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Title

Chlorides Retention of Brackish Water using Moringa Oleifera Seeds

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الملخص

تستكشف هذه الدراسة استخدام بذور المورينجا أوليفيرا كعامل امتصاص حيوي طبيعي، قابل للتحلل، ومنخفض التكلفة لإزالة الكلور من المياه قليلة الملوحة. تم الحصول على الظروف المثلى في هذه التجربة باستخدام 5 جرام من بذور المورينجا أوليفيرا مع 60 دقيقة من التحريك ودرجة حموضة 7.2 عند درجة حرارة الغرفة. هذا يسلط الضوء على إمكاناتها كحل مستدام لتنقية المياه.

الكلمات المفتاحية: بذور المورينجا أوليفيرا ، معالجة المياه، إزالة الكلور، المواد الممتزة الطبيعية، المياه شبه مالحة، تنقية مستدامة.

Abstract

This study explores the use of Moringa Oleifera seeds as a natural, biodegradable, and inexpensive biosorbent for the dechlorination of brackish water. The optimal conditions obtained in this experiment were a Moringa Oleifera mass of 5g with 60 minutes of agitation and a pH of 7.2 at ambient temperature. This highlights their potential as a sustainable solution for water purification.

Keywords: Moringa Oleifera, biosorption, dechlorination, brackish water, natural adsorbents, sustainable water treatment.

Résumé

Cette étude explore l'utilisation des graines de Moringa Oleifera comme biosorbant naturel, biodégradable et peu coûteux pour la déchloration de l'eau saumâtre. Les condition optimal obtenu dans cette expérience et une masse de Moringa Oleifera égale à 5g avec 60min d'agitation et pH=7.2 dans la température ambient. ce qui souligne leur potentiel comme solution durable pour la purification de l'eau.

Mots clés: Graines de Moringa Oleifera, biosorption, eau saumâtre, adsorbants naturels, traitement durable de l'eau.

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GENERAL INTRODUCTION

GENERAL INTRODUCTION

Water, often referred to as "blue gold," is an essential resource for all forms of life, including humans. It is the most abundant component of the human body, making up about 65% of its composition. Any variation in its availability can pose significant and sometimes irreversible risks. Water is also vital for human activities such as domestic consumption, agriculture, and industry. On the Earth's surface, water is distributed among various reservoirs in a highly unequal manner: oceans, freshwater, etc. Freshwater is the most critical resource for humanity, playing a crucial role in all social, economic, and environmental activities. It underpins life on our planet, acts as a driving or limiting factor for all forms of social and technological development, and can be a source of well-being or hardship, of cooperation or conflict [1].

Traditional water treatment techniques, such as chemical precipitation, membrane filtration, and activated carbon adsorption, typically require significant operational expenses and involve complex processes. Moreover, the reliance on chemical additives in these methods can lead to secondary pollution, posing additional environmental concerns.

As environmental concerns intensify and regulatory standards become more stringent, there is a growing focus on advanced water treatment technologies that can effectively address emerging contaminants and meet higher purification requirements. Among these technologies, adsorption has emerged as a leading method due to its adaptability, high efficiency, and capacity to remove a broad spectrum of pollutants [2].

Consequently, there is increasing interest in developing water purification methods that are sustainable, economically viable, and environmentally benign. In this regard, natural adsorbents have attracted significant attention as promising alternatives to conventional treatment approaches [3].

Among the innovative natural solutions explored for sustainable water treatment, the seeds of *Moringa Oleifera* have gained considerable attention due to their multifunctional properties. Traditionally known for their coagulating ability in removing turbidity and pathogens from water, recent research has also highlighted their potential in the dechlorination of brackish or chlorinated water. *Moringa Oleifera* seeds contain bioactive compounds such as proteins and enzymes that can interact with residual chlorine, reducing its concentration to safer levels. This is particularly valuable in regions where chemical treatment is costly or environmentally unsustainable. The use of *Moringa Oleifera* not only represents a low-cost, biodegradable, and locally available alternative

but also aligns with the growing demand for green technologies in water purification. Its effectiveness in reducing chlorine levels makes it a promising candidate for pre-treatment in desalination processes and for improving the quality of water intended for agricultural or domestic use[4].

The biodegradable nature of *Moringa Oleifera* seeds ensures that their use in water treatment does not contribute to secondary environmental pollution.

The primary objective of this study is to investigate the use of a natural material: *Moringa Oleifera* seeds (MOS) for the dechlorination of brackish water.

This manuscript is organized into three chapters, each presenting a key aspect of the study:

- Chapter 1 is dedicated to a general overview of the adsorption phenomenon, along with a presentation of the various mathematical models used for the quantitative analysis of the experimental results.
- Chapter 2 Aims to provide a comprehensive summary about brackish water.
- Chapter 3 focuses on the materials, reagents, and methods employed in this study. It details the characterization techniques and experimental protocols used throughout the research.
- Chapter 4 is devoted to the presentation of the different obtained results.

Based on the overall interpretation of the experimental results, a general conclusion is drawn.

1.1. Definition

Adsorption is a key process in water treatment that involves the accumulation of molecules or particles at the surface of a solid material, known as the adsorbent, from a surrounding liquid or gas phase, referred to as the adsorbate. In contrast to absorption, where substances penetrate into the interior of a material, adsorption takes place solely on the surface of the adsorbent. This distinction is essential for understanding the mechanisms and behavior of adsorption, especially in water treatment applications [5].

1.2. Types of Adsorption

Adsorption is classified into physical adsorption (physisorption) and chemical adsorption (chemisorption). A thorough understanding of the underlying principles and distinctions between these adsorption types is critical for the design of efficient treatment systems and the optimization of contaminant removal in environmental engineering applications.

1.2.1. Physical Adsorption (Physisorption):

Physisorption primarily arises from weak intermolecular forces such as London dispersion forces, dipole-dipole interactions, and hydrogen bonding between adsorbate molecules and the surface of the adsorbent. This type of adsorption is largely governed by van der Waals forces, which become significant when the attractive interactions between the solid surface and gas molecules surpass the cohesive forces holding the gas molecules together.

Physisorption forces consist of two types:

- Dispersion forces (van der Waals).
- Polar forces resulting from the presence of an electric field in the micro pores.

The reversible nature of physisorption sets it apart from chemisorption, as adsorbate molecules can detach from the adsorbent surface when conditions are appropriately adjusted [6].

1.2.2. Chemical Adsorption (Chemisorption):

Chemisorption involves the formation of chemical bonds between the adsorbent and adsorbate, which are significantly stronger than the van der Waals forces governing physisorption. Unlike physisorption, chemisorption is generally irreversible, making desorption more difficult. As a result, the adsorbed molecules often experience substantial changes in their chemical structure, highlighting the depth and specificity of the interaction.

Furthermore, the energy involved in chemisorption is significantly greater than that of physisorption, reflecting the complexity of the chemical bonding process. This higher energy

requirement highlights the specific and selective nature of chemisorption, which depends on the chemical affinity between the adsorbate and the adsorbent. The process is highly exothermic, with heat release typically ranging from 20 to 50 kcal/mol [7].

Chemisorption is characterized by:

- A prolonged equilibrium attainment between the adsorbed phase and the fluid medium
- An increase in the amount of adsorbed material with temperature
- Liberation of heat during adsorption comparable to reaction heats approximately tenfold higher than physical adsorption.
- Irreversibility
- Marked specificity, implying that certain adsorbents are fixed onto a particular adsorbent (Table 1.1).

Table 1.1: Comparison of Physisorption and Chemisorption [8]

Characteristic	Physisorption	Chemisorption
Mechanism	Attraction between molecules and surface via van der Waals forces.	Formation of chemical bonds between molecules and surface.
Bond Strength	Relatively weak bonds.	Strong chemical bonds.
Reversibility	Reversible process.	Often irreversible.
Heat of Adsorption	Lower heat of adsorption (typically less than 10 kJ/mol).	Higher heat of adsorption (typically 40 to 100 kJ/mol).
Specificity	No specific affinity.	Specific affinity between adsorbate and adsorbent.
Temperature Effect	Adsorption decreases with increasing temperature.	Adsorption increases with increasing temperature.
Equilibrium Time	Equilibrium reached relatively quickly.	Equilibrium may take longer to establish.
Examples	Adsorption of gases on activated carbon.	Reaction of hydrogen with a metal surface.

1.3. Adsorption Isotherms and Kinetics

Adsorption isotherms and kinetics are critical for understanding adsorption mechanisms in water treatment processes. This section provides an in-depth exploration of these foundational concepts, emphasizing their relevance and detailing various isotherm models, including Langmuir, Freundlich, and BET. It also examines kinetic models such as first-order, second-order, pseudo-first-order, and pseudo-second-order kinetics. Additionally, the section discusses experimental approaches for determining isotherms and kinetic parameters, offering comprehensive insights into analytical methodologies and data interpretation techniques[9].

1.3.1. Introduction to Adsorption Isotherms

Adsorption isotherms serve as fundamental tools in adsorption science, enabling a detailed understanding of the equilibrium relationship between the concentration of adsorbate in the bulk solution and the amount adsorbed onto the surface of the adsorbent at equilibrium. A thorough grasp of adsorption isotherms is essential for assessing adsorption capacity, elucidating underlying mechanisms, and enhancing the efficiency of water treatment processes. These isotherms are essential analytical tools that provide critical insights into the complex interactions between adsorbents and adsorbents, help characterize the surface properties of adsorbent materials, and evaluate the performance of adsorption systems. Through the study of these isotherms, researchers and practitioners can deepen their understanding of adsorption behavior, thereby advancing more effective water treatment strategies and contributing to sustainable approaches for environmental remediation and resource management [10].

1.3.2. Adsorption Kinetics

Adsorption kinetics describe the rate at which adsorption occurs over time, offering key insights into the dynamic behavior of adsorption processes. This section examines four widely used kinetic models first-order, second-order, pseudo-first-order, and pseudo-second-order kinetics providing detailed formulations and explanations for each to facilitate a deeper understanding of their application in water treatment studies.

The process of adsorption (Figure 1.1), driven by molecular diffusion, typically reaches equilibrium within seconds to minutes. However, when microporous adsorbents are involved, the process may extend over longer periods due to the slower diffusion of molecules through pore structures that are comparable in size to the adsorbate molecules. The transition from the liquid phase containing the adsorbate to the solid phase, where the solute adheres to the adsorbent surface, occurs through several distinct stages [11].

- External diffusion: This process involves the transfer of solute molecules from the bulk liquid phase to the external surface of the adsorbent particles.
- Internal diffusion: Within the fluid occupying the pores, solute molecules migrate from the external surface of the adsorbent particles toward their interior through the pore network.
- Surface diffusion: In some adsorbents, an additional contribution may arise from the surface diffusion of adsorbed molecules along the internal pore surfaces at the scale of individual adsorbent grains.

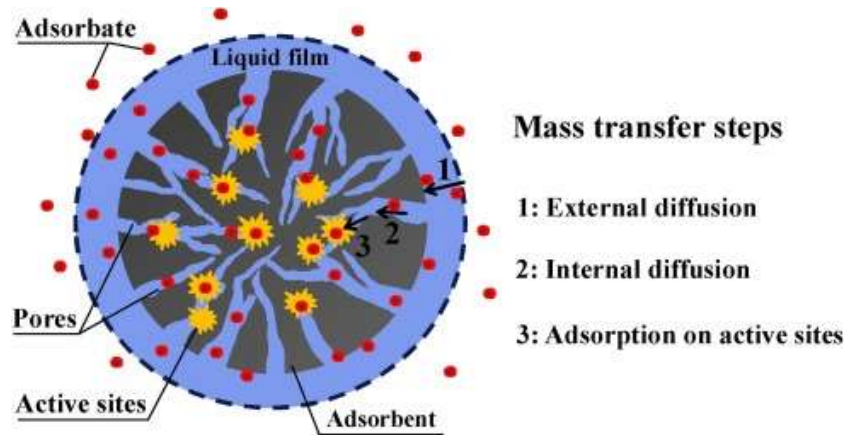


Figure 1.1: Mass Transfer Steps in Adsorption Process [12]

1.3.2.1. Modeling of adsorption kinetics

➤ Pseudo-first-order Kinetics equation

The pseudo-first-order kinetic model describes adsorption as a single-step process in which the adsorption rate is directly proportional to the concentration of the adsorbate in the bulk solution. It assumes that the rate-limiting step is the physical attachment of adsorbate molecules to the surface of the adsorbent. The model is mathematically expressed as follows:

$$\frac{dq}{dt} = k_1 \times (Q_e - Q_t) \quad (\text{Eq. 1.1})$$

Q_e and Q_t : adsorbed quantities of MO at equilibrium and at time t per unit mass of material (mg g⁻¹).

K_1 : pseudo first-order adsorption rate constant (min⁻¹).

In integrating and linearizing equation 1, we arrive at equation which allows us to obtain **k_1** and

Qe. For linearization, we need to plot $\ln(Q_e - Q_t)$ function of time

$$\ln(Q_e - Q_t) = \ln Q_e - \frac{K_1}{2.303} t \quad (\text{Eq. 1.2})$$

➤ Pseudo-second-order Kinetics

The pseudo-second-order kinetic model assumes that adsorption occurs primarily through chemisorption or surface reactions, where the rate of adsorption is proportional to the square of the adsorbate concentration in the bulk solution. This model implies that the process involves the formation of chemical bonds between the adsorbate and the surface of the adsorbent. The pseudo-second-order kinetics can be mathematically represented as:

$$Q_t = \frac{Q_e^2 \times K_2 \times t}{1 + (Q_e \times k_2 \times t)} \quad (\text{Eq. 1.3})$$

k₂: pseudo second-order adsorption rate constant (g. mg⁻¹. min⁻¹)

To integrate and linearize (Eq. 1.3), we arrive at (Eq. 1.4) which allows us to obtain **k₂** and **Q_e**. For linearization, we need to plot **t/Q_t** against time

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \quad (\text{Eq. 1.4})$$

1.4. Adsorption capacity

The adsorption capacity of an adsorbent refers to the amount of adsorbate (by mass or volume) retained per unit mass of the adsorbent at a given temperature. This capacity is influenced by several factors, including the molecular size and solubility of the adsorbate, as well as the surface area, structural characteristics, and chemical composition of the adsorbent. The adsorption capacity is commonly represented by the following equation:

$$Q_e = \frac{(C_e - C_t) \cdot V}{m} \quad (\text{Eq. 1.5})$$

Where:

Q_e : the adsorption capacity

C_e and C_t : the initial and current substrate concentrations

V : the solution volume

m : the adsorbent mass

This equation quantifies the efficiency of the adsorption process by relating the initial and equilibrium concentrations of the adsorbate to the volume of the solution and the mass of the adsorbent.

1.5. Types of adsorption Isotherms

An adsorption isotherm is a graphical representation that illustrates the relationship between the amount of adsorbate retained by an adsorbent and the equilibrium pressure or concentration of the adsorbate at a constant temperature. It reflects various adsorption mechanisms, including micro pore filling, multilayer adsorption, and capillary condensation. Brunauer proposed a classification system for theoretical adsorption–desorption isotherms, which provides valuable insights into the nature of the adsorption process and the structural properties of the adsorbent[13]. as shown on (figure 1.2)

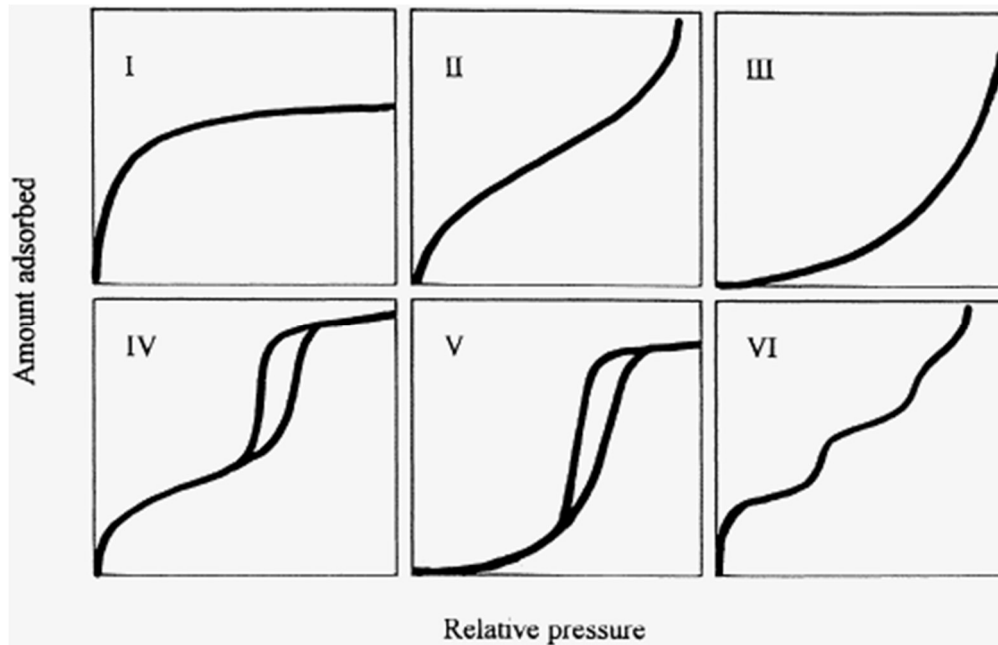


Figure 1.2: Classification of Adsorption Isotherms [14].

Type I (Langmuir Isotherm): This type of isotherm is characteristic of adsorption in microporous materials with relatively low external surface areas, such as activated carbons and zeolites. It typically exhibits a steep initial uptake at low pressures, followed by a plateau as the system approaches saturation. This behavior reflects the rapid filling of micro pores and the limited availability of adsorption sites, ultimately resulting in monolayer coverage [15].

Type II: This type of isotherm is typical of non-porous or macro porous adsorbents, where adsorption proceeds through the formation of multiple layers. The isotherm features a distinct inflection point in the initial region of the curve, indicating the completion of monolayer coverage. Beyond this stage, additional layers of adsorbate molecules accumulate, leading to a gradual increase in the overall amount adsorbed [15].

Type III isotherms: This type of isotherm characterizes adsorbents with weak adsorbate–adsorbent interactions, typically observed in non-porous materials with low surface affinity for the adsorbate. The amount of adsorption increases continuously without reaching a plateau, indicating ongoing multilayer adsorption even at low relative pressures. Such behavior suggests that adsorbate–adsorbate interactions dominate over adsorbate–adsorbent interactions [15].

Type IV isotherms: These isotherms are characteristic of mesoporous materials with pore sizes ranging from 2 to 50 nm. While the isotherm initially resembles Type II, it exhibits a pronounced hysteresis loop attributed to capillary condensation occurring within the mesoporous. This hysteresis signifies that the adsorption and desorption processes follow different pathways, highlighting the complex nature of mesoporous structures [15].

Type V isotherms: These isotherms resemble Type III but are observed in mesoporous materials. They are characterized by weak adsorbate–adsorbent interactions and exhibit a hysteresis loop resulting from capillary condensation. This behavior suggests that the adsorbate tends to condense within the mesoporous rather than forming a uniform multilayer on the adsorbent surface [15].

Type VI isotherms: This type of isotherm represents stepwise multilayer adsorption occurring on highly uniform surfaces. Each distinct step corresponds to the sequential formation of additional adsorbate layers. Such isotherms are uncommon and are typically observed in materials possessing very uniform adsorption sites, where each step signifies the completion of another molecular layer [15].

1.6. Factors Influencing Adsorption Performance

Adsorption plays a vital role in numerous applications, including environmental remediation, wastewater treatment, and the purification of industrial systems. Optimizing adsorption processes requires a thorough understanding of the factors that affect their efficiency. This section explores four critical factors influencing adsorption performance: solution chemistry, temperature effects, adsorbate concentration, and the properties of the adsorbent material [16].

1.6.1. Effect of Solution Chemistry

Solution chemistry has a significant influence on the adsorption process, with three key parameters playing a critical role in determining its effectiveness.

➤ pH

The pH of a solution plays a crucial role in determining the surface charge of both the adsorbent and the adsorbate. In metal ion adsorption, for example, the surface charge of the adsorbent is influenced by the solution's pH, which in turn affects the adsorption capacity. Typically, lower pH levels enhance metal ion adsorption due to the increased availability of active sites on the adsorbent surface[17].

➤ Ionic Strength

Electrolytes in the solution impact the ionic strength, which in turn affects adsorption capacity. Solutions with high ionic strength can weaken the electrostatic interactions between the adsorbate and adsorbent, resulting in reduced adsorption efficiency. In contrast, low ionic strength conditions may promote adsorption by minimizing competition among ions for available adsorption sites[17].

➤ Presence of Competing Ions

The presence of additional ions in the solution, whether chemically similar or different from the target adsorbate, can lead to competition for available adsorption sites on the adsorbent surface. This competitive adsorption can considerably influence both the overall adsorption capacity and the selectivity of the adsorbent toward specific ions. Consequently, understanding the relative affinity of various ions for the adsorbent surface is essential for accurately predicting adsorption behavior, especially in complex solutions containing multiple ionic species. Such knowledge helps in designing and optimizing adsorption systems for real-world applications where mixed ion environments are common [17].

1.6.2. Influence of Temperature on Adsorption

Temperature significantly influences both the kinetics and equilibrium of the adsorption process. In most cases, adsorption is exothermic, so increasing the temperature tends to reduce the adsorption capacity. However, this trend is not universal—certain adsorption processes are endothermic or display more complex temperature-dependent behaviors. Therefore, a thorough understanding of the thermodynamic properties of the adsorption system is crucial for accurately predicting how temperature variations will impact adsorption performance [18].

1.6.3. Role of Adsorbate Concentration

The concentration of the adsorbate in the solution has a direct influence on the adsorption capacity of the adsorbent. At lower concentrations, a large number of adsorption sites remain unoccupied, allowing for efficient uptake of the adsorbate and resulting in high adsorption efficiency. As the concentration increases, these active sites gradually become occupied, eventually leading to saturation, beyond which further increases in adsorbate concentration result in minimal gains in adsorption capacity. Analyzing adsorption isotherms is essential for understanding this relationship, as they reveal how adsorbate concentration affects the extent and nature of adsorption under equilibrium conditions [19].

1.6.4. Effect of agitation

Agitation significantly enhances the adsorption process by improving mass transfer, reducing boundary layer thickness, and preventing particle aggregation. It increases contact between adsorbate molecules and the adsorbent surface, accelerating equilibrium and maximizing adsorption capacity. The optimal agitation speed, determined experimentally, ensures effective adsorption without causing mechanical issues. This understanding is essential for designing efficient industrial adsorption systems, particularly in wastewater treatment [20].

1.6.5. Impact of Adsorbent Properties on Performance

The adsorption performance of a material is largely determined by its inherent properties. Key factors influencing its effectiveness include:

Surface Area: Adsorption capacity is often closely linked to the surface area of the adsorbent. Materials with larger surface areas offer more active sites, thereby enhancing their overall adsorption performance.

Pore Structure: The pore structure of the adsorbent including pore size distribution and pore volume plays a critical role in determining the accessibility of adsorption sites and the diffusion of

adsorbate molecules within the material. Adsorbents with well-defined and optimized pore structures often demonstrate improved adsorption capacity and faster kinetics.

Surface Chemistry: The surface functional groups and chemical composition of an adsorbent dictate its affinity toward specific adsorbents. Modifying or functionalizing the surface chemistry can enhance both the selectivity and efficiency of the adsorption process [21].

1.6.6. Parameters of adsorption

Various parameters and characteristics of both the adsorbent and the adsorbate can significantly impact the adsorption process, especially in terms of adsorption capacity and kinetics.

1.6.7. Characteristics of the Adsorbed Molecule

Size of the Adsorbed Molecules: Mechanically, the adsorbate molecules must be smaller than the pore diameter of the adsorbent to allow efficient diffusion into the porous structure and access to adsorption sites.

Solubility: Studies have indicated that adsorption constants generally increase as the solubility of a compound decreases. Additionally, various researchers have proposed different correlations between the adsorption constant and the physicochemical properties of organic molecules [22].

Acidity Constant (pKa): Many organic compounds act as weak acids or bases, with the pH controlling whether these molecules exist in ionized or neutral forms. The specific form of the molecule influences which components of the matrix are involved in the adsorption process. Most studies suggest that adsorption retention reaches its maximum when the pH is equal to the compound's pKa [23].

Polarity and Polarizability of the Adsorbed Molecule: Adsorption is strongly affected by the size of the compound (including surface area and volume) as well as its functional groups such as alcohols, aldehydes, ketones, carboxylic acids, amines, sulfur, and halogens which contribute to different levels of polarizability [23].

1.7. Adsorbents

Adsorbents are solid materials that facilitate the accumulation of molecules or particles from a liquid or gas phase onto their surface through the process of adsorption. This surface-based interaction contrasts with absorption, where substances penetrate into the bulk of the material. Adsorption is influenced by factors such as surface area, porosity, and the chemical nature of the adsorbent's surface.

- **Synthetic adsorbents**

The most common industrial adsorbents are the following: activated carbon, zeolites, activated alumina, Silica gels, polymer adsorbents...

- **Natural Adsorbents (Sorbents)**

Natural adsorbents are primarily composed of agricultural and industrial wastes that possess inherent properties enabling significant adsorption capacity. Various by-products and residues from agriculture or the agri-food industry can be employed in adsorption processes (biosorption) as cost-effective and environmentally friendly adsorbents, such as:

- Fruit waste: live pits, almond, apricot and peach shells, pomegranate and orange peel....
- Industrial wastes: carbon derived from tire rubber, treatment sludge, bagasse pith that is a significant waste from the sugarcane industry...
- Algae and seafood waste: such as green algae, chitin from the cell wall of some fungi.

Biosorption presents several benefits, including the low cost of adsorbents, high removal efficiency, reduced production of chemical and biological sludge, and the potential for bio-sorbent regeneration. As such, natural sorbents represent an excellent and sustainable alternative to conventional chemical remediation methods [24].

1.8. *Moringa Oleifera*: A Natural Adsorbent

Moringa Oleifera, commonly known as the drumstick tree or horseradish tree, is a highly valued plant native to the Indian subcontinent. A member of the Moringaceae family, it is widely recognized for its diverse and beneficial applications across multiple fields. Notably fast growing and highly resilient to drought, *Moringa Oleifera* can flourish in a variety of climatic conditions, making it particularly valuable in regions experiencing water scarcity and agricultural constraints.

Its slender, pinnate leaves, fragrant white flowers, and long, drumstick-like seedpods distinguish the tree. These pods contain the seeds, which are especially significant in water treatment applications. *Moringa Oleifera* seeds are small, round, and brownish-black in color, and they have been extensively studied for their natural coagulant and adsorptive properties in the treatment of wastewater.

These cationic polypeptides, known as *Moringa* seed coagulant proteins (MCPs), possess distinctive properties—most notably, coagulation and antimicrobial activities—that are highly beneficial in wastewater treatment. The coagulating action of MCPs promotes the aggregation and subsequent removal of suspended solids and various contaminants, thereby improving water

clarity and reducing turbidity. In addition, their antimicrobial activity contributes to the inactivation of pathogenic microorganisms, further enhancing the safety and microbiological quality of the treated water [25].

The inclusion of *Moringa Oleifera* seeds in water treatment processes offers numerous advantages [26]:

- ✓ **Natural Coagulant:** *Moringa Oleifera* seeds contain cationic proteins that function as natural coagulants, effectively facilitating the removal of suspended particles and reducing turbidity in wastewater treatment processes.
- ✓ **Reduction of Organic Load:** The seeds contribute to the reduction of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) by promoting the coagulation and subsequent removal of organic matter from wastewater.
- ✓ **Heavy Metal Removal:** *Moringa Oleifera* seeds have demonstrated the ability to adsorb heavy metals such as lead (Pb), cadmium (Cd), and arsenic (As), thereby significantly reducing their concentrations in treated water.
- ✓ **Antimicrobial Properties:** *Moringa Oleifera* seeds also exhibit notable antimicrobial activity, which contributes to the reduction of pathogenic microorganisms in wastewater, thereby enhancing the microbiological quality of treated water. Furthermore, as a natural and biodegradable material, *Moringa* seeds are environmentally friendly and do not introduce harmful residues, minimizing the risk of secondary pollution often associated with synthetic chemical treatments.
- ✓ **Cost-Effectiveness:** *Moringa Oleifera* seeds are inexpensive and widely available, making them a cost-effective and accessible solution for water treatment, particularly in resource-limited and developing regions.
- ✓ **Simplicity of Use:** The water treatment process using *Moringa Oleifera* seeds is simple, low-tech, and easy to implement, making it highly suitable and accessible for small-scale and rural communities with limited resources.
- ✓ **Improvement in Water Quality:** The use of *Moringa Oleifera* seeds can significantly enhance water quality by reducing turbidity, color, and contaminant concentrations, thereby making the water safer for a wide range of applications.
- ✓ **Enhanced Settling of Solids:** The coagulating properties of *Moringa Oleifera* seeds promote the aggregation and settling of suspended solids, thereby facilitating their more efficient removal during sedimentation.

- ✓ **Versatility:** *Moringa Oleifera* seeds have proven effective in treating a variety of wastewater types, including domestic, industrial, and agricultural effluents.
- ✓ **Promotion of Sustainable Practices:** The use of *Moringa Oleifera* seeds in water treatment supports sustainable and environmentally friendly practices, aligning with global initiatives aimed at reducing dependence on chemical coagulants.

Moringa Oleifera, commonly referred to as the “drumstick tree” or “miracle tree,” belongs to the Moringaceae family and is native to northern India. This fast-growing species can attain heights of 10 to 12 meters, with a trunk diameter reaching up to 45 cm, and is characterized by its thick, greyish-white bark. The tree bears pinnately compound leaves ranging from 30 to 60 cm in length, each consisting of 5 to 9 light green, elliptical leaflets measuring approximately 1 to 2 cm.

The tree produces small, fragrant flowers that range in color from white to cream, arranged in panicles measuring 10 to 25 cm in length. The tree bears hanging, triangular seedpods ranging from 20 to 45 cm long, which contain dark brown seeds. These seeds are round and equipped with three thin wings, and are released when the mature pods naturally split open. Additionally, *Moringa Oleifera* develops a deep taproot system, which allows it to tolerate and thrive in arid and drought-prone environments.

The tree is highly valued for its diverse applications. Its nutrient-rich leaves are packed with essential vitamins and minerals, serving as an important dietary component. The seeds exhibit natural coagulant properties, making them effective in water purification processes. Additionally, oil extracted from the seeds is widely used in the cosmetic and food industries. The tree’s versatility has earned it recognition for its significant contributions across multiple fields, including nutrition, environmental sustainability, and industry (Figure 1.3).



Figure 1.3: Moringa Oleifera Plant

1.8.1. Characteristics of Moringa Oleifera:

Table 1.2: Characteristics of Moringa Oleifera [27]

Category	Details
Name	Moringa Oleifera
Family	Morongaceae
Order	Brassicales
class	Magnoliopsida
kingdom	Planatae
Genus	Moringa
Species	Oleifera
Leaf type	Pinnately compound
Seed type	Round with three thin wings
Height	10 to 12 meters
Economic uses	Nutritional supplement, water purification, medicinal, oil production

2.1. Definition

Brackish water refers to water whose salinity lies between that of freshwater and seawater, typically ranging from 0.5 to 30 grams of salt per liter (0.5–30‰). It commonly arises in estuaries and coastal lagoons where freshwater mixes with ocean water, creating environments with fluctuating salt concentrations. They are sometimes surface waters, but more often groundwater that has become loaded with salts by dissolving certain salts present in the soils they have passed through. Their composition therefore depends on the nature of the soils they have traversed and the speed at which they move through these soils. The main dissolved salts are CaCO_3 , CaSO_4 , MgCO_3 , and NaCl [28].

2.2. Brackish water used: Hammam Alwen (therapeutic) water

Hammam Alwen, situated in Blida, Algeria, is well-known for its therapeutic thermal springs, which are extensively used in balneotherapy a healing practice that utilizes mineral-enriched waters to promote health and wellness. The waters at Hammam Alwen are particularly notable for their iron-rich (ferruginous) and chloride-sodium composition, with temperatures ranging between 29°C and 41°C. These characteristics make them especially beneficial in the treatment of ailments such as rheumatism and various skin disorders.

In balneotherapy, the mineral content of the water is a key factor in its curative effects. The high iron levels can help enhance blood circulation and reduce inflammation, while chloride and sodium ions are known to promote muscle relaxation and pain relief. The thermal nature of the water further stimulates blood flow, aiding in tissue repair and relieving discomfort from musculoskeletal conditions.

Treatment sessions at Hammam Alwen typically involve soaking in the mineral waters, which can be directed toward specific areas of the body as needed. The natural buoyancy and resistance of the water support gentle exercise and mobility therapy, improving joint flexibility and muscle strength without overloading the body.

In summary, the distinctive mineral composition and thermal qualities of Hammam Alwen's waters position it as a significant location for those seeking natural, non-invasive treatments for a range of physical health issues (Figure 2.1).



Figure 2.1: Hammam Alwen lake

Introduction:

This chapter provides a comprehensive overview of the experiments carried out in this study, covering the preparation methods of the various solutions, the experimental procedures implemented, and the characterization techniques applied throughout the research.

3.1. Chemical products

The chemicals listed in (Table 3.1), along with their respective properties, were utilized to formulate the matrices and prepare the aqueous solutions under the various experimental conditions.

Table 3.1: Chemical products used

Product	Purity (%)	Density (g/cm ³)	Purchased from
Ethylenediamine tetraacetic acid (EDTA)	99	1.5	Cynor
AgNO ₃	99	4.35	Sigma-Aldrich

3.2. Preparation of Moringa Oleifera Seeds (MOS)

The bio sorbent was derived from Moringa Oleifera seeds, unmodified state, without undergoing any chemical treatment. The seeds were washed carefully with tap water, followed by air-drying for five days until the seeds hardened. This drying process was carried out under ambient conditions to preserve the physicochemical properties of the biosorbent (Figure 3.1).



Figure 3.1: Moringa Oleifera Seeds

3.3. Characterization of the biosorbent

3.3.1. Characterization of the biosorbent by FTIR

The biosorbent was characterized using Fourier Transform Infrared Spectroscopy (FTIR) to identify functional groups present on the surface.

3.3.2. Determination of pH_{pzc}

Additionally, the pH at the point of zero charge (pH_{pzc}) was determined to understand the surface charge properties of the biosorbent.

The point of zero charge is a critical property of material surfaces, as it provides an indication of their acidic or basic nature. It is defined as the pH at which the surface carries no net electrical charge meaning the total positive charges equal the total negative charges. This parameter plays a significant role in adsorption processes, particularly when electrostatic interactions contribute to the adsorption mechanism [29].

A straightforward and rapid method was employed to determine the pH_{pzc} of the sample. The point of zero charge was assessed following the procedure outlined below.

Operating mode

- ✓ Take 100mL of distilled water in a beaker then add a mass of 0.5g of solid (adsorbent).
The solution obtained is denoted S1.
- ✓ Fill the burette with the hydrochloric acid solution HCl 0.1M.
- ✓ Determine the initial pH of solution S1.
- ✓ Dose the S1 solution drop by drop with the HCl hydrochloric acid solution until the pH value is completely stabilized. Note the variation in pH.

N.B: Repeat the same steps for the 0.1M NaOH sodium hydroxide solution.

The surface charge was calculated using the equations provided below.

✓ Case of HCl : $Q_a = (C_a + [OH^-] - [H^+]) / m$ Eq. 3.1

✓ Case of NaOH : $Q_b = (-C_b + [OH^-] - [H^+]) / m$ Eq. 3.2

With:

Q : Charge of surface (mol.g⁻¹)

C_a : Concentration of acid (mol.L⁻¹)

C_b : Concentration of base (mol.L⁻¹)

m : test sample in g

3.4. Parametric study of the retention of chlorides on MOS

3.4.1. Effect of Contact Time

Contact time is a key factor in adsorption studies, as it reveals the period necessary for the adsorbate–adsorbent system to achieve equilibrium.

Beakers containing 200ml of our brackish water placed on a vibration plate then 1g is added of MOS.

The contact times between the adsorbent and adsorbate for each beaker were set respectively to 5, 10, 30, 40, 60, 120, and 240 (min).

The concentration levels of chloride (Cl-) was determined by using Mohr method (annex) .

The results were presented as curves illustrating removal efficiency over time, allowing for the determination of the optimal contact duration.

$$R\% = \frac{C_i - C_f}{C_i} \times 100 \quad \text{Eq. 3.3}$$

C_i : Initial concentration

C_f : Final concentration

3.4.2. Effect of sorbent mass

The objective is to identify the optimal sorbent dosage that achieves maximum dechlorination.

Variant masses of MOS were mixed with the same volumes (V=200 mL) of our water in beakers

The chosen mass range is 0.2, 0.5, 1.5, 5 and 10g of MOS.

The same operating conditions and analytical methods described previously were applied. The results were ultimately presented in the form of a curve. showing the yield (R%) of chloride concentration [Cl-] in function of mass.

3.4.3. Effect of pH

pH is a crucial parameter in adsorption studies, as it can affect the structural and ionization properties of the adsorbent, as well as the solubility, chemical form, and adsorption behavior of the adsorbate.

In this work, we investigated the effect of pH on the adsorption levels by MOS by adjusting our water pH level to the following values : 2, 5, 10 and 12 (proposed by our promoter), by using

hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions depending on the required pH level.

The results were expressed in a curve showing the yield (R%) of chloride concentration [Cl⁻] in function of pH to determine the optimal adsorption conditions.

3.4.4. Effect of temperature

The temperature effect has been done in order to study the effect of temperature on MOS in the adsorption process.

After fixing optimal conditions for mass, time and pH we used 3 samples in different temperatures : 30°C , 40°C , 70°C (the normal temperature is 22°C), those temperature were chosen at random because of the lack of the needed materials in the laboratories, the process of maintaining the heat was difficult to do.

The results were expressed in a curve showing the yield (R %) of chloride concentration [Cl⁻] in function of temperature.

4.1. Characterization of brackish water

Samples of the brackish water were collected and characterized. Obtained results are summarized in the table 4.1.

Table 4.1: Characterization of brackish water of Hammam Alwen

Element	Unit	Value
pH		6.8-7.2
Ca ²⁺	mg/mol	1760
Mg ²⁺		1445
Hardness		3600
Cl ⁻		1152.125

4.2.Characterization of MOS by FTIR

The FTIR (Fourier Transform Infrared) analysis of *Moringa Oleifera* seed powder provides insight into its functional composition, which is crucial for its application in environmental remediation, particularly in water treatment. The spectrum (Figure 4.1) reveals a broad absorption peak around 3288 cm⁻¹, corresponding to O–H stretching vibrations, indicative of hydroxyl groups commonly found in alcohols and phenolic compounds [30].

Peaks at approximately 2922 cm⁻¹ and 2853 cm⁻¹ are associated with C–H stretching of aliphatic chains, suggesting the presence of lipids and long-chain hydrocarbons [30,31].

A distinct band near 1657 cm⁻¹ corresponds to C=O stretching vibrations, typical of amide groups from proteins [31,32].

Additional peaks in the 1450–1000 cm⁻¹ region—particularly around 1375 cm⁻¹, 1232 cm⁻¹, and 1035 cm⁻¹—are attributed to C–N stretching and C–O bending, confirming the presence of amines, esters, and polysaccharides [30,31,32].

These functional groups enhance the biosorption properties of *Moringa Oleifera* seeds by facilitating mechanisms such as hydrogen bonding, ion exchange, and complexation with various pollutants, including heavy metals and dyes. The diversity of chemical functionalities supports the material's efficiency as a low-cost, biodegradable, and environmentally sustainable option for wastewater treatment technologies [30–32].

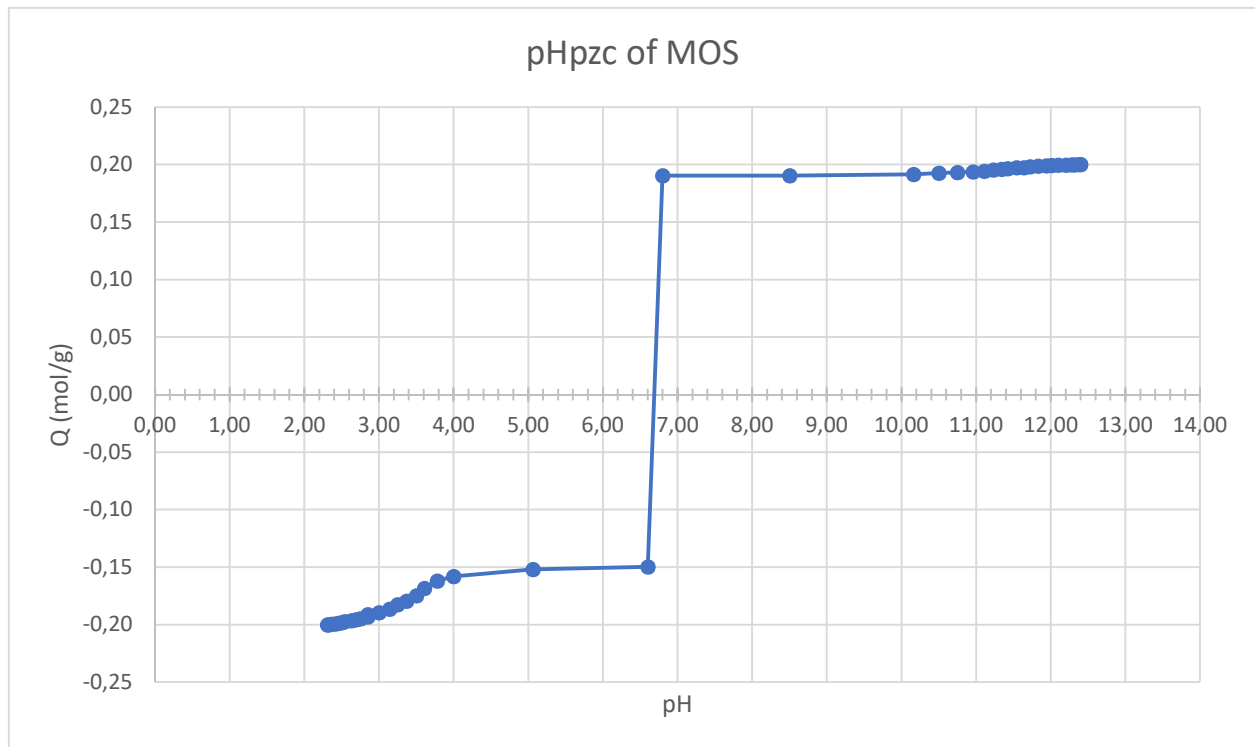


Figure 4.2: pH_{pzc} of MOS

4.4. Results of the retention study of chloride using *Moringa Oleifera* seeds (MOS):

4.4.1. Effect of contact time:

Figures 4.3 and 4.4 show a rapid increase in adsorption capacity, followed with the same efficiency between 30min and 40min with 53.84%, the other increase until it reaches the peak in our case at 60min with 69.23% than it keep having the same efficiency in 2h and 4h. Moringa seeds are rich in proteins that carry positively charged amino groups (NH_3^+) in water, those positively charged groups can electrostatically attract negatively charged chloride ions (Cl^-). Over time, more Cl^- ions come into contact with those groups, especially as water keeps circulating.

The adsorption capacity of the chloride is the most efficient at 60min, so it was considered as sufficient for maximum adsorption.

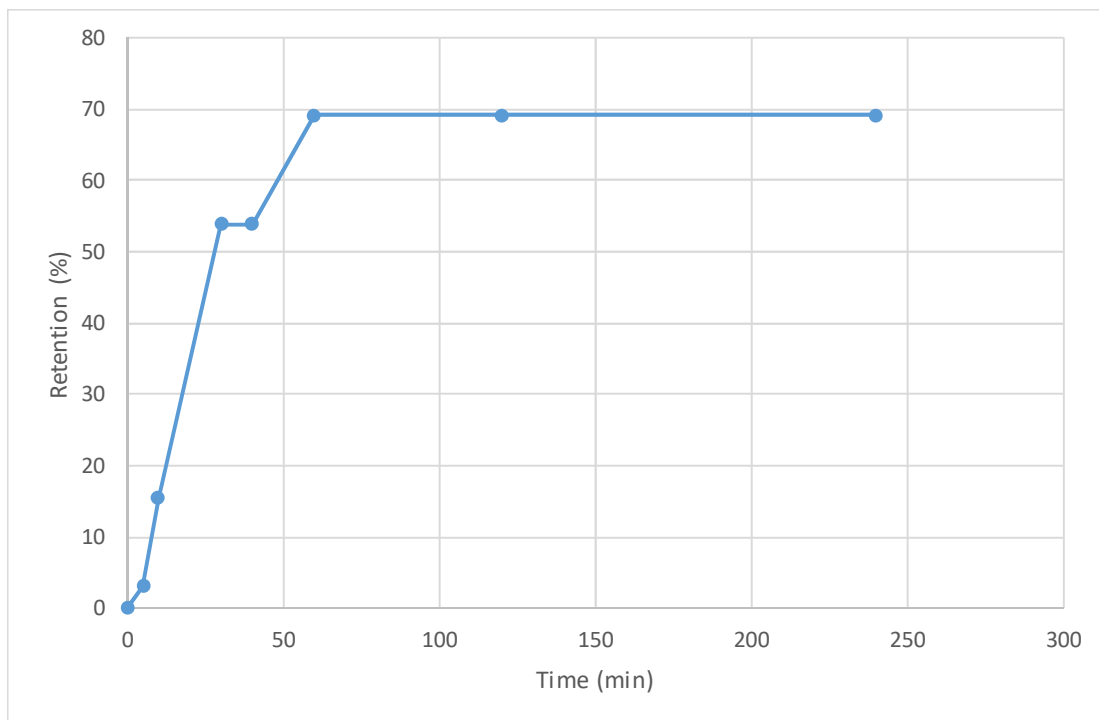


Figure 4.3: adsorbed yield of chloride as a function of time on MOS

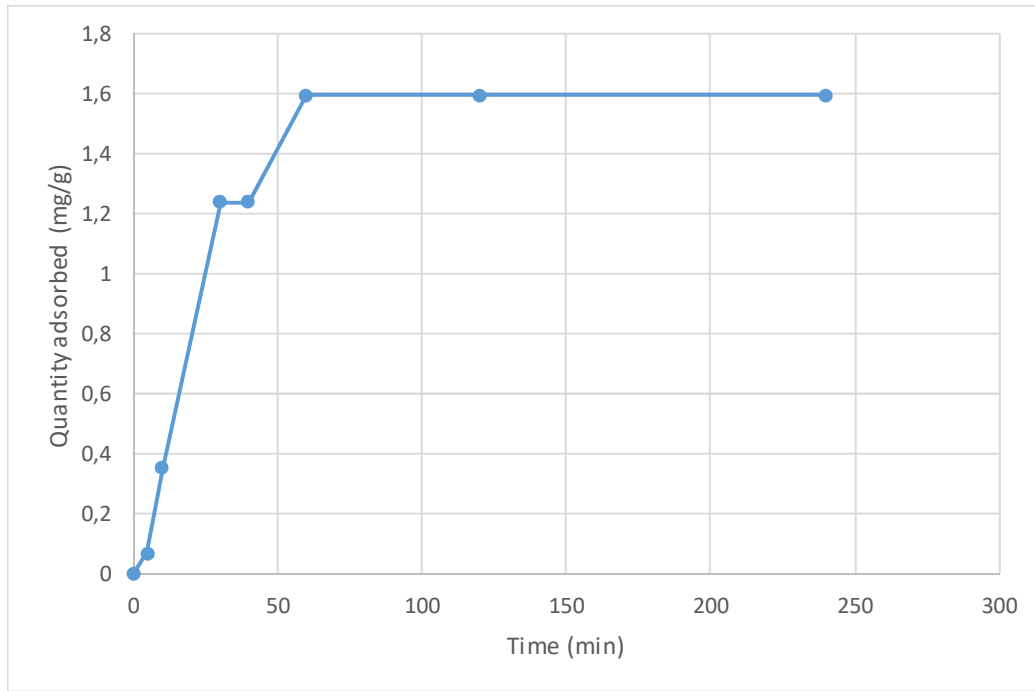


Figure 4.4: Adsorbed quantity of chloride as function of time on MOS

4.3.2. Effect of mass:

The figures 4.5 and 4.6 show that as the adsorbent mass increases, the removal efficiency (R %) also increases, from 7.7% at 0.2g to 76.9% at 0.5g.

This is attributed to the number of active sites available for adsorption, which enhance overall removal.

The adsorption capacity decreases with increasing mass at 10g 46.1%, this declined is likely due to particle aggregation, reducing the effective surface area and active sites.

There is an optimal mass beyond which efficiency drops, 5g of MOS was chosen then for the rest of the work.

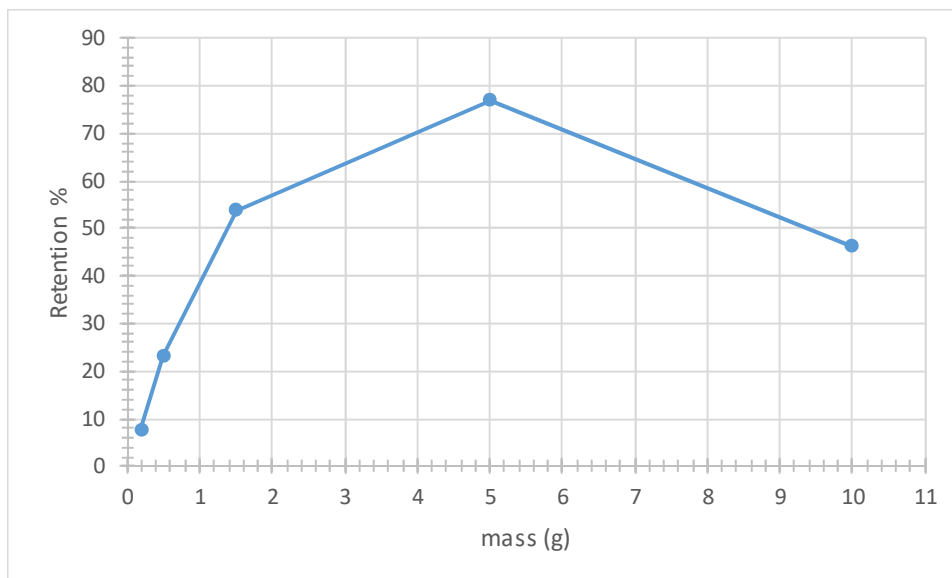


Figure 4.5: adsorbed yield of chloride as a function of mass on MOS

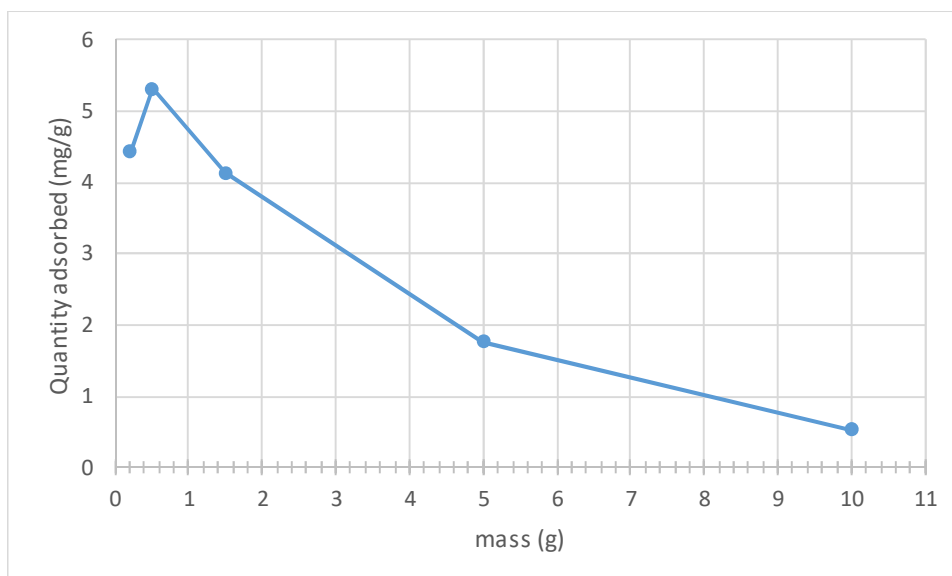


Figure 4.6: Adsorbed quantity of chloride as function of mass on MOS

4.3.3. Effect of pH:

The adsorption capacity of the chloride by MOS is influenced by small degree by the pH of the solution. At neutral pH of 6.8, the efficiency is moderate at 76.92% (Figures 4.7 and 4.8). As the pH decreases to 2 the efficiency increases to 87.69%, indicating that acidic conditions enhance the adsorption.

However, as the pH increases above neutral, the efficiency drops by small degrees, with 73.84 at pH 10 and 69.23 at pH 12.

The adsorption of chloride is the most effective under acidic conditions, with an optimal pH around 2 highlighting the importance of the pH in adsorption.

In acidic conditions, the surface of many adsorbents becomes protonated (positively charged), the positive surface attracts negatively charged Cl^- ions enhancing adsorption.

In basic condition the surface becomes negatively charged leading to repulsion of Cl^- reducing removal efficiency.

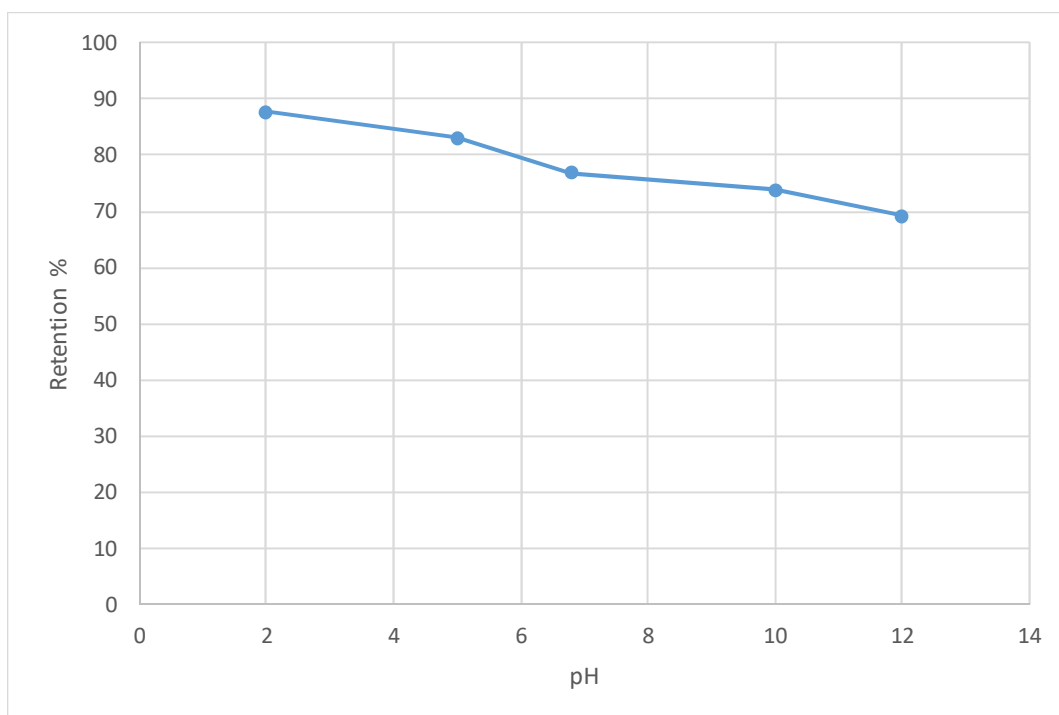


Figure 4.7: Adsorbed yield of chloride as a function of pH on MOS

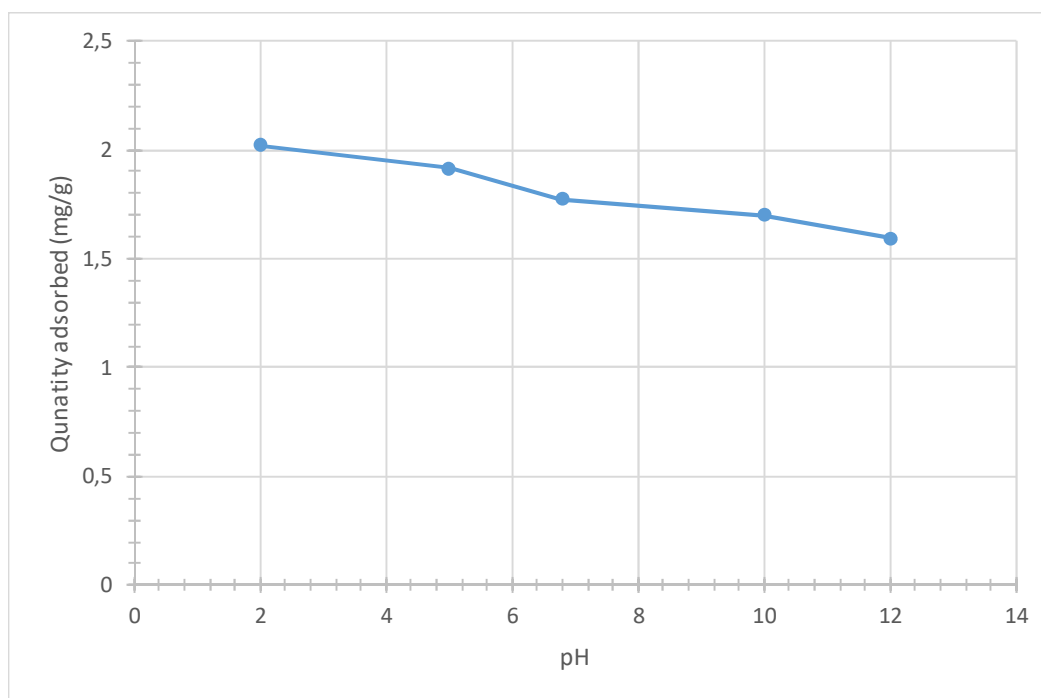


Figure 4.8: Adsorbed quantity of chloride as function of pH on MOS

4.3.4. Effect of the temperature:

Obtained results (Figures 4.9 and 4.10) show that the adsorption capacity of the chloride by MOS decreases markedly with temperature. At 295.15°K and at 303°K with 76.92% the efficiency is at maximum,

As the temperature decreases to 343°K the efficiency decrease to 46.15%, demonstrating in our case the optimal conditions for the adsorption is at lower temperature enhances the adsorption capacity, highlighting the importance of temperature in optimizing the adsorption process. At high temperature give more kinetic energy to chloride ions and water molecules, this can lead to desorption the reverse of adsorption, where previously adsorbed CL^- ions detach from Moringa surface and return to the solution.

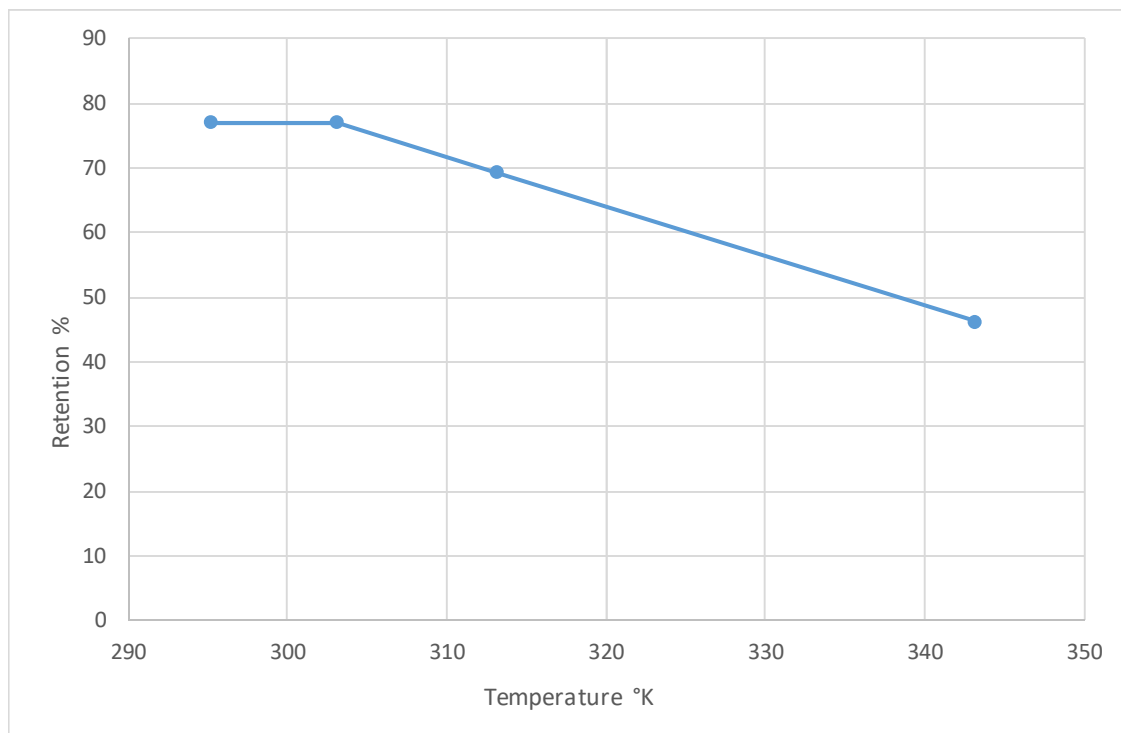


Figure 4.9: adsorbed yield of chloride as a function of temperature on MOS

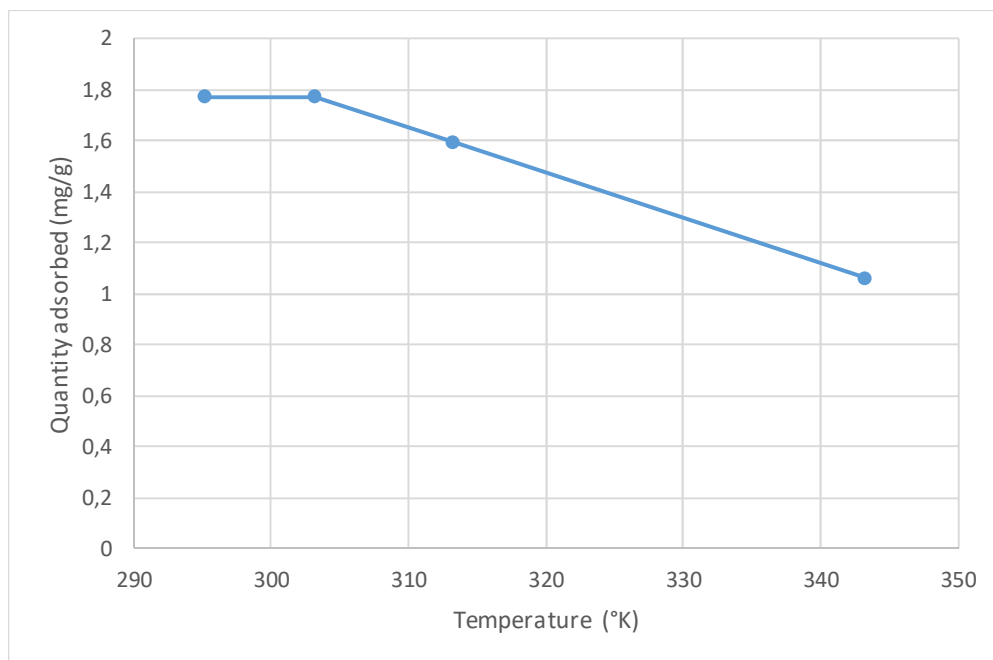


Figure 4.10: Adsorbed quantity of chloride as function of temperature on MOS

4.4. Thermodynamic study of chloride retention by MOS

Thermodynamic parameters relating to the sorption process, the free energy change (ΔG , KJ.mol⁻¹), enthalpy change (ΔH , J.mol⁻¹) and entropy change (ΔS , J.mol⁻¹), were calculated using the following equations:

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

$$\Delta G = \Delta H - T \Delta S$$

where R is the universal gas constant (8.314 J. K⁻¹mol⁻¹), T the absolute temperature (°K) and K is the equilibrium constant.

Values of the thermodynamic parameters are shown in Table 4.2. The values of the free energy change (ΔG) were negative, indicating the spontaneity of the adsorption process. The positive value of ΔS indicates the increased randomness in the system of the solid/solution interface during the adsorption of chlorides. Further, the positive value of ΔH confirmed that the sorption on a biomaterial of chlorides is endothermic process.

Table 4.2: Thermodynamics values of chlorides biosorption MOS

T(°K)	295.15	303.15	313.15	343.15
ΔH (kJ/mol)	2.55			
ΔS (J/mol.K)	75.03			
ΔG (kJ/mol)	-22.14	-22.74	-23.49	-25.74

4.5. Adsorption kinetics modeling

Adsorption kinetics modeling involves describing how adsorbate molecules are removed from a solution and accumulate on the surface of an adsorbent over time. The goal is to understand the rate and mechanism of adsorption.

4.5.1. pseudo-first-order kinetic model

plotting the curve of $\ln (Q_e - Q_t)$ versus time (t) allows for determination of the rate constant K1 and the equilibrium adsorption capacity Q_e . The results are shown in the figure 4.11.

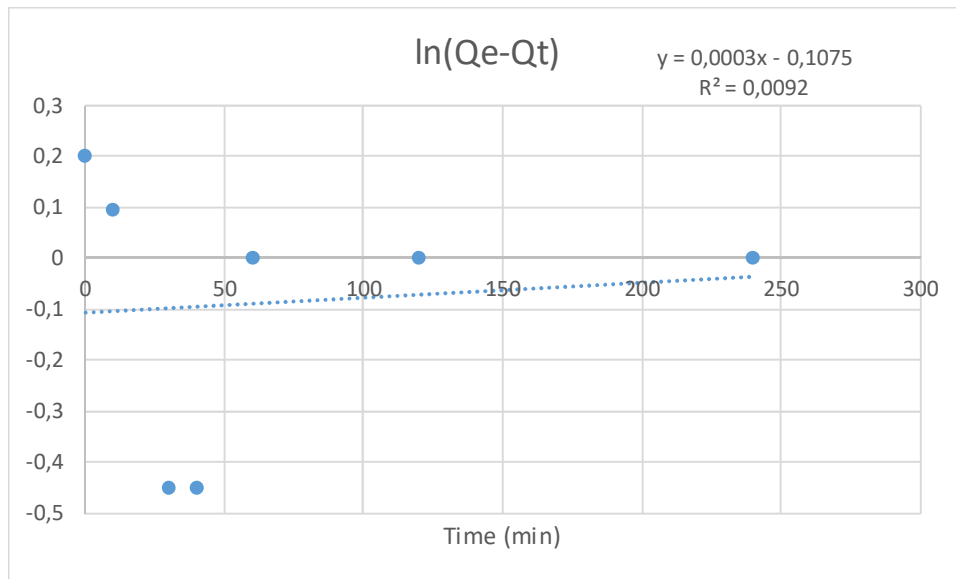


Figure 4.11 : pseudo-first-order model of chloride adsorption on MOS

4.5.2. pseudo-second-order kinetic model

the plot of t/Q_t versus time (t) is used to determine the rate constant K_2 . The results are illustrated in the figure 4.12.

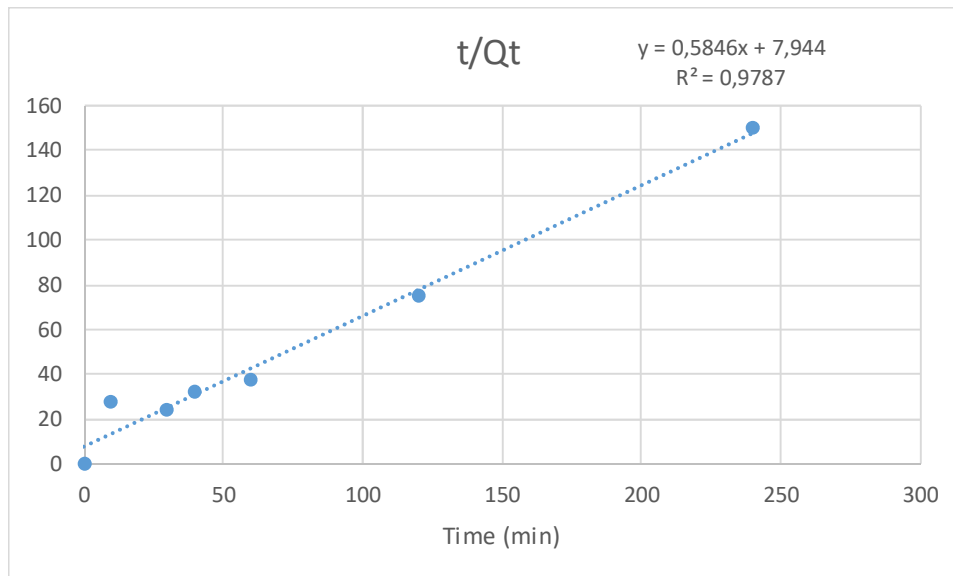


Figure 4.12 : pseudo-second-order model of chloride adsorption on MOS

Based on the kinetic modeling results, the adsorption data fits the pseudo-second-order model significantly better than pseudo-first-order model. the pseudo-first-order regression yielded a poor correlation coefficient ($R^2 = 0.0092$), an unrealistically high equilibrium; adsorption capacity ($Q_e = 3333,33 \text{ mg/g}$), and a negative rate constant, indicating a poor and physically invalid fit. In contrast, the pseudo-second-order model provided an excellent fit to the data, with a high correlation coefficient ($R^2 = 0.9787$), a realistic Q_e value of 1.71 mg/g , and a valid positive rate constant ($k = 0.043 \text{ g/mg.min}$). therefore, the pseudo-second-order is more appropriate for describing the adsorption kinetics in this study.

(Table 4.3) summarizes the parameters of the pseudo-first-order and second-order-models of Chloride adsorption on MOS.

Table 4.3: Parameters of the pseudo-first-order and second-order-models

	Pseudo-first-order	Pseudo-second-order
$Q_e (\text{mg/g})$	3333.33	1.71
$K \text{ g}/(\text{mg} \cdot \text{min})$	$-8.4 \cdot 10^{-7}$	0.043
R^2	0.0092	0.9787

General Conclusion

General Conclusion

This study successfully investigated the use of *Moringa Oleifera* seeds (MOS) as a natural, biodegradable, and cost-effective biosorbent for the dechlorination of brackish water. Addressing the critical environmental and public health challenges posed by residual chlorine and salinity in water, this research aimed to offer a sustainable alternative to conventional, often costly and environmentally damaging, water treatment methods.

The experimental findings consistently demonstrated the efficacy of MOS in significantly reducing chlorine levels without introducing secondary pollutants, highlighting its potential as a sustainable solution for water purification. Key parameters influencing the adsorption process were systematically examined:

- **Contact Time:** An optimal contact time of 60 minutes was identified, achieving a high removal efficiency of 69.23%, attributed to the electrostatic attraction between positively charged amino groups on MOS and negatively charged chloride ions.
- **Adsorbent Mass:** Increasing the mass of MOS generally enhanced chloride removal, with an optimal dosage of 5g yielding 76.9% efficiency. This was linked to the increased availability of active adsorption sites.
- **pH Influence:** The adsorption of chloride was most effective under acidic conditions, with an optimal pH of approximately 2, reaching an impressive 87.69% efficiency. This is because acidic environments promote protonation of the MOS surface, enhancing the attraction of chloride ions.
- **Temperature Effects:** Adsorption efficiency was found to decrease with increasing temperature. Optimal conditions were observed at lower temperatures (22°C and 30°C), where efficiency reached 76.92%, suggesting that higher temperatures may lead to desorption of chloride ions.

Overall, this research underscores the promising role of *Moringa Oleifera* seeds as an eco-friendly and economically viable biosorbent for water treatment. The findings contribute valuable insights into the adsorption mechanisms and optimal operating conditions for chloride removal, paving the way for the development and implementation of sustainable water purification technologies, particularly in regions where access to advanced treatment infrastructure is limited. Further research could explore the long-term performance, regeneration capabilities, and application in diverse water matrices to fully realize the potential of MOS in environmental engineering.

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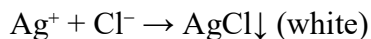
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ANNEX

Precipitation Reactions:



Operating Procedure

-Test sample: 10 ml of sample.

-Reagent: silver nitrate AgNO_3 .

-Indicator: potassium chromate K_2CrO_4 at 5%

In a 100 ml Erlenmeyer flask, pour 10 ml of sample, add 5 drops of K_2CrO_4 . Dropwise add the AgNO_3 solution placed in the burette. Stir the mixture vigorously during the titration so that the adsorption equilibrium has time to establish. The end of the titration is indicated by the brick-red color.

Complexometric titrations of Ca^{2+} and Mg^{2+} (total hardness)

Operating procedures

-Take a 50 ml volume of water to be analyzed in a 250 ml Erlenmeyer flask.

-Add 4 ml of ammoniacal buffer solution at pH=10.

-Add a small spatula tip of Eriochrome Black T. The coloration turns dark red or violet. The pH must be 10.

Titrate with an N/50 concentration EDTA solution contained in the precision burette until the color changes from red to blue, verifying that the coloration no longer changes with the addition of an extra drop of EDTA.

-Perform two trials (keep a control color) to determine V_1 .

Expression of results

The total concentration of calcium and magnesium, expressed in milliequivalents per liter, is given by the expression:

$$C' = 1000 \times (C \times V_1) / V_2$$

C' : concentration in milliequivalents per liter of the EDTA solution.

V_1 : Volume in ml of the EDTA solution

V_2 , Sample volume.

Complexometric titrations of Ca^{2+}

Operating procedures

- Take a volume $V_1 = 50$ mL of tap water in a 250 ml Erlenmeyer flask.
- Add 2 mL of soda (2N). The pH must be between 12 and 13.
- Add a small spatula tip of murexide.
- Titrate by stirring with an EDTA solution of molar concentration $C = 0.02$ eqg.L⁻¹ until the color changes from red to blue, where V is the number of milliliters poured.
- Perform two trials (keep a control color) to determine V Magnesium hardness is deduced by the difference between total hardness and calcium hardness.

Expression of results:

For a 50 ml test portion, the calcium content is equal to:

$$\text{Ca (mg/L)} = (V \times 0.4008 \times 1000) / 50$$

$$\text{CaCO}_3 \text{ (mg/L)} = (V \times 1000) / 50$$