PREPARATION AND CHARACTERIZATION OF CHITOSAN FOR HEAVY METAL IONS REMOVAL

AĞIR METAL İYONLARININ UZAKLAŞTIRILMASI İÇİN KİTOSAN HAZIRLANMASI VE KARAKTERİZASYONU

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To my family

ETİK

Hacettepe Üniversitesi Fen Bilimleri Enstitüsü, tez yazım kurallarına uygun olarak hazırladığım bu tez çalışmasında;

- tez içindeki bütün bilgi ve belgeleri akademik kurallar çerçevesinde elde ettiğimi,
- görsel, işitsel ve yazılı tüm bilgi ve sonuçları bilimsel ahlak kurallarına uygun olarak sunduğumu,
- başkalarının eserlerinden yararlanılması durumunda ilgili eserlere bilimsel normlara uygun olarak atıfta bulunduğumu,
- atıfta bulunduğum eserlerin tümünü kaynak olarak gösterdiğimi,
- kullanılan verilerde herhangi bir değişiklik yapmadığımı,
- ve bu tezin herhangi bir bölümünü bu üniversite veya başka bir üniversitede başka bir tez çalışması olarak sunmadığımı

beyan ederim.

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ABSTRACT

PREPERATION AND CHARACTERIZATION OF CHITOSAN FOR HEAVY METAL IONS REMOVAL

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Chitosan and cross-linked chitosan with epichlorohydrin beads was prepared with the aim of reversibly adsorb and release of heavy metal ions from aqueous solutions.

The present work was orgnized in three main parts. During the first part of the study, chitosan beads was prepared by dissolving 3.0 g chitosan in 100 mL 2% acetic acid solution, and the solution was dropped into 2 M sodium hydroxide solution. The prepared chitosan beads puted into a flask with 100 mL sodium hydroxide (pH 10), and some amount of epichlorohydrin was added as cross-linking agent and stirred at 60°C for 6 h. the chitosan and cross-linked chitosan beads washed extensively with distilled water and stored for use.

The characterization of the prepared chitosan and crosslinked chitosan was carried out by using Swelling Test, Elemental Analysis method, Scanning Electron Microscopy (SEM) image, specific surface area measurements, and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The surface area of chitosan beads was 1.15 m^2/ g while the surface area of cross-liked chitosan beads was 0.55 m^2/g.

In the secondpartof the study, adsorption of metal ions from aqueous solutions onto chitosan and cross-linked beads was investigated in batch processes. The effect of the initial metal ions concentration, pH of the medium, temperature, weight of adsorbent materials, rate of stirring, and adsorption time on the adsorption capacity was examined. The last part of this study the selectivity ofchitosan and cross-linked chitosan by epichlorohydrin for removing of heavy metal ions from natural water samples was investigated.

The maximum adsorption capacity of chitosan beads for aqueous solutions of selected metal ions (Cu(II), Hg(II), As(III) and As(V)) was obtained by experiments as 204 mg/g (3.21 mmol/g), 550mg/g (2.74 mmol/g), 100 mg/g (1.33 mmol/g), and 200mg/g (2.70 mmol/g) respectively.The maximum adsorption capacity of cross-linked chitosan beads was128mg/g (2.02 mmol/g), 84 (0.42mmol/g), 50 mg/g (0.66 mmol/g), and 181mg/g (2.42 mmol/g) for Cu(II), Hg(II), As(III) and As(V) respectively.

Competitve adsorption studies were done with the solution that contains all four heavy metal ions. The adsorbtion capacity of Cu(II) ions are higher than the Hg(II), As(III) and As(V). The adsorption capacities for Cu(II), Hg(II), As(III) and As(V) ions were found to be 25 mg/g (0.39mmol/g), 20mg/g (0.10 mmol/g), 13mg/g (0.18 mmol/g), and 18 mg/g (0.23 mmol/g), respectively for chitosan. And 17 mg/g (0.27 mmol/g), 5.07mg/g (0.02 mmol/g), 9.28 mg/g (0.12mmol/g), and 12.37 mg/g (0.16mmol/g), respectively for cross-linked chitosan.

Chelation behavior of heavy metal ions could be modelled using both the Langmuir and Freundlich isotherms. The results were fitted to the Langmuir isotherms. In order to examine the controlling mechanism of adsorption process, kinetic models were used to test experimental data. The result suggested that the pseudo-second order adsorption mechanism is predominant and that the overall rate of the adsorption process appeared to be controlled by chemical process.

Key words: Heavy metal removal, Chitosan, Cross-linked chitosan, AAS.

Özet

AĞIR METAL İYONLARININ UZAKLAŞTIRILMASI İÇİN KİTOSAN HAZIRLANMASI VE KARAKTERİZASYONU

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Kitosan ve epiklorohidrin ile çapraz bağlanmış kitosanpartikülleri sulu ortamdan ağır metallerin tersinir biçimde adsorpsiyonu ve uzaklaştırılması için hazırlandı.

Bu çalışma üç ana bölüm olarak organize edildi. Çalışmanın ilk kısmında, kitosan partikülleri 3.0 g kitosanın %2 asetik asit içeren 100 mL çözeltide çözünmesi ve ardından 2 M sodyum hidroksit çözeltisine aktarılmasıyla hazırlandı. Hazırlanan kitosanpartikülleri 100 mL sodyum hidroksit (pH 10) ile bir cam balona boşaltıldı ve bir miktar epiklorohidrin çapraz bağlayıcı madde olarak eklendi ve bu karışım 60 °C de 6 saat karıştırıldı. Kitosan ve çapraz bağlanmış kitosanpartikülleridistile su ile bolca yıkandı ve kullanım için hazır bekletildi.

Hazırlanmış kitosan ve çapraz bağlı kitosankarakterizasyonu Şişme Testi, Elementel Analiz yöntemi, Taramalı Elektron Mikroskopu (SEM) görüntülemesi, spesifik yüzey alanı ölçümleri ve FourierTransformInfrared (FTIR) spektroskopisi tekniği ile gerçekleştirildi.Kitosanpartiküllerinin yüzey alanı 1.15 m^2/g iken çapraz bağlı kitosan partiküllerinin yüzey alanı 0.55 m^2/g olarak tespit edildi.

Çalışmanın ikinci kısmında, sulu çözeltilerden metal iyonlarının kitosan ve çapraz bağlı kitosanpartikülleri üzerine adsorpsiyonubatch sistemde incelendi. Adsorpsiyonkapasitesiüzerine başlangıç metal iyonu derişimi, ortam pH' ı, sıcaklık, adsorbent miktarı, karıştırma hızı ve adsorpsiyon süresinin etkileri incelendi. Çalışmanın son kısmında, kitosan ve epiklorohidrin ile çapraz bağlanmış kitosanın doğal su örneklerinden ağır metal uzaklaştırılması için seçiciliği test edildi.

Kitosan partiküllerinin sulu çözeltilerde seçilmiş metal iyonları (Cu(II), Hg(II), As(III), As(V)) için maksimum adsorpsiyon kapasitesi sırasıyla 204 mg/g(3.21 mmol/g), 550mg/g(2.74

mmol/g), 100 mg/g (1.33 mmol/g) ve 200mg/g(2.70 mmol/g) olarak elde edildi. Çapraz bağlı kitosan partiküllerinin maksimum adsorpsiyon kapasitesi ise sırasıyla 128 mg/g(2.02 mmol/g), 84mg/g(0.42 mmol/g), 50 mg/g (0.66 mmol/g) ve 181mg/g(2.42 mmol/g) idi. Ağır metal iyonlarının şelatlaşma davranışı hem Langmuir hem de Freundlich izotermleri kullanılarak modellerdirildi. Sonuçlar Langmuir izotermlerine uygun bulundu. Adsorpsiyonprosesinin kontrol mekanizmasını incelemek amacıyla deneysel verilerin test edilmesi için kinetik modeller kullanıldı. Sonuçlar yalancı ikinci derece adsorpsion mekanizmasının daha baskın olduğunu ve bütününde adsorpsiyonprosesininkimyasal bağlanma kontrollü göründüğünü önermektedir. Yarışmalı adsorpsiyon çalışmaları bütün bu dört ağır metal iyonlarını içeren çözelti ile gerçekleştirilmiştir.

Anahtar kelimeler: Ağır metal uzaklaştırılması, Kitosan, Çapraz bağlı kitosan, AAS.

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1. INTRODUCTION

Heavy metal pollution in the aquatic environment has become a major concern because of the toxicity of heavy metals to aquatic life, human beings and ecological systems [1].Rapid industrialization and the increase in population have all contributed to the heavy metal pollution in the eco-system [2]. The importance of heavy metal pollution control has increased significantly in recent decades[3].

Metal ions at very low levels such as copper, iron, and zinc are considered essential for normal body functions. Metal ions are toxic at high concentrations. The difference between the ranges essentiality and toxicity is very narrow for heavy metal ions. The toxicity of heavy metals may be caused by mechanisms that include blocking essential functional groups of bimolecular and disrupting the integrity of biomembranes [4].These metal ions are metabolic poisons and enzyme inhibitors; they can cause mental retardation and semi-permanent brain damage [5].Toxic metals are released into the environment in a number of different ways: burning of fossil fuels,coal combustion, battery industry, mining and smelting of metallic ferrous ores, municipal wastes, electric device manufacturing among others [6], fertilizers manufacturing [7], sewage waste-waters, and automobile emissions…etc., the effective removal of heavy metal ions from water or industrial effluents is very important and has attracted considerable research and practical interest [8].Conventional methods that have been used to remove heavy metal ions from various industrial effluents usually include chemical precipitation, flocculation, membrane separation, ion exchange, evaporation, electrolysis [3], reverse osmosis, neutralization, cementation [9 -11], solvent extraction, and adsorption etc.. [5]; [8].The main limitation of these techniques is their low efficiency in the removal of trace levels of metal ions [2].Among these methods, adsorption is one of the most promising treatments for the removal of metal ions because it is simple, cost-effective, extensively used [12],easy handled[5]. A lot of adsorbents including agricultural wastes [13], natural zeolites [14], clays [15], and polymer adsorbents, have been widely reported to remove metal ions from aqueous solutions. However, the further applications of these materials are limited by their low adsorption capacities or efficiencies.

The necessity to reduce the amount of heavy metal ions to acceptable levels in wastewater streams and subsequent possible re-use of these metal ions, has led to an increasing interest in selective polymer adsorbents [5].The adsorption on polymer sorbents is reported to be the best method for removal of metal ions in a low concentration such as ppm level. Nonspecific sorbents, such as activated carbon, metal oxides, silica, and ion-exchange resins have been used[2].Activated carbons used in wastewater treatment are traditionally obtained from precursors such as wood, lignite and animal bones. However, the interest for the application of alternative and low-cost raw materials in the production of this adsorbent has increased during last years [16], specific sorbents have been considered as one of the most promising techniques. Specific sorbents consist of a ligand that interacts with the metal ions specifically and a carrier matrix that may be an inorganic material(e.g. aluminum oxide, silica or glass) orpolymer microbeads (e.g. polystyrene, chitosan, cellulose, polymaleic anhydride or polymethylmethacrylate)[2].The increasing number of publications on adsorption of toxic compounds by modified polysaccharides shows that there is a recent increasing interest in the synthesis of new low-cost adsorbents used in wastewater treatment [17]. Chitosan, a type of biopolymer, is a good adsorbent to remove various kinds of anionic and cationic dyes as well as heavy metal ions. Chemical modifications of chitosan that lead to the formation of chitosan derivatives, grafting chitosan and chitosan composites have gained much attention [18].

In this study two forms of chitosan biopolymer areprepared for the removal of heavy metal ions. Chitosan is a natural heteropolymer of glucosamine and N-acetyl glucosamine residues[19],Chitosan, is a non-toxic, environmentally friendly biopolymer[20],and has a wide variety of applications in the fields of biotechnology, biomedical, environmental, microbiology, and pharmaceutical studies [19], in addition, it is one of the most promising alternative adsorbents for removing heavy metal ions and dyes. Besides,chitosan is used in the preparation of some biotechnological materials such as cell-stimulating materials, antibacterial agents, blood anti-coagulants (heparinoids), photography, cosmetics,artificial skin, chitin and chitosan based dressings, food and nutrition, opthalmology, paper finishing, solid-state batteries, and drug-delivery systems [19],[20].

Chitosan, which is one of the most representative biopolymers, has recently received considerable interest for the removal of heavy metals due to its excellent metal-binding capacities and low cost. Chitosan, poly (*b*-1-4)-2-amino-2-deoxy-D-glucopyranose, is produced by partially alkaline *N*-deacetylation of chitin, which can be widely found in the exoskeleton of shellfish and crustaceans as the second most abundant natural biopolymers after cellulose. It is known as an outstanding sorbent of extremely high affinity for transition and post transition metal ions selectively because the amino (-NH_2) and/or hydroxyl(-OH) groups on chitosan chains serve as coordination sites [21].

Determination of trace ions in natural samples is of great interest because of its adverse effects on human health. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Electro- thermal Atomic Absorption Spectrometry (ETAAS), are employed in trace ions analysis[22], as well as Flame Atomic Absorption Spectrometry (FAAS)is widely used for these determinations due to the common availability of the instrumentation, the speed and simplicity of the procedures and the precision and accuracy of the techniques [23]. As a result (FAAS) is cheap and its usage is easier than other instruments [24]. In addition, most of the concentrations of the metal ions in environmental samples are readily determined using this technique.

There are three main objectives of this research. The first one is to prepare chitosan and cross-linked chitosan by epichlorohydrin and study of characterization of these two polymers by Elemental Analysis, Fourier-Transform Infrared Spectroscopy (FTIR), determination of surface area of the chitosan beads and Scanning Electron Microscopy(SEM).The second one is to study the selectivity of chitosan and cross-linked chitosan for removing of heavy metal ions from aqueous solutions with different pH values, incubation time, temperature, concentrations and at different rate of stirring. The last objective is to study the selectivity of chitosan and cross-linked chitosan by epichlorohydrin for removing of heavy metal ions from natural water samples.

2. THEOREATICAL

In the last years, environment contamination by heavy metals has gained much attention due to the significant impact on public health [25]. Industrialization and urbanization have resulted in increased releases of toxic heavy metals into the natural environment comprising soils, lakes, rivers, ground waters and oceans [26].

2.1. Heavy Metals

A heavy metal is a member of an ill-defined subset of chemical elements that exhibit metallic properties. Many different definitions of the term heavy metal have been proposed, based on density, atomic number, atomic weight, chemical properties or toxicity. Heavy metals are natural constituents of the Earth's crust. They are stable and cannot be degraded or destroyed, and therefore they tend to accumulate in soils and sediments [27].

Heavy metal solutions are widely used in industrial activities such as metal finishing, electroplating, painting, dying, photography, surface treatment, printed circuit board manufacture, etc... Most of the heavy metal ions are well-known toxic and carcinogenic agents, while metal residues in the environment pose a threat not only for human health, but also have serious detrimental effects for the aquatic eco-system. The presence of heavy metals in the aquatic environment has forced international environmental agencies to introduce strict regulations with regard to metal discharge, especially from industrial activities [9]. Heavy metals they are metabolic poisons that generally cause poisoning by binding to enzymes thereby decreasing their activity [28].

2.1.1. Toxicities of Heavy Metals

The symptoms of the toxic effects of heavy metals may vary widely at the physiological level, but the basic toxicity mechanisms at the molecular level may be limited. The toxicities of heavy metals may be caused by the following mechanisms:

(1) Blocking the essential functional groups of biomolecules such as enzymes: Specific amino acid residues, such as serine-OH, cysteine-SH and histidine-N often constitute the active sites of enzymes. Hg(II), for example, binds strongly cysteine-SH′s, blocking an enzymatic activity.

(2) Displacing essential metal ions from biomolecules: A metal ion may displace a native ion, if its affinity to the binding site is stronger than that of the native one. Often a biomolecule with a foreign metal ion loses its activity.

(3) Modifying the active conformation of biomolecules, especially enzymes and perhaps polynucleotide's: A coordination of a cation may change the conformation of a protein, rendering it non-functional.

(4) Disrupting the integrity of biomembranes: A metal cation may bind the negatively-charged head(s) of phospholipids and the integral protein residues of the membrane.

(5) Modifying some other biologically active agents: For example Cd(II) and Pb(II) appear to potentiate the endotoxins produced by bacteria. This might be due to their effect to block some enzymes which degrade to endotoxin.

(6) Binding with bioanions, resulting in a decreased level of essential bioanions, especially PO_4^{3-}or a displacement of an essential cation from biominerals: For example, Pb(II), having a size similar to that of Ca(II), could replace Ca(II) in a bone mineral. As a result the mechanical strength of the bone may be affected. The size and the electric charge would be an important factor in these effects. One of the basic toxic effects of Pb(II) is considered to be binding of PO_4^{3-} , rendering its cytoplasmic level very low [29].

2.1.2.Effects of Heavy Metals on Human Health

Most of heavy metals (Fe, Zn, Cu, Mo, Co, Cr, V, Mn, and Ni) are essential nutrients for plants animals and microorganisms. Only in high concentrations they become toxic. All living organisms possess both mechanisms to store and transport metals for use in metallo-proteins or cofactors and to protect themselves against the toxic effects of metal excess. In a biological system the normal concentration range of each metal is narrow. Deficiency or excess of heavy metals causes pathological changes. According to a biological significance heavy metal ions may be arranged in the following order: iron > zinc > copper> molybdenum > cobalt > chromium > vanadium > manganese > nickel [30].

The heavy metals hazardous to humans include lead, mercury, cadmium, arsenic, copper, zinc, and chromium. Heavy metals toxicity and the danger of their bioaccumulation in the food chain represent one of the major environmental and health problems of our modern society [7]. The lack of Zn could result in a weakness immunity system, depression, Copper is known as an important element in both industry and biological systems. It is an essential nutrient for all high plants and animals. It is critical for energy production in the cells, also involved in nerve conduction, connective tissue, the cardiovascular system and immune system. In addition, copper is closely related to estrogen metabolism and is required for women's fertility and to main pregnancy. Dietary ingestion of copper is indispensable for good health. According to national surveys, the average dietary intake of copper in the US is approximately 1.0–1.1mg/ day for adult women and 1.2–1.6mg/day for adult men [33].

However, excess copper may be absorbed in the intestinal tissues that lead to intestinal disorders (nausea, vomiting, diarrhea and stomach cramps), impaired healing and reduced resistance to infections [32], serious lesions in the central nervous system and even permanent damage especially for children and liver or kidney damage or even death[34], Therefore, a precise, accurate and rapid measurement of copper is of great importance [33].The World Health Organization (WHO) recommended 1.5 mg/L as the maximum acceptable concentration of this metal in drinking water on account of its toxicity [35].Copper, as one of extensively used materials in the mechanical manufacturing industry, electroplating, light industry, architecture [36],electronics, automotive, and so forth, has caused many actual or potential sources of pollution. Effluent containing copper ions from many industries has posed a risk to both human beings and ecological environment. Therefore, copper ions removal from wastewater has become an important subject today [12].

2.1.2.2. Mercury

The heavy metal mercury, Hg, atomic number 80 and atomic weight 200.59 a silver white, heavy liquid at typical ambient temperatures and pressures. Mercurys melting point is -38.89C$^{\circ}$ under atmospheric pressure. Mercury is the only metal which is a liquid at room temperature[37];(Figure 2.2).

(2) Forms of mercury with relatively low toxicity can be transformed into forms with very high toxicity through biological and other processes;

(3) Methyl mercury can be bioconcentrated in organisms and biomagnified through food chains, returning mercury directly to man and other upper trophic level consumers in concentrated form;

(4) Mercury is a mutagen, teratogen, and carcinogen, and causes embryocidal, cytochemical, and histopathological effects;

(5) High mercury content in some species of fish and wild life from remote locations emphasize the complexity of natural mercury cycles and human impacts on these cycles and

(6) The anthropogenic use of mercury should be reduced, because the difference between tolerable natural background levels of mercury and harmful effects in the environment is exceptionally small.

The toxicity of mercury depends strongly on its redox state. The most toxic form of mercury is the highly reactive Hg^{2+}, which binds to the amino acid cysteine in proteins. In contrast, the danger of elemental mercury (Hg°) and organo-mercury compounds lies in their transport routes. Mercury vapor is easily inhaled, enters the blood stream in the lungs and is thus distributed throughout the body. Within cells, it is oxidized to reactive Hg^{2+}. The toxicity of monomethylmercury ($MeHg^{+}$) or dimethylmercury (Me_2Hg) is caused by its ability to penetrate membranes within seconds and also to cross the blood–brain barrier. Symptoms of mercury poisoning are mainly neuronal disorders but also damage to the cardiovascular system, kidney, bones, etc. The three major sources of Hg emissions are natural, anthropogenic and re-emitted sources. Urban discharges, agricultural materials, mining and combustion and industrial discharges are the principal anthropogenic sources of Hg pollution in the environment. Hg was used extensively in gold extraction; in the 1800s, it was used in the chloralkali industry, in the manufacture of electrical instruments, and as a medical antiseptic; and since 1900, it has been used in pharmaceuticals, in agricultural fungicides, in the pulp and paper industry and in the production of plastics. Mercury undergoes complex physical, chemical and biological transformations in the environment, being the principal ones: (a) the transport of Hg(II)through the atmosphere, its photochemical oxidation to reactive Hg(II) and subsequent deposition on soils, lakes, rivers and the sea; (b) the methylation of Hg(II) by reducing bacteria in anoxic habitats, its uptake by aquatic organisms and accumulation in the food web, resulting in high mercury concentrations in fish and chronic low level exposure of humans. Hg contamination can be much more widespread than that observed for other metals, due to atmospheric transport, or to biomagnification through the food chain, reaching fish and humans [38]. Mercury is used in thermometers, barometers, manometers, and other scientific apparatus.

Methylmercury (CH_3Hg), It affects the immune system, alters genetic and enzyme systems, and damages the nervous system, including coordination and the senses of touch, taste, and sight. Methylmercury is particularly damaging to developing embryos, which are five to ten times more sensitive than adults. Exposure to methylmercury is usually by ingestion, and it is absorbed more readily and excreted more slowly than other forms of mercury. Elemental mercury, Hg^0, the form released from broken thermometers, causes tremors, gingivitis, and excitability when vapors are inhaled over a long period of time.Short-term exposure to high levels of metallic mercury vapors may cause lung damage, nausea, vomiting, diarrhea, increases in blood pressure or heart rate, skin rashes, and eye irritation[41]. Although it is less toxic than methylmercury, elemental mercury may be found in higher concentrations in environments such as gold mine sites, where it has been used to extract gold. If elemental mercury is ingested, it is absorbed relatively slowly and may pass through the digestive system without causing damage. Ingestion of other common forms of mercury, such as the salt $HgCl_2$, which damages the gastrointestinal tract and causes kidney failure, is unlikely from environmental sources[40].

Mercury, is ubiquitous in the environment. Figure 2.3.

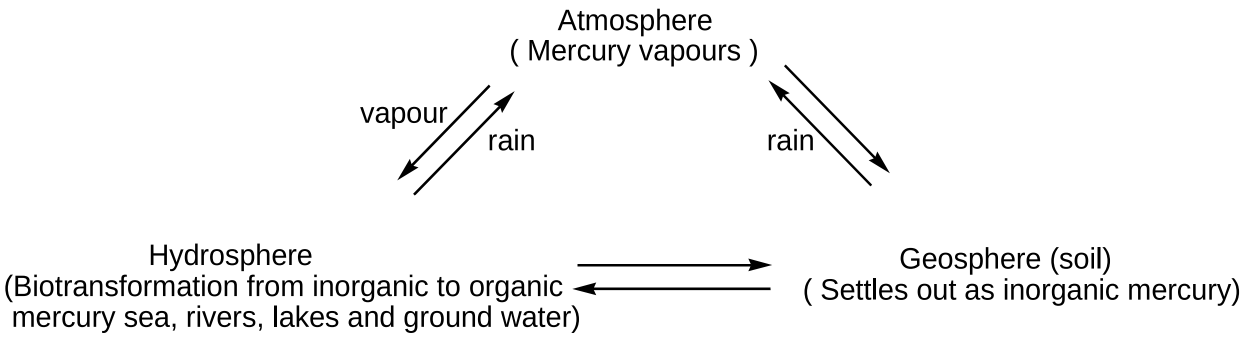


Figure 2.3 Mercury and environment

There have been numerous studies dedicated to the study of mercury toxicity. We have shortlisted a few below for the better understanding towards low dose mercury toxicity [42]. (Table2.1).

Table 2.1.Effect of low dose mercury toxicity on various organ systems

Nervous system Adults	Memory loss, including alzheimer like dementia, deficit in attention, hypoesthesia, ataxia, dysarthrea, subclinical finger tremor impairment of hearing and vision, sensory disturbances, increased fatique
Children/infants	Deficit in language (late talking) and memory deficit in attention, autism
Motor system Adult	Disruption of fine motor function, decreased muscular strength, increased tiredness
Children/infants	Late walking
Renal system	Increases plasma creatinine level
Cardiovascular system	Alter normal cardiovascular homoeostasis
Immune system	Decrease overall immunity of the body, exacerbates lupus like autoimmunity, multiple sclerosis, autoimmune thyroiditis or atopic eczema
Reproductive system	Decreases rate of fertility in both males and females, birth of abnormal offsprings

hematopoieticand nervous systems. Two forms of inorganic arsenic are found in natural waters, depending on the redox potential: As(V) and As(III)[44], lower level exposure can cause nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, and a sensation of “pins and needles” in hands and feet, Ingestion of very high levels can possibly result in death and long-term low level exposure can cause a darkening of the skin and the appearance of small “corns” or “warts” on the palms, soles, and torso[41].

Arsenic is introduced in water through natural and anthropogenic sources: release from mineral ores, probably due to long term geochemical changes, and from various industrial effluents like metallurgical industries, ceramic industries, dye and pesticides manufacturing industries and wood preservatives. Two predominant species found in natural waters are inorganic forms of arsenic namely; arsenate As(V) and arsenite As(III) and their presence depend on the pH and redox conditions[45].

Arsenic is present in water as a result of both natural and anthropogenic activities. Inorganic arsenic can occur in the environment in several forms. In natural waters, and thus in drinking water, it is mostly found in trivalent (arsenic (III) (As(III))) or pentavalent (arsenic(V) (As(V))) states. Drinking water poses the greatest threat to public health from arsenic Arsenic dissolved in water is acutely toxic and can lead to a number of health problems. Usually arsenic is built up in the body through drinking water and food contaminated with arsenic and causes increased risks of cancer in the skin, lungs, liver, kidney, and bladder. Consumption of arsenic also leads to disturbance of the cardiovascular and nervous system functions and concentrations eventually lead to death. People drinking water contaminated with arsenic with equal to or greater than 50 ppb are prone to increased risks of lung and bladder cancer and of arsenic-associated skin lesions. The US Environmental Protection Agency (USEPA) in 2001 adopted a new standard for arsenic in drinking water at 10 ppb, replacing the old standard of 50 ppb. [46]. But the guideline of Asconcentration limit value recommended by WHO in drinking waters has been 10μg/L since1993. The European Union, USA, Canada, Japan, and Vietnam have accepted this value in their regulatory systems, but other countries (Bangladesh, Bolivia, India, etc.) still operate at present to the 50μg/L standard [45].

2.2. Adsorption

Adsorption is the accumulation of atoms, molecules, or ions at the surface of a solid or liquid as the result of physical (Van der Waals adsorption) or chemical forces(activated adsorption) depending on the type of forces between the adsorbate and the adsorbent. We can distinguish between two types of adsorption process depending on which of these two force types plays the bigger role in the process. In physical adsorption, the individuality of the adsorbate and the adsorbent are preserved. In chemisorption, there is a transfer or sharing of electron or breakage of the adsorbate into atoms or radicals who are bound separately [47].

It differs from absorption, in that an adsorbed substance remains at the surface while an absorbed substance spreads throughout the absorbing material. An adsorbed substance is termed an adsorbate while the material on which adsorption occurs is the substrate. The release of an adsorbate is termed desorption [48].

Adsorption is one of the most effective and simplest approaches to removing toxic and recalcitrant pollutants from aqueous systems, and activated carbon is one of the most widely used adsorbents for this purpose [49]. Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. Abundant information on the use of activated carbon for such purposes can be found in scientific literature Because of their great capacity to adsorb pollutants. This capacity is mainly due to their structural characteristics and their porous texture, which gives them a large surface area, and their chemical nature, which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages. It is non-selective, quite expensive, and the higher the quality, the greater the cost. The regeneration of saturated carbon by thermal and chemical procedure is also expensive, and results in loss of the adsorbent. This had led many workers to search for more economic and efficient adsorbents. Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various adsorbents, in particular natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. Starch and chitin may have potential as inexpensive, readily available materials and are classified as low-cost sorbents[17].However, their adsorption capacities, mechanical strength, and other properties need further improvement for wider application [50]. A large variety of nonconventional adsorbents have been examined for their ability to remove various types of pollutants from water and wastewater. The adsorption capacity of several low-cost-adsorbents, mainly biopolymers, which are obtained from renewable sources, has been investigated. Most of them, including chitosan, adsorb selectively several metallic ions [20].

2.2.1. Adsorption Kinetics

The adsorption on a solid takes places in several stages;

(1) External diffusion; the mass transfer by diffusion of the adsorbate molecules from the bulk fluid phase through a stagnant boundary layer surrounding each adsorbent particle to the external surface of the solid.

(2) Internal diffusion; transfer of the adsorbate to the interior of the particle by migration of the adsorbate molecules from the relative small external surface of the adsorbent to the surface of the pores within each particle and by the diffusion on the adsorbate molecule through the pores of the particles.

(3) The actual adsorption process; the molecule in the pores are adsorbed from the solution to solid phase. This stage is relatively fast, compared to the first two steps: hence, local equilibrium is usually assumed between these two phases[51].

The adsorption process is affected by the following factors:

- Surface area of adsorbent
- Nature of adsorbate
- pH
- Temperature
- Solute concentration
- Time of contact
- Nature of contacting

2.2.2. Adsorption Equilibrium

Adsorption capacity of the adsorbent can be determined by making a contact between the adsorbate and adsorbent. If adsorption is the removal mechanism, then the residual concentration will be reached that will remain unchanged with time, which is also known equilibrium, and the process is adsorption equilibrium. Two types of adsorption processes are mentioned:

(1) Physical adsorption, which is a reversible phenomenon. It results from the action of van der Waals forces. It is usually dominant at low temperatures and is multilayered.

(2) Chemisorption is generally irreversible, because chemical interactions are involved between the adsorbate and adsorbent moiety. Factors affecting the adsorption process are pH, temperature, adsorbent quantity, and particle size including other chemical properties of the adsorbate and adsorbent [52].

2.2.3. Adsorption Isotherms

It is the relationship between the amount of adsorbate adsorbed on the surface of adsorbent and equilibrium concentration of the adsorbate at a certain temperature and other condition. The equilibrium data is formulated into an isotherm model. Brunauer [53], classified adsorption isotherm in six types. These types may be monolayer, multilayer or condensation in pores/capillaries. An isotherm model is suitable tool to assess the adsorption capacities in batch and column study. Batch study consists of contacting an adsorbate with a definite quantity of adsorbent in batch stirred system. The mixture is agitated to facilitate the adsorption process. In column study, adsorbent is packed in a column reactor and almost no flow or movement of adsorbent takes place inside the column. Different theoretical and empirical models have been proposed to describe the different types of isotherms in batch study. Most commonly used models are discussed here which are generally used for the interpretation of adsorption isotherms [52].

The equilibrium isotherm is fundamental in describing the interactive behaviour between the solutes and adsorbent. It is also essential in the design of an adsorption system. Three of the most commonly used isotherms, namely, the Langmuir, Freundlich and BET isotherms. Thermodynamic parameters such as Gibbs free energy change (ΔG^0), enthalpy changes

(ΔH^0) and entropy change (ΔS^0) can be estimated using equilibrium constants changing with temperature. The standard Gibbs free energy change of the sorption reaction is given by:

$$\Delta G^0 = -RT\ln K$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \text{……………………………………..} 2.1$$

Where *K is* the equilibrium constant, which can be obtained according to the method reported by Ramnani and Sabharwal, [54]; ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the plot of ln *K* against 1/*T*. The negative values of ΔG^0 reflect the feasibility of the process, and the values become more negative with increase in temperature. The positive value of ΔH^0 showed the endothermic nature of the adsorption. The positive value of ΔS^0 suggested an increase in randomness at the solid–solution interface during the adsorption of the element on polymeric material [1].

2.2.3.1. Freundlich Isotherm

The equilibrium relationship in absorbers can often be described by a Freundlich relationship. Freundlich provided there is: No association or dissociation of the molecule after they are adsorbed on the surface. A complete absence of chemisorption.

In other words for Freundlich isotherm to be valid, the adsorption must be purely a physical process with no change in the configuration of the molecules in the adsorbed state. Freundlich proposed the equation:

$$q = kc^{1/n} \text{…………………………………………..} 2.2$$

where k, n are empirical constants dependent on the adsorption rate and on the temperature, c is the equilibrium concentration of the solute in the solution in mg/L, q is the amount of solute adsorbed on the unit mass of the adsorbent for certain period of time (mg/L) according to the Freundlich equation, the amount adsorbed increases infinitely with increasing pressure.

2.2.3.2. Langmuir Isotherm

The Langmuir model was originally developed to represent chemisorption on asset of distinct localized adsorption sites. The derivation of Langmuir adsorption isotherm involves five implicit assumptions.

(1) The adsorbed gas behaves ideally in the vapor phase.

(2) The adsorbed gas is confined to monomolecular layer.

(3) The surface is homogeneous, that is, the affinity of each binding site for gas molecules in the same.

(4) There is no lateral interaction between adsorbate molecules.

(5) The adsorbate gas molecules are localized, that is, they do not move around on the surface.

The commonly quoted form is:

$$q = nKC/(1 + KC) \text{…………………………………..2.3}$$

Where n is a temperature independent constant which is supposed to represent affixed number of surface sites, K is a temperature dependent equilibrium constant.

2.2.3.3. BET Isotherm

In 1938, Brunauer, Emmett and Teller showed how to extend Langmuir approach to multilayer adsorption and their equation has come to be known as the BET equation. The basic assumption that each molecule in the first adsorbed layer is considered to provide one site for the second and subsequent layers. That the molecules in the second and subsequent layers, which are in contact with other sorbet molecule rather than with the surface of the adsorbent are considered to behave essentially as the saturated liquid, while the equilibrium constant for the first layer of molecule in contact with the surface of the absorbent is different. The resulting equation for the BET equilibrium isotherm is [55].

$$\frac{1}{q_e \; C_0 - C_e} = \frac{1}{kq_m} + \; k - 1 \; (C_0 - C_n)/(C_0 - C_n) \text{…………2.4}$$

Where q_m is the amount of adsorbate in a monolayer per unit mass of adsorbent, q_e is the ratio of mass of adsorbed solute to that of adsorbent, C_e is the equilibrium adsorbate concentration C_0 and C_n are respectively the initial and removable adsorbate concentration and k is a constant parameter[51].

2.3. Biosorption of Heavy Metals

Biosorption has recently received a great deal of attention due to the low cost of the materials used in these applications and for the environmentally friendly impact of the treatment of exhausted sorbents. Several types of biomass have been tested for the recovery of precious metals, including fungal biomass,algal biomass but also polymers of biological origin.[56], [57], the term biosorption refers to many modes of non-active metal uptake by biomass.

There are many different types of biosorbents like:

- Active biomass belonging to algae, bacteria or fungi.
- Non active kind of biosorbent which is essentially a waste product or a byproduct of a fermentation process.
- Abundant natural materials or polymers.

The advantage of biosorption is that the biomass used, could be a raw material which is either abundant, a waste from another industrial operation or could be cheaply available. There are certain broad range biosorbents which can collect all heavy metals from the solution with a small degree of selectivity. Metal sequestration can occur by complexation, chelating, ion-exchange or coordination. Other mechanisms are physical such as adsorption or precipitation. Any of these mechanisms may be important in immobilizing the metal on the biosorbent. Since the biomaterials that are used for sorption are complex a number of these mechanisms could be occurring simultaneously. Naturally abundant biosorbents such as chitin and chitosan are recognized as excellent metal ligands, forming stable complexes with many metal ions, and serving as effective protein coagulating agents.

An overview of some of the literature follows. Reported adsorption capacities are noted when possible to give some idea of sorbent effectiveness. Sorption depends heavily on experimental conditions such as pH, metal concentration, ligand concentration, competing ions, and particle size [58].There are several chemical groups that could potentially attract and sequester metal ions: acetamido groups in chitin, amino and phosphate groups in nucleic acids, amino, amido, sulfhydryl and carboxyl groups in proteins and hydroxyls in polysaccharides [59].

2.4. Polymeric Adsorbents

In the past decades, polymeric adsorbents have been emerging as potential alternative to activated carbon in term of their vast surface area, perfect mechanical rigidity, adjustable surface chemistry and pore size distribution, and feasible regeneration under mild conditions. Generally, polymeric adsorbents can effectively trap many of the ubiquitous organic pollutants. To further improve adsorption performance of a given polymeric adsorbent toward other pollutants such as highly water-soluble compounds (e.g., sulfonated pollutants) and heavy metal ions, surface modification or functionalization has proved to be an effective approach because the functional groups bound to the polymeric matrixes are expected to provide specific interaction with the target pollutants [49]. Biosorbents gain wide attention as these are available in large quantities worldwide and are eco-friendly. The use of adsorbents containing natural polymers has received reorganization, in particular polysaccharides such as chitin and its derivate chitosan [50].

2.4.1. Polymer-Metal Complexes

Polymer science has emerged as an active discipline of material science. This field impinges an area of commodity, engineering and specialty polymer, there by stimulating interest all over the globe in exploiting never domains. One such branch that has emerged is polymer–metal complex comprising an organic polymer containing coordinating sites, complexes with metals. This is of relatively recent origin and an interdisciplinary approach taking into its fold areas viz. chemistry, metallurgy, environmental, and material sciences.

Polymeric materials with the ability to create complexeswith metal ions are very common, originatingfrom both natural and synthetic source. Recentprogress made in design and synthesis of novel coordinationpolymers has brought a variety of polymeric materialsthat exhibit the structural diversities and attractiveproperties which can be further utilized in various fields, like catalysis, sewage treatment, optics, luminescence and sensor technology or polymer drug grafts[60].

Polymer metal complex is composed of polymer and metal ions; where the metal ions are bound to the polymer ligand by a coordinate bond. A polymer ligand contains anchoring site like nitrogen, oxygen, or sulphur obtained either by polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and low molecular weight compound having coordinating ability. The synthesis results in an organic polymer with inorganic function. The metal atoms attached to polymer backbone and to exhibit characteristic catalytic behavior which are distinctly different from their low molecular weight analogue. Indeed many synthetic polymers –metal complexes have been found to possess high catalytic efficiency in addition to semi conductivity, heat resistance and biomedical potentials.

Complexation reaction and their resultant coordination structure are studied mostly by spectroscopic, such as UV-Visible, FTIR, NMR, ESR, etc. These spectra often show characteristics specific for polymeric ligand structure. The stability of the polymeric complex usually differs from that of a monomeric complex [61].

2.4.2. FactorsAffect Polymer-Metal Complex Formation

The factors which affect chelate formation include:

(1) The basic strength of chelating group. There is relationship between the basicity of chelating group, as measured by pKa, and the stability of the chelate it forms.

(2) The electronegativity of the donor atoms of the basic group in the chelating agent. Atoms of lower electro negativity tend to form stronger bonds, e.g. nitrogen and sulphur are better than oxygen. Thus diphenylthiocarbazone (dithozone) forms more stable chelates than does its oxygen analogue, diphenylcarbazone.

(3) Ring size: Five or six membered rings are most stable, since these have minimum strain. The functional groups of the base must be so situated in the molecule that they permit the formation of a stable ring. Chelate stability increases with the number of rings that are formed, possibly owing to increasing number of water molecules that are displaced from their metal coordination sphere by one molecule of the poly functional reagent.

(4) The metal ion characteristics such as charge/ionic radius ratio (ionic potential). As the ratio increase, the stability of metal complex usually rises, provided the metal ion has available binding orbitals for the electron pairs it accepts.

The electronegativity of the metal also plays part. The electronegativity, measured as the energy necessary to remove electrons from the metal atom expresses the electron – attracting ability of the metal ions. The approximate order of the stability of complexes of limited number of divalent ions towards a number of chelating agents has been given as; Pb >Cu >Ni >Co >Zn >Cd >Fe >Mn >Mg.

(5) Resonance and steric effect. The stability of chelate structure is enhanced by contribution of resonance structure of the chelate ring, thus copper acetyl acetone has greater stability than the copper of salicylaldoxime, if the chelated complexes are used in separation processes, all of these factors must be taken into care. The success of the polymeric ligand is determined by the capacity when removing metal ions from wastewater or from toxic mediums, the polymeric ligands can be used to remove some special and important metal ions from medium for regaining. After purification, these metal ions can be used in either process. The important parameters during removing metal ions from dilute aqueous solution for regaining are;

(1)The solubility of the polymer ligand that forms complex,

(2)The capacity of the chelate polymer,

(3)The concentration of the metal salt,

Other methods such as ion exchange systems that are used for metal regaining from aqueous solution has disadvantage because these systems can make reactions in heterogeneous phase.

The purposes of the employing polymers that include chelating groups in separation techniques as a suitable material are[51].

(1) These materials are stable.

(2) It can be used for many times, they are reusable.

(3) The obtained yield is high by using low energy.

(4) They are permeable.

2.5. Polysaccharides

Polysaccharides have been proposed as the first biopolymers to have formed on Earth. Polysaccharides are complex carbohydrates formed from monosaccharides. A number of monosaccharide molecules such as those of glucose, become linked by glycosidic bonds with the elimination of a molecule of water for each monosaccharide added. When a polysaccharide has multiple molecules of the same type, it is described as homopolysaccharide. For example, starch and celluloseis composed of only glucose. When a polysaccharide molecule is formed by more than one type of monosaccharide molecules, it is described as a heteropolysaccharide,for example, chitin[62].

Polysaccharides, is stereoregular polymers of monosaccharides (sugars), are unique raw materials in that they are: very abundant natural polymers (they are referred to as biopolymers); inexpensive (low-cost polymers); widely available in many countries; renewable resources; stable and hydrophilic biopolymers; and modifiable polymers. They also have biological and chemical properties such as non-toxicity, biocompatibility, biodegradability, polyfunctionality, high chemical reactivity, chirality, chelation and adsorption capacities. The excellent adsorption behavior of polysaccharides is mainly attributed to:

(1) High hydrophilicity of the polymer due to hydroxyl groups of glucose units.
(2) Presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups).
(3) High chemical reactivity of these groups.
(4) Flexible structure of the polymer chain.

In spite of these properties and advantages some problems can occur. For example, chitosan is soluble in acidic media and therefore cannot be used as an insoluble sorbent under these conditions, except after physical and chemical modifications.

One of the most important and useful feature of chitin and starch is their good chemical reactivity. They possess a large number of reactive groups (hydroxyl and/or acetamido groups) present at the 2-, 3-, and 6-positions in the glucose unit. These groups allow direct substitution reactions (esterification or etherification reactions) or chemical modifications (hydrolysis, oxidation or grafting reactions, and enzymatic degradation), usually referred to as chemical derivatization, yielding different polysaccharide derivatives for specific domains of applications.

The starch and chitin derivatives can be classified in three main classes of polymers:

(1) Modified polymers such as cationic starches, carboxymethylchitin.

(2) Derivatized biopolymers, including chitosan, cyclodextrins and their derivatives.

(3) Polysaccharide-based materials such as resins, gels, membranes,composite materials.

The modification of the existing polysaccharides is one possible method of obtaining more polar sorbents. The possible chemical derivatization of starch and chitin is also an interesting property because it is well known that the grafting of ligands can improve their adsorption properties. By incorporating some functional (hydrophobic) groups either into the backbone of the network structure or as pendant groups it is possible to prepare materials with strong adsorption properties. The chemical modification of the starch and chitin also allows preparation of two derivatized polysaccharides, cyclodextrin and chitosan, respectively[17].

2.5.1.Starch and Cellulose

Starch is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds, butcellulose is a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linkedD-glucose units,(Figure 2.5).

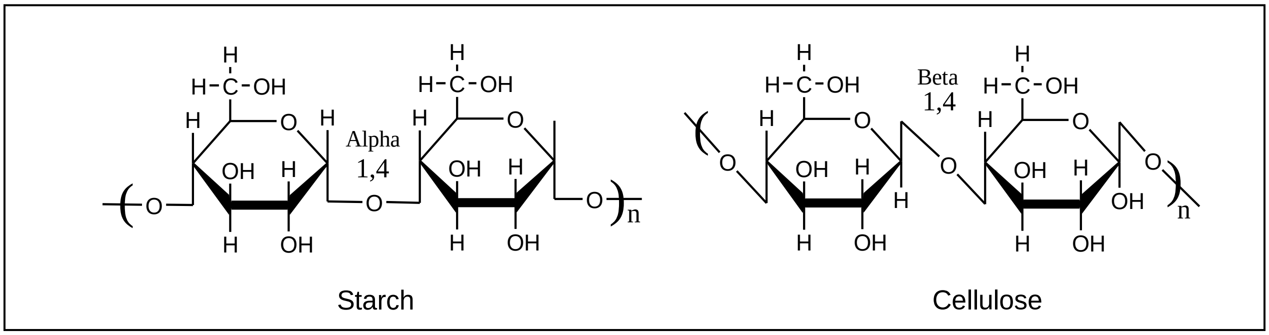


Figure 2.5. Structures of starch and cellulose

2.5.2.Alginic Acid

Alganic acid, or alginate, is an anionicpolysaccharide, It is a linear copolymer with homopolymeric blocks of (1-4)-linked β-D-mannuronate (M) and its C-5 epimer α-L-guluronate (G) residues, respectively, covalenôly linked together in different sequences or blocks, (Figure 2.6).

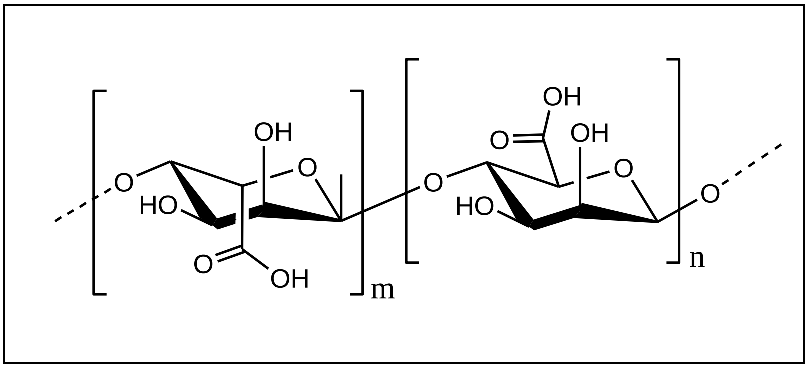


Figure 2.6. Structure of alginic acid

2.5.3.Dextran

Dextran is a complex, branched glucan (polysaccharide made of many glucose molecules), The straight chain consists of α-1, 6glycosidic linkages between glucose molecules, while branches begin from α-1, 3 linkages (Figure 2.7).

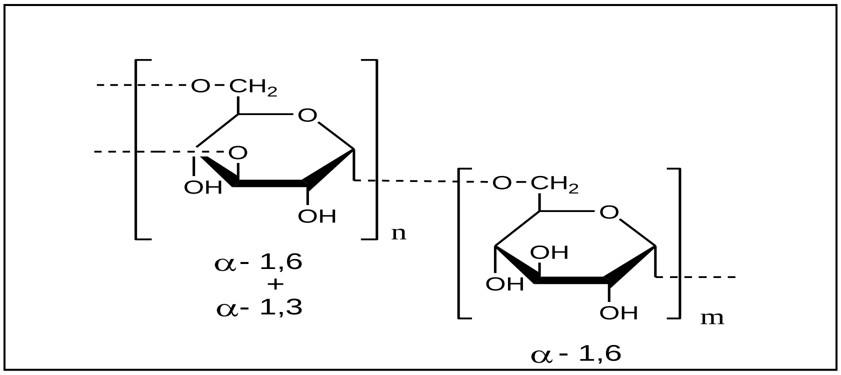


Figure 2.7. Strucure of dextran

2.5.4.Chitin

Chitin is a long-chain polymer of a *N*-acetylglucosamine, a derivative of glucose, In terms of structure, chitin may be compared to the polysaccharide cellulose and, in terms of function, to the protein keratin, (Figure 2.8).

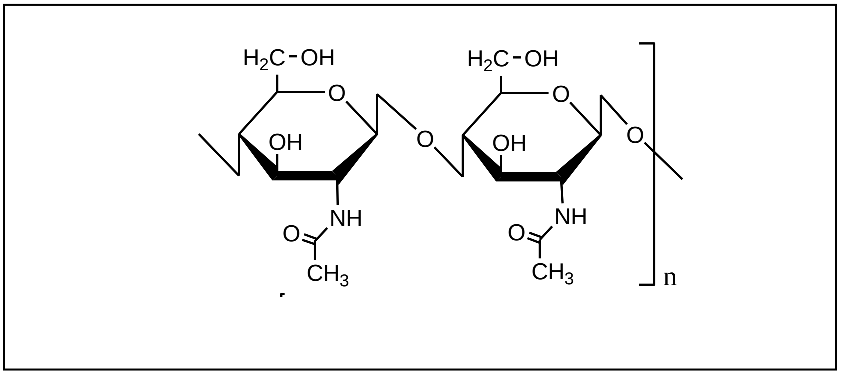


Figure 2.8. Structure of kitin

Chitin is a modified polysaccharide that contains nitrogen; it is synthesized from units of *N*-acetylglucosamine (to be precise, 2-(acetylamino)-2-deoxy-D-glucose). These units form covalent β-1, 4 linkages (similar to the linkages between glucose units forming cellulose). (Chitin is a natural linear biopolymer,of N-acetyl-D-glucosamine linked by B(1–4) glycosidic bond).Therefore, chitin may be described as cellulose with one hydroxyl group on each monomer substituted with an acetylamine group. This allows for increased hydrogen bonding between adjacent polymers, giving the chitin-polymer matrix increased strength.

The name chitinis derived from the Greek word chiton, meaning a coat of mail, and was apparently first used by Bradconnot in 1811.

It is recognized to be the second most abundant biopolymer on earth, next to cellulose. It occurs primarily as a structural component in the exoskeleton of crustaceans, insects, in the pens of squids; it is also found to lesser extents in other animals, plants, fungi and bacteria[63].Deacetylation of chitin with concentrated strong alkaline produces poly-D-glucosamine or chitosan, which has a high density of amino group, and is soluble in weakly acidic solvents such as acetic acid or formic acid. It appears that the physicochemical properties of chitin and chitosan are widely different, which are governed by three principal factors, i.e. source of raw material, molecular weight and degree of deacetylation[63].

Chitosan is more efficient than chitin in terms of adsorption capacity due to the presence of a large number of free amino groups on chitosan chain. The efficiency of the polymeric sorbents depends on various physico-chemical parameters such as particle size, surface area, pore diameter, pore volume, degree of cross linking and particle size distribution.

The fraction of deacetylation for commercial chitosan samples is usually lower than 95%. Higher deacetylation degree may be achieved at the expense of supplementary deacetylation steps, which contribute to partial depolymerization, and high costs when appropriate and sophisticated processes are employed for deacetylation. Highly deacetylated products are generally reserved for biomedical applications. The presence of acetylglucosamine and glucosamine units contributes to the existence of heterogeneities in the polymer. Amino groups are strongly reactive with metal ions. Indeed, nitrogen atoms hold free electron doublets that can react with metal cations. Amine groups are thus responsible for the uptake of metal cations by a chelation mechanism. However, the amine groups are easily protonated in acidic solutions.

Due to its perfect properties of chitosan among potential applications and uses the following must be mentioned:

(1) Medical (bandages and sponges, artificial blood vessels production, preparation of surgeon implants, artificial skin, tumor inhibition, skin burns treatment, eye fluid and lenses production), pulp and paper industry (surface treatment, photographic paper production, carbonless paper production).

(2) Cosmetics (make-up powder, nail polish, moisturizer production).

(3) Biotechnology (enzyme immobilization, protein separation, chromatography applications).

(4) Food (removal of dyes and acids preservative, color stabilization agent, preparation of functional food, animal feed additive).

(5) Agriculture (seed coating, hydroponic fertilizers production, controlled agrochemicals release).

(6) Water treatment (removal of metal ions, flocculant/coagulant of proteins, amino acids, dyes, heavy metal ions, filtration) [68], [69].

2.5.5.1. RawChitosan

The principal characteristics of chitosan that may affect its sorption properties are its deacetylation degree, crystallinity and, to a lesser extent, molecular weight. The deacetylation degree controls the fraction of free amine groups that will be available for interactions with metal ions. The amine groups on chitosan are much more reactive than the acetamide groups on chitin. The free electron doublet of nitrogen on amine groups is responsible for the sorption of metal cations. The protonation of amine groups in acidic solutions is responsible for the electrostatic attraction of metal anions[57].

2.5.5.2. Modification of Chitosan

Chitosan can easily be modified by chemical or physical processes to prepare chitosan derivatives (obtained by grafting new functional groups),Figure 2.11, or to condition the polymer (by preparation of membranes, gel beads, fibers, hollow fibers). These processes may be used for controlling the reactivity of the polymer (improving the affinity of the sorbent for the metal, changing the selectivity series for sorption, changing the pH range for optimum sorption) or enhancing sorption kinetics.

Recently, there has been a growing interest in chemical modification of chitosan to improve its molecular weight and its solubility to widen its application. Among various methods, copolymerization is the common way to improve chitosan properties such graft as increasing chelating or complexation properties, enhancing adsorption properties etc. The high adsorption capacities of modified chitosan for metal ions can be of great use for the recovery of valuable metals or the treatment of contaminated effluents[70].

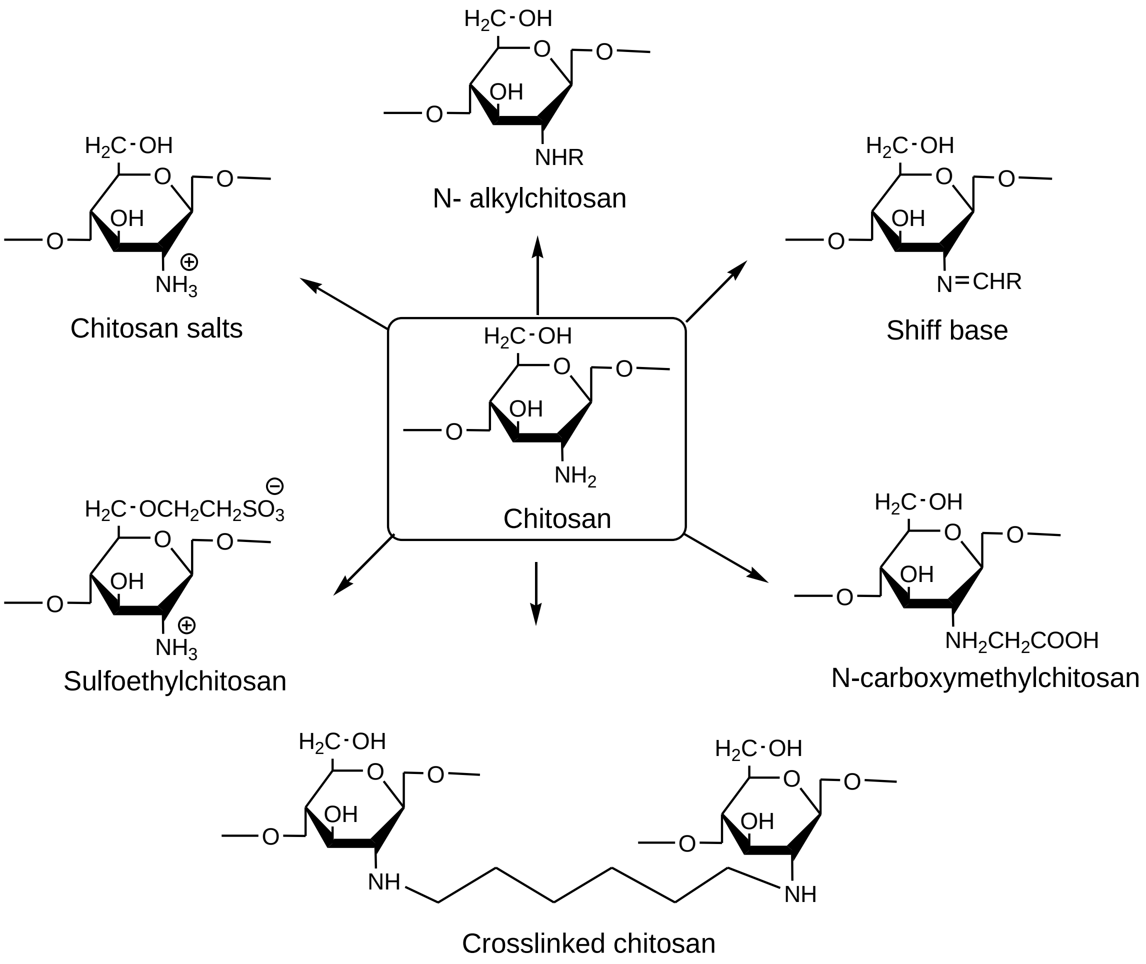
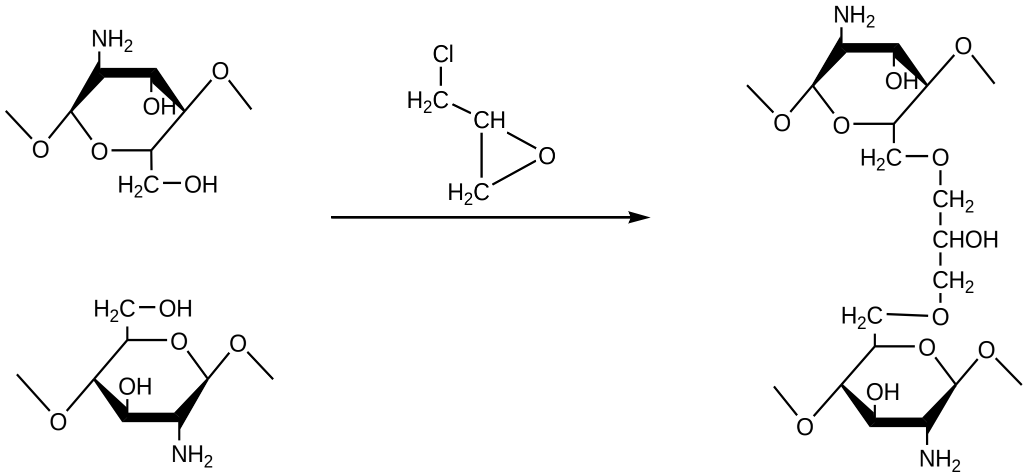


Figure 2.11. Examples of chemical derivatization of chitosan

Chemical modification is more common, which involves either grafting a specific group onto the chitosan backbone or cross-linking. This is done to increase metal sorption capacities or improve selectivity of the polymer for a certain species. Modification is also done to prevent dissolving of the polymer when soluble chitosan is not required and the sorption is performed at acidic solutions. Cross-linking can be done using cross-linking agents such as glutaraldehyde, cyclodextrin and epichlorohydrin. However cross-linking step might reduce the uptake efficiency of chitosan especially in the case of glutaraldehyde. Reaction of the chitosan amine groups with glutaraldehyde leads to the formation of imine functional groups thereby reducing the number of amine groups. Epichlorohydrin and ethylene glycol can also be used since they react with -OH groups of chitosan,Figure 2.12,therefore they should not affect the residual amine functional groups for binding. The adsorption capacity depends on the extent of cross-linking and generally decreases with increase in the extent of cross-linking.



(1) (2)

Figure 2.12. Schematic representation for the cross-linking reaction of chitosan with epichlorohydrin

Epichlorohydrin is a cross-linking mono-functional agent used to form covalent bonds with the carbon atoms of the hydroxyl groups of chitosan, resulting in the rupturing of the epoxide ring and the removal of a chlorine atom.

Figure 2.12;explain the reaction of chitosan (1) with valuable metals or the treatment of contaminated effluents. Epichlorohydrin in an acidic condition might be cross linked at hydroxyl groups to form the epichlorohydrin cross-linked chitosan product (2), therefore, in the present case, the pHs and molar ratios of epichlorohydrin to chitosan conditions established were appropriated for the cross-linking reaction between chitosan and epichlorohydrin in the homogeneous reaction [66].

2.5.5.3. Interaction Mechanisms

Despite the large number of papers dedicated to the sorption of metal ions, most of them focus on the evaluation of sorption performances and only a few of them aim at gaining a better understanding of sorption mechanisms. However, it is accepted that amine sites are the main reactive groups for metal ions, though hydroxyl groups (especially in the C-3 position) may contribute to sorption. These reactive groups may interact with metal ions through different mechanisms depending on the metal, the pH, and the matrix of the solution. The free electron doublet on nitrogen may bind metal cations at pH close to neutrality (or weak acidity). On the other hand, the protonation of amine groups in acidic solutions gives the polymer a cationic behavior and consequently the potential for attracting metal anions. It is important to observe that the sorption of a metal may involve different mechanisms (chelation versus electrostatic attraction) depending on the composition of the solution, the pH, since these parameters may affect the protonation of the polymer (repulsion of metal cations) and the speciation of metal ions. The chelation of metal cations by ligands in solution may result in the formation of metal anions, which therefore turns the chelation mechanism on chitosan to an electrostatic attraction mechanism on protonated amine groups of the polymer[57].

2.5.5.4. Chelation

The theory of hard and soft acids and bases (HSB), as defined by Pearson, describes the ability of ions to interact or enter into coordinate bonding with other ions or with ligands and shows that this depends on the availability of their outermost electrons and empty molecular orbitals. This must be considered on top of any electrostatic effects due to ion-ion, ion-dipole, and ion-higher multipole interactions. The last type of effect is governed primarily by the charge and size of the ion. The first type of effect can be described by means of the softness parameters and the Lewis acid/base parameters of the ions. The HSAB concept provides a description of the capacities of ions to prefer ligands of the same kind (soft–soft and hard–hard) to those of different kinds when forming coordinative bonds. Softness of ions generally goes hand in hand with their polarizability, and hardness with their electrostatic field strength[57].

Metal chelating agents for the removal of metallic impurities in wastewaters is an excellent application for large-scale use of chitosan. Therefore, much attention hasbeen drawn to this polymer and to the possibilities of modifying it in order to improve its selectivity. Chitosan has been described as a suitable natural polymer for the collection of metals ions, since the amine groups and hydroxyl groups on the chitosan chain can act as chelation sites for metal ions.Cross-linking of chitosan reduces the metal adsorption capacity, it enhances the resistance of chitosan against acid, alkali and chemical. Cross-linking treatment decreases adsorption performances involving a decrease in the number of free amine groups, a decrease in the accessibility to the internal sites or block a number of adsorption sites [8].

2.6. Characterization of Polymeric Adsorbents

2.6.1. Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is one of the most important methods for the identification and characterization of chemical structures. Its greatest use lies in its unique application to the identification of chemical functional groups from vibrational spectra [69].

2.6.2.Scanning Electron Microscope (SEM)

SEM is a very widely used technique to study surface topography. A high energy (typically 10 KeV) electron beam is scanned across the surface. The incident electrons cause low energy secondary electrons to be generated, and some escape from surface. The secondary electrons emitted from the sample are detected by attracting them onto a phosphor screen. This screen will glow and the intensity of the light is measured with a photomultiplier. Some of the incident electrons may strike an atomic nucleus and bounce back into the vacuum. These electrons are known as backscattered primaries and can be detected with a backscattered electron detector. Backscattered electrons can also give information on the surface topography and on the average atomic number of the area under the electron beam. The surface sensitivity of the SEM can be done by raising the voltage on the sample to just below the incident primary beam energy [70].

2.6.3. Elemental Analysis

Elemental analysis on carbon, hydrogen and nitrogen is the most essential - and in many cases the only - investigation performed to characterize and/or prove the elemental composition of an organic sample.

2.6.4. Determination of Surface Area of Polymeric Adsorbents

The determination of specific surface by means of the BET theory is based upon the phenomenon of physical adsorption of gases on the external and internal surfaces of a porous material. The BET (Brunauer, Emmett and Teller) Theory is commonly used to evaluate the gas adsorption data and generate a Specific Surface Area result expressed in units of area per mass of sample (m^2/g).

2.6.5. Optical Atomic Spectrometry

Optical atomic spectrometry involves the monitoring of electronic transitions of gas-phase atoms to perform quantitative determination of elements in samples. The three types of atomic spectrometry are atomic emission, atomic absorption, and atomic fluorescence [71].

2.6.5.1. Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is the measurement of the absorption of optical radiation by atoms in the gaseous state[72]. it is a common technique used in many analytical chemistry protocols, as well applications requiring a high degree of precision and accuracy, such as food & drug safety, clinical diagnostics, and environmental sampling. Atomic absorption spectrometers may be used to analyze the concentration of over 70 different elements in a given sample solution[73], [74], and it is a mature analytical method, which is present in almost any analytical laboratory as a working horse for elemental determinations of metals. Innovation, however, is still going on with respect to the introduction of the sample into the atomizer and the increase of the analyte sampling efficiencies and residence times in the atomizer [75].

Atomic absorption spectrometry relies on the Beer-Lambert law to determine the concentration of a particular analyte in a sample. The absorption spectrum and molar absorbance of the desired sample element are known, and each element will preferentially absorb light at a particular wavelength, due to each element having a defined and discrete quantity of energy required to promote its electron into higher orbital’s (excited state) [73].

Every element has a specific number of electrons associated with its nucleus. The normal and most stable orbital configuration of an atom is known as the "ground state." If energy is applied to an atom, the energy will be absorbed and an outer electron will be promoted to a less stable configuration known as the "excited state." Since this state is unstable, the atom will immediately return to the "ground state," releasing light energy.The process of atomic absorption is illustrated in Figure 2.13.

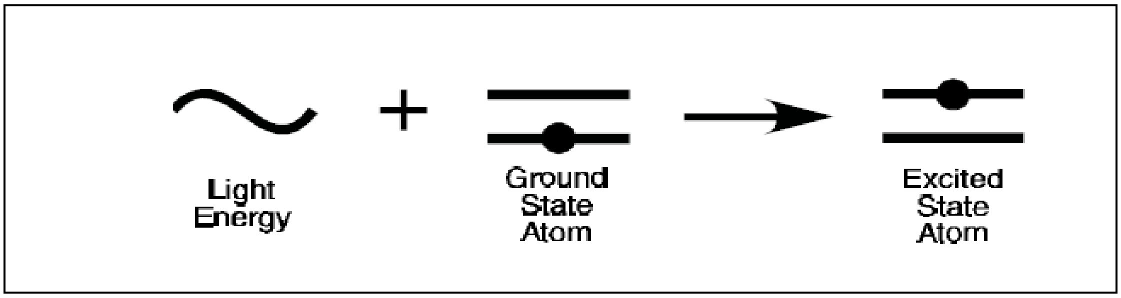


Figure 2.13.Atomic Absorption Process

The "ground state" atom absorbs light energy of a specific wavelength as it enters the "excited state." As the number of atoms in the light path increases, the amount of light absorbed also increases. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte can be made. The use of special light sources and careful selection of wavelengths allow the specific determination of individual elements.

Atomic absorption spectrometry (AAS) incorporates a light source whose beam travels through the atom cell and to a detection system. Neutral gaseous atoms absorb the light, reducing the intensity of the beam. According to Beer’s law, the absorbance is directly proportional to the concentration of atoms in the atom cell.

A standard solution of known concentration of atoms can be used to establish the relationship, usually by performing a standard regression analysis. A typical AAS consists of a primary light source, an atom source, a monochromator, a detector, an electronic system to process the data, and a display system to report the results Figure 2.14; [76].

There are two basic types of atomic absorption instruments: single-beam and double-beam.

- **Single Beam**

A schematic diagram of a single-beam atomic absorption instrument is shown in Figure 2.15.

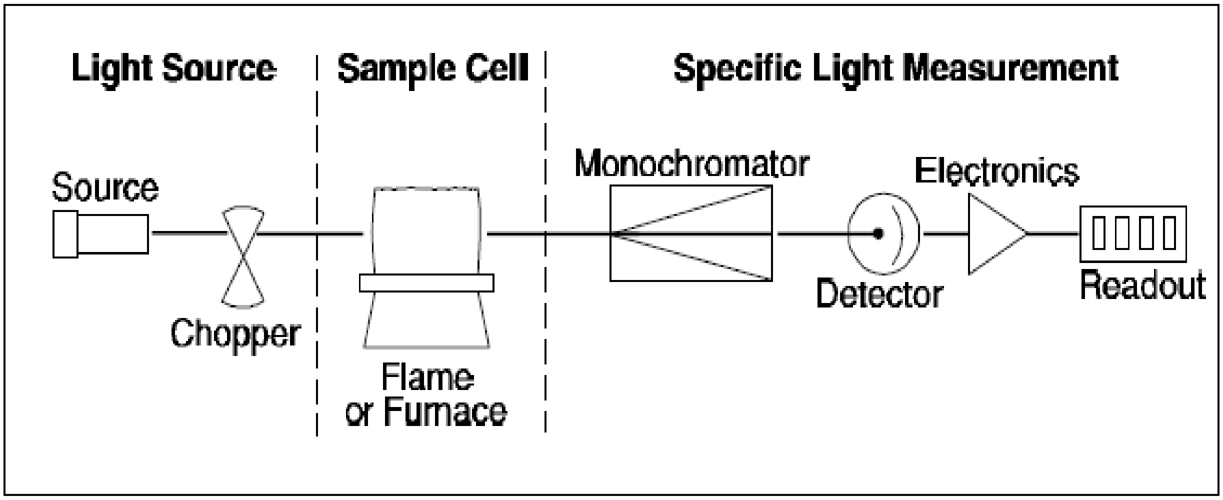


Figure 2.15.Single-Beam Atomic Absorption Spectrometer

In single beam the light source (hollow cathode lamp or electrodeless discharge lamp) emits a spectrum specific to the element of which it is made, which is focused through the sample cell into the monochromator. The light source must be electronically modulated or mechanically chopped to differentiate between the light from the source and the emission from the sample cell. The monochromator disperses the light and the specific wavelength of light isolated passes to the detector, which is usually a photomultiplier tube. An electrical current is produced depending on the light intensity and processed by the instrument electronics. The electronics will measure the amount of light attenuation in the sample cell and convert those readings to the actual sample concentration. With single-beam systems, a short warm-up period is required to allow the source lamp to stabilize.

- **Double Beam**

A schematic diagram of a double-beam system is shown in Figure 2.16.

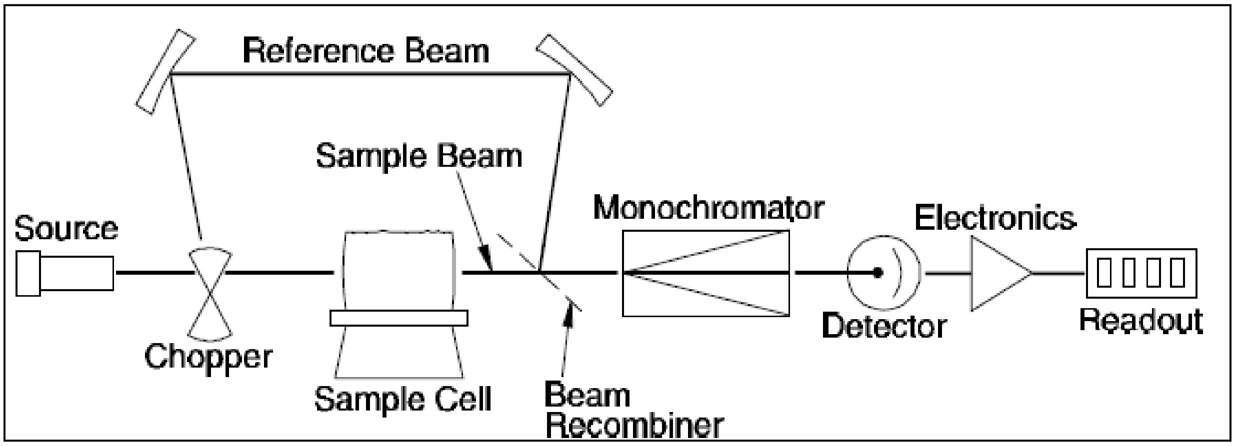


Figure 2.16.Double-Beam Atomic Absorption Spectrometer

The light from the source lamp is divided into a samplebeam, which is focused through the sample cell, and a reference beam, which is directed around the sample cell. In a double-beam system, the readout represents the ratio of the sample and reference beams. Therefore, fluctuations in source intensity do not become fluctuations in instrument readout, and stability is enhanced. Generally, analyses can be performed immediately with no lamp warm-up required.

2.6.5.1.2. Radiation Sources

In AAS the radiation source is a device to generate electromagnetic radiation with given properties; the radiation can be generated for example in a low pressure electrical discharge or in low pressure plasma [77]. Since atoms absorb light at very specific wavelengths, it is necessary to use a narrow-line source which emits the narrow-line spectra of the element of interest. Narrow-line sources provide high intensity and make atomic absorption a specific analytical technique. The main sources used for atomic absorption are the hollow cathode lamp(HCL) and the electrodeless discharge lamp(EDL).

- **Line Sources**

Line source are spectral radiation sources in which the analyte element is volatilized and excited so that it emites its spectrum. Excitation can be caused by a low pressure electrical (glow) discharge, by micro or radio waves, or by thermal energy.

By using line source in AAS it is possible to do without high-resolution monochromators, since concomitant elements cannot in principle absorb radiation from the element-specific radiation source. A prerequisite is elements nevertheless that the analyte must be presentin high spectral purity in the source. If there are several elements in the radiation source spectral interference in the area of the analytical line, caused by more than one line passing the exit slit of the monochromator and falling on the detector, must beavoided [78].

- **Hollow Cathode Lamp(HCL)**

The hollow cathode lamp is an excellent, bright, stable line source for most elements. However, for some volatile elements, EDLs are available. EDLs are typically more intense than hollow cathode lamps and, therefore, may offer better precision and lower detection limits for someelements,Figure 2.17. Shows how a hollow cathode lamp is constructed.

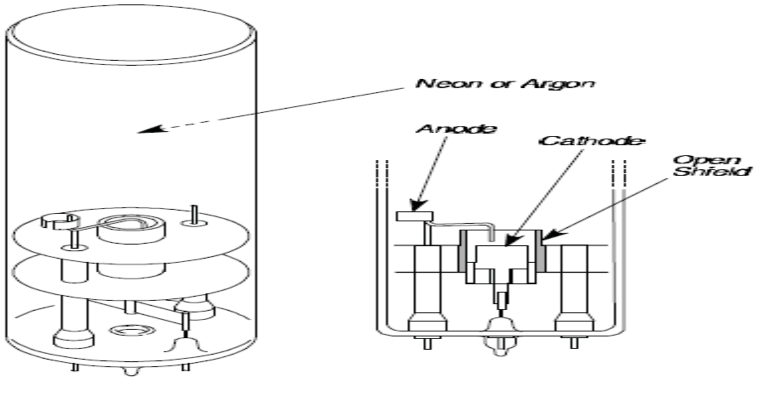


Figure 2.17. Diagram of a Hollow Cathode Lamp

The cathode is a hollowed-out cylinder constructed entirely or in part of the metal whose spectrum is to be produced. The anode and cathode are sealed in a glass cylinder filled with neon or argon at a pressure of about 1 k Pa[88]. The glass cylinder has a quartz or UV glass window for optimum transmittance of the emitted radiation.Cathode containing one or more analyte elements. The anode is mostly made of tungsten or nickel. The optimum fill gas is selected that gives the best lamp intensity while taking into consideration spectral interferences from either neon or argon. A red glow is observed in lamps filled with neon; while argon filled lamps have a blue glow. Hollow cathode lamps are available for more than 60 elements.The hollow cathode emission process is illustrated in Figure 2.18.

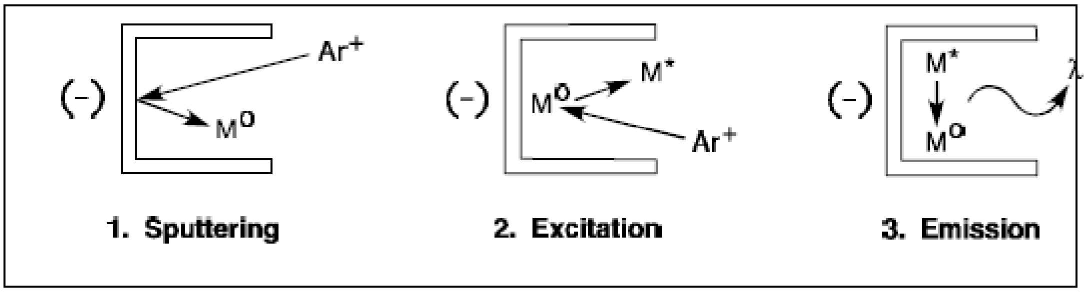


Figure 2.18. Hollow Cathode Lamp Emission Process

An electrical potential is applied between the anode and cathode and some of the fill gas atoms are ionized. The positively charged ions collide with the negatively charged cathode and dislodge metal atoms in a process called "sputtering." Sputtered metal atoms are further excited to emission through impact with the fill gas.

Hollow cathode lamps have a finite lifetime. With extended use, the sputtering process removes some of the metal atoms from the cathode and these are deposited elsewhere. Fill gas is absorbed in the sputtered metal, on the glass walls and also absorbed into the glass from bombardment. Lamps for volatile elements age faster due to more rapid sputtering of the cathode.

- **Multielement Lamps**

The cathode of a hollow cathode lamp is generally constructed from a very pure metal resulting in a very pure emission spectrum. It is, however, possible to construct a cathode from a mixture or alloy of several metals. The resulting "multielement" lamp can be used as a source for all the metals contained in the cathode. There is a wide variety of multielement lamp combinations available. Not all metals can be used in combination due to metallurgical properties or spectral limitations, and with multielement lamps care must be taken to ensure that no spectral interferences caused by overlapping of lines occur in the regions of the analytical lines.While lamps containing combinations of two or three elements can typically be used without problems, lamps with more elements cannot recommended for all applications [78].

- **Electrodeless Discharge Lamps (EDLs)**

For most elements, the hollow cathode lamp is a completely satisfactory source for atomic absorption. In a few cases, however, the quality of the analysis is impaired by limitations of the hollow cathode lamp. The primary cases involve the more volatile elements, where low intensityand short lamp life are a problem. The atomic absorption determination of these elements can often be dramatically improved with the use of brighter, more stable sources such as the "electrodeless discharge lamp" (EDL).

Figure 2.19, shows the design of the electrodeless discharge lamp. A small amount of the metal or salt of the element for which the source is to be used is sealed inside a quartz bulb.

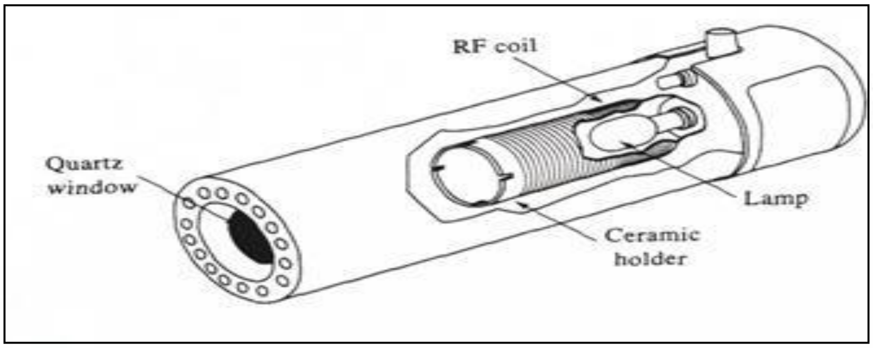


Figure 2.19. Electrodeless Discharge Lamp

This bulb is placed inside a small, self-contained radio frequency coil (RF) generator or"driver." When power is applied to the driver, an RF field is created. The coupled energy will vaporize and excite the atoms inside the bulb, causing them to emit their characteristic spectrum. With most spectrometer models, an accessory power supply is required to operate an EDL.

Electrodeless discharge lamps are typically much more intense and, in some cases, more sensitive than comparable hollow cathode lamps. They therefore offer the analytical advantages of better precision and lower detection limits where an analysis is intensity-limited. In addition to providing superior performance, the useful lifetime of an EDL is typically much greater than that of a hollow cathode lamp for the same element. Electrodeless discharge lamps are available for a wide variety of elements, including most of the volatile metals.

- **Continuum Sources**

In a continuum source the radiation is distributed continuously over a greater wavelength range. In AAS, continuum sources are used mainly for sequential or quasi-simultaneous background measurement and correction. Deuterium lamps and halogen lamps are mostly used for this purpose.The deuterium lamp is a spectral lamp with deuterium as the discharge gas in quartz bulb. For some applications hydrogen has also been used as the discharge gas. The deuterium lamp emits a sufficiently high radiant power in the short wavelength range from about 190 nm to 330 nm[77]. Figure 2.20, shows the design of the deuterium lamp.

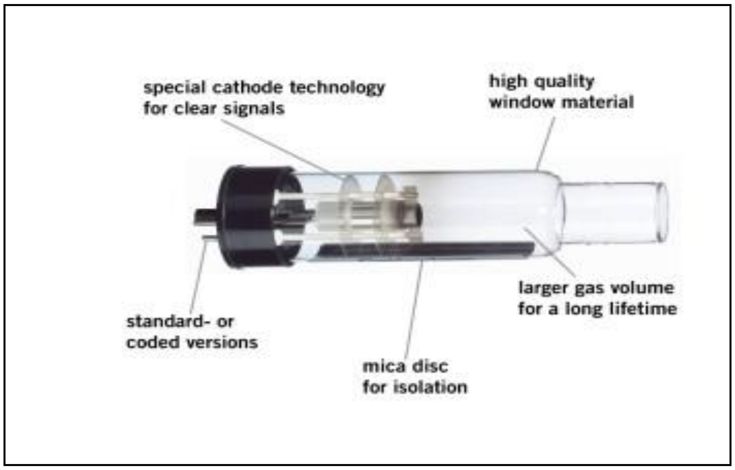


Figure 2.20. Deuterium Lamp

2.6.5.1.3. Atomizers and Atomizer Units

The *atomizer* is the "place"in which the analyte is atomized, i.e. the flame, the graphite tube, or the quartz tube. The *atomizerunit* encompasses, in addition to the atomizer, all assemblies required for operation, for example a burner with nebulizer and gas supply, or a graphite furnace with power supply. The portion of the atomizer through which the measurement radiation beam passes is termed the *absorption volum*e or *observation volume*.

The task of the atomizer unit is to generate as many free atoms in the ground state as possible and to maintain them in the absorption volume for as long as possible. To meet the requirements of the Beer-Lambert law the distribution of the atoms should be as homogeneous as possible in the absorption volume, i.e. over the length and cross-section of the atomizer. The atomization step, i.e. the transfer of the sample, and especially the analyte, into free atoms in the gaseous state, is without doubt the most important process in an analysis by AAS. The success or failure of a determination is dependent on the atomization step. The sensitivity of a determination is directly proportional to the degree of atomization of the analyte and to the residence time of the analyte atoms in the absorption volume. Ultimately, all known non-spectral interferences in AAS are nothing more than influence on the number of analyte atoms generated, either absolute or per time unit, or on their spatial distribution in the atomizer.

The most important criteria for the selection of a suitable atomizer for a given analytical task are the concentration of the analyte in the analytical sample, the amount of sample available, and the state of the sample (solid, or liquid). Furnace techniques exhibit higher sensitivity than flames. A further important criterion is the analyte itself, since atomizers vary considerably in their suitability for atomizing individual analyte as a result of the temperature and chemical environment of various atomizer types[72].

- **Flame Atomization**

The flame technique is the oldest of the AAS techniques. For many years it was theworkhorse"For the determination of secondary and trace elements and also for main constituents and even nowadays it is difficult to imagine a routine analytical laboratory without this technique due to its simplicity and economy.

In flame atomization, either an indeterminate volume or a fixed aliquot of the measurement solution is converted into an aerosol in a nebulizer and transported into the flame. The flame must possess enough energy not only to vaporize but also to atomize the sample. The chemical composition of the flame can have a major influence on these processes. Nowadays two flametypes are used almost exclusively: the air-acetylene or nitrous oxide-acetylene flames.The properties of these two flames, and also two further flame types that are occasionally used, are presented in Table 2.1.

The burning velocities listed in the fourth column of the table are of considerable importance, because flames are stable in certain ranges of flow rates only. If the flow rate does not exceed the burning velocity, the flame propagates itself back into the burner, giving flashback. As the flow rate increases, the flame rises until it reaches a point above the burner where the flow velocity and the burning velocity are equal. This region is where the flame is stable.

Table 2.2. Spectroscopic flames for AAS with their properties.

Oxidant	**Fuel gas**	**Maximum flame temperature(°C)**	**Maximumburning velocity(cm/s)**	**Remarks**
Air	Acetylene	2250	158	Most commonly used flame
Nitrous oxide	Acetylene	2700	160	For difficultly volatilized and atomized substances
Air	Hydrogen	2050	310	Flame of high transparency; for easily ionized elements
Air	Propane/butane	1920	82	For easily ionized elements

- *Nebulizer-Burner System*

Nowadays, premix burners are used almost exclusively in AAS because the laminar flame offers excellent conditions for performing determinations with minimum interference. In system of the type the measurement solution is aspirated by a pneumatic nebulizer and sprayed into a spray chamber. The sample aerosol is mixed thoroughly with the fuel gas and the auxiliary oxidant in the chamber before leaving the burner slot, above which the flame burning. Depending on the burner head, the flame is generally 5cm to 10cm long and a few millimeters wide. Normally the radiation beam passes through the entire length of the flame. The burner head is usually interchangeable to permit the use of various flame types. A typical premix burner is depicted in Figure 2.21.

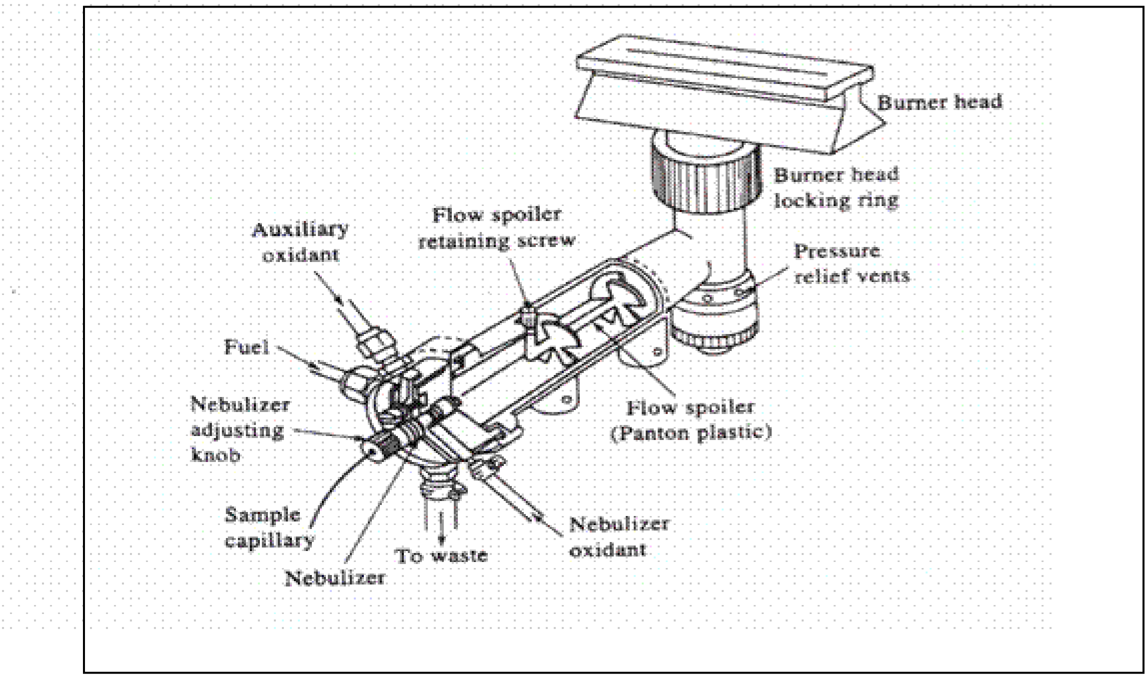


Figure 2.21. Premix burner optionally permitting the use of a flow spoiler or an impact bead.

- **Electrothermal Atomizers**

Furnace is used primarily to atomize solids, slurries, and solutions for atomic absorption. A common design consists of a graphite tube with an inside diameter of a few millimeters

Figure 2.22. Since the furnace tube is heated by passing electrical current through the graphite, the method is also called electrothermal atomization. The furnace can accept a small graphite flat platform inside, an L'vov platform. When an L'vov platform is present, the sample is placed on the platform instead of on the inner surface of the furnace. The platform only touches the furnace sides along its lower edge, so the heat from the furnace walls does not heat the along its lower edge, so the heat from furnace walls dose not heat the sample directly. The sample is heated primarily by radiated heat, which tends to produce more uniform heating.

Different sample require different heating protocols. For example, if the sample is a solution or slurry, the first step is removing the solvent by heating at about 100 °C. Sometimes it is beneficial to heat the furnace to an intermediate, higher temperature to vaporize some of the matrix interferents. This operation is called the char step or pyrolysis step, and, for it to be effective, the analyte should be present in a heat-stable chemical from so none is lost. Subsequently, the temperature is raised as rapidly as possible atomization temperature.

For atomic absorption, graphite furnace allows the sample material to reside in the light path somewhat longer than in a flame. On the other hand, the background tends to be larger, sample material may be lost, and interactions of the analyte and furnace are possible. Various matrix modifiers may be added to sample to suppress theses effects to some degree. The modifiers form complexes with analyte, which raise it vaporization temperature. This helps to retain the material during the char step. The matrix modifiers are specific for given elements [72].

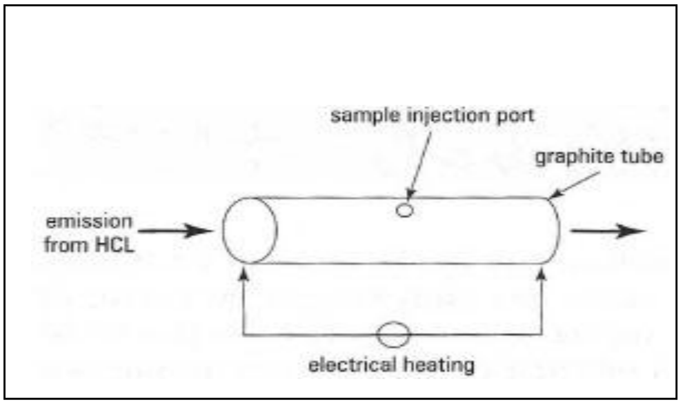


Figure 2.22. Illustration of one kind of graphite furnace

- **Chemical Vaporization**

For chemical vapor generation atomizers and atomizer units used to determine those analytes that can be vaporized in the atomic state or as molecules (e.g. as hydrides or ethyl compounds) by chemical reaction at ambient temperature. These analytes are essentially mercury by Cold Vapor Atomic Absorption Spectrometry (CV-AAS) after reduction with stannous chloride or sodium borohydrideand antimony, arsenic, bismuth, germanium, lead, selenium, tellurium, and tin by Hydride-Generation Atomic Absorption Spectrometry (HG-AAS). For hydride generation, the gaseous hydrides of the metals are chemically produced by the addition of sodium borohydride. The gaseous hydrides and hydrogen produced by the reaction are then swept by an argon purge into a heated quartz cell. The same, or very similar, apparatus is used for both.[78], [73].

Table 2.3. Advantages and disadvantages of both flame and electrothermal atomizers

AAS Atomization Method	Advantages	Disadvantages
Flame	*Faster than furnace methods *Result are highly reproducible	*Handles only liquid samples *Flame is a source of noise *Wastes sample solution *Residence time of atoms in optical path of flame is very small
Graphite Furnace	*Handles smaller sample sizes *Handles solid and liquid samples *High sensitivity *Low amount of noise *Lower detection limits for many elements *Sample solution is not wasted	*Much more time consuming *More severe matrix effects *Low precision *Analytical range is low compared to flame and plasma atomization analysis is usually limited to metals

2.6.5.1.4. Interferences in Atomic Absorption Spectrometry

Atomic absorption is a very specific technique with few interference. The interferences that do exist fall into six categories: chemical interferences, ionization interferences, matrix interferences, emission interferences, spectral interferences, and background absorption. Since the interferences in atomic absorption are well-defined, it is easy to eliminate or compensate for them. The following pages discuss these interferences and how to correct for them.

- **Chemical Interferences**

The most common interferences in atomic absorption are chemical interferences. If the sample being analyzed contains a thermally stable compound with the analyte that is not totally decomposed by the energy of the flame, a chemical interference exists. As a result, the number of atoms in the flame capable of absorbing light is reduced. Chemical interferences can normally be overcomed or controlled in two ways: the use of a higher temperature flame or the addition of areleasing agent to the sample (or standard) solution.

- **Ionization Interferences**

Ionization interferences occur when the flame temperature has enough energy to cause the removal of an electron from the atom, creating an ion. As these electronic rearrangements deplete the number of ground state atoms, atomic absorption is reduced. Ionization interferences can be controlled by the addition of an excess of an easily ionized element to the blank, standards, and samples. Forthis purpose, the alkali metals (K, Na, Rb, and Cs) which have very low ionization potentials are normally used.

- **Matrix Interferences**

Matrix interferences can cause either a suppression or enhancement of the analyte signal. Matrix interferences occur when the physical characteristics (viscosity, burning characteristics, and surface tension) of the sample and standard differ considerably. This can happen when the sample solution contains a high concentration of dissolved salts or acid, when different solvents are used for sample and standard solutions, or when the sample and standard solutions are at radically different temperatures.To compensate for matrix interferences, try to match as closely as possible the matrix components in the sample, standard, and blank. Any reagent added to the samples during preparation should also be added to the standards and the blank. When organic solvents are being used, the standard and sample solutions must be prepared with the same solvent. All solutions should be allowed to come to the same temperature before the determination is begun. When there is no other way to compensate for the matrix interference, the method of additions can be used.

- **Emission Interferences**

At high analyte concentrations, the atomic absorption analysis for highly emissive elements sometimes exhibits poor analytical precision, if the emission signal falls within the spectral bandpass being used. There are several ways to compensate for this interference, including decreasing the slit width, increasing the lamp current, diluting the sample, and using a cooler flame.

- **Spectral Interferences**

A spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the bandwidth of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. When multielement lamps are being used, a combination of elements may exist that will generate the possibility of a spectral interference. The slit width normally used with single-element lamps may be large enough to pass an absorbing wavelength of another element present in a multielement lamp. This can be overcome by using a smaller slit or selecting an alternate wavelength.

- **Background Interferences**

Background absorption is interference in atomic absorption for which the method of additions will not compensate. There are two causes of background absorption: light scattering by particles in the flame and absorption of light by undissociated molecular forms of matrix materials in the flame. To compensate for this problem, the background absorption must be measured and subtracted from the total measured absorption to determine the true atomic absorption component. Fortunately, background absorption can be distinguished from the absorption due tothe element of interest. The element can absorb only the narrow line emitted by the source lamp; background absorption is less specific and extends over a broad wavelength band. The most common way to compensate for background absorption is to use a background corrector, which utilizes a continuum source (deuterium arc lamp in the ultraviolet or a tungsten-iodide lamp for visible wavelengths). A continuum source emits light over a broad spectrum of wavelengths instead of at specific lines. With background correction, simultaneous compensation is obtained at the samewavelength used to measure atomic absorption. With this system, light from the primary source and the continuum source are passed alternately through the flame. The element being determined effectively absorbs light only from the primary source, while background absorption affects both beams equally. Therefore, when the ratio of the two beams is measured electronically, the effect of the background absorption is eliminated and the true atomic absorption signal is obtained.

For flame AA analyses, background correction is most commonly performed using the continuum source technique. Alternate techniques, such as Zeeman Effect background correction, are also commonly employed for graphite furnace AA analyses.

2.6.5.1.5. Optics

The spectral range of interest for atomic absorption spectrometry begins in the near infrared at 852.1 nm, the wavelength of cesium, and reaches down into the vacuum UV below 200 nm. At the present time, the instrumental limit for a non-flushed instrument and using a flame is 193.7 nm, the wavelength of arsenic.

Atomic absorption spectrometry therefore covers much the same wavelength range that is of interest for atomic emission spectrometry or UV/VIS spectrometry. In principle it should then be possible to employ proven monochromators in atomic absorption. However, it has been shown that the requirements in AAS with respect to resolution and dispersion of the monochromator are different from those of other techniques. One of the greatest

3. Experimental

3.1.Preparation of chitosan and cross-linked chitosan beads

3.1.1. Materials

Chitosan was purchased from Boao Bio-Technology Company, Shanghai (China). Epichlorohydrin (ECH) was purchased from Tianjin no.1 Chemical Reagent Factory (China).

3.1.2. Preparation methods

3.1.2.1. Preparation of chitosan beads

Chitosan beads were prepared as described. Simply, 3.0 g chitosan (deacetylation degree is 90%, average molecular weight 503,495) was dissolved in 100 mL, 2 %(v/v) acetic acid. The solution was dropped through needle into 2M sodium hydroxide solution, and the gelled spheres formed instantaneously. The formed chitosan beads remained in sodium hydroxide for 24 hand was washed with distilled water and stored in distilled water for use.

3.1.2.2. Preparation of cross-linked chitosan beads by epichlorohydrin

The wet non-cross-linked beads were put into a flask with 100mL sodium hydroxide solution (pH 10), some amount of cross-linking agent, epichlorohydrin was added and stirred at 60°C for 6 h. (Figure 3.1), The cross-linked chitosan beads were then washed extensively with distilled water to remove any unreacted epichlorohydrin,and stored in distilled water for use [79].

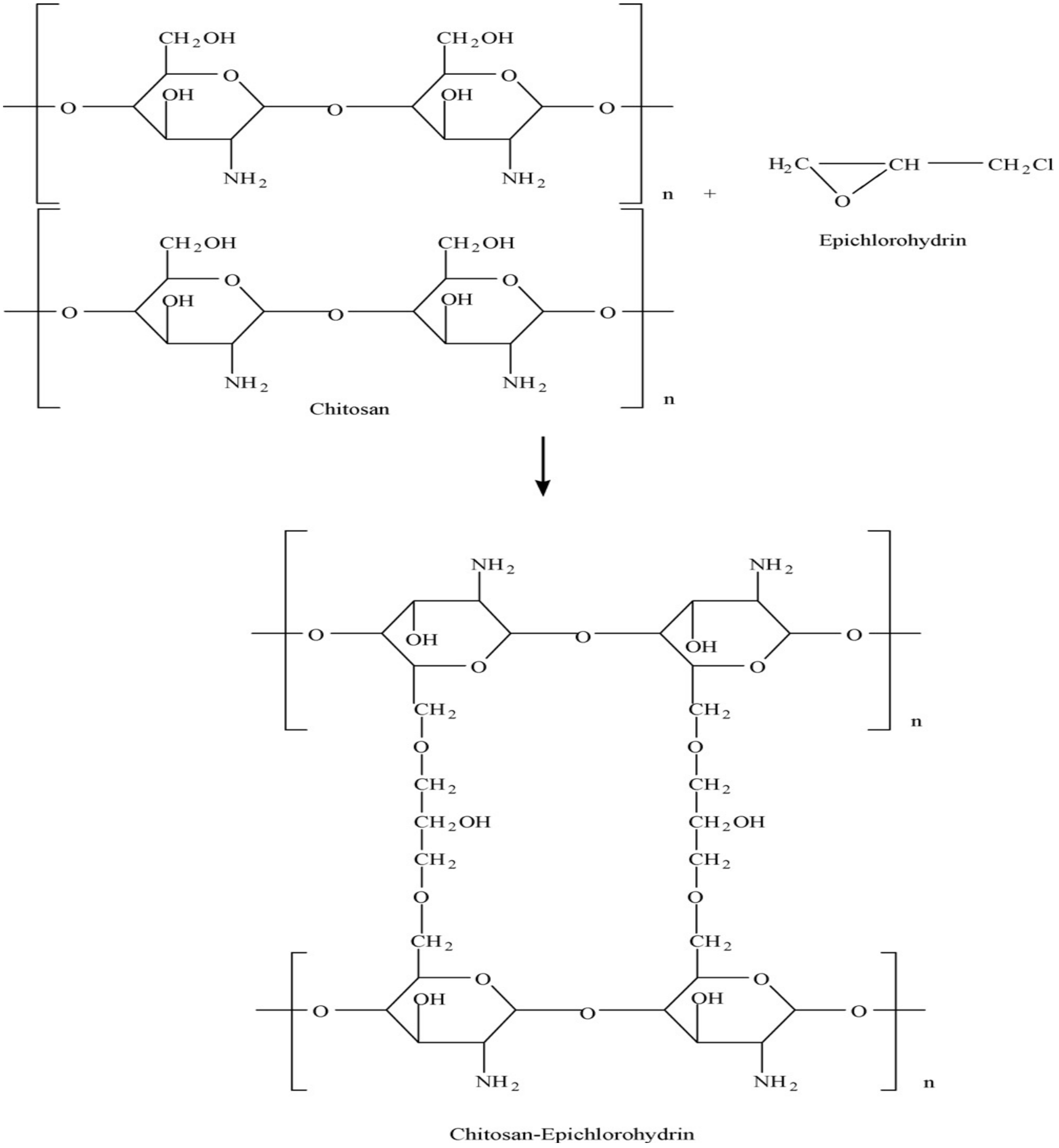


Figure 3.1: Schemmatic representation of chitosan cross-linked by epichlorohydrin [80].

3.2. Characterization of chitosan and cross-linked chitosan

3.2.1. Swelling studies

Chitosan and cross-linked chitosan beads were tested with regard to their solubility in5% (v/v) acetic acid, distilled water and 0.10 M sodium hydroxide solution by adding 0.10 g of chitosan and cross-linked chitosan beads into these solutions for a period of 24 h with stirring.

The swelling studies of chitosan and cross-linked chitosan beads were carried out in distilled water at room temperature for a period of 24 h. The percentage of swelling ratio of these beads was calculated by using the following equation:

$$\text{Percentage of swelling } \% = \frac{W_S - W}{W} \times 100 \text{ ……………………..….} 3.1$$

Where$W_S$is the weight of swollen beads (g) and W is the weight of dry beads (g).

3.2.2. Elemental analysis

Percentage of Carbon, Nitrogen, and Hydrogenin chitosan and cross-linked chitosan with epichlorohydrin beads were obtained by FLASH 2000 Series, Organic Elemental Analyzer, (CHNS/O Analyzer), Thermo Scientific, USA.

3.2.3. Surface morphology

The surface morphology of the chitosan and crosslinked chitosan beads was examined using scanning electron microscopy (SEM), (JEOL, JEM 1200 EX; Tokyo, Japan).The samples were initailly dried in oven at 55 °C for 48 hours before being analyzed. The surface of the sample was then scanned at the desired magnification to study the morphology of the beads.

3.2.4.Measurement of surface area

The surface area of the chitosan and cross-linked chitosan was measured by Quadrasorb SI (Surface Area Analyzer and Pore Size Analyzer from Quantachrome Instruments, USA).

3.2.5. FTIR studies

FTIR spectra of chitosan and cross-linked chitosan beads were obtained by using a FTIRspectrophotometer(model: Thermo, Nicolet iS10, USA). The dry samples (about 0.1 g) was thoroughly mixed with KBr (0.1g, IRGrade, Merk, Germany), and pressed into a pellet form and the FTIR spectrum was then recorded.

3.3. Adsorption studies of heavy metal ions by chitosan and cross-linked chitosan

3.3.1. Reagents and apparatus

All chemicals were of analytical-reagent grade. Standard solutions of 1000mg/L Cu(II) were prepared from Cu $(NO_3)_2.3H_2O$salt in deionized water, standard solutions of 1000mg/L Hg(II) solution was prepared from $HgCl_2$ salt, As(III) solution was prepared from As_2O_3 salt in deionized water and As(V) solution was prepared from $NaSO_2$. From these solutions, other dilute standard solutions were prepared daily. Otherchemicals were analytical grade and used as received. Deionized water of 18.1 MΩ/cm resistivity was obtained from a Banstead, Nanopure Diamond Purification System. Neo Met, Istek, Inc, Model 240 L pH meter was also usedto measure pH values. Thermo Electron LED, GmbH magnetic stirrer was used for stirring the ionic solutionswith polymers.The concentration of Cu(II), Hg(II),As(III) and As(V) ions were measured by Atomic Absorption Spectrophotometer (AAS, Perkin Elmer AAnalyst 800) equipped with a deuterium lamp correction. The working conditions were given in Table 3.1

Table 3.1. The working conditions for determination of Cu(II), Hg(II), As(III)and As(V) in Flame Atomic Absorption Spectrophotometer

Element	Wavelength (nm)	Bandwidth (nm)	Lamp current (mA)	Flame composition(L / min)	
				Acetylene	Air
Cu(II)	324.8	0.7 H	15 (HCL)	2.2	17.0
Hg(II)	253.7	0.7 H	185(EDL)	2.2	17.0
As(III)	193.7	0.7 H	385(EDL)	2.2	17.0
As(V)	193.7	0.7 H	385(EDL)	2.2	17.0

3.3.2. Adsorption studies

Adsorption of Cu(II), Hg(II), As(III)and As(V)metal ions from aqueous solutions were studied in batch systems. Aqueous solutions (50 mL) containing different amount of metal ions (2.5 – 500 mg/L), were incubated with (0.1-2g) chitosan and chitosan cross-linked with epichlorohydrin. Samples with different pH values (in the range 4.5 – 9),adjested useconjugate acid/ base buffer solutions at room temperature were mixed with beads and stirred magnetically at speed of (300 -1000 rpm). The effect of contact time (5–420 min), were also examined. The amount of metal ions removal was calculated from the difference between metal ions taken by the chitosan beads and that remained in the solution. The amount of adsorption per unit mass of the sorbent was calculated by using the following expression:

$$Q\ \ mg\ \ g\ = \frac{(C_0-C)V}{m} \text{……………………………………..(3.2)}$$

where Q is the amount of metal ion adsorbed onto unit mass of the polymer(mg/g); C_o and C are the initial and final concentrations after treatment for certain period of time, respectively (mg/L); V is the volume of aqueous solution (L); and m is the mass of adsorbentused (g).The removal percentage(RP %), were calculated according to following equation:

$$RP\ \% = \frac{(C_0 - C)\times 100}{C_0} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3.3)$$

C_o and C are the initial and final concentrations, respectively (mg/L)[81].

3.3.3.Studies of adsorption isotherm

Adsorption isotherms of metal ions adsorbend into chitosan and cross-linked chitosan were determined for Cu(II), Hg(II), As(III) and As(V) metal ions in aqueous solutions. 0.25g of the polymeric beads were stirred in 50mL of metal ion solutions (concentration between 2.5 to 500 mg/L) at several time intervals (5 to 420 min). Adsorption data at a pH ranged from 5 to 7 were modelled using Langmuir and Freundlich isotherms.

3.4. Selectivity Experiments

In order to show the behavior of chitosan and cross-linked chitosan, competitive adsorption were also studied. The competitive adsorption experiments were carried out with 5 mg/L aqueous solution of Cu(II), and 50 mg/L aqueous solutions of Hg(II), As(III), and As(V) ions and the mixure of these ions in the similar manner as described previously. Experiments were performed at a constant pH =5.5, with 0.25 g sorbent for 120 min at 700 rpm and the concentration of these metal ions weredetermined by using AAS.

4. RESULTS AND DISCUSSIONS

4.1. Characterization of chitosan and cross-linked chitosan

4.1.1. Swelling studies

Solubility of chitosan is associated with molecular weight, degree of deacetylation andionic composition of the solutions. It was shown inTable 4.1;the cross-linked chitosan was found to be insoluble in acidic and alkaline medium as well as distilled water. It is well known that the high hydrophilicity of chitosan beads or raw chitosan due to a primary amine group makes chitosan easily soluble in dilute acetic or formic acid solutions to yield a hydrogel in water. A convenient proof of cross-linking is the swelling behaviour of the cross-linked chitosan beads in dilute acetic acid. Thus, cross-linking treatment should be necessary to reinforce the chemical stability of the beads in such acidic solution. Meanwhile, the less swelling behaviour of cross-linked chitosan beads was important so they can be used in an adsorption column. The percentage of swelling of chitosan and cross-linked chitosan beads are given in Table 4.2.

Table 4.1. Solubility effect of chitosan and crosslinked chitosan beads.

Beads	**Solubility effect**		
	5% (v/v) Acetic acid	**Distilled water**	**0.10 M NaOH**
Chitosan	Soluble	Insoluble	Insoluble
Cross-linked chitosan	Insoluble	Insoluble	Insoluble

Table 4.2. Swelling behaviour of chitosan and crosslinked chitosan beads

Beads	Swelling (%) by distilled water
Chitosan	22.69
Cross-linked chitosan	20.25

4.1.2. Elemental analysis

Table 4.3. Shows the elemental analysis results of the chitosan and crosslinked chitosan beads

Beads	C%	N%	H%
Chitosan	41.05	7.16	6.60
Cross-linked chitosan	39.27	5.38	6.36

The percentage of C, N and H in chitosan was also studied and obtained 39.43%, 8.41%, and 7.30% respectively.The percentage ofC, N and H in cross-linked chitosan by epichlorohydrin 29%, 7.44%, and 4.78% respectively.

4.1.3. Surface morphology

The morphology of chitosan and cross-linked chitosan are given in Figures 4.2, and 4.3.It can be seen that the chitosan surface has a membrane aspect and does not present porosity, which indicates that it is likely not to have diffusion problems and thus the sorption process could be fast [82].The surface of cross-linked chitosan with epichlorohydrin was noted to have much asperity and to be more coarsely grained.

4.1.4. Measurement of the surface area

Measurement of the polymers surface area a very important paramater, the surface area of chitosan and crosslinked chitosanbeads was determined byN sorption isotherm in a BETapparatus and application of the BET theory (Table 4.4).

Table 4.4. Measurement of the surface area of the chitosan and crosslinked chitosan beads.

Beads	**Surface area (BET)^a (m^2/g)**
Chitosan	1.15
Cross-linked chitosan	0.55

4.1.5. FTIR studies

FTIR results are given in Figure 4.1.

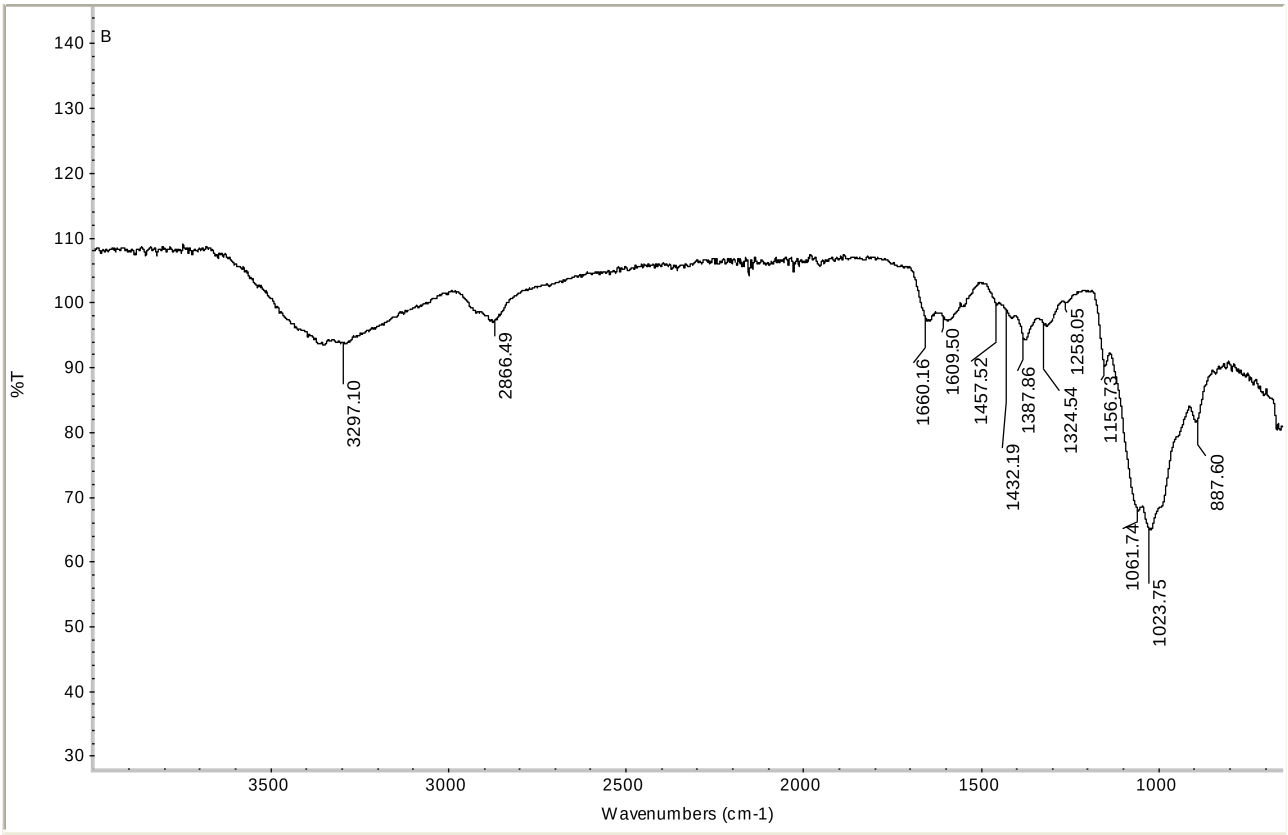
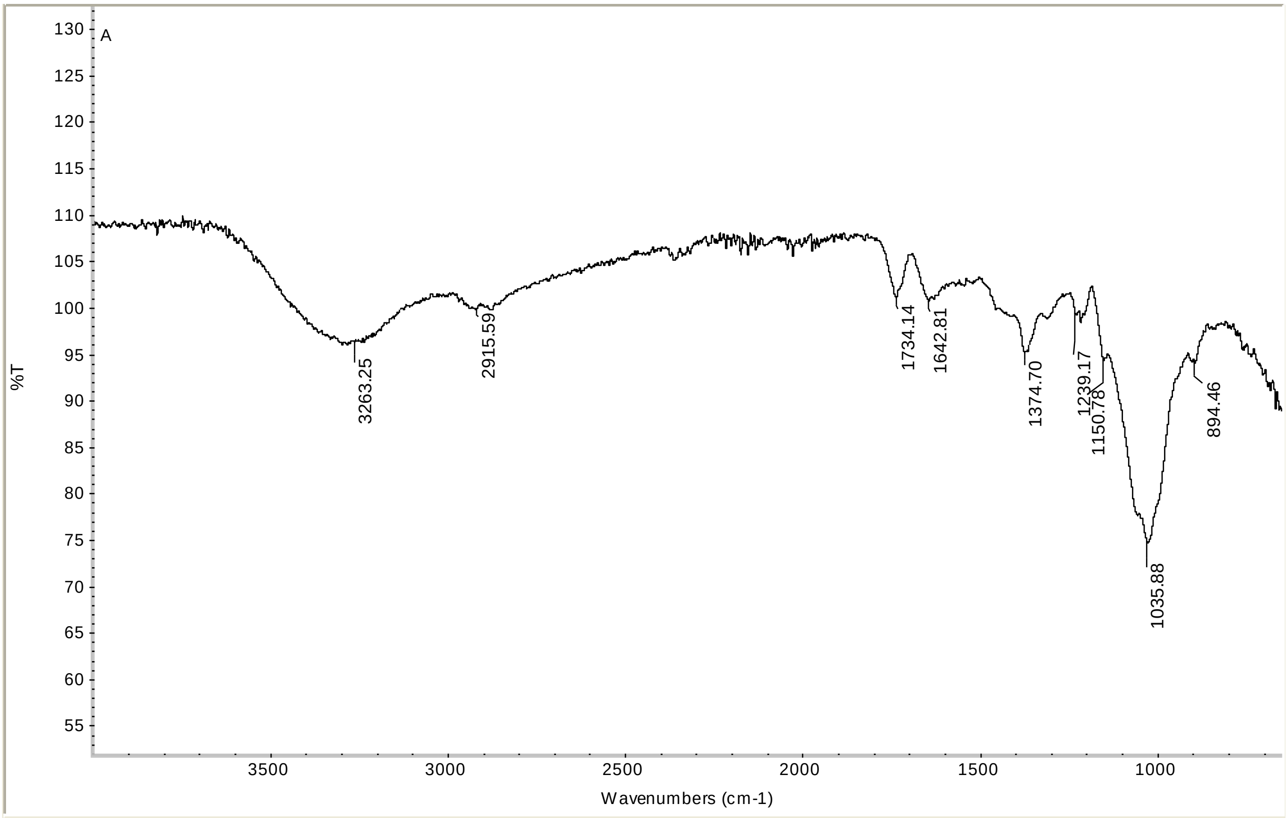


Figure 4.1.(a). FT-IR spectra ofChitosan



(b) FT-IR spectra of Cross-linked chitosan by epichlorohydrin.

The FTIR Spectra of chitosan and cross-linked chitosan are shown in Figure 4.1. A broad band in 3000-3500 cm^{-1}, which was stretching vibrations of N-H and O-H.

The absorption of aliphatic C-H shift from 2866 cm^{-1} (Chitosan) to 2915 cm^{-1}(crosslinked chitosan), absorption at 1734 cm^{-1} that means polymeric strucure has either carbonyl group C=O or you have C=N. The bands at 1156 cm^{-1}represent a symmetric stretching of C-O-C birdge. 1061.74 cm^{-1} and 1023.75 cm^{-1} showsskeletal vibrations involving C-O stretching. The peak around 894.46 cm^{-1} to1150.78 cm^{-1} assigned saccharine structure. A band at 1642.81 cm^{-1} was characterized asamide absorption. The absorption bands at 1258.05 and 1061.74cm^{-1} can be attributed from the hydroxyl groups of chitosan.

C_3position) may contribute to sorption. Most studies of the chelation mechanism have been focused on the adsorption of copper.

Copper adsorption on chitosan and cross-linked chitosan has been investigated by a number of research groups. Wan and colleagues investigated Cu(II) ion adsorption capacity of chitosan immobilizedon sand as compared to chitosan or sand used alone [6].According to Fangqiang Xuet althe maximum adsorptioncapacity of Cu(II) by chitosan was 176 mg/g [84]

Different adsorption capacities for Cu(II) onto chitosan were reported depending on the raw material: crab shells (20.8 mg/g), shrimp shells (123.1 mg/g) and prawn shells (33.4 mg/g); on the chemical modification: chitosan–Ca–alginate (50.4 mg/g), chitosan–PVA (47.8 mg/g), chitosan/ECH cross-linked (35.5 mg/g) and chitosancoated with alumina (86.2 mg/g); and on the particle size: 2.84 mg/g (250–355 μm), 2.60 mg/g (355–500 μm) and 1.81 mg/g (710–1000 μm). Furthermore, the rate of metallic ion sorptiononto chitosan depends on the raw material (shrimp, crab or lobstershells), on the preparation method and on chemical and physicalmodifications[85].

This study compared the adsorption behaviour of Cu(II) on chitosan without cross-linking and the crosslinked chitosan with epichlorohydrin, identifying which groups are responsible for the metal-chitosan interaction. The study also investigated the effect of key paramers, such as pH, Cu(II) ion concentration, etc [86].

Rhazi et al. 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 ($[Cu(–NH_2)]^{+2}$, $2OH^-$, H_2O) is suggested; whereas at pH>5.8, the complex ($[Cu(–NH_2)_2]^{+2}$, $2OH^-$) is considered (Figure 4.9) [57].

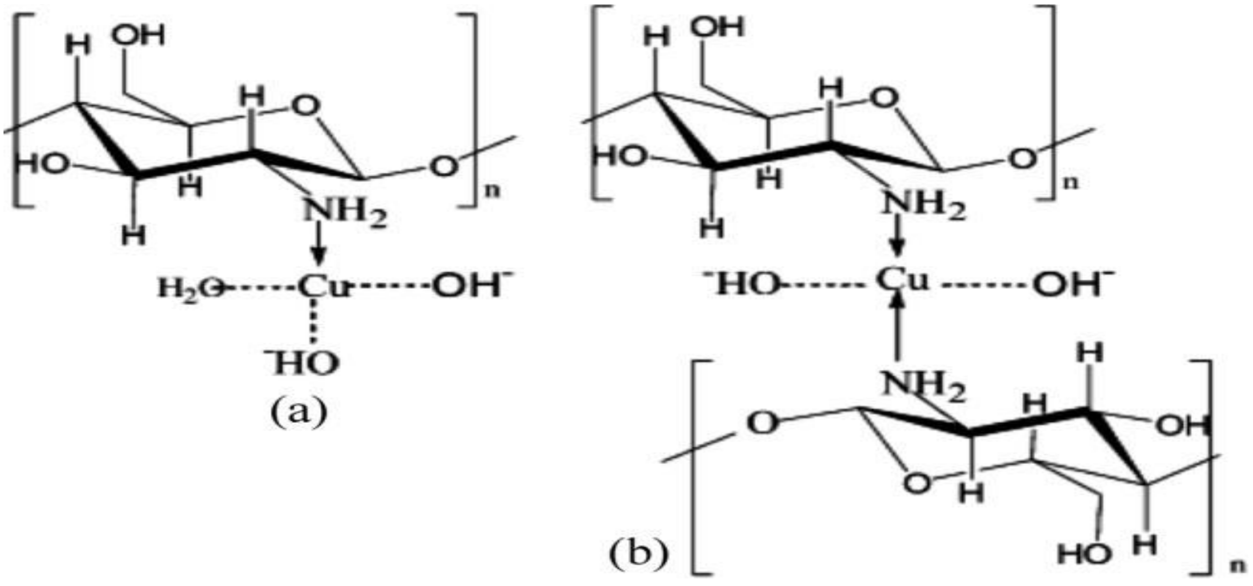


Figure4.9.Proposed structures of Cu-Chitosan complex (a) at pH between 5.3 - 5.8 and (b) at pH>5.8.

The maximum adsorption capacity for Cu(II) obtained in this study is given in Table 4.5.

Table 4.5. Cu(II) adsorption parameters from studies with chitosan without crosslinking and crosslinked chitosan by epichlorohydrin.

Sorbent	Initial conc.(mg/L)	Final conc. (mg/L)	RP %	Q_{max}(mg/g)	Q_{max}(mmol/g)
Chitosan	500	455	8.8	204	3.21
Cross-linked chitosan	500	471	5.8	128	2.02

From all these parameters, and the above results in Table 4.5 and the results in Figure(4.4-4.8), it was suggested that metal binding capacity of chitosan was markedly decreased by the presence of cross-linking agent.

The maximum capacity of the chitosan without cross-linking for Cu(II) ion it is 204mg/g, (3.21 mmol/g)and on the cross linked chitosan around 128mg/g (2.02 mmol/g).

indicate that the efficiency of adsorption of Hg(II) by chitosan depends upon the period of treatment, the particle size, initial concentration of Hg(II) and quantity of chitosan [65].
This study compared the adsorption behaviour of Hg(II) on chitason without crosslinking and the cross-linked chitosan with epichlorohydrin, identifying which groups are responsible for the metal-chitosan interaction. The study also investigated the effect of key parameters, such as pH, Hg(II) ion concentration, etc. The results were listed in Table 4.6.

Table 4.6. Hg(II) adsorption parameters from studies with chitosan and cross-linked chitosan

Sorbent	**Initial conc.(mg/L)**	**Final conc.(mg/L)**	**RP %**	**Q_{max}(mg/g)**	**Q_{max} (mmol/g)**
Chitosan	500	378	24.22	550	2.74
Cross-linked chitosan	500	481	3.74	84	0.42

From all these parameters,and the above results in Table 4.1 and the results in Figure.(4.10- 4.14), it was suggested that metal binding capacity of chitosan was markedly decreased by the presence of cross-linking agent.

A few studies for treatment and removing of this heavy metal ion by chitosan.In this study, the maximum capacity of the chitosan without cross-linking for Hg (II) ion it is550mg/g, (2.74 mmol/g),and on the cross linked chitosan around84 mg/g.(0.42 mmol/g).
In other studies maximum adsorption capacity of chitosan for Hg (II) was obtained about 815 mg/g and123.8 mg/g chitosan at pH 6, respectively. Choong and Wolfgag [87] have studied mercury removal by chitosan derivative, maximum removing capacity was 2.3 mmol/ g at pH 7 for chitosan beads which has reacted with ethylendiamine. But the effect of several parameters such as pH and particle size of adsorbent on the adsorption of Hg to chitosan system has not been considered [87, 88].According to P. Miretzkya, A. Fernandez Cirelli, the cross-linking may reduce the adsorption capacity as it diminishes the quantities of free amino groups, but this loss of capacity may be necessary to ensure stability of the polymer [38].

Table 4.7. As(III) adsorption parameters from studies with chitosan without crosslinking and crosslinked chitosan by epichlorohydrin(ECH)

Sorbent	Initial conc.(mg/L)	Final conc.(mg/L)	RP %	Q_{max}(mg/g)	Q_{max} (mmol/g)
Chitosan	500	478	4.40	100	1.33
Cross-linked chitosan	500	488	2.21	50	0.66

From all these parameters, and the above results in table 4.7 and the results in Figures(4.15- 4.19), it was suggested that metal binding capacity of chitosan was markedly decreased by the presence of cross-linking agent.

The maximum capacity of the chitosan without cross-linking for As(III) ion it is 100mg/g, (1.33 mmol/g) and on the cross-linked chitosan around 50mg/g, (0.66 mmol/g).

- **Adsorption capacity of As(V) ion**

This study compared the adsorption behaviour of As(V) on chitosan and the cross-linked chitosan with epichlorohydrin, identifying which groups are responsible for the metal-chitosan interaction. The study also investigated the effect of key parameters, such as pH, As(V) ion concentration, etc. For comparing the As(V) adsorbility between, medium cation concentration solutions (about 50 mg/L), were prepared to obtain the removal percentage and adsorption capacity for each absorbent. The results were listed in Table 4.8.

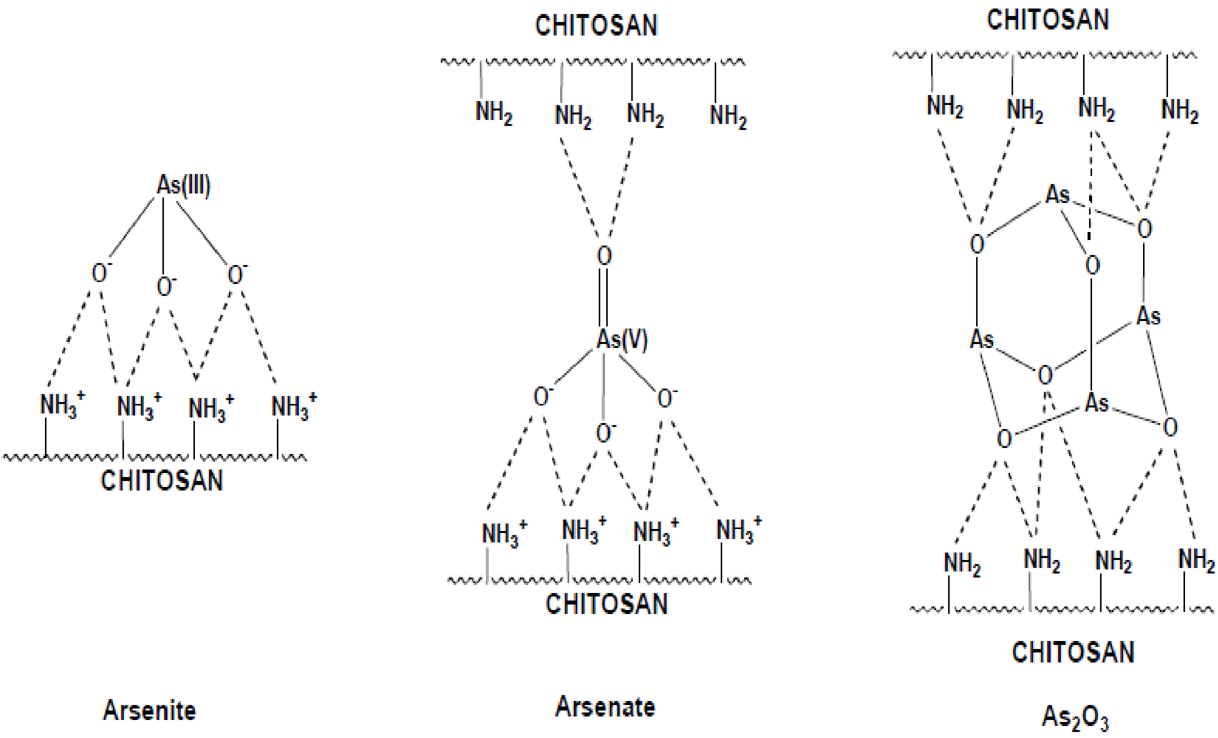
Table 4.8. As (V) adsorption parameters from studies with chitosan and cross-linked chitosan by epichlorohydrin.

Sorbent	**Initial conc.(mg/L)**	**Final conc.(mg/L)**	**RP %**	**Q_{max}(mg/g)**	**Q_{max} (mmol/g)**
Chitosan	500	455	8.90	200	2.69
Cross-linked chitosan	500	460	8.00	181	2.42

From all these parameters, and the above results in Table 4.8 and the results in Figures (4.20- 4.24), it was suggested that metal binding capacity of chitosan was markedly decreased by the presence of cross linking agent.

The maximum capacity of the chitosan for As(V) ion it is 200mg/g, (2.69 mmol/g), and on the cross-linked chitosan around 181mg/g, (2.42 mmol/g).
It is generally believed that electrostatic interactions, metal chelation and ion pairs formations are the three main mechanisms hypothesized to occur when a metal is adsorbed by chitosan. Surface adsorption, chemi- and physisorption, diffusion and adsorption-complexation mechanisms may also occur, as a consequence of ion-exchange, hydrogen bonds, hydrophobic and Van der Waals interactions. The occurrence of interactions between chitosan and anionic molecules (dyes) was studied by thermodynamic methods

recognizing that chemisorption (ion-exchange, electrostatic attractions) is the most prevalent mechanism with the pH as the main factor affecting adsorption.



Arsenite

Arsenate

As_2O_3

Figure 4.25**.** A model of interaction between chitosan and As(III) (arsenite), As(V) (arsenate) species and (arsenic oxide)As_2O_3.

We hypothesized a model of interaction between chitosan and As(III) (arsenite)/As(V) (arsenate) species or arsenic oxide As_2O_3 that we have presented in Figure 4.25. The arsenite anion may preferentially form electrostatic interactions with protonated chitosan amino groups. Arsenate may instead interact with the polymer through electrostatic interactions and hydrogen bonds. For what concerns the arsenic oxide As_2O_3, the interaction might occur mainly through hydrogen bonds[89].

Cross-linked materials possess several characteristics,properties and advantages.Homogeneous cross-linked materials are easy toprepare with relatively inexpensive reagents andare available in a variety of structures with avariety of properties, and also in numerousconfigurations, e.g. gels, particles of irregularshape or regular beads, membranes, coatings,films, fibers, capsules and sponges.They are insoluble in acidic and alkaline mediumsas well as organic solvents. Cross-linked gels arevery stable hydrophilic polymers. They becomemore resistant to shear, high temperature and lowpH compared to their parent polysaccharide.After cross-linking, they maintain their properties,original characteristics (except the cristallinity)and strength in acidic and basic solutions. Thesecharacteristics are important for an adsorbent sothat it can be used in a lower pH environment.Furthermore, the swelling behavior of the beads inwastewater can be optimized.Cross-linking reduces the amount of the crystallinedomains in the polysaccharide and can then changethe crystalline nature of the raw polymer. Thisparameter significantly influences the sorptionproperties because it may control the accessibilityto sorption sites.Cross-linked beads also have other advantages such as faster kinetics, increased ease of operationand interesting diffusion properties. Due to the hydrophilic nature of their crosslinking units,materials possess a remarkably high swelling capacity in water, and consequently their networksare sufficiently expanded as to allow a fastdiffusion process for the pollutant [17].

The stability, mobility and accessibility of thepolysaccharide. Although cross-linking enhancesthe resistance of polysaccharide against acid, alkaliand chemicals it involves a loss in the chainflexibility, a reduction of the mobility ofchelating groups and their accessibility, and as aresult causes a significant decrease in pollutantuptake efficiency and adsorption capacities of theadsorbent. However, this loss of capacity may benecessary to ensure the stability of material.[17].

4.3. Evaluation of sorption performance

Evaluation of sorption performance and the usability of a specified sorbent for the treatment of metal-bearing solutions must take into account the following parameters: sorption isotherms, uptake kinetics, uptake selectivity (and effect of competitor ions) and finally the possibility of desorbing the metals for recovery and the recycling of the sorbent.

Chitosanis non-toxic, hydrophilic, biocompatible, biodegradableand anti-bacterial, which has led to a diverse range ofapplications in the biomedical field and in cosmetic, foodand textile industries. Chitosanappears to be more useful as compared to chitin, since ithas a large number amine and hydroxyl groups that canserve as chelating sites and can be chemically modified[90].

Some of the amine sites are sometimes involved in some kind of inter- and intra-molecular bonds. The crystallinity of the polymer may make some groups inaccessible to the metal ions.Another important parameter is the chain length or the degree of polymerization.Also the degree of mixing of the metal-chitosan complex and the physical state of the chitosan affected the capacity of chitosan.Chitosan solubility has been widely investigated. It is an important property which can be controlled by polymer weight, type and concentration of the acid used for dissolving the polymer and the presence of metal ions in the solution. Polymer and the presence of metal ions in the solution, can bind to the polymer and affect its solubility. Chitosan was found to be soluble in nearly all monovalent and multivalent acids. Chitosan is soluble in formic, acetic, citric, pyruvic and lactic acids. It does not dissolve in other organic acids.

4.3.1. Adsorption isotherms

4.3.1.1. Langmuir adsorption model

An adsorption isotherm is used to characterize the interactions of each molecule with the adsorbents. This provides a relationship between the concentration of the molecules in the solution and the amount of metal ions adsorbed on the solid phase when the two phases are at equilibrium. The Langmuir adsorption model assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which is capable of holding only one molecule. These sites are also assumed to be energetically equivalent and distant from each other so that there are no interactions between molecules adsorbed on adjacent sites.

During the batch exeriments, adsorption isotherms were used to evaluate adsorption properties. The Langmuir adsorption isotherm is expressed by Eq 4.1. The corresponding transformations of the equilibirium data for metal ions molecules gave rise to a linear plot, indicating that the Langmuir model could be applied in these systems and described by the equation [91-93]:

$$Q = Q_{max} b \,.\, Ceq / (1+bCeq) \quad \text{………………………………………………………...…} \quad (4.1)$$

4.3.1.2.Freundlich isotherm model:

The other well-known isotherm, which is frequently used to describe adsorption behavior, is Freundlich isotherm. This isotherm is another form of the Langmuir approach for adsorption on a heterogeneous surface. The amount of adsorbed molecule is the summation of adsorption on all binding sites. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer. This empirical equation takes the form:

$Q_{eq} = K_F(C_{eq})^n$……………………………………………………………………………. (4.3)

Where, $K_F$and n are the Freundlich constants. This equation can be linearized so that

$LnQ_{eq} = lnK_F + (n.\ lnC_{eq})$……………………………………………………………….. (4.4)

The plot of ln Q_{eq} versus ln C_{eq} was employed to generate the intercept of ln K_F and the slope of n (Figure 4.28, 4.29, 4.30, and 4.31).

The adsorption isothmers of metal ions chitosan and cross-linked chitosan were found to be linear over the whole concentration range studies and correlation coefficients [91-96].

Table 4.10. Langmuir and Freundlich adsorption isotherm constants for metal ions adsorbed by chitosan cross-linked by epichlorohydrin beads.

		Langmuir constants			**Freundlich constants**		
Metal ion	**Q_{exp} (mg/g)**	**Q_{max}**	**b (L/mg)**	**R^2**	**K_F**	**1/n**	**R^2**
Cu(II)	128	166	0.012	0.958	2.768	0.704	0.905
Hg(II)	84	111	0.012	0926	1.735	0.860	0.743
As(III)	50	62	0.011	0.951	1.677	0.600	0.792
As(V)	181	250	4.78×10^{-3}	0.87	5.129	0.575	0.941

Equilibrium data, commonly known as adsorptionisotherms, are the basic requirements for the designof adsorption systems. Obtaining equilibrium data fora specific adsorbate/adsorbent system can be performedexperimentally, with a time-consuming procedurethat is incompatible with the growing need foradsorption systems design. Analysis of equilibriumdata is important for developing an equation that canbe used to compare different adsorbents under differentoperational conditions and to design and optimizean operating procedure.Various adsorption isothermmodels, such as the Langmuir and Freundlichmodels, have commonly been used to predict theadsorption efficiency and potential of an adsorbent.Therefore, semireciprocal (Ceq/q_{max}eq versus Ceq) of theexperiment data for the adsorption of Cu(II), Hg(II), As(III) and As(V) ions is plotted for the chitosan and crosslinked chitosan. Theability of the Freundlich model to fit the experimentaldata was also examined. For this case, the plot of In Ceq vs. In q_{max} was employed to generate the interceptvalue of K_F and the slope of 1/n.The Langmuir and Freundlich adsorption constantscalculated from the corresponding isotherms with thecorrelation coefficients are presented in Table 4.9. and Table 4.10. for chitosan and cross-linked chitosan respectively.Themaximum theoretical adsorption capacity of Cu(II),Hg(II), As(III) and As(V) calculated from Langmuir equationwas 250, 1000, 142, and 333 mg/ g. or (3.93, 4.98, 1.89 and 4.44 mmol/g chitosan beads) respectively. And 166, 111, 62, and 250 mg/g or (2.62, 0.55, 0.83, and 3.33 mmol/g cross-linked chitosan beads) respectively.

The correlation coefficients show that the adsorptionprocess could be described by the Langmuir equation.This was also supported by the root mean square values.The magnitudes of K_F and 1/ n (Freundlich constants)show easy separation of Cu(II), Hg(II), As(III) and As(V) ions from aqueous medium and indicate favorableadsorption. The intercept K_F value is an indicationof the adsorption capacity of the adsorbent; theslope 1/n indicates the effect of concentration on theadsorption capacity and represents adsorption intensity [4].

4.4. Adsorption kinetics

In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, kinetic models were used to test experimental data. The kinetic models (Pseudo-first and second-order equations) can be used in this case assuming that the measured concentrations are equal to adsorbent surface consentrations. The first-order rate equation of Lagergren is one of the most widely used for adsorption of solute from a liquid solution. It may be represented as follows:

$$\Delta qt / dt = k_1 (q_{eq} – qt) \ldots\ldots \quad (4.5)$$

Where $k_1$is the rate constant of pseudo-first order adsorption (min^{-1}) and $q_{eq}$and qt denote the amountsof adsorbed metal ions at equilibrium and at time t (mg/g), respectively. After integration by appling boundary conditions, qt=0 at t=0 and qt=qt at t=t, gives

$$Log [q_{eq}/ (q_{eq}-qt)] = (k_1t) / 2.303 \ldots\ldots \quad (4.6)$$

Equation 4.6 can be rearranged to obtain a linear form

$$Log (q_{eq}-qt) = log (q_{eq}) – (k_1t) / 2.303 \ldots\ldots \quad (4.7)$$

A plot oof log (q_{eq}) versus t should give a straight line to confirm the applicability of the kinetic model. In a true first-order process log (q_{eq}) should be equal to the interception point of a plot of Log (q_{eq}-qt) via t.

In addition, a pseudo-second order equation based on adsorption equilibrium capacity may be expressed in the form,

$\Delta qt / dt = k_2 (q_{eq} – qt)^2$………………………………………………………………….. (4.8)

Where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-first order adsorption process. Integrating equation 4.8, q and appling the boundary conditions, qt=0 at t=0 and qt=qt at t=t, leads to

$[1/ (q_{eq} – qt)] = (1/ q_{eq}) + k_2t$……………………………………………………….…… (4.9)

Or equivalently for linear from

$(t/ qt) = (1/ k_2q_{eq}^2) + (1/ q_{eq})\ t$……………………………………………………….……. (4.10)

A plot of t/ qt versus t shoud gives a linear relationship for the applicability of the second-order kinetics. The rate constant (k_2) and adsorbtion at equilibrium (q_{eq}) can be obtained from the intercept and slope, respectively.

Table 4.11. The first and second order kinetic constants for the chitosan beads

Metal ion	**Experimental**	**First-order kinetic**			**Second-order kinetic**		
		slope	**intercept**		**slope**	**intercept**	
	Q_{eq} (mg/g)	**K_1 (1/min)**	**q_{eq} (mg/g)**	**R^2**	**K_2 (g/mg.min)**	**q_{eq} (mg/g)**	**R^2**
Cu(II)	9	0.028	7.13	0.99	0.006	10.2	0.99
Hg(II)	185	0.028	182	0.98	0.0009	100	0.99
As(III)	41	0.016	30.1	0.95	0.0009	47	0.98
As(V)	48	0.014	35.2	0.88	0.0005	58	0.96

Table 4.12. The first and second order kinetic constants for the cross-linked chitosan beads

	Experimental	**First-order kinetic**			**Second-order kinetic**		
		slope	**intercept**		**slope**	**intercept**	
Metal ion	**Q_{eq} (mg/g)**	**K_1 (1/min)**	**q_{eq} (mg/g)**	**R^2**	**K_2 (g/mg.min)**	**q_{eq} (mg/g)**	**R^2**
Cu(II)	8	0.024	6.58	0.97	0.004	9	0.98
Hg(II)	86	0.019	59.4	0.93	0.0005	200	0.998
As(III)	36	0.017	30.2	0.97	0.0006	44	0.97
As(V)	44	0.016	39.9	0.98	0.0003	56	0.92

The validity of the modelis checked by the regression coefficient (R^2) [97].For the Lagargren first-order kinetic model, a plot of log (q_{eq}- qt) against taccording to the eqation shouldgive a straight line to confirm the applicability of the kinetic model. In a true first-order process log qeqshould be equal to the intercept of a plot of log (q_{eq}- qt) against t. On the other hand, a plot of 1/qt vs. 1/t from the equation should give a linear relationship for theapplicability of the second-order kinetic. The rate constant(k_2) and adsorption at equilibrium (q_{eq}) can beobtained from the intercept and slope, respectively,and there is no need to know any parameter beforehand.The comparison of experimental adsorptioncapacities and the theoretical values estimated fromthe first- and second-order equation are presented inTable 4.11 and 4.12. for chitosan and cross-linked chitosan respectively. The Lagargren model was not enough orsatisfactory to explain the experimental kinetic data.Whereas, the theoretical q_{eq} values for the adsorptionof heavy metal ions on the chitosan beads were near toclose to the experimental q_{eq} values in the case of second-order kinetic. This suggests that the rate-limitingstep may be the chemical adsorption not the masstransport limitation. Increasing metal ion concentrationin the aqueous solutions seems to reduce theexternal diffusion of the adsorbate and enhancesintraparticular diffusion[4].

4.5. Competitive adsorption of metal ions:

The competitive adsorption of Cu (II), Hg (II), As (III) and As (V)from a mixture was also investigated. Theseexperiments were performed at a constant pH of 5.5 and at room temp.using solution containing 5 mg/ L aqueous solution of Cu (II), and 50 mg/ L aqueous solutions for Hg (II), As (III), and As (V) ions fromeach metal ion. The adsorbed capacity of Cu(II) ionsis higher than other metal ions(Hg(II), As (III) and As (V)). Theadsorption capacities for Cu (II), Hg (II), As (III) and As (V)ions in Table 4.13, and 4.14

Table 4.13. Competitive adsorption of metal ions on chitosan

Ions	**mg adsorbed ion/ g polymer**	**Mmoladsorbed ion/ g polymer**
Cu(II)	25	0.39
Hg(II)	20	0.10
As(III)	13	0.18
As(V)	18	0.24

Table 4.14. Competitive adsorption of metal ions on cross-linked chitosan

Ions	**mg adsorbed ion/g polymer**	**Mmoladsorbed ion/g polymer**
Cu(II)	17	0.27
Hg(II)	5	0.02
As(III)	9	0.12
As(V)	12	0.16

5. CONCLUSION

- In this study we prepared chitosan and crosslinked chitosan by epichlorohydrin as crosslinked agents. Chitosan is a hydrophilic product derived from N-deacetylation of chitin in the presence of hot alkali, chitin it is a natural polysaccharide found in the exoskeletons of crrustaceans such as shrimps, crabs, prawns and lobsters.
- Chitosan is widely regarded as a promissing polymeric material of great scientific interest, due to its exellent properties, such as abundance, non toxicity, hydrophilicity, biocompatibility, biodegrability, adsorption properties, antibacterial properties and wide application potential.
- Chitosan is very efficient at removing metal ions through several mechanisms including metal chelation (for metal cations) and ion exchange (in the case of metal anions). The free doublet of nitrogen in amine functions is responsible of the formation of complexes between metal cations and chitosan.
- Chitosan is a unique polymer among natural polysaccharides: its amine groups are protonated in acidsolutions and associated to counter ions that can beexchangedwith metal anions [98].
- The major limitation of chitosan however, it is solubility in most dilute mineral and organic acid solutions. Attempts have been made to improve its chemical stability under acidic conditions by chemical modification using cross-linking agents.
- In this study we modified the chitosan by cross-linking reaction with epichlorohydrin,Epichlorohydrin is a cross-linking mono-functional agent used to form covalent bonds with the carbon atoms of the hydroxyl groups of chitosan, resulting in the rupturing of the epoxide ring and the removal of a chlorine atom, but the cross-linking may be decrease the adsorption capacity of adsorbent.
- The characterization of prepared chitosan and cross-linked chitosan was studied such as solubility test, swelling test by distelled water, measurment of the surface area of the polymers by BET methods, FTIR analysis to obtain the main functional groups in the polymer structures.

- The surface morphologyof chitosan has a membrane aspect and does not present porosity, which indicates that it is likely not to have diffusion problems and thus the sorption process could be fast . The surface of cross-linked chitosan with epichlorohydrin was noted to have much asperity and to be more coarsely grained.
- The percentage of chitosan and cross-linked chitosan swelling by distelled water that obtained 22.96% and 20.25% respectively.The surface area of chitosan beads was 1.15 m^2/ g while the surface area of cross-liked chitosan beads was 0.55 m^2/g.
- Due to elemental analysis results,the percentage of C, N and H in chitosan was also studied and obtained 39.43%, 8.41%, and 7.30% respectively. The percentage of C, N and H in cross-linked chitosan by epichlorohydrin 29%, 7.44%, and 4.78% respectively.
- In the FTIR spectra of chitosan and cross-linked chitosan a broad band in 3000-3500 $cm^{-1,}$ this was stretching vibrations of N-H and O-H. The peak in 3297.10 cm^{-1}, which can be assigned to O-H group. The absorption of aliphatic C-H shift from 2866 cm^{-1} (Chitosan) to 2915 cm^{-1}, absorption at 1734 cm^{-1} that mean you have carbonyl group C=O or you have O-C birdge). 1061.74 cm^{-1} and 1023.75 cm^{-1} (skeletal vibrations involving C-O stretching.
  C=N formed your polymer structure. The bands at 1156 cm^{-1} (a symmetric stretching of C-The peak around 894.46 cm^{-1} to1150.78 cm^{-1} assigned saccharine structure. At 1642.81 cm^{-1} was characterized of amide absorption. The absorption bands at 1258.05 and 1061.74cm^{-1} can be attributed from the hydroxyl groups of chitosan.
- The morphology of prepared chitosan beads were also studied by scanning elctrom microscope (SEM), chitosan and crosslinked chitosan. It can be seen that the chitosan surface has a membrane aspect and does not present porosity, which indicates that it is likely not to have diffusion problems and thus the sorption process could be fast. And the surface of cross-linked chitosan with epichlorohydrin was noted to have much asperity and to be more coarsely grained.
- The maximum adsorption capacity of chitosan beads for the Cu(II), Hg(II), As(III), and As(V) ion solution it is 204 mg/g (3.21 mmol/g), 550.23 mg/g(2.74 mmol/g), 100 mg/g (1.33 mmol/g), and 200mg/g (2.69 mmol/g) respectively.

- The maximum adsorption capacity of cross-linked chitosan beads for the Cu(II), Hg(II), As(III), and As(V) ion solution it is 128mg/g (2.02 mmol/g), 84 (0.4231mmol/g),50 mg/g (0.66 mmol/g), and 181mg/g (2.42 mmol/g) respectively.
- The maximum theoretical adsorption capacity of Cu(II),Hg(II), As(III) and As(V) calculated from Langmuir equation was 250, 1000, 142, and 333 mg/ g. or (3.93, 4.98, 1.89 and 4.44 mmol/g chitosan beads) respectively. And 166, 111, 62, and 250 mg/g or (2.62, 0.55, 0.83, and 3.33 mmol/g cross-linked chitosan beads) respectively.
- In the adsorption kinitecs the first-order model was not enough or satisfactory to explain the experimental kinetic data. Whereas, the theoretical q_{eq} values for the adsorption of heavy metal ions on the chitosan beads were near to close to the experimental q_{eq} values in the case of second- order kinetic. This suggests that the rate-limiting step may be the chemical adsorption not the mass transport limitation. Increasing metal ion concentration in the aqueous solutions seems to reduce the external diffusion of the adsorbate and enhances intraparticular diffusion.
- The competitive adsorption of Cu(II), Hg(II), As(III) and As(V) from a mixture was also investigated. These experiments were performed at a constant pH of 5.5 and at room temp. using solution containing 5 mg/ L aqueous solution of Cu(II), and 50 mg/ L aqueous solutions for Hg(II), As(III), and As(V) ions from each metal ion. The adsorbtion capacity of Cu(II) ions are higher than those obtained for Hg(II), As(III) and As(V). The adsorption capacities for Cu(II), Hg (II), As(III) and As(V) ions were found to be 25 mg/g (0.3934mmol/g), 20.18 mg/g (0.1006 mmol/g), 13.65 mg/g (0.1821 mmol/g), and 17.73mg/g (0.2367 mmol/g), respectively for chitosan. And 17.23 mg/g (0.2711 mmol/g), 5.07 mg/g (0.0253 mmol/g), 9.28 mg/g (0.1239 mmol/g), and 12.37 mg/g (0.1651 mmol/g), respectively for cross-linked chitosan.

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Projects and budgets from Thesis: -

Published Articles fromThesis: -

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