies between 0 and 1 (Gerente et al., 2007).</td>
</tr>
<tr>
<td>Temkin</td>
<td>$q_e = \frac{RT}{b_F} \ln(A_F C_{eq})$</td>
<td>$R$ is the universal gas constant, $T$ is absolute temperature, $A_F$ and $b_F$ are constants (Gerente et al., 2007).</td>
</tr>
<tr>
<td>Dubinin–Radushkevich</td>
<td>$q_e = q_D \exp\left(-B_D \varepsilon^2\right)$</td>
<td>$q_D$ is the Dubinin–Radushkevich monolayer capacity, $B_D$ is a constant related to the mean free energy of sorption per mole of the sorbate, $\varepsilon$ is the Polyanin potential which is related to equilibrium concentration, $P$ is the pressure of adsorbed species and $P_o$ is the saturated vapour pressure (Do, 1998).</td>
</tr>
<tr>
<td>Toth</td>
<td>$q_e = \frac{q_{e,\text{max}} a_T C_{eq}}{1 + (a_T C_{eq})^{1/t_T}}$</td>
<td>$a_t$ is a constant which plays the role of the inverse of an adsorptive potential, and the exponent $t_T$ characterizes the heterogeneity of the adsorbent. $t_T$ is usually less than unity (Do, 1998).</td>
</tr>
<tr>
<td>Langmuir–Freundlich (Sips)</td>
<td>$q_e = \frac{q_m a_S^{1/b_S} C_{eq}^{1/b_S}}{1 + (a_S C_{eq})^{1/b_S}}$</td>
<td>$a_S$ and $b_S$ (dimensionless) are the parameters of the isotherm (Do, 1998).</td>
</tr>
</tbody>
</table>
Brunauer et al. (1940) classified the isotherms for physical adsorption into five types (see Figure 3.1). Type I is the typical Langmuir adsorption isotherm exhibited by microporous adsorbents. Isotherms of Types II and III are observed in adsorbents with a wide range of pore sizes. Type IV suggests the formation of two surface layers, and type V is observed when the intermolecular attraction effects are large (Ruthven, 1984).

![Figure 3.1 Types of characteristic isotherms (Brunauer et al., 1940)](image)

### 3.1.1 The Freundlich Isotherm

The Freundlich equation is one of the earliest empirical equations used to describe equilibrium data (see Table 3.2). This model can be applied to non-ideal sorption. It often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interactions.

To linearize Eq. 3.1, logarithms are taken:

\[
\log q_e = \log a_F + b_F \log C_{eq} \quad (3.9)
\]

Numerical values of \( a_F \) and \( b_F \) can be found from the intercept and slope of the linear form of the plot.

The Freundlich equation does not consider all sites on the adsorbent surface to be equal. Furthermore, it is assumed that, once the surface is covered, additional adsorbed species can still be accommodated. In other words, multilayer adsorption is predicted by this equation (van Loon and Duffy, 2005).

### 3.1.2 The Langmuir Isotherm

The Langmuir isotherm is an empirical isotherm derived from a proposed kinetic mechanism. The Langmuir model assumes (Coulson and Richardson, 2002):

- The energy is the same all over the surface.
- Adsorbed molecules do not interact.
- Molecules adsorb at fixed sites and do not migrate over the surface.
- At the point of maximum adsorption, only a monolayer is formed. The molecules of adsorbate are deposited only on the free surface of the adsorbent (Figure 3.2).
These conditions are seldom satisfied: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the adsorption mechanism is clearly not the same for the first as for the last molecules. The fourth condition is the most troublesome, as more molecules can often adsorb on the monolayer. This problem is solved by the BET isotherm. Moreover, a modified form of the Langmuir isotherm can also describe a bi-layer deposition.

The shape of the Langmuir isotherm is a gradual positive curve that flattens to a constant value (see Figure 3.1, type I). The Langmuir model is represented by Eq. 3.2 (see Table 3.2). The values of $q_{e,max}$ and $b$ can be determined by linearization of this equation, followed by linear regression or by non-linear fitting using the original form of the isotherm equation.

This model has been widely applied to describe the adsorption of several metallic ions onto chitosan or its derivatives, such as the adsorption of Au(III) onto N–carboxymethyl chitosan and chitosan (Wang Ngah and Liang, 1999), adsorption of As(III) and As(V) onto chitosan (Gerente et al., 2005), adsorption of Cu(II) onto flake– and bead–types of chitosan (Wu et al., 2000), and the adsorption of Fe(II) and Fe(III) onto chitosan and cross-linked chitosan beads (Wan Ngah et al., 2005). In general, most fits of the Langmuir isotherm show good agreement.

### 3.2 Kinetic Sorption Mechanisms

Metal sorption kinetics are influenced by sorption reactions and the mass transfer steps that govern the transfer of metal ions from the bulk of the solution to the sorption sites on the surface and inside adsorbent particles, i.e. external and intra-particle diffusion.

In turn, these mechanisms depend on the physical form of the chitosan (flakes, gel, beads, etc), the intrinsic structure of chitosan (deacetylation degree, crystallinity, and molecular weight), the nature of the metal and the solution, as well as, process conditions (temperature and pH). Simplified models can be used to test experimental batch data and identify the rate-controlling mechanisms for the adsorption process. Of these models, the pseudo first-order model, the pseudo second-order model, and the intra-particle diffusion model are the most widely used to describe the sorption of metal ions onto chitosan (Gerente et al., 2007). The main kinetic equations are shown in Table 3.3.
The kinetics of the adsorption process can be studied by carrying out a separate set of adsorption experiments at constant temperature to follow the adsorption with time. The adsorption rate can be determined quantitatively and tested by the pseudo-first-order and pseudo-second-order models. This information is useful for further applications of system design in the treatment of natural water and waste effluents.

**Table 3.3 Kinetic Model Equations for Metal Ion Adsorption (Gerente et al., 2007)**

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order equation of Lagergren</td>
<td>[ \frac{dq_t}{dt} = k_1(q_e - q_t) ] (3.10)</td>
<td>( q_e ) and ( q_t ) are the sorption capacities at equilibrium and at time ( t ) respectively, and ( k_1 ) is a pseudo-first-order sorption rate constant.</td>
</tr>
<tr>
<td>Pseudo-second-order equation</td>
<td>[ \frac{dq_t}{dt} = k_2(q_e - q_t)^2 ] (3.11)</td>
<td>( q_e ) and ( q_t ) are the sorption capacities at equilibrium and at time ( t ) respectively. ( k_2 ) is the pseudo-second-order sorption rate constant.</td>
</tr>
<tr>
<td>Elovich model equation</td>
<td>[ \frac{dq_t}{dt} = \alpha_E \exp(-\beta_E q_t) ] (3.12)</td>
<td>( q_t ) is the sorption capacity at time ( t ), ( \alpha_E ) is the initial sorption rate, and ( \beta_E ) is the desorption constant.</td>
</tr>
</tbody>
</table>

### 3.2.1 The Pseudo-First-Order Equation

The Lagergren rate equation (see Table 3.3) was the first rate equation for sorption in a liquid/solid system based on solid capacity (Ho and McKay, 1999). This equation can be linearized for use in the kinetic analysis of experimental results (Gerente et al., 2007):

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t
\] (3.13)

According to Gerente et al. (2007), the main disadvantages of this model are:

- the linearized equation Ec. 3.13 does not give theoretical \( q_e \) values that agree with experimental \( q_e \) values, and
- the plots are only linear over approximately the first 30 minutes. Beyond this initial 30 minute period, the experimental data and theoretical results do not correlate well.

This model has been widely applied for the adsorption of metallic ions onto chitosan, such as the adsorption of Au(III) (Wan Ngah and Liang, 1999), adsorption of As(III) and As(V) (Gerente et al., 2005), adsorption of Cu(II) (Wu et al., 2000; Wan Ngah et al., 2004), adsorption of Cr(VI) and Cu(II) (Sağ and Aktay, 2002). In some cases, the pseudo-first-order model fits the experimental data well and allows the evaluation of \( k_1 \). In the other cases, the pseudo-second-order has been much more successful.
3.2.2 The Pseudo-Second-Order Equation

If the rate of adsorption has a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed by Eq. 3.11. The linear form of the pseudo-second-order equation is given by:

\[
\frac{t}{q(t)} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

(3.14)

With this equation there is no problem in assigning an effective \( q_e \), because \( q_e \) and \( k_2 \) can be obtained from the slope and intercept of the plot of \( t/q_t \) vs. \( t \) (Gerente et al., 2007).

The pseudo-second-order model has also been applied to experimental data for the adsorption of metallic ions onto chitosan. Adsorption of Cu(II) onto chitosan beads (Wan Ngah et al., 2004) has been effectively described using this model.

3.3 Diffusion-Controlled Sorption Models

3.3.1 Intra-particle Diffusion-Controlled Adsorption

To investigate the internal diffusion mechanism during the adsorption of metal ions onto chitosan, the intra-particle diffusion equation has been used, considering that adsorption is usually controlled by an external film resistance and/or mass transfer is controlled by internal or intra-particle diffusion (Gerente et al., 2007).

For adsorption onto spherical particles with constant diffusion coefficient, Crank (1970) proposed the following equation:

\[
\frac{q_t}{q_e} = 6 \left( \frac{D_i t}{r^2} \right)^{0.5} \left[ 1 + \frac{1}{\sqrt{\pi}} + 2 \sum \text{ierfc} \left( \frac{n_i r}{\sqrt{D_i t}} \right) \right] - \frac{3D_i t}{r^2}
\]  

(3.15)

In the earlier stages of the adsorption process, when \( t \) is relatively small, equation (3.15) reduces to:

\[
q_t = \frac{6q_e D_i^{0.5}}{\pi^{0.5} r} t^{0.5}
\]  

(3.16)

or

\[
q_t = k_i t^{0.5}
\]  

(3.17)

where

\[
D_i = \frac{\pi k_i^2 r^2}{36q_e^2}
\]  

(3.18)
The coefficient $k_i$ is determined from the initial linear slope of $q_t$ versus $(time)^{0.5}$.

According to Weber and Morris (1963), if the intra-particle diffusion is the rate-limiting step in the adsorption process, the graph of $q_t$ vs. $t^{0.5}$ should yield a straight line passing through the origin. McKay and Allen (1980) suggested that three linear sections on the plot $q_t$ vs. $t^{0.5}$ can be identified. That means that two or three steps can occur. The first portion represents external surface adsorption or an instantaneous adsorption stage. The second portion is a gradual adsorption stage, where the intra-particle diffusion is the controlling factor. The third portion is a final equilibrium stage where the intra-particle diffusion starts to decelerate due to extremely low solute concentrations in the solution (Wu et al., 2000).

3.4 Chemical Speciation

The adsorption of metal ions can be influenced by the presence of others species such as anionic ligands e.g., carbonates, bicarbonates, cyanides, hydroxide, chlorides (Gerente et al., 2007).

The metals present in aqueous solutions are distributed as soluble species such as free ions, neutral and charged complexes. The speciation or specific distribution will depend on the total concentration of each metal, and the acidity, redox potential, pH, and temperature. In many aqueous systems of industrial interest, both strong and weak electrolytes are present. The experimental determination of the speciation in real systems presents considerable difficulties. Therefore, a combination of experimental measurements such as metal solubility and a non-ideal thermodynamic model is usually used in order to establish the solution speciation under real conditions.

There have been significant developments in the modelling of electrolytic aqueous systems. Zemaitis et al. (1986), Pitzer (1991), Wolery (1992) and Stumm and Morgan (1996) have produced models for calculating the metal speciation in multi-component aqueous solutions. Generally, the trend is towards the use of equilibrium models with fewer physical parameters, broader applicability, and greater predictive capability. Today, there are numerous computer codes and associated databases for modelling the complex geochemical processes that occur when aqueous solutions (e.g. groundwater, saline waters, and effluent streams) react with soil, rock or solid waste materials. This software allows the user to create and evaluate models that include the effects of dissolution and precipitation reactions, complexation, adsorption, ion exchange, solute transport, diffusion and convection. The species distribution can be calculated under different conditions of concentration, pH, redox potential and temperature. Software can handle both dilute waters and high-ionic-strength brines. The main codes are: EQ3/6 (Wolery, 1992), PHREEQC (Parkhurst et al., 1980), MINTEQA2 (Allison et al., 1991) and HSC (Roine, 1999).

3.4.1 The PHREEQC Program

PHREEQC version 2 is a computer program for simulating chemical reactions and transport processes in natural or polluted water. The program is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces.
PHREEQC calculates concentrations, molalities and activities of aqueous species, pH, redox potential (pe), saturation indices, and mole transfers of phases to achieve equilibrium as a function of specified reversible and irreversible geochemical reactions. PHREEQC can be used as a speciation program to calculate saturation indices and the distribution of aqueous species. Analytical data for mole balances can be defined for any valence state or combination of valence states for an element. The distribution of redox elements among their valence states can be based on a specified redox potential (pe) or any redox couple for which data are available.

PHREEQC allows the concentration of an element to be adjusted to obtain equilibrium (or a specified saturation index or gas partial pressure) with a specified phase. Solution compositions can be specified with a variety of concentration units. The input to PHREEQC is a free format and is based on chemical symbolism. Balanced equations, written in chemical symbols, are used to define aqueous species, exchange species, surface-complexation species, solid solutions, and pure phases, which eliminate the use of index numbers to identify elements or species.
4 EXPERIMENTAL PART

This section describes the materials used, the experimental set up, and the main experiments performed:

- to determine the optimum pH for the uptake of Cu(II), Zn(II), Hg(II), and As(V) onto chitosan (Paper II),
- to obtain adsorption isotherms at optimum pH for each metallic ion (Paper II),
- to determine the Langmuir parameters at optimum pH for each metallic ion (Paper II),
- to study the adsorption kinetic at different concentrations and particle size in batch and column experiments (Cu and Zn in Paper III),
- to investigate the regeneration of the adsorbent (Paper II), and
- to study the application of chitosan to remove metallic ions from natural water and wastewater (Papers I and III)

4.1 Material

4.1.1 Chitosan

Chitosan, with a deacetylation degree of approximately 59%, was used in the experimental part. The average particle density was 0.1892 g cm\(^{-3}\). The flake sizes were distributed from <0.22mm to 0.71 mm.

4.1.2 Metallic Ions Solutions

These solutions were obtained from a stock standard (1000 mg L\(^{-1}\)) of Cu(II), Zn(II), Hg(II), and As(V). Deionised water was used to prepare all the solutions. The pH of the metallic ion solutions was adjusted by adding drops of 1.25 N hydrochloric acid or 0.5 – 3.0 % sodium hydroxide. The pH was measured by a 410A Orion pH meter.

4.2 Experimental Set-up

Figure 4.1 shows the equipment used to perform the equilibrium adsorption experiments: (a) Lab-Line rotator (model 1346) and (b) Barnstead-Lab-Line shaker (model 30105). Desorption experiments and the uptake of metallic ions from natural water and wastewater were also performed using this equipment.

![Figure 4.1 Equipment used to carry out adsorption equilibrium experiments.](image)
The experimental set-up shown in Figure 4.2a was used to study the adsorption kinetics in batch experiments, using a magnetic stirrer (IKA Works Ceramag Midi) and a pH meter (410A Orion) to control the pH of the solution during the adsorption process.

Experimental studies in chitosan-packed columns were performed in a cylindrical column with a height of 20 cm and an internal diameter of 2.3 cm (Figure 4.2b). A Watson-Marlow 502S peristaltic pump was used to adjust the flow rate and to feed the column with the metallic ion solution.

![Figure 4.2 Experimental set-up used to carry out adsorption kinetic experiments (a) in batch and (b) in an adsorbent-packed column.](image)

4.3 Production of Chitin and Chitosan on a Laboratory Scale

Raw material was provided by CAMANICA S.A., a shrimp-processing company. The chitin extraction process was based on chemical deproteinization, demineralization, and depigmentation of the shrimp shells on a laboratory scale. Chitosan was obtained by the deacetylation of chitin.

3 kg of shrimp shells were placed in 15 L of a 10% sodium hydroxide solution. The mixture was stirred for 1 hour at room temperature. Later, the solid was separated from the liquid and washed with soft water (without Ca$^{2+}$ and Mg$^{2+}$ ions). The solid was placed in 12 L of 1.8N hydrochloric acid for 12 hours at room temperature to remove minerals such as calcium and magnesium carbonate. Subsequently, the liquid was removed and the solid was washed with soft water. 12 L of 0.38% sodium hypochlorite was poured into the vessel containing the solid and the suspension was agitated until the pigmentation of the solid disappeared (about 15 minutes). The white solid (chitin) was washed and dried in an oven at 50 ºC for 12 hours. At the end, 735 g of chitin were produced.

The deacetylation of chitin was performed as follows. 150 g of chitin was mixed with 1.125 L of 50 % sodium hydroxide and the suspension was kept in an oven at 110 ºC for one hour. The mixture was washed with soft water several times to remove residual sodium hydroxide, until pH 8 was achieved. The material was dried in an oven at 50 ºC.
4.4 Experiments

The experiments to study the adsorption of Cu, Zn, Hg, and As onto chitosan, the study of desorption, and the application of chitosan for the uptake of metallic ions from natural water and wastewater were carried out in duplicate.

4.4.1 Influence of pH on Metals Adsorption Capacity

To study the influence of pH on the metallic ion adsorption capacity of the chitosan, experiments were conducted at different initial pH values. Some of the experimental conditions are given in Table 4.1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Mass of Chitosan (g)</th>
<th>pH initial range</th>
<th>Concentration of metallic ion (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.10</td>
<td>3 – 6</td>
<td>50</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.20</td>
<td>3 – 6</td>
<td>50</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.20</td>
<td>4 – 8</td>
<td>50</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.50</td>
<td>3 – 7</td>
<td>50</td>
</tr>
</tbody>
</table>

To gain a better understanding of the pH-dependence and the adsorption mechanism for these metals, adsorption experiments were also conducted under controlled pH conditions. The pH of the metal solutions was controlled by the addition of 0.012 – 1.25 N hydrochloric acid or 0.01 – 3.0 % sodium hydroxide solutions. The pH was measured by a 410A Orion pH meter. High pH values were not studied to avoid precipitation.

Adsorption experiments were performed by mixing the adsorbent with 40 mL of a solution of a single metallic ion. Batch experiments were carried out at room temperature using an agitation speed of 200 rpm for 2 hours. At the end of this time, the suspension was filtered, and the filtrate was collected to determine the ion concentration. Cu and Zn were determined by GBC 932 Plus Atomic Absorption; As and Hg were determined using a HG3000 Hydride Generator.

4.4.2 Adsorption Equilibrium

Adsorption equilibrium studies were performed by placing chitosan in contact with 40 mL of single ion solutions of different concentrations. The experiments were performed at room temperature and at the optimum initial pH for each metallic ion until equilibrium was reached (see Table 4.2).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Initial pH optimum</th>
<th>Mass of Chitosan (g)</th>
<th>Concentration of metallic ion (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>6.0 ± 0.1</td>
<td>0.20</td>
<td>25 – 750</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>6.0 ± 0.1</td>
<td>0.20</td>
<td>50 – 750</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>4.0 ± 0.1</td>
<td>0.20</td>
<td>0.1 – 500</td>
</tr>
<tr>
<td>As(V)</td>
<td>3.0 ± 0.1</td>
<td>0.50</td>
<td>5 – 500</td>
</tr>
<tr>
<td></td>
<td>5.2 ± 0.2 (constant)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
During the arsenic adsorption process, the pH was kept at constant conditions (see Table 4.2) to avoid the solubilisation of chitosan and to improve the arsenic adsorption. After equilibrium, the metallic ion solutions were filtered and analyzed by atomic absorption.

### 4.4.3 Adsorption Kinetics in Batch Experiments

Kinetics studies for Cu(II), Zn(II), Hg(II), and As(V) were carried out at the optimum initial pH (see Table 4.2). In the case of arsenic, the pH of solution was kept constant during the adsorption process (pH<pKa chitosan). The experiments were performed at two initial concentrations (20 and 50 mg L\(^{-1}\) for Cu(II) and Zn(II), 5 and 20 mg L\(^{-1}\) for Hg(II), and 1 and 5 mg L\(^{-1}\) for As(V)) and with different particle size fractions of the chitosan (<0.22mm and 0.22 – 0.45 mm).

An amount (1.25 – 5.0 g) of adsorbent was mixed with 1000 mL of a single metal solution for a total contact time of 450 min, at room temperature using an agitation speed of 450 rpm. To monitor the adsorption process, 5 mL samples were taken at different times. The pH of the solution was measured during the process.

The samples were filtered and the residual metallic ion content was determined by atomic absorption. In order to evaluate the kinetic mechanism of the adsorption process, the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were tested with experimental data.

### 4.4.4 Experiments in Columns

Experiments in columns were performed with two different adsorbent particle size fractions (0.45 – 0.56 mm and 0.56 – 0.71 mm) and different liquid flow rates (1.1 – 2.72 mL s\(^{-1}\)), at room temperature (25 ± 1 °C). The bed height was kept at 16.5 cm. The experimental conditions are summarized in Table 4.3.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cu(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of metallic ion solution (L)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Inlet Concentration (mg L(^{-1}))</td>
<td>12.60</td>
<td>11.45</td>
</tr>
<tr>
<td>Inlet pH</td>
<td>6.1</td>
<td>6.1</td>
</tr>
<tr>
<td>Mass (g)</td>
<td>10.60</td>
<td>10.60</td>
</tr>
<tr>
<td>Average flow (Q) (mL s(^{-1}))</td>
<td>2.72</td>
<td>2.72</td>
</tr>
</tbody>
</table>

A peristaltic pump was used to feed the solution containing the single metallic ion into the column. During the adsorption process, samples of the effluent were collected every 5 minutes (at larger flows) and 10 minutes (at smaller flows). The metallic ion concentration was determined by atomic absorption. The pH of samples was also
measured by means of a 1346 Orion pH meter. The breakthrough curves were drawn as a function of the bed volume (BV) passed through the column.

### 4.4.5 Batch Desorption Experiments

The desorption experiments were conducted by placing known amounts of exhausted adsorbent (dry mass varying between 0.4 and 2.0 g) in contact with potential regenerating solutions of different concentrations (see Table 4.4). The experiments were performed at room temperature using an agitation speed of 200 rpm. The amount of desorbed metallic ion was determined using the same process as stated before.

#### Table 4.4 Conditions used to determine desorption of metals from chitosan.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Regenerating Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>25 mL of 1 M (NH₄)₂SO₄</td>
</tr>
<tr>
<td></td>
<td>25 mL of 0.5, 1.0, and 2.0 M NaOH</td>
</tr>
<tr>
<td>Zinc</td>
<td>25 mL of 1.0 M (NH₄)₂SO₄</td>
</tr>
<tr>
<td></td>
<td>25 mL of 0.1 M HCl</td>
</tr>
<tr>
<td></td>
<td>25 mL of 0.5, 1.0, and 2.0 M NaOH</td>
</tr>
<tr>
<td>Mercury</td>
<td>20 mL of 0.5, 1.0, and 2.0 M NaCl</td>
</tr>
<tr>
<td>Arsenic</td>
<td>50 mL of 0.1 and 1.0 M NaOH</td>
</tr>
<tr>
<td></td>
<td>50 mL of 1.0 M NaCl</td>
</tr>
<tr>
<td></td>
<td>50 mL of 1.0 M (NH₄)₂SO₄</td>
</tr>
</tbody>
</table>

### 4.4.6 Removal of Metal Ion from Natural and Wastewater

The uptake of metallic ions from natural water (groundwater and rivers) and wastewater (mining industry) was studied using chitosan flakes, in column and batch experiments.

#### Removal of arsenic using column experiments

Four water samples from drilled wells were taken from the Limon Mine Community. Analyses of pH, temperature, conductivity, potential, and dissolved oxygen (DO) were carried out in situ with electrometric methods. The metallic ion contents (Fe, Mn, Mg, Ca, Cu, Pb, and Zn) were determined by atomic absorption. For arsenic a Hydride Generator was used. The experiments were performed using a column 12.5 cm in height, and 3.7 cm in diameter. The operating conditions were pH 3 and 7, the bed volume was 98.2 cm³, and the flow was 4 mL s⁻¹.

#### Removal of mercury from natural water in batch experiments

Water samples were taken from different points: creeks, wells, and a gold extraction site, around La Libertad Community in Chontales, Nicaragua. The samples were filtered and mercury was determined using a Hydride Generator technique. Adsorption experiments were performed in batch mode. 0.2 g of chitosan was mixed with 40 mL samples at the pH of the natural water and an agitation speed of 200 rpm for one hour.
Removal of copper and zinc from gold ore tailing solutions in batch experiments

The tailing samples were taken from two different points: mining effluents (fresh tailings) and tailings ponds, Santa Rosa (Figure 4.3). Physico-chemical characterization is comprised of the determination of pH, temperature, and total suspended solids (TSS), in situ; and the determination of metallic ions (Cu, Zn, Al, Ca, Mg, Mn, Pb, K, and Na) by atomic adsorption. Speciation of cyanide and related compounds present in gold ore tailing solutions was carried out using the PHREEQC program.

![Figure 4.3](image)

Figure 4.3 (a) Gold ore tailing effluents and (b) Santa Rosa’s tailing ponds (Triton Minera S.A., El Limón, Nicaragua)

Cu and Zn removal tests from gold ore tailing solutions were carried out in batch experiments. The pH of the tailing solutions was decreased by carefully adding small amounts of dilute hydrochloric acid up to about pH 6. An amount of 0.2 grams of chitosan (<0.22 mm particle size) was placed in contact with 40 mL of tailing solution. The samples (in duplicate) were in contact for 60 minutes on a shaker at 200 rpm and room temperature. The samples were filtered and analyzed by atomic absorption.

4.5 Evaluation of Experimental Data

4.5.1 Adsorption Capacity

The adsorption capacity, $q_e$, was calculated from the difference between the initial single metal concentration in aqueous solutions, $C_o$, and the equilibrium concentration, $C_{eq}$, according to

$$q_e = \frac{(C_o - C_{eq})V}{W}$$

(4.1)

where $V$ is the volume of aqueous solution (L) and $W$ is the mass of the chitosan (g).

4.5.2 Adsorption Isotherms

The Langmuir isotherm model (Eq. 3.2) was used to evaluate the adsorption equilibrium data. The linear form of the Langmuir equation is given by,

$$\frac{C_{eq}}{q_e} = \frac{1}{q_{e,max}} \frac{C_{eq}}{q_{e,max}b} + \frac{1}{q_{e,max}b}$$

(4.2)
Linearized plots of \( \frac{C_{eq}}{q_e} \), versus the equilibrium concentrations, \( C_{eq} \), were obtained for each metal. Numerical values of \( q_{e,max} \), the maximum adsorbable concentration of metallic ions, and \( b \), the adsorption equilibrium constant were determined from the slope and intercept of the linear form of the Langmuir isotherm, and by non-linear fitting of the Langmuir equation.

4.5.3 Adsorption Kinetics

To identify the rate-controlling mechanisms during the adsorption of copper, zinc, mercury, and arsenic, three steps were considered:

- Mass transfer of the metallic ion from the bulk solution to the chitosan surface,
- Adsorption of the metallic ion onto sites, and
- Internal diffusion of the metallic ion onto chitosan.

For this purpose, simplified models were applied to evaluate the experimental batch data for each metal (see Table 4.5). The goodness of the fit was estimated in terms of the coefficient of determination, \( R^2 \).

<table>
<thead>
<tr>
<th>Model</th>
<th>Plots</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first-order model</td>
<td>( \log(q_e - q(t)) ) versus ( t )</td>
</tr>
<tr>
<td>(Eq. 3.13)</td>
<td></td>
</tr>
<tr>
<td>Pseudo second-order model</td>
<td>( \frac{t}{q(t)} ) versus ( t )</td>
</tr>
<tr>
<td>(Eq. 3.14)</td>
<td></td>
</tr>
<tr>
<td>intra-particle diffusion model</td>
<td>( q(t) ) versus ( t^{1/2} )</td>
</tr>
<tr>
<td>(Eq. 3.17)</td>
<td></td>
</tr>
</tbody>
</table>

Numerical values of pseudo-second-order constants, \( k_2 \) and \( q_e \), were determined from:

- The slope and intercept of the straight lines of \( \frac{t}{q(t)} \) versus \( t \), and
- Non-linear fitting of the pseudo-second-order equation.
5 RESULTS AND DISCUSSION

5.1 Production of Chitin and Chitosan

Chitin was obtained from shrimp shells with a yield of 24.5%. According to Muzzarelli (1977), shrimp shells consist mainly of chitin, protein/caroteins, and calcium carbonate with an average composition of 25, 35, and 40% by weight, respectively. This implies that the production of chitin was high (approximately 98%) on the laboratory scale. On the other hand, the chitosan yield was 35.4% by weight with respect to chitin. This value is low compared to other studies, where yields up to 86% have been reported (Agulló et al., 2004). The processes of washing and separation by sedimentation of solids and suction of the liquid phase are considered to be the main contributors to losses of bio-material because of the small particle size of the product. This material may not sediment and can be suctioned by the pump. To increase the production of chitosan, the separation step must be improved.

The IR spectrum of chitosan is shown in Figure 5.1. This was obtained by Magna 550 IR Spectrometry. This IR spectrum exhibits an adsorption band at 1065 cm\(^{-1}\) due to CO stretching, at 1430 cm\(^{-1}\) due to CH bending, at 1660 cm\(^{-1}\) due to amino groups bending vibration, and an adsorption band at 3420 cm\(^{-1}\) due to hydroxyl group stretching vibration. A deacetylation degree of 59.9% was obtained by applying Eq. 2.1.

![Figure 5.1 IR Spectrum of chitosan produced at laboratory level.](image)

5.2 Influence of pH on Adsorption Capacity

The adsorption of copper (II), zinc (II), mercury (II), and arsenic (V) on chitosan flakes in different pH ranges was studied to elucidate the influence of solution pH on the adsorption capacity and to establish the optimum pH for the adsorption of each metallic ion (Paper II). Due to the behaviour of these heavy metals in aqueous solution, where Cu, Zn and Hg act as metallic cations and As acts as a metal oxoanion, this topic is divided into two sections: the first shows the adsorption behaviour of metal cations and the second presents the arsenic adsorption onto the sorbent.
5.2.1 Adsorption Capacity for Metal Cations

The adsorption capacity for (a) Cu(II), (b) Zn(II), and (c) Hg(II) is shown in Figure 5.2 as a function of initial pH under controlled and uncontrolled conditions. The results of adsorption experiments with metal cations at different initial pH, without pH-control during the adsorption process, show no significant differences in adsorption capacity. These samples exhibit a final pH range of 7.16–7.46 for copper, 7.73–7.82 for zinc, and 7.15–7.87 for mercury. The differences between these pH-values are rather small, which explains the similarity between adsorption capacities regardless of initial pH. On the other hand, adsorption experiments with controlled pH-values exhibit a strong dependence of adsorption capacity on the pH of the solution, the adsorption capacity for metal cations increasing with increasing pH.

![Graphs showing adsorption capacity for metal cations under controlled and uncontrolled pH conditions.](image)

**Figure 5.2** Influence of initial pH on adsorption capacity of chitosan for (a) copper, (b) zinc, (c) mercury, and (d) arsenic under controlled and uncontrolled pH conditions.
The cause of the increase in the pH during the experiments without pH-control can be by a rupture of internal hydrogen bonds caused by a swelling of chitosan, followed by the protonation of amino groups with water as proton donor (Argulló et al., 2004), according to the following reaction:

\[
\text{Chitosan–NH}_2 + \text{H}_2\text{O} \Leftrightarrow \text{Chitosan–NH}_3^+ + \text{OH}^-
\]  

(5.1)

In addition, chitosan acts as a weak base. At low pH, amino groups of chitosan take the protons available in aqueous solution, according to:

\[
\text{Chitosan–NH}_2 + \text{H}^+ \Leftrightarrow \text{Chitosan–NH}_3^+
\]  

(5.2)

This reduces the concentration of H\(^+\) ions and raises the pH of the solution.

The low adsorption capacity in acidic solution can be explained by the competition between protons and metallic ions for available amino adsorption sites (Wan Ngah et al., 2004), and by electrostatic repulsion (Jeon and Höll, 2003). The following relation shows the influence of pH on the uptake of metallic ions:

\[
\text{Chitosan–NH}_3^+ + \text{M}^{2+} \Leftrightarrow \text{Chitosan–NH}_2 - \text{M}^{2+} + \text{H}^+
\]  

(5.3)

The equilibrium of this reaction is shifted to the left at higher H\(^+\) ion concentrations (lower pH), reducing the number of binding sites for metallic ions. In addition, the protonation of amino groups in acidic solutions induces an electrostatic repulsion of metal cations that reduces the number of binding sites available for metallic ions. On the other hand, at higher pH, there is a decrease in H\(^+\) ions in the solution and both the competition for binding sites and the electrostatic repulsion decrease and the adsorption performance is improved.

The speciation and distribution of metal–ion species in the solution is an important parameter which determines the effect of pH on sorption capacity. Speciation at a given pH can affect adsorption performance, if this means the existence of species that cannot interact with the adsorbent. At near neutral pH, the cations Cu(II) and Zn(II) are found as free ions in aqueous solutions and they can be adsorbed onto chitosan by chelation according to:

\[
\text{Chitosan–NH}_2 + \text{M}^{2+} \Leftrightarrow \text{Chitosan–NH}_2 - \text{M}^{2+}
\]  

(5.4)

On the other hand, mercury speciation showed that this cation exits mainly as a hydroxy-complex and it can, therefore, be adsorbed by chelation at near neutral pH.

### 5.2.2 Arsenic Adsorption Capacity

Figure 5.2d shows the influence of pH on the arsenic adsorption capacity of chitosan under uncontrolled and controlled pH conditions. At an uncontrolled pH, there is no significant dependence of adsorption capacity on the initial pH of the solution. When the final pH of the solution was measured, this was slightly above a neutral pH, regardless of the initial pH. The protonation constant of chitosan is log K\(_p\) = 6.3 and about 20\% of amino groups are protonated at a pH of about 6.9 (Juang et al., 1999).
This means that chitosan was only partly cationic and protonated. For this reason, the adsorption capacity for arsenic was obtained low.

On the other hand, at a controlled pH, the adsorption capacity increased with decreasing pH of the solution. Thus, the protonation of the amino groups significantly increased the adsorption capacity of chitosan. This implies that ionic exchange is the most important adsorption mechanism.

The speciation of arsenic suggests that arsenates were present mainly as $\text{H}_2\text{AsO}_4^-$ and $\text{HAsO}_4^{2-}$ in this pH range (Figure 5.3). Both could be adsorbed by ion exchange onto cationic sites of chitosan. When the pH is below 3, arsenic speciation favours the uncharged $\text{H}_3\text{AsO}_4$ species. The adsorption capacity in Figure 5.2d was therefore close to an optimum value, favoured by both protonation of the amino groups as well as arsenic speciation. This conclusion is also supported by the work of Dambies et al. (2002).

![Figure 5.3 Arsenate speciation at different pH and at 50 mg L$^{-1}$ arsenic concentration using the PHREEQC program.](image)

The optimum initial pH for each metallic ion which gives the maximum adsorption capacity is shown in Table 5.1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>6.0$^1$</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>6.0$^1$</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>4.0$^1$</td>
</tr>
<tr>
<td>As(V)</td>
<td>3.0$^2$</td>
</tr>
</tbody>
</table>

$^1$ At uncontrolled pH conditions.

$^2$ At controlled pH conditions.
5.3 Adsorption Isotherm

Adsorption isotherms of copper, zinc, mercury, and arsenic onto chitosan flakes at optimum initial pH (see Table 4.2) are shown in Figure 5.4. The adsorption experiments were performed under uncontrolled pH conditions, except in the case of arsenic where the pH of the solution was kept at 5.3±2 (Paper II).

Adsorption isotherms for Cu(II), Zn(II), Hg(II), and As(V) were modelled using the Langmuir equation (Eq. 4.2) to test whether the adsorbent exhibited this kind of behaviour (Paper II). The results revealed that data for the adsorption of Cu(II) and Zn(II) correlated well ($R^2>0.99$). On the other hand, the correlations in the case of Hg(II) and As(V) ($0.9<R^2<0.99$) were less good. These equations suggest that the Langmuir model describes the adsorption of metallic ions on chitosan reasonably well.

Figure 5.4 Comparison between experimental data of adsorption isotherm for copper, zinc, mercury, and arsenic, and non linear modelled using Langmuir equation at the optimum initial pH.
Figure 5.4 shows that the Langmuir model fitted the experimental data well. This does not necessarily mean that the hypothesis that the model is valid for these sorption systems is verified.

The values of the maximum adsorption capacity, $q_{e,\text{max}}$, and the Langmuir adsorption equilibrium constant, $b$, for Cu(II), Zn(II), Hg(II), and As(V) are shown in Table 5.2. The values of maximum adsorption capacity show that chitosan produced on a laboratory scale has a good capacity to adsorb Cu(II), Zn(II), and Hg(II), and a lower capacity to adsorb As(V).

The adsorption capacity of chitosan found in this work differs from other results reported in literature. Ng et al. (2002) reported a copper adsorption capacity of 2.834 and 2.838 mg Cu g$^{-1}$ at pH 3.5 and 4.5, respectively. Juang et al. (1999) reported an adsorption capacity of 174 mg Cu g$^{-1}$. The mercury adsorption capacity was lower than that reported by Jeon and Höll (2003). On the other hand, Boddu et al. (2007) estimated the maximum sorption capacity for arsenic to be 96.46 mg As g$^{-1}$.

Table 5.2 Experimental constants of Langmuir isotherms for metallic ions onto Chitosan.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Linear equation</th>
<th>Non linear optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{e,\text{max}}$ (mg g$^{-1}$)</td>
<td>$b$ (L mg$^{-1}$)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>78.7</td>
<td>0.14</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>52.6</td>
<td>0.08</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>106.4</td>
<td>0.51</td>
</tr>
<tr>
<td>As(V)</td>
<td>21.3</td>
<td>0.01</td>
</tr>
</tbody>
</table>

These significant differences in sorption capacities cannot be explained solely by the degree of deacetylation. Other parameters such as crystallinity and structural factors that affect the specific surface area and the availability of adsorption sites must be considered. Studies of lead sorption on chitosan showed that the sorption capacity was a function of the particle size (Ng et al., 2003).

5.4 Adsorption Kinetics by Batch Experiments

5.4.1 Effects of Initial Concentration and Particle Size

Figure 5.5 shows the concentrations of Cu(II), Zn(II), Hg(II), and As(V) adsorbed onto chitosan as a function of time, at the optimum initial pH. The results show the effects of the initial metal concentration in the solution and the flake size. The rate of adsorption of these metals was fast in the initial stages of the process, but gradually decreased later on the way toward equilibrium. However, the reduction in adsorption rate was much more pronounced for copper. As expected, the time to reach equilibrium increased with increasing initial metallic ion concentration in the solutions.

The experimental results reveal that the particle size has a significant influence on the rate of metal uptake in the case of copper (Figure 5.5a). It is particularly noticeable at high initial metal concentrations where the adsorption rate decreases rapidly with time. This suggests that diffusion within particles controls copper sorption. It is known that chitosan flakes have a low porosity (Guibal, 2004), and a larger flake size will
obviously restrict diffusion within the particles. However, the fact that the particle size did not have the same effect at low metal concentrations suggests that, besides the resistance against diffusion, other mechanisms influence the process (Paper III).

In the present experimental conditions, the particle size used had only a slight influence on the adsorption rate of zinc (Figure 5.5b) and mercury (Figure 5.5c). Obviously the process requires less time to reach equilibrium. These results are almost independent of the initial solution concentration. The results for mercury adsorption differ from the results presented by Shafaei et al. (2007), who found that the adsorption of mercury increases with decreasing particle size.

Figure 5.5 The influence of initial metallic ion concentration and particle size on adsorption kinetic of Cu(II), Zn(II), Hg(II), and As(V) in batch experiments. The experiments were performed at optimum initial pH, at a temperature of 25 °C, and an agitation rate of 450 rpm.
Arsenic exhibits an interesting behaviour (see Figure 5.5d). The adsorption capacity increased at the beginning of the process and decreased later. This phenomenon was more evident at the smaller particle size. The reason may be the increase in pH during the adsorption process or the solubility of chitosan at low pH.

To gain a better understanding of the effect of pH on arsenic adsorption, experiments with different particle sizes and under controlled and uncontrolled pH conditions were conducted. These experiments were performed in duplicate and a similar behaviour was observed in both cases. Figure 5.6a shows the adsorption capacity of arsenic as a function of contact time for different particle sizes and at controlled and uncontrolled pH levels. Figure 5.6b shows the pH as a function of time during the process. The results reveal that there is an inverse relation between the arsenic adsorption capacity and the pH of the solution, i.e. the arsenic adsorption capacity decreases when the pH of the solution increases.

![Figure 5.6](image_url)

**Figure 5.6** (a) Arsenic adsorption as a function of time at different particle sizes and at controlled and uncontrolled pH levels. The initial concentration of arsenic was 1.0 mg L$^{-1}$. (b) pH as a function of contact time.

Under uncontrolled pH conditions and different particle sizes, it was observed that the adsorption capacity initially increased since the pH of the solution was low (approximately 3.5). The amino groups of chitosan are then protonated, allowing arsenic ions to be bonded to those groups by electrostatic attraction, according to:

$$\text{Chitosan–NH}_2 + H^+ + Y^- \rightleftharpoons \text{Chitosan–NH}_3^+ Y^-$$

(5.5)

where $Y^-$ represents arsenate species.

However, as the adsorption process progresses the pH of the solution increases. This means that the hydrogen ion concentration decreases and the reaction equilibrium is displaced towards the left hand.
At a controlled pH, the arsenic adsorption capacity also increases. The pH of the solution was kept at 5.3 ± 0.2 by adding hydrochloric acid during the adsorption process. Nevertheless, a decrease of arsenic adsorption capacity was also observed at smaller particle sizes. This can be explained by the solubility of chitosan in acid media where a portion of the chitosan suffers dissolution due to the small particle size (<0.22mm). On the other hand, this effect is reduced when the absorbed particle size is larger (0.22 – 0.45mm). In this case, Figure 5.6a shows that the arsenic adsorption capacity achieved a maximum value and that this remains constant during the adsorption process.

5.4.2 Adsorption Dynamics of Copper

Pseudo-first-order equation, pseudo-second-order equation, and intra-particle diffusion models were tested with experimental data for copper (Paper III). The results shown in Figure 5.7b reveal that copper adsorption best can be described by a pseudo-second-order equation ($R^2$ values between 0.992 and 0.999), except for adsorption from solutions with an initial concentration of 50 mg L$^{-1}$ using an adsorbent particle size fraction of 0.22 – 0.45 mm ($R^2 = 0.964$). The best correlation for the intra-particle diffusion model was obtained for this size fraction as shown in Figure 5.7c ($R^2 = 0.993$). Cheung et al. (2003) found that at a high initial concentrations (>40 mg L$^{-1}$) and with an adsorbent particle size of 0.355 – 0.500 mm, the pseudo-second-order does not fit the experimental data well ($R^2 < 0.984$). This can mean that the mechanism of copper adsorption may depend on the initial concentration and on the adsorbent particle size. At low concentrations and small particle sizes, the pseudo-second-order adsorption mechanism is predominant and the overall rate of copper adsorption is therefore controlled by adsorption reactions and not by mass transport (Chiou and Li, 2003).

It has previously been pointed out that the intra-particle diffusion model can present multilinearity, and three stages can be distinguished (Wu et al., 2000). The plot corresponding to copper adsorption at an initial concentration of 50 mg L$^{-1}$ and the largest particle size fraction (Figure 5.7c) does not show the stage corresponding to the diffusion of metallic ions through the external film. This suggests that the stirring was strong enough to eliminate this resistance. The only remaining stage corresponds to the process where intra-particle diffusion is the rate-limiting step.
5.4.3 Adsorption Dynamics for Zinc, Mercury, and Arsenic

A pseudo-first-order equation, pseudo-second-order equation, and intra-particle diffusion model for Zn, Hg, and As were tested with experimental data at different particle sizes and at different initial concentrations.

The results of the models for Zn(II) are shown in Figure 5.8, which reveal that there is no good fit between experimental data and the pseudo-first-order model (Paper III).
The best correlation ($R^2 > 0.99$) was obtained for the pseudo-second-order model. Therefore, the rate-limiting step may be the adsorption mechanism. Figure 5.8d shows that the experimental data for zinc were also well described by the pseudo-second-order model. A similar behaviour was observed for the adsorption of Zn on chitosan derivates (Li et al., 2007) and on other biosorbents (Reddad et al., 2002). On the other hand, the plots of intra-particle diffusion for that metal show two main steps, the first of which can be attributed to the adsorption stage and the second to the equilibrium stage.

The plots of the pseudo-first-order equation, the pseudo-second-order equation, and the intra-particle diffusion model for Hg are displayed in Figure 5.9. The results show that the best correlation ($R^2 > 0.999$) was obtained for the pseudo-second-order model, and that the adsorption is therefore also the rate-limiting step. In addition, Figure 5.9d shows
that the experimental mercury concentration data fit the pseudo-second-order model well.

![Graph](image)

Figure 5.9 Kinetic models for the removal of mercury of different particle sizes and different initial concentrations.

The plots of intra-particle diffusion also show two main steps: (1) the adsorption stage and (2) the approach to an equilibrium stage. Similar results were observed by Campos et al. (2007), who found that intra-particle diffusion is not the limiting step in mercury adsorption.

The results shown in Figure 5.10 reveal that there is no good correlation between experimental data and pseudo-first-order model for arsenic. On the other hand, good correlations ($R^2 > 0.999$) were obtained for the pseudo-second-order model (see Figure 5.10b). Figure 5.10d shows that the experimental data are well fitted using a non linear
pseudo-second-order equation. However, different behaviour was reported by Gerente et al. (2005) whose experimental data were better described with a first order kinetic model.

![Graphs showing kinetic models for the removal of arsenic of different particle sizes and different initial concentrations.](image)

**Figure 5.10** Kinetic models for the removal of arsenic of different particle sizes and different initial concentrations.

The parameters $q_e$ and $k_2$ for Cu(II), Zn(II), Hg(II), and As(V) corresponding to the pseudo-second-order equation are depicted in Table 5.3. The results also show that the rate constant decreases when the initial solution concentration and the particle size increase.

The kinetics of copper sorption onto chitosan and its derivates have been widely studied in the literature. Although these studies agree with the suitability of the pseudo-second-order equation shown in the present study, some values of the rate constant, $k_2$, obtained
here differ from values reported in the literature. The results probably depend on the type of adsorbent (raw material origin and production process) and on the experimental conditions (Paper III).

Table 5.3 Values of $q_e$ and $k_2$ for Cu, Zn, Hg and As determined according to the pseudo-second-order model at different initial solution concentrations and for different adsorbent particle sizes

<table>
<thead>
<tr>
<th>Metallic ion</th>
<th>Initial Conc. (mg L$^{-1}$)</th>
<th>Adsorbent particle size (mm)</th>
<th>Linear Model</th>
<th>Non Linear Optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>$k_2$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>$q_e$ (mg g$^{-1}$)</td>
</tr>
<tr>
<td>Copper</td>
<td>20</td>
<td>&lt;0.22</td>
<td>16.29</td>
<td>4.07 x 10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.22–0.45</td>
<td>16.05</td>
<td>1.48 x 10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>&lt;0.22</td>
<td>36.9</td>
<td>9.58 x 10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.22–0.45</td>
<td>28.33</td>
<td>7.07 x 10$^{-4}$</td>
</tr>
<tr>
<td>Zinc</td>
<td>20</td>
<td>&lt;0.22</td>
<td>3.75</td>
<td>4.36 x 10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.22–0.45</td>
<td>4.13</td>
<td>1.34 x 10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>&lt;0.22</td>
<td>8.98</td>
<td>1.05 x 10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.22–0.45</td>
<td>8.57</td>
<td>9.39 x 10$^{-3}$</td>
</tr>
<tr>
<td>Mercury</td>
<td>5</td>
<td>&lt;0.22</td>
<td>2.5</td>
<td>5.46 x 10$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.22–0.45</td>
<td>2.5</td>
<td>2.63 x 10$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>&lt;0.22</td>
<td>10.07</td>
<td>4.57 x 10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.22–0.45</td>
<td>10.12</td>
<td>2.48 x 10$^{-2}$</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1</td>
<td>0.22–0.45</td>
<td>0.17</td>
<td>2.10 x 10$^{0}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.22–0.45</td>
<td>0.41</td>
<td>5.73 x 10$^{-1}$</td>
</tr>
</tbody>
</table>

Sağ and Aktay (2002) reported a pseudo-second-order rate constant, $k_2$, for copper adsorption onto chitosan at two different concentrations, 30 and 60 mg L$^{-1}$, and for a particle size fraction of 0.25 – 0.42 mm. The values of $k_2$ were 1.35 x 10$^{-3}$ and 7.69 x 10$^{-4}$ g mg$^{-1}$ min$^{-1}$ respectively. These values are in agreement with the results reported in this work under similar conditions. Wan Ngah et al. (2004) estimated the rate constant for copper adsorption to be 5.20 x 10$^{-3}$ g mg$^{-1}$ min$^{-1}$, for an initial solution concentration of 5 mg L$^{-1}$ and a particle size fraction <0.25 mm. This value is greater than the value obtained in this work for an initial solution concentration of 20 mg L$^{-1}$ and a chitosan particle size fraction <0.22 mm.

5.5 Adsorption of Metallic Ions in Columns

Figure 5.11 shows the breakthrough curves for copper and zinc adsorbed onto chitosan at different particle sizes and with different solution flow rates (Paper III). In order to analyze the results, the maximum permissible metal concentrations established by MARENA (Ministry of Environment and Natural Resources, Nicaragua) (Table 5.6) were used to define the breakthrough point. The results show that the Cu(II) sorption kinetics depend to some extent on particle size and solution flow rate, and that the best results were obtained for the smallest particles and lowest flow rate. Under these
conditions, Cu is eluted in about 50 BV and reaches the breakthrough point at 60 BV (see Figure 5.11a).

![Breakthrough curves of copper and zinc using chitosan flakes of different particle sizes and different solution flow rates.](image)

**Figure 5.11** Breakthrough curves of (a) copper (II) and (b) zinc (II) using chitosan flakes of different particle sizes and different solution flow rates.

The Zn(II) breakthrough curves (Figure 5.11b) show that the particle size had no significant influence on the adsorption kinetic in the range of sizes examined. On the other hand, the solution flow rate affected the adsorption of zinc. The elution of Zn, for the largest particle size, started at 20 BV and the breakthrough point was reached at approximately 30 BV, almost independently of the solution flow rate.

### 5.6 Desorption Experiments

The regeneration of chitosan has been studied less than the adsorption process; therefore, a preliminary screening for a suitable desorbing solution was conducted (Paper II).

The study of copper and zinc desorption from chitosan was performed using different regenerating solutions: 1M ammonium sulphate, (NH₄)₂SO₄, at pH 1, and sodium hydroxide, NaOH, at different concentrations. The results showed that copper and zinc desorption with (NH₄)₂SO₄ was about 90% and 80% respectively. Sodium hydroxide was shown to be an excellent regenerating agent for zinc, but it was not able to remove copper from the sorbent (Figure 5.12a). Similar desorption results were obtained with 0.5 and 1 M of NaOH solutions but, when a 2 M NaOH solution was used, the Zn desorption decreased considerably. Zinc desorption with NaOH may be explained by the formation of tetrahydroxozinc ion, Zn(OH)₄²⁻, at high pH values which can lead to electrostatic repulsion between these ions and the amino groups of chitosan.

Sodium chloride was suggested as a good regenerating solution to remove mercury from chitosan, as well as Na₂S₂O₃, KI, and KSCN (Kobayashi et al., 1985). Due to their non-toxic properties and low cost, aqueous solutions of sodium chloride of various concentrations were tested for the mercury desorption. The results are shown in Figure 5.12b. They revealed that 1M NaCl solution was more efficient than both 0.5 and 2M
NaCl solutions. The 1M solution removed 2.5 times more mercury than the 0.5M solution and 10 times more than the 2M solution. Desorption results for NaCl solutions may be due to the formation of metal ion–stable complexes at high chloride concentrations. According to the speciation of mercury (II), three main chlorides complex can be found: tetrachloromercury (II) ion, HgCl$_4^{2-}$, trichloromercury (II) ion, HgCl$_3^-$, and mercury chloride, HgCl$_2$. The electrostatic repulsion between these mercury–species and the amino groups of chitosan can promote desorption.

Sodium hydroxide, sodium chloride, and ammonium sulphate were potential regenerating solutions for arsenic desorption. The results showed that a 1M NaOH solution was the most effective regenerating agent (see Figure 5.12c).

The efficiency of desorption with sodium hydroxide may be explained by the increase in pH. At low pH, the amino groups of chitosan are associated with hydrogen ions according to Eq. 5.2 to form Chitosan–NH$_3^+$, which capture the arsenic anions from solution (Eq. 5.5). When the pH increases the number of hydrogen ions available decreases, and this means that there are no Chitosan–NH$_3^+$ groups to bind the arsenic anions. These anions are released to aqueous solutions.

### 5.7 Case Studies

#### 5.7.1 Removal of Arsenic from Water Wells in the El Limon Community

The main characteristics of the water wells are shown in Table 5.4. The arsenic concentration of the Limon drilled well waters was lower than the maximum permitted by CAPRE guidelines (10 μg L$^{-1}$). The highest arsenic concentration, 8.40 μg L$^{-1}$, was found in Well 1. The arsenic species found in the samples are dissociated products of As(V) (H$_2$AsO$_4^-$ and HAsO$_4^{2-}$).
Table 5.4  Physical and chemical characterization of water wells from the Limon Mine Community.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Samples</th>
<th>Admissible Maximum Value¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>28.3</td>
<td>27.9</td>
</tr>
<tr>
<td>pH</td>
<td>6.45</td>
<td>6.70</td>
</tr>
<tr>
<td>pE</td>
<td>4.86</td>
<td>4.27</td>
</tr>
<tr>
<td>Arsenic (µg L⁻¹)</td>
<td>8.40</td>
<td>6.90</td>
</tr>
</tbody>
</table>

¹ CAPRE guidelines for drinking water quality

The arsenic removal data in columns packed with chitosan using samples taken from wells of the Limon Community are displayed in Table 5.5. Under the conditions examined (pH 3 and 7), the arsenic presents in the water was removed almost totally at both pH values. This is expected since the amount of arsenic in the treated water was far less than the capacity of the chitosan packed in the column. The results showed that it is possible to reduce the arsenic concentration in effluents with low arsenic concentrations to very low values (Paper I).

Table 5.5  Arsenic removal data from Limon’s drilled well water samples. Flow rate = 4 ml s⁻¹, V_L = 98.2 cm³

<table>
<thead>
<tr>
<th>Sample</th>
<th>Arsenic Concentration (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_initial</td>
</tr>
<tr>
<td>1</td>
<td>8.40</td>
</tr>
<tr>
<td>2</td>
<td>6.90</td>
</tr>
<tr>
<td>3</td>
<td>7.50</td>
</tr>
<tr>
<td>4</td>
<td>8.10</td>
</tr>
</tbody>
</table>

5.7.2  Removal of Copper and Zinc from Gold Ore Tailing Solutions

Table 5.6 shows the physico-chemical characterization of gold mine tailing solutions. The total suspended solids (TSS) concentration in the samples was greater than the maximum permissible value established by MARENA. TSS includes minerals, colloids, and other non-visible materials that affect the quality of the effluents (Paper III).

The cyanide concentration in the mining effluents was obviously high (73.0 mg L⁻¹) since it comes directly from the plant. It is reduced substantially in the tailing ponds by the dilution and natural degradation of the cyanide. On the other hand, the metallic ion concentrations (except for copper) are lower than the levels recommended by MARENA.

The speciation of copper and zinc in gold ore tailing solutions depends very much on their oxidation states, the metallic ion concentrations, the cyanide concentration, the redox potential, the temperature, and the pH of the solution. To elucidate the distribution of the species of copper and zinc, the PHREEQC program was used. The input data were the experimental values reported in Table 5.6. The results for copper and zinc speciation are graphically represented in Figure 5.13 (Paper III).
Table 5.6 Characterization of gold ore tailing solutions from El Limón Mine

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mining effluents</th>
<th>Tailing ponds</th>
<th>MARENA¹ Maximum permissible</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.0</td>
<td>7.7</td>
<td>6 – 9</td>
</tr>
<tr>
<td>pE</td>
<td>4.0</td>
<td>4.0</td>
<td>–</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>32.0</td>
<td>31.6</td>
<td>45</td>
</tr>
<tr>
<td>Total suspended solids, TSS (mg L⁻¹)</td>
<td>1162</td>
<td>991</td>
<td>50</td>
</tr>
<tr>
<td>Cyanide (mg L⁻¹)</td>
<td>73.0</td>
<td>0.60</td>
<td>1.0²</td>
</tr>
<tr>
<td>Iron (mg L⁻¹)</td>
<td>2.11</td>
<td>0.91</td>
<td>5</td>
</tr>
<tr>
<td>Copper (mg L⁻¹)</td>
<td>5.36</td>
<td>0.34</td>
<td>0.5</td>
</tr>
<tr>
<td>Zinc (mg L⁻¹)</td>
<td>0.23</td>
<td>0.07</td>
<td>1</td>
</tr>
<tr>
<td>Aluminium (mg L⁻¹)</td>
<td>1.82</td>
<td>1.51</td>
<td>2</td>
</tr>
<tr>
<td>Calcium (mg L⁻¹)</td>
<td>234.33</td>
<td>141.96</td>
<td>–</td>
</tr>
<tr>
<td>Magnesium (mg L⁻¹)</td>
<td>0.21</td>
<td>1.4</td>
<td>–</td>
</tr>
<tr>
<td>Manganese (mg L⁻¹)</td>
<td>0.02</td>
<td>ND</td>
<td>2</td>
</tr>
<tr>
<td>Lead (mg L⁻¹)</td>
<td>0.34</td>
<td>0.11</td>
<td>2</td>
</tr>
<tr>
<td>Arsenic (μg L⁻¹)</td>
<td>34.73</td>
<td>60.7</td>
<td>500²</td>
</tr>
<tr>
<td>Mercury (μg L⁻¹)</td>
<td>35.42</td>
<td>1.7</td>
<td>–</td>
</tr>
</tbody>
</table>

¹ Ministerio del Ambiente y Recursos Naturales, Nicaragua.
² Metal Mining Effluent Regulations for Canada.

According to the calculations, the copper and zinc in the mining effluents are mostly found as tricyanocuprate(II) ion, Cu(CN)₃⁻, and tetracyanozinc(II) ion, Zn(CN)₄²⁻, respectively. Despite of the presence of other metallic ions such as Fe(III), the high cyanide concentration makes possible the formation of Cu-CN and Zn-CN complexes. In the tailing ponds, however, the major species are copper(II) cyanide, Cu(CN)₂, and zinc ion, Zn²⁺, respectively. The absence of any Zn-CN complex can be due to the low
concentration of cyanide (0.6 mg L\(^{-1}\)) and the presence of iron ions in the solution which can form a strong complex with cyanide ions, Fe(CN)\(_6^{3-}\).

The distribution of Cu(II) and Zn(II) species in the tailing solutions is different when the pH of the solution is reduced to 6. The main species of Cu(II) and Zn(II) in mining effluents are Cu(CN)\(_2\) and Cu(CN)\(_3\); Zn\(^{2+}\), and Zn(CN)\(^{-}\); respectively, while in the tailing ponds the main species are Cu(CN)\(_2\), Cu\(^{2+}\); and Zn\(^{2+}\). The availability of cyanide ions depends strongly on the pH of the solution. At pH 6, the cyanide is principally found as HCN, since these ions can be associated with hydrogen ions, H\(^{+}\), present in this solution, according to:

\[
M(CN)_{n}^{n-} + yH^{+} \rightarrow M(CN)_{n-y}^{n+y-} + yHCN
\]  
(5.6)

The results for Cu and Zn removal from gold ore tailing solutions are shown in Table 5.7, which indicates that the copper and zinc present in tailing ponds were removed almost totally under the conditions examined; while the removal of these metallic ions from mining effluents was lower.

The speciation results in tailing ponds show that the copper and zinc are mostly found as free metallic ions. In addition, the concentrations of Cu and Zn are lower than in mining effluents and they can therefore be adsorbed by chitosan, regardless of the presence of other metallic ions in the solution (Paper III).

<table>
<thead>
<tr>
<th>Metallic ion</th>
<th>Sample</th>
<th>Initial Conc. (mg L(^{-1}))</th>
<th>Final Conc. (mg L(^{-1}))</th>
<th>%Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Mining effluents</td>
<td>5.36</td>
<td>0.12</td>
<td>97.8</td>
</tr>
<tr>
<td></td>
<td>Tailing ponds</td>
<td>0.34</td>
<td>&lt;0.01</td>
<td>~100</td>
</tr>
<tr>
<td>Zinc</td>
<td>Mining effluents</td>
<td>0.23</td>
<td>0.10</td>
<td>71.2</td>
</tr>
<tr>
<td></td>
<td>Tailing ponds</td>
<td>0.07</td>
<td>&lt;0.01</td>
<td>~100</td>
</tr>
</tbody>
</table>

The lower uptake of Cu and Zn from mining solutions can, however, be due to various factors: high concentrations of Cu and Zn, the speciation of these metals, the presence of other metallic ions such as Fe, Pb, and Hg, which can reduce the number of binding sites for the adsorption of copper and zinc ions, and the effect of cyanide ions during the adsorption process. Indeed, the speciation results showed that a fraction of these metals are present as Metal-CN complex.

Other studies have demonstrated that metallic ion sorption can be inhibited by cyanide ions if sufficiently stable complexes are formed. Sankararamakrishnan et al. (2007) found that cyanide ions can inhibit the adsorption of cadmium onto chitosan even at low anion concentrations. Similar results were reported for the uptake of gold and silver, where cations were found as Au(CN)\(_2\); (Niu and Volesky, 2003) and Ag(CN)\(_2\); (Lasko and Hurst, 1999). Despite the effects of cyanide ions, the copper concentration after removal using chitosan was nevertheless lower than the maximum level value recommended by MARENA (<0.5 mg L\(^{-1}\)).
6 CONCLUSIONS

The study showed that the solution pH strongly affects the adsorption capacity of chitosan. It was observed that the greatest adsorption of Cu (II), Zn (II), and Hg (II) occurs at high pH, whereas the greatest adsorption of As (V) takes place at low pH.

The Langmuir isotherm fits the experimental data well for the ions studied. The adsorption capacity of the metals on chitosan follows the sequence Hg>Cu>Zn>As. Although it was found that arsenic is effectively removed by chitosan, the practical application has the drawback that the adsorption of arsenic on chitosan is more effective under acidic conditions.

The large differences between adsorption capacities reported in literature suggest that there are important structural differences related to the raw material and the production of chitosan that deserve further study.

The present study showed that the adsorbent particle size strongly affects the copper adsorption capacity. The kinetics for the adsorption of copper, zinc, mercury, and arsenic onto chitosan are best described by a pseudo-second-order equation, except for copper adsorption at high initial concentrations and large particles size, where intra-particle diffusion is the rate-controlling mechanism.

The copper breakthrough curves were affected by both particle size and flow rate, whereas zinc breakthrough curves was affected only by flow rate. The breakthrough for copper and zinc are reached at about 60 and 30 bed volumes, respectively.

The metallic ions can easily be removed from chitosan by treatment with regenerating solution ((NH₄)₂SO₄, NaCl, and NaOH). However, the use of these results demands additional information about the interactions between the metals and the influence of other ions simultaneously present in the water and the regeneration of the adsorbent.

The uptake of arsenic from natural water demonstrated that it is possible to reduce the arsenic concentration from effluents with low arsenic concentration to very low values. On the other hand, the copper and zinc adsorption from mining effluents using chitosan can be affected by the cyanide ions and other ions present in the solution, which can compete for the available amino adsorption sites on chitosan. Tests conducted with mining effluents showed that chitosan is effective for removal of Cu(II) and Zn(II) ions up to 97% and 71%, respectively.
**NOTATION**

Latin letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_F$</td>
<td>Freundlich isotherm constant</td>
<td>$(\text{mg}^{1-b_F} \text{L}^{b_F} \text{g}^{-1})$</td>
</tr>
<tr>
<td>$a_R$</td>
<td>Redlich Peterson isotherm constant</td>
<td>$((\text{L mg}^{-1})^{\beta_R})$</td>
</tr>
<tr>
<td>$a_S$</td>
<td>Sips isotherm constant</td>
<td>$(\text{L mg}^{-1})$</td>
</tr>
<tr>
<td>$a_t$</td>
<td>Toth isotherm constant</td>
<td>$(\text{L mg}^{-1})$</td>
</tr>
<tr>
<td>$A_T$</td>
<td>Temkin constant</td>
<td>$(\text{L g}^{-1})$</td>
</tr>
<tr>
<td>$b$</td>
<td>Langmuir adsorption equilibrium constant</td>
<td>$(\text{L mg}^{-1})$</td>
</tr>
<tr>
<td>$b_F$</td>
<td>Freundlich exponent</td>
<td>--</td>
</tr>
<tr>
<td>$b_R$</td>
<td>Redlich-Peterson exponent</td>
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</tr>
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<td>$b_S$</td>
<td>Sips isotherm constant</td>
<td>--</td>
</tr>
<tr>
<td>$b_T$</td>
<td>Temkin constant</td>
<td>$(\text{J mol}^{-1} \text{mg}^{-1} \text{g})$</td>
</tr>
<tr>
<td>$B_D$</td>
<td>Dubinin–Radushkevich constant</td>
<td>$((\text{J}^{-2} \text{mol}^2))$</td>
</tr>
<tr>
<td>$B_V$</td>
<td>Bed volume</td>
<td>--</td>
</tr>
<tr>
<td>$C_{eq}$</td>
<td>Equilibrium concentration</td>
<td>$(\text{mg L}^{-1})$</td>
</tr>
<tr>
<td>$C_S$</td>
<td>Concentration at which all sites are saturated</td>
<td>$(\text{mg L}^{-1})$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Intraparticle diffusion coefficient</td>
<td>$(\text{cm}^2 \text{s}^{-1})$</td>
</tr>
<tr>
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<td>Pseudo-first-order reaction rate constant</td>
<td>$(\text{min}^{-1})$</td>
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<tr>
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<td>Pseudo-second-order rate constant</td>
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<td>Dissociation equilibrium constant</td>
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<td>BET constant</td>
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<td>$K_p$</td>
<td>Protonation constant</td>
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<tr>
<td>$K_R$</td>
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</tr>
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<td>$M$</td>
<td>Molecular weight</td>
<td>$(\text{kg kmol}^{-1})$</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure of adsorbed species</td>
<td>(kPa)</td>
</tr>
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<td>Vapour pressure</td>
<td>(kPa)</td>
</tr>
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<td>$q_e$</td>
<td>Equilibrium adsorption capacity</td>
<td>$(\text{mg g}^{-1})$</td>
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<td>$q_{e,max}$</td>
<td>Maximum adsorption capacity</td>
<td>$(\text{mg g}^{-1})$</td>
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<td>Dubinin–Radushkevich monolayer capacity</td>
<td>$(\text{mg g}^{-1})$</td>
</tr>
<tr>
<td>$q_t$</td>
<td>Adsorption capacity at time $t$</td>
<td>$(\text{mg g}^{-1})$</td>
</tr>
<tr>
<td>$Q$</td>
<td>Average flow rate</td>
<td>$(\text{mL s}^{-1})$</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial coordinate</td>
<td>(cm)</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>$(8.314 \text{J K}^{-1} \text{mol}^{-1})$</td>
</tr>
<tr>
<td>$t$</td>
<td>Contact time</td>
<td>(min)</td>
</tr>
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<td>$t_T$</td>
<td>Toth isotherm exponent</td>
<td>--</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
<td>(K)</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume of aqueous solution</td>
<td>(L)</td>
</tr>
<tr>
<td>$V_F$</td>
<td>Total water volume passed through the column</td>
<td>(L)</td>
</tr>
<tr>
<td>$W$</td>
<td>Mass of adsorbent</td>
<td>(g)</td>
</tr>
</tbody>
</table>

Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_E$</td>
<td>Initial sorption rate</td>
<td>$(\text{mg g}^{-1} \text{min}^{-1})$</td>
</tr>
<tr>
<td>$\beta_E$</td>
<td>Desorption constant during any given experiment.</td>
<td>$(\text{g mg}^{-1})$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Polyanii potential</td>
<td>$(\text{J mol}^{-1})$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity</td>
<td>$(\text{kg m}^{-1} \text{s}^{-1})$</td>
</tr>
</tbody>
</table>
REFERENCES


