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THEME

Removal of mercury from wastewater by adsorption on zinc oxide

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Abstract

The pollution by heavy metals, particularly mercury (Hg), is a major environmental issue due to their toxicity, persistence, and bioaccumulation in the food chain. Industrial, mining, and agricultural activities are the main sources of mercury contamination. Various physico-chemical methods have been developed to eliminate mercury from used waters, including cementation, chemical precipitation, and adsorption. Zinc oxide (ZnO) is an effective adsorbent due to its specific surface, porosity, and functional groupings. However, few studies have evaluated its potential for mercury elimination. This study aims to experimentally study mercury elimination in aqueous solution using zinc oxide adsorption. The results will provide valuable data for developing large-scale treatment processes.

Keywords: adsorption, mercury ions, zinc oxide (ZnO)

Résumé

La pollution par les métaux lourds, en particulier le mercure (Hg), est un problème environnemental majeur en raison de leur toxicité, de leur persistance et de leur bioaccumulation dans la chaîne alimentaire. Les activités industrielles, minières et agricoles sont les principales sources de contamination par le mercure. Diverses méthodes physico-chimiques ont été développées pour éliminer le mercure des eaux usées, y compris la cémentation, les précipitations chimiques et l'adsorption. L'oxyde de zinc (ZnO) est un adsorbant efficace en raison de sa surface spécifique, de sa porosité et de ses groupements fonctionnels. Cependant, peu d'études ont évalué son potentiel d'élimination du mercure. Cette étude vise à étudier expérimentalement l'élimination du mercure en solution aqueuse par adsorption d'oxyde de zinc. Les résultats fourniront des données précieuses pour développer des processus de traitement à grande échelle.

Mots-clés: adsorption, ions de mercure, oxyde de zinc (ZnO)

ملخص

ويمثل التلوث بالمعادن الثقيلة، ولا سيما الزئبق، مشكلة بيئية رئيسية بسبب سميتها وثباتها وتراكمها البيولوجي في السلسلة الغذائية. وتشكل الأنشطة الصناعية والتعدين والزراعية المصادر الرئيسية للتلوث بالزئبق. تم تطوير طرق فيزيائية كيميائية مختلفة لإزالة الزئبق من مياه الصرف الصحي، بما في ذلك التدعيم والترسيب الكيميائي والامتزاز. أكسيد الزنك هو امتزاز فعال بسبب سطحه المحدد ومساميه ومجموعاته الوظيفية. ومع ذلك، فإن القليل من الدراسات قد قيمت إمكانية إزالة الزئبق. تهدف هذه الدراسة إلى التحقيق التجريبي في القضاء على الزئبق في المحلول المائي عن طريق امتزاز أكسيد الزنك. وستوفر النتائج بيانات قيمة لتطوير عمليات تجهيز واسعة النطاق

الكلمات الرئيسية: الامتزاز، أيونات الزئبق، أكسيد الزنك

General Introduction

General Introduction

Water pollution by heavy metals, especially mercury (Hg), is a major environmental problem due to its toxicity, persistence and bioaccumulation in the food chain. Industrial, mining and agricultural activities are the main sources of mercury contamination of water.

Several physico-chemical methods have been developed to remove mercury from wastewater, including cementation, chemical precipitation and adsorption. Among these techniques, adsorption on metal oxide-based materials has proven to be particularly effective.

Zinc oxide (ZnO) is a promising adsorbent due to its large specific surface area, porosity and the presence of functional groups on its surface that facilitate the binding of Hg ions. However, few studies have evaluated its potential for the removal of mercury from wastewater.

The aim of the present work is to experimentally study the removal of mercury (Hg^{2+}) from aqueous solution by adsorption on zinc oxide. The parameters influencing the adsorption process such as pH, adsorbent dose, initial Hg concentration, temperature and contact time will be optimized. Adsorption kinetics and isotherms will also be determined to understand the mechanisms involved.

The results of this study will provide a better understanding of the potential of zinc oxide to remove mercury from wastewater and provide useful data for the development of large-scale treatment processes.

Our work is divided into three parts:

The first part presents an extensive bibliography and consists of three chapters:

- ➢ The first chapter provides a general overview of mercury, its effects on the environment and human health, and elimination processes.
- ➢ The second chapter presents a review of the knowledge of the adsorption process. A description of the different models that are used to exploit the experimental results.
- ➢ The third chapter presents a general overview of adsorbents.

- The fourth chapter presents a description of zinc oxide and its properties.

The second part presents all the experimental materials and methods;

The last part is dedicated to the exploitation of the results;

Finally, a general conclusion summarizes the main results obtained.

Bibliographic part

CHAPTERI

General overview of mercury

Chapter I

General overview of mercury

I.1.Introduction:

Mercury occurs naturally in the environment and exists in many forms. Like lead and cadmium, mercury is a constituent of the earth and a heavy metal. In its pure state, it is known as “elemental” or “metallic” mercury. Mercury is rarely found in nature as a pure, liquid metal, but rather in inorganic compounds and salts. Mercury can be bound to other compounds as mono-valent or divalent mercury (also known as Hg(I) and Hg(II) or Hg^{2+},respectively). Many inorganic and organic mercury compounds can be formed from Hg(II).[1]

At present, mercury is recognized as a hazardous metal whose use in certain sectors of industry is either banned or in the process of being eliminated. These include the use of mercury cathodes in the chlorine industry, thermometry, and other applications. Additionally, mercury is present in trace amounts in a number of modern consumer products, including laptop computers, batteries, telephones, certain high-tech lighting equipment, and anti-lock brakes in cars manufactured in 2002. The number of individuals utilizing mercury or mercury-based products is on the decline, and the chemical industry is subject to rigorous monitoring and control of its emissions. The production of mercury is currently minimal, and the majority of the mercury used is derived from the recycling of waste containing this element and from byproducts generated by the mining and metallurgical industries.

I.2.Basic facts about mercury

Mercury is a heavy metal that occurs naturally in the environment in various chemical forms. The elemental form of mercury is a shiny silvery metal. It is the only metal that exists in a liquid state under normal conditions of temperature and pressure, without the phenomenon of supercooling. This is because it has a significant vapor pressure, which allows it to vaporize quite easily. Mercury was employed for a considerable period in the production of thermometers and batteries prior to its prohibition in 1999. [2][3]

I.2.1.Origin - etymology

In ancient times, mercury was regarded as the primordial metal from which all other metals were derived, and also as the metal most akin to gold. It was therefore named after the planet closest to the Sun (Mercury). Mercury was sometimes considered to be a liquid state of silver, which gave rise to the names ‘liquid silver’, ‘living silver’ or ‘quick silver’, which were sometimes used. The atomic symbol 'Hg' is derived from the Latin name 'hydrargyrum', which is derived from the Greek 'hydrargyros' meaning 'water and silver'. This name is used to describe the silvery appearance and liquid state of mercury.[2]

I.2.2.The properties of mercury

Mercury is the chemical element with atomic number 80 and symbol Hg. It belongs to group II of the periodic table, has an atomic mass of 200.59 g/mol and an atomic nucleus of approximately 1.54 Å.

I.2.2.1. General Properties

Table I-1: General properties[3, 4]

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Names	***Mercury***
Z Symbol	80Hg
Chemical series	Transition metals
Group, period, bloc	12, 6,d
Density	13 579.40 kg/m3
MOHS hardness	1.5
Color	Silver white

I.2.2.2. Atomic properties

Table I-2: Atomic properties[4]

Atomic mass	200.59 g/mol
Atomic ray	150 (171) pm
Covalent radius	149 pm
Van der Waals radius	155pm
Configuration (Xe)	4f14 5 d10 6s2
Electrons per energy level	2, 8, 18, 32, 18, 2
Crystallized Structure	Rhombohedral
Oxidation states	1,2

I.2.2.3. Chemical properties

Mercury metal Hg° has an atomic number of 80 and an atomic weight of 200.59. It provides: [3][4]

Mercury ions:Hg^{+}- Hg^{+}ou Hg_2^{2+}

And mercuric ions :Hg^{++}

- They correspond respectively to mercurous compounds: Hg_2 X_2(Hg_2Cl_2, Hg_2SO_4…) and mercuric compounds: HgX_2 (HgS, HgCl_2 ...).
- It gives organ metallic derivatives: R-Hg-R, which is very reactive, and mixed derivatives: R-Hg-X, according to the mercuration process.
- Mercury slowly oxidizes in the air.
- It is insoluble in water, usual solvents and alkalis.
- Metallic mercury is oxidized in dry air. In the presence of moisture, mercury undergoes oxidation. The oxides formed are HgzO at room temperature.
- It is not damaged by dilute hydrochloric and sulphuric acids, but dissolves in hot dilute nitric acid and in concentrated sulphuric acid.
- One of the particularities of mercury is that it forms, with other metals, specifically called amalgams.

I.2.2.4. Physical properties

Mercury metal can be frozen and transformed into a solid at a temperature of -38.85°C. It can be transformed into a gas when boiled at 365.6°C. The density of mercury is 13.59 grams per cubic centimeter. [5]

The substance in question exhibits two particularly noteworthy physical properties.

- The surface tension is exceptionally high.
- It is also a good conductor of electricity.

Surface tension is a property of liquids that gives them the appearance of being covered by a skin. In addition to its conductivity with regard to electricity, this property is employed in a mercury switch, which is used to turn light on and off.

The other liquid metal is mercury. Indeed, there is only one other liquid element, bromine. Bromine is a non-metallic substance. At a temperature of 38.85°C, mercury can be frozen, or transformed into a solid. At 365.6°C, it can be transformed into a gas (boiled). Its density is 13.59 grams per cubic centimeter.

Mercury is also a highly conductive material with regard to electricity. This property is employed in a variety of functional products. One such device is the mercury switch, which is used to turn lights on and off. A small quantity of mercury is placed in a glass capsule of minimal dimensions.

A capsule can be constructed in such a way that it can tilt back and forth. As the capsule tilts, mercury flows from one end to the other. The presence of mercury at one end of the capsule will result in the generation of an electric current through a circuit. Conversely, in the absence of mercury, no current will flow. Mercury switches are relatively simple to manufacture and can be produced in a relatively short time. [6]

(Figure I.1): Mercury is the only metal that is liquid at room temperature.

I.3.Mercury in the environment

Mercury is a chemical element that is present in the earth's crust and is found in various forms in the environment, including elemental, inorganic and organic. It is released naturally into the environment through the process of degassing, which occurs in the earth's crust, volcanoes, soil and rock erosion, among other factors. Since the advent of industrialization, a proportion of the mercury present in the environment has also been derived from anthropogenic sources. [7]

Mercury can be transported through various compartments of the earth's ecosystem. It can be transported from the soil to lakes and rivers, evaporate from their surface, be eroded by the wind or propelled by volcanoes and carried into the air by the wind, then deposited on the ground, land or water. This process then begins anew.

I.3.1.Mercury distribution in the environment

Mercury is naturally present in the environment, whether in water, air or soil. [8]

3.1.1Air and precipitation

In the atmosphere, approximately 90% of mercury is present in its elemental form, Hg0. The remaining portion is constituted by dimethylmercury, other methylated and dimethylated mercury derivatives, and less than 1% particulate mercury.

The presence of mercury in rainwater can be attributed to the solubility of Hg0 in water, its oxidation and subsequent adsorption to aerosols. The monomethylated form, resulting from the decomposition of dimethylmercury, accounts for less than 1% of the mercury present in precipitation. The residence time of atmospheric particles and the associated mercury is relatively brief, typically on the order of a few days. In contrast, in the vapor phase, the residence time of mercury in the atmosphere is of the order of a year. This implies that a considerable proportion of the dry fallout will impact the fields in the vicinity of the sources, whereas the volatile forms will contribute to the homogenized, diffuse fallout on a hemispheric scale.

I.3.1.2 Water

The most prevalent form of mercury in water is divalent mercury, whether or not it is complexed by organic species.

In aqueous environments, two essential chemical reactions are in competition: reduction and methylation.

The first process is conducive to atmospheric recycling, while the second is conducive to bioaccumulation. The reduction or methylation of Hg^{2+} in aquatic systems modifies the chemical behavior of the element, determining its mobility, bioavailability and toxicity.

I.3.1.3 Soil rocks

This phenomenon occurs naturally in cinnabar (HgS). Mercury is found in igneous, metamorphic and sedimentary rocks, with the highest levels occurring in ultrabasic and alkaline rocks. Among sedimentary rocks, oil shales are the richest in mercury.

Cinnabar is composed of 86.2% mercury. Ores of lead and zinc also contain traces of mercury.

Mercury, which is naturally present in the soil, also originates from atmospheric and sedimentary deposits of surface water.

I.4.Mercury toxicity

I.4.1. Effects on human health

Mercury is a naturally occurring metal. Mercury enters the environment through the natural breakdown of minerals in rocks and soil that have been exposed to wind and water. The dispersion of mercury from natural sources has remained relatively consistent over time. Nevertheless, the concentration of mercury in the environment is consistently on the rise, and this can be attributed to human activity.[9]

The majority of the mercury released by human activities is emitted into the atmosphere during the combustion of fossil fuels, mining, smelting and the burning of solid waste. Some activities result in the direct release of mercury into the soil or water. For instance, the application of agricultural fertilizers and the discharge of industrial wastewater may contribute to this phenomenon.All the mercury released into the environment ends up in the soil or surface water.

I.4.2.Effects on the environment

Mercury spilt on the ground is rapidly immobilized. It is fixed by iron, aluminium and manganese oxides and by organic matter. It binds with organic matter in the form of very stable organic complexes.

The speciation and behavior of mercury in soils are influenced by a number of factors, including pH, concentration of organic matter, redox potential, cation exchange capacity, chloride concentration, aeration, mineralogical composition of the soil and soil texture.[7]

Soil is known to contain mercury derived from the bedrock on which it was formed. Consequently, the soil will be characterized by a higher concentration of mercury than the bedrock from which it originated. For instance, soils formed on quartz sands contain minimal quantities of mercury, whereas those formed on shale are considerably more enriched.

I.5. Mercury abatement methods

I.5.1. Adsorption

In the field of chemistry, adsorption is a surface phenomenon whereby atoms, ions or molecules (referred to as adsorbates) attach themselves to a solid surface (referred to as the adsorbent) from a gaseous or liquid phase or a solid solution. In the case of an adsorbed atom, we refer to it as an atom. [5]

Adsorbent materials:

- Activated carbon: Widely used, economical, but limited adsorption capacity.
- Alumina: Good adsorption capacity for Hg (II), but more expensive than activated carbon.
- Ion exchange resins: Selective for Hg (II), but can be sensitive to other metal ions.
- Nonmaterial: offer a large adsorption surface and high efficiency, but can be costly and difficult to synthesize

- **Factors influencing adsorption :**
  - pH: The optimum pH varies depending on the adsorbent, generally between 6 and 8.
  - Temperature: Adsorption is generally more favorable at low temperatures.
  - Mercury concentration: Adsorption efficiency decreases with increasing mercury concentration.

- **Adsorbent regeneration :**

  - Saturated adsorbents can be regenerated by chemical (e.g. NaOH) or thermal (e.g. heating) methods.

I.5.2. Filtration

Filtration is a separation process that separates the constituents of a mixture comprising both a liquid phase and a solid phase through the use of a porous medium. The application of a filter allows for the retention of particles within a heterogeneous mixture that are larger than the filter's pore size. [5,7]

- **Types of filters:**
  - Membrane filters: Effective against mercury particles > 0,1 µm.
  - Sand filters: Effective for mercury particles > 1 µm.
  - Deep filters: Effective for mercury particles > 5 µm.
- **Pre-treatments:**
  - Filtration may be preceded by coagulation/flocculation for particle-laden liquids.
  - Oxidation may be required to convert elemental Hg to Hg(II) prior to filtration.

I.5.3. Precipitation:

Precipitation refers to all forms of water in a liquid or solid state originating from the atmosphere. These hydrometeors, having undergone condensation and aggregation processes inside clouds, have become too heavy to remain suspended in the atmosphere and fall to the ground or evaporate into virga before reaching it.

Precipitants:

- Sodium sulphide: Precipitates Hg (II) as insoluble HgS.
- Sodium hydroxide: Precipitates Hg(II) as insoluble $Hg(OH)_2$.
- Sodium chloride: Precipitates Hg(II) as insoluble $HgCl_2$.

- **Factors influencing precipitation:**
  - pH: The optimum pH varies according to the precipitating agent.
  - Mercury concentration: The quantity of precipitating agent required depends on the mercury concentration.
  - Temperature: Precipitation is generally more favorable at low temperatures.

I.5.4. Oxidation:

Oxidation is a fundamental chemical process that involves the loss of electrons from an atom or molecule. It plays a crucial role in many everyday reactions, from the rusting of metal to the burning of fuel.

- **Oxidizing agents:**
    - Potassium permanganate: Oxidizes elemental Hg to Hg(II).
    - Iron(III) chloride: elemental Hg oxide to Hg(II).
    - Hydrogen peroxide: Elemental Hg oxide to Hg(II).

- **Coupling with other techniques:**
    - Oxidation can be followed by filtration or precipitation to remove Hg(II)

I.5.5. Extraction par solvent:

- **Solvents:**
    - Chloroform: Widely used, but toxic and volatile.
    - Dichloromethane: Less toxic than chloroform, but still volatile.
    - Liquid ionic solvents: Offer a more environmentally friendly alternative to traditional organic solvents.
- **Factors influencing extraction:**
    - Type of solvent: The choice of solvent depends on the form of mercury and the contaminated matrix.
    - pH: pH can affect extraction efficiency.
    - Temperature: Extraction is generally more favorable at higher temperatures.

Major considerations:

- **Cost:** The cost of mercury removal technologies varies depending on the method chosen, the amount of mercury to be removed and the contaminated matrix.
- **Regulations:** It is important to comply with local and national regulations for mercury disposal.
- **Safety:** Mercury disposal is a complex and potentially dangerous process. It is important to use qualified professionals for the management and disposal of mercury.

I.6.Properties and characteristics of zinc oxide (ZnO)

Zinc oxide is a binary inorganic compound with the chemical formula ZnO. It is an odorless, tasteless white powder that is insoluble in water. [10]

I.6.1.Physical properties:

- Crystal structure: Wurtzite (hexagonal) or blende (cubic)
- Color: White, but may turn yellow on heating
- Density: 5,61 g/cm^3
- Melting point: 1975 °C
- Boiling point: 2240 °C
- Refractive index: 2,008
- Good electrical and thermal conductivity
- Piezoelectric and semi-conductive properties

I.6.2.Chemical properties:

- Amphoteric oxide: Reacts with acids and bases.
- Soluble in strong acids and alkaline solutions
- Insoluble in water and alcohol
- Reacts with halogens to form zinc halides
- Photo luminescent: Emits visible light when exposed to ultraviolet light
- Wide band gap (3.37 eV): Transparent in the visible and near ultraviolet range

Uses:

- White pigment in paints, cosmetics and rubberss
- Sun protection agent
- Catalyst in many chemical reactions
- Food additive
- Semiconductor in transistors, diodes and lasers
- Piezoelectricity in sensors and transducers

Characterization:

- X-ray diffraction (XRD): Determination of crystal structure

- Infrared absorption spectroscopy (IR): Identification of functional groups
- Raman spectroscopy: Analysis of molecular vibration modes
- Scanning electron microscopy (SEM): Observation of surface morphology
- Elemental analysis: Determination of chemical composition

Zinc oxide is an important material with a wide range of applications. Its unique properties make it a valuable choice for many industries.

CHAPTER II

General information on the phenomenon of adsorption

Chapter II

General information on the phenomenon of adsorption

II.1.Introduction

The adsorption separation process is a highly significant technology in the present era, employed extensively for the purification and depollution of a diverse range of materials and applications, including those in the petroleum, petrochemical and chemical industries, as well as in environmental and pharmaceutical fields.

This chapter will provide an overview of adsorption, with a view to elucidating its significance and elucidating the factors that influence adsorption.

II.2.General definition of adsorption

Adsorption is defined as the process whereby molecules of a fluid (gas or liquid) attach themselves to the surface of a solid. The phase constituted of adsorbed molecules is designated as the 'solute' or 'adsorbate', while the solid is referred to as the 'adsorbent'. The surface of the solid is comprised of the external and internal surfaces created by the network of pores and cavities within the adsorbent. [7, 11, 12]

II.3. Adsorption theory

Adsorption theory is a set of models and concepts that explain the phenomena of adsorption, which is the attachment of molecules or ions to a solid surface. The following section presents a selection of key theories and models.[13] :

II.3.1.The Langmuir theory is a theoretical model that describes the adsorption of molecules on a surface. It was developed by Irving Langmuir and is based on the assumption that adsorption sites are energetically identical and that adsorption is localized on these sites. This theory, developed by Irving Langmuir, is based on the assumption that adsorption sites are energetically identical and that adsorption is localized on these sites. It is employed to delineate chemical adsorption and serves as the foundation for the Brunauer, Emmett and Teller (BET) theory.

II.3.2.TheBrunauer, Emmett and Teller (BET) theory is a theoretical framework that describes the adsorption of gases onto solid surfaces. This theory represents an extension of Langmuir's theory for the physical adsorption of gases. The theory takes into account the interactions between the adsorbed molecules and the adsorption sites, as well as the interactions between the adsorbed molecules themselves. The BET theory is employed to elucidate the physical adsorption of gases on solid surfaces.

II.3.3.The Flory-Huggins theory is a theoretical framework that describes the behaviour of molecules in solution. This theory is employed to elucidate the phenomenon of adsorption in solutions. The theory considers the interactions between adsorbed molecules and solvent molecules, as well as the interactions between adsorbed molecules themselves.

II.3.4.Density Functional Theory (DFT) This theory is founded upon the statistical mechanics of confined fluids and is employed to elucidate the phenomenon of molecular adsorption. It considers the physico-chemical characteristics of both the adsorbent and the adsorbate.

II.3.5.The theory of gas kinetics is concerned with the kinetics of gases. This theory is employed to elucidate the processes of adsorption and desorption. The theory considers the interactions between the adsorbed molecules and the adsorption sites, as well as the interactions between the adsorbed molecules themselves.

These theoretical frameworks and computational models are employed to elucidate and anticipate adsorption phenomena, which are of paramount importance in a multitude of domains, including water treatment, gas purification, and chemical production.

II.4. Adsorption processes

The various adsorption processes are methods used to separate and purify substances by attaching molecules or ions to a solid surface. The following section will present a brief overview of the principal adsorption processes:[11]

II.4.1. Fixed-bed adsorption

A process that is commonly employed for the purification of gases and liquids. In this process, the adsorbent material is arranged in the form of a bed within a column. The compounds to be adsorbed traverse the bed and are retained on its surface. This type of adsorption is an effective method for separating unwanted compounds from fluids by retaining them in the adsorbent bed.

II.4.2. Fluidized bed adsorption

Fluidized bed adsorption is a similar process to fixed bed adsorption, but with a slight difference. In this process, the adsorbent material is held in suspension in a stream of gas or liquid, creating a fluidized bed. The compounds to be adsorbed come into contact with the suspended adsorbent particles, resulting in effective adsorption. This process is often used for applications where intensive contact between the fluids and the adsorbent material is required.

II.4.3. Column adsorption

In this process, the adsorbent material is arranged in the form of a column. The compounds to be adsorbed pass through this column and are retained on its surface. This is an effective technique for separating unwanted compounds from fluids.

II.4.4. Direct injection adsorption

The adsorbent is transported by the off-gas and collected on a downstream filter. This method also improves adsorption kinetics and reduces pressure drops.

II.4.5. Adsorption in a wheel concentrator

This process uses a rotating wheel to adsorb molecules or ions. This allows continuous production and efficient regeneration of the adsorbents.

II.4.6. Dynamic adsorption

A method that involves modulating temperature, total pressure or concentrations in order to regenerate adsorbents in situ. It is frequently employed in conjunction with other regeneration techniques.

II.4.7. Membrane adsorption:

The adsorbent is immobilized on a porous membrane, allowing selective passage of the adsorbate, offers efficient separation of adsorbate and adsorbent, facilitates regeneration, allows continuous and compact operations and can be more expensive than other adsorption methods.

II.5.Types of adsorption

Depending on the amount of energy brought into play between the adsorbent and the adsorbate, the forces responsible for the adsorption phenomenon may be physical or chemical, leading to two types of adsorption: physical adsorption (**‘physisorption’**) and chemical adsorption **‘chemisorption’**[18].

II.5.1.Physical adsorption

Physical adsorption or physisorption involves very weak interactions between molecular entities such as Van der Waals forces of attraction and forces due to electrostatic polarization interactions; it is reversible and not very specific. Physical adsorption is rapid and generally limited by diffusion phenomenal.

II.5.2.Chemical adsorption

Known as chemisorption, this is an irreversible phenomenon due to a strong covalent chemical bond between the surface atoms of the solid and the adsorbed molecules. This type of adsorption involves high attraction energies, which lead to high adsorption heats.

II.6. Effect of the various factors influencing adsorption

The theory of the adsorption of liquids by solids is considerably less developed than that of the adsorption of gases or vapors by solids. This is undoubtedly due to a number of factors that make the study of such phenomena difficult to interpret. These factors include: [12] :

II.6.1. Specific surface area

The specific surface area, also known as the mass area, represents the total surface area per unit mass of the product accessible to atoms and molecules. An understanding of this surface area enables the reactivity of a sample to be more effectively controlled when it is brought into contact with other materials. This is because the rate of reaction varies with the state of division of the materials.

II.6.2. The pH

The pH has been demonstrated to exert a significant influence on the adsorption characteristics. In the majority of cases, the optimal results are achieved at the lowest pH. This property is particularly pertinent to the adsorption of acidic substances.

II.6.3. Concentration

For low dissolved concentrations, the adsorption rate is generally observed to obey Freundlich's law.

II.6.4. Adsorption speed

Physical adsorption in the liquid phase is much slower. The viscosity of the solution must be a factor affecting the speed of adsorption, and it is likely that reducing the viscosity by heating will increase the speed. This is one of the reasons why solid adsorbents are used to decolorize solutions at high temperatures.

II.6.5.The nature of the adsorbent

Since the substances to be adsorbed must move in a more or less viscous solvent, the adsorbent used in the liquid phase generally has different characteristics to those used in the gas phase.

II.6.6.The nature of the adsorbate

The physico-chemical properties of the adsorbate are decisive and play a key role in its adsorption onto a solid adsorbent surface. Molecular structure is one of the main parameters influencing adsorbate retention. The more voluminous the molecular structure, the more difficult it is for certain solid phases to retain it.

II.6.7. Temperature

Adsorption is an exothermic process and its progress must be encouraged by lowering the temperature, with some very rare cases of endothermicity being reported.

II.6.8. Porosity

Generally speaking, the adsorbent materials most commonly used in practice have a high porosity. The importance of this parameter lies in the geometric selectivity of the molecules to be adsorbed. It seems that the greatest diffusion in the pores will be influenced by the diameter of the pores. To characterize the porosity of an adsorbent material, it is necessary to determine its total porosity as well as the fractions due to macropores (greater than 30nm), mesopores (between 30 and 1.5 nm) and micropores (radius less than 1.5 nm). The pore volume vp expressed in cm3 /g is determined by the mercury porosimeter method.

II.7. Adsorption isotherms

An adsorption process can be described using an adsorption isotherm. Such an isotherm is a curve representing the relationship between the quantity of solute adsorbed per unit mass of adsorbent qe or X/m and the concentration of solute in solution Ce. Such a curve is obtained from the results of laboratory tests carried out at a constant temperature. To do this, known quantities of adsorbent are introduced into volumes of water to be treated and, after a given contact time, the residual concentration of solute in solution is measured [13].

The quantity of solute adsorbed is calculated using equation:

$$qe = \frac{(C0 - Ceq).V}{m} = X/m$$

Where :

C_0: initial solute concentration (mg/l)

Ce: equilibrium solute concentration (mg/l)

qe: quantity of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g)

X: quantity of solute adsorbed at equilibrium (mg); $X = (C_0 - Ce).V$

m: mass of adsorbent (g)

V: volume of solution (l)

Some authors have compiled a large number of Langmuir isotherms and found that there are 4 types, which have been linked fairly precisely to various binding modes.

II.8. Adsorption isotherm models

The phenomenon of adsorption has been established by several mathematical and empirical models, each of which is based on assumptions and approximations. Widely used models include:

8.1. Langmuir model

Langmuir's theory has been used to study the adsorption of gas molecules onto metal surfaces. Langmuir's isotherm is difficult to use for natural systems where single layer adsorption on a single type of site is rarely encountered. The isotherm is represented by the following equation [10,12]

$$\frac{Ceq}{qe} = \frac{1}{Kl.\mathrm{qm}} + \frac{1}{\mathrm{qm}} Ceq$$

Where:

Ceq: equilibrium concentration of adsorbate (mg/L).

qe: quantity of substance adsorbed per unit mass of adsorption (mg/g).

K_L: constant corresponding to the adsorption energy.

q_m: maximum adsorption capacity.

II.8.2.Freundlich model

In 1962, Freundlich proposed another model to describe adsorption in a gaseous or liquid medium. This model is represented by a two-parameter equation (Kf and n) and consists of an exponential distribution of adsorption site energies on the surface of the support and is characterised by adsorption at localised sites.

This model is described by :

$$\boldsymbol{qe} = \boldsymbol{KfCeq1/n}$$

Given that:

qe: the quantity of adsorbed entities per gram of adsorbent at equilibrium (mg/g).
Ceq: the concentration of adsorbate in the solution at equilibrium (mg/l).
Kf: Freundlich constant (l/mg).
n: Freundlich energy parameter.

When the value of n is between 1< n < 1, this indicates favorable adsorption.
On the other hand, if the value is n< 1, this indicates poor adsorption.

The two Freundlich parameters Kf and n can be determined experimentally by logarithmic transformation of the expression to give:

$$\boldsymbol{lnqe} = \boldsymbol{lnKf} + \boldsymbol{1/nlnCeq}$$

II.8.3.Temkin model

Temkin's isotherm takes into account the fact that the heat of adsorption of all the molecules in the capping layer decreases linearly with capping deue to the decrease in adsorbent-adsorbate interactions. Adsorption is therefore characterized by a uniform distribution of surface binding energies. The Temkin isotherm is expressed as

$$q_e = (RT \,/\, b_t\,)ln(K_t \cdot C_e)$$

Or in linear form:

$$q_e = B_1lnK_t + B_1lnC_e$$

With $B_1 = Rt/bt$ (J/mol), Temkin's constant for the heat of sorption and Kt (l/g) the adsorption equilibrium constant corresponding to the maximum binding energy.

II.9. Classification of adsorption isotherms:

Not all adsorbent-adsorbate systems behave in the same way. Experimentally, four main classes can be distinguished: S (Sigmoid), L (Langmuir), H (High affinity) and C (Constant partition). Figure (II.1) shows this classification.

After this description we turn to the interpretation of the different classes of isotherms. We start with the most common: the Langmuir isotherm [13,11]

II.9.1.Class L

At low solution concentrations, the L class isotherms show a downward concavity, reflecting a decrease in the number of free sites as adsorption progresses. This phenomenon occurs when the forces of attraction between the adsorbed molecules are weak. It is often observed when the molecules are adsorbed flat, which minimizes their lateral attraction. It can also occur when the molecules are adsorbed vertically and when adsorption competition between the solvent and the solute is low. In this case, the adsorption of isolated molecules is strong enough to make lateral interactions negligible.

II.9.2. S Class

At low concentrations, the isotherms in this class have an upward-facing concavity. Adsorbed molecules encourage the subsequent adsorption of other molecules (cooperative adsorption). This is due to the molecules attracting each other by Van Der Waals forces, and grouping together in islands in which they pack against each other. This behavior is favored when the solute molecules are adsorbed. Vertically, as is the case for molecules with a single functional group, and on the other hand, when the molecules are in strong adsorption competition with the solvent.

II.9.3. H Class

The initial part of the isotherm is almost vertical, and the quantity adsorbed appears large at almost zero concentration of the solute in the solution. This phenomenon occurs when the interactions between the adsorbed molecules and the solid surface are very strong. The class H isotherm is also observed when micelles or polymers formed from solute molecules are adsorbed.

II.9.4. C Class

The isotherms in this class are characterized by a constant partition between the solution and the substrate up to a plateau. Linearity shows that the number of free sites remains constant during adsorption. This means that the sites are created during adsorption. This implies that isotherms of this class are obtained when the solute molecules are able to modify the texture of the substrate by opening pores that had not previously been opened by the solvent. [13]

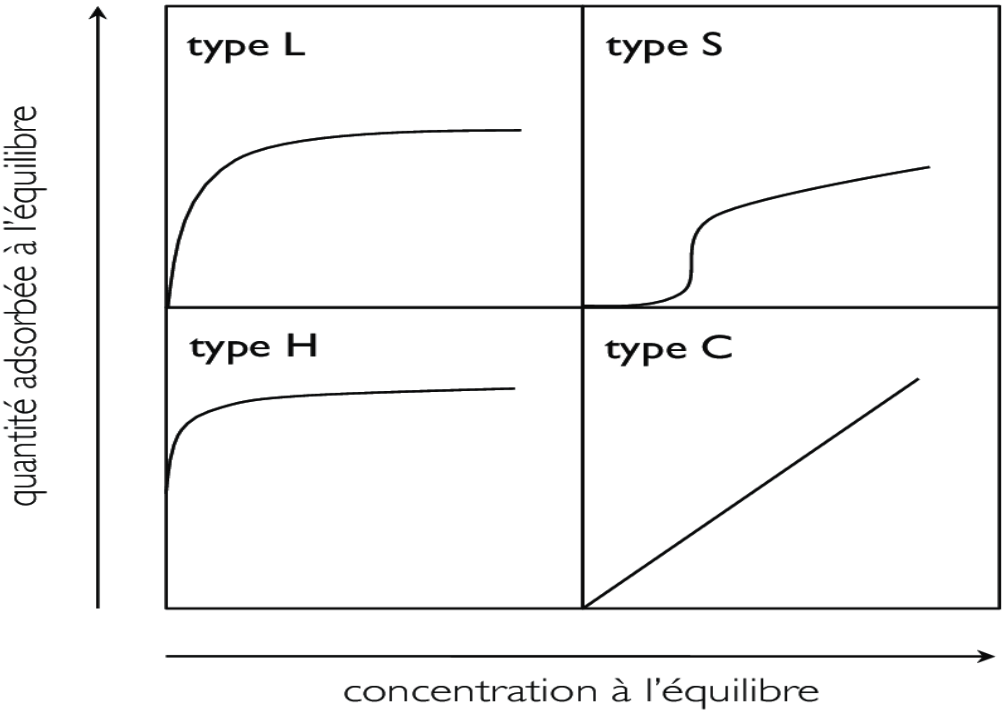


Figure II.1: The four types of isotherms according to Giles

II.10. Adsorption processes used in the chemical industry

Adsorption processes are widely used in the chemical industry to separate and purify substances. Here are a few examples of these uses [18].

II.10.1. Gaseous separation:

Adsorption is frequently used to remove impurities from gases. Adsorbents like activated carbon or molecular sieves are employed to selectively adsorb contaminants such as moisture, CO_2, sulfur compounds, and volatile organic compounds (VOCs) from process streams, ensuring the purity of gases used in various chemical processes.

II.10.2. Liquid separations:

Adsorption plays a crucial role in the purification of liquids. Activated carbon, zeolites, silica gel, and other adsorbents are utilized to remove organic impurities, colorants, odors, and trace contaminants from liquids such as water, solvents, and process streams.

II.10.3 Fractionation of hydrocarbons:

Adsorption is used to separate hydrocarbons according to their molecular weight and chemical structure.

II.10.4. Solvent recovery:

Solvent recovery is a crucial process in the chemical industry aimed at reclaiming and reusing solvents used in various processes, thereby reducing costs, minimizing waste, and enhancing sustainability. Adsorption plays a significant role in solvent recovery processes, particularly through techniques such as pressure Swing Adsorption (PSA) and activated Carbon Adsorption..

II.10.5. Purification of industrial gases:

Adsorption is a versatile and effective technique for the purification of industrial gases, offering high efficiency, selectivity, and scalability for a wide range of applications in various industries, including petrochemicals, energy production, semiconductor manufacturing, and environmental protection, and it is used to purify industrial gases such as CO2 and industrial gases.

II.10.6 Drug production:

Adsorption plays a pivotal role in numerous stages of pharmaceutical production, including purification, separation, formulation, and drug delivery. It contributes to the development of safe, effective, and high-quality pharmaceutical products.

II.10.7 Water and effluent treatment:

Adsorption is used to remove pollutants such as pesticides, chlorinated solvents, sulphur compounds, odors, VOCs and heavy metals from water and effluents.

II.10.8Air Pollution Control

Adsorption technologies are utilized for the control of air pollutants emitted from industrial processes. Adsorbents are employed to capture and remove harmful gases and volatile organic compounds (VOCs) from exhaust gases before their release into the atmosphere, helping to mitigate environmental pollution.

II.10.9.Gas Storage and Separation

Adsorption is utilized for gas storage and separation applications. Adsorbents with tailored pore structures, such as metal-organic frameworks (MOFs) and activated carbons, are employed to selectively adsorb and store gases like hydrogen, methane, and carbon dioxide, as well as for gas separation processes such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA).

II.10.10. Air Pollution Control

Adsorption technologies are utilized for the control of air pollutants emitted from industrial processes. Adsorbents are employed to capture and remove harmful gases and volatile organic compounds (VOCs) from exhaust gases before their release into the atmosphere, helping to mitigate environmental pollution.

These applications demonstrate the importance of adsorption in the chemical industries for separating and purifying substances, which is essential for the production of chemical products and for protecting the environment.

CHAPTER III

Adsorbents

Chapter III

Adsorbents

III.1. Introduction

Strictly speaking, all solids are adsorbents. However, only adsorbents with sufficient specific surface area (surface area per unit mass) can be of practical interest. Industrial adsorbents generally have a specific surface area of more than 100 m2 /g, and even several thousand m2 /g. These adsorbents are necessarily microporous, with pore sizes below 2 nm, or mesoporous, with pore sizes between 2 nm and 50 nm (according to the IUPAC classification).

According to the literature, a good adsorbent should have a highly developed pore structure and a very high specific surface area. These two characteristics allow the adsorption equilibrium (maximum adsorption) to be reached in the shortest possible time. An adsorbent must be: [19].

- Cheap and readily available.
- Adaptable (versatile) to potential applications, while being chemically, thermally and/or mechanically stable
- Have a high adsorption capacity for a wide range of pollutants
- Have fast adsorption kinetics
- Highly selective.
- Effective while remaining independent of the physico-chemical conditions of the solution (concentration, pH, ionic strength, temperature, possible presence of competitors or inhibitors, etc.).
- Easily regenerated if necessary.

III.2.The characteristics of adsorbents

Adsorbents, which are used in various fields such as water purification, air filtration, gas separation and even in chemical engineering for separation and purification processes, have several general characteristics: [20]

1. **High specific surface area:** The specific surface area is an essential measure of the sorption capacity of an adsorbent. It refers to the available surface area per unit weight of adsorbent. The higher the specific surface area, the more partitioned the adsorbent

2. **Porosity:** They are often porous, with a pore network structure that provides a large internal surface area for adsorption.
3. **Selectivity:** Some adsorbents are selective for certain substances, i.e. they can selectively adsorb certain compounds while allowing others to pass through.
4. **Adsorption capacity:** They have a high adsorption capacity, which means that they can effectively adsorb large amounts of substances on their surface. This is usually measured in milligrams of molecules per gram of adsorbent (mg/g).
5. **The structure of the adsorbent:** The adsorption of a substance increases as the particle size and pore size of the adsorbent decrease. However, if the pore diameter is smaller than the diameter of the molecules, the adsorption of this compound will be negative, even if the surface of the adsorbent has a high affinity for the compound. The pore size distribution plays an important role in the overall kinetics of the adsorption process.
6. **Reversibility:** The adsorbent must be capable of releasing the adsorbed substance when the conditions change, giving it a degree of reversibility in the adsorption process.
7. **Chemical stability**: Adsorbents must be chemically stable to maintain their adsorption properties when exposed to different substances and environmental conditions.
8. **Type of adsorbent**: The type of adsorbent can influence the adsorption capacity and adsorption rate. Natural adsorbents, such as clays and zeolites, have different properties to synthetic adsorbents, such as macromolecular resins.
9. **Regeneration**: Some adsorbents can be regenerated, i.e. the adsorbed substances can be removed from their surface, allowing them to be reused.
10. **Low cost:** Ideally, adsorbents are inexpensive to produce and use, making them attractive for a wide range of applications. These characteristics make adsorbents valuable tools in many purification and separation processes.

III.3. Mineral Adsorbents

Mineral adsorbents can exist in their natural or synthetic state. Adsorbents play a vital role in the mineral products industry for a variety of applications, including the separation, purification, recovery and refining of ores and derived products. The choice of the appropriate adsorbent depends on the specific nature of the mineral product, the impurities to be removed and the final objective of the treatment. [21]

III.3.1. Clays

Clays are aluminosilicates. They are natural products that are activated to improve their adsorption properties.

III.3.2. Zeolites

Zeolites are adsorbents with a three-dimensional aluminosilicate crystalline framework composed of SiO_4 and AlO_4 tetrahedra, with the general formula (AlO_2M, $nSiO_2$), where M is usually an alkali or alkaline-earth metal.

There are more than 100 species of zeolites, which differ in the value of n and in their crystallographic structure. They have a microporous structure of cavities and channels, which gives them adsorptive properties. They are available in powder, granular or extruded form. Their specific surface area does not exceed 900 m^2/g, but they have good selectivity [22].

III.3.3. Activated aluminas

Activated aluminas are obtained by flash thermolysis of aluminiumtrihydroxide$Al(OH)_3$, resulting in a product of approximate composition Al_2O_3, 0.5 H_2O, with a porous structure due to the elimination of water molecules. The surface of the pores is covered with Al-OH groups and adsorption is preferentially by hydrogen bonding.

Activated aluminas are amorphous, moderately polar and hydrophilic adsorbents. They have a specific surface area of 300 m^2 /g [23].

III.3.4. Silica gel

Silica gels are prepared from $Si(OH)_4$ in the aqueous phase, obtained by acidification of a sodium silicate, or from a silica sol. The Si-OH groups form hydrogen bonds.

There are two types of silica gel: microporous, which are relatively hydrophilic, and macroporous, which are versatile and, as the name suggests, differ in the size of their pores. Their specific surface area can range from 300 to 800 m^2 /g [24].

These materials are used to adsorb pollutants such as pesticides, chlorinated solvents, sulphur compounds, odours, VOCs and heavy metals from water and wastewater.

In summary, the adsorbents used for mineral products are mainly natural materials. These materials are activated to increase their porosity and adsorption capacity, making them effective in adsorbing pollutants from water and wastewater.

III.4. Factors to consider when selecting an adsorbent for mineral products:

1. Type of mineral product and impurities: The physico-chemical properties of the mineral product and the impurities to be removed determine the most appropriate type of adsorbent.

2. Adsorption selectivity: The adsorbent must be able to selectively adsorb the target impurities while allowing the desired mineral product to pass through.

3. Adsorption capacity: The ability of the adsorbent to adsorb a sufficient quantity of impurities is essential for optimum efficiency**.**

4. Operating conditions: The temperature, pressure and pH conditions of the process must be compatible with the properties of the adsorbent.

5. Cost and regeneration: The cost of the adsorbent and the ability to regenerate and reuse it are important economic factors to consider.

III.5. Organic adsorbents

In the field of organic products, adsorbents play a crucial role in various processes, including the separation, purification, decolorization and deodorization of organic compounds. The choice of the appropriate adsorbent depends on the specific nature of the organic product, the impurities to be removed and the final objective of the treatment [25].

III.5.1. Activated carbon

Activated carbon is the most widely used adsorbent in industry. It is mainly obtained from carbonaceous materials (wood, shells, oil residues, etc.). It consists of carbon particles that have been chemically or physically treated to increase their porosity and therefore their adsorption potential. It has been shown that activated carbon is a non-selective material that often physically adsorbs contaminants, mainly by van der Waals forces [23].

III.6. Polymer-based adsorbents

Polymer-based adsorbents are materials composed primarily of polymers (long chains of repeating units) that are designed to adsorb substances from a fluid or gas phase. These materials are used in a variety of applications, ranging from water purification to gas separation and chemical processing. [25]

The advantage of using polymers for adsorption lies in their tunable properties. Polymer structures can be modified to have specific chemical functionalities, pore sizes, surface areas, and mechanical properties, all of which can be tailored to optimize adsorption performance for particular applications.

Here are some key points about polymer-based adsorbents:

1. Versatility: Polymer-based adsorbents can be tailored to adsorb a wide range of substances, including organic compounds, heavy metals, and gases.

2. Customization: The properties of polymer-based adsorbents can be customized through various techniques such as copolymerization, cross-linking, and functionalization with specific chemical groups.

3. High surface area: Some polymer-based adsorbents can have high surface areas, which increase their adsorption capacity per unit mass or volume.

4. Regeneration: Depending on the application, polymer-based adsorbents can often be regenerated by desorbing the adsorbed substances, allowing for multiple uses and cost-effectiveness.

5. Cost-effectiveness: In many cases, polymer-based adsorbents can be more cost-effective than traditional adsorbents like activated carbon, especially when tailored for specific applications.

6. Durability: Polymer-based adsorbents can be engineered to have good mechanical strength and chemical stability, enhancing their durability and longevity in various operating conditions.

7. Environmental applications: Polymer-based adsorbents are widely used in environmental remediation processes, such as wastewater treatment and air purification, due to their effectiveness in removing pollutants.

Examples of polymer-based adsorbents include polymeric resins, ion exchange resins, and various types of functionalized polymers like chelating resins and molecularly imprinted polymers (MIPs). Each type has its own set of advantages and is chosen based on the specific requirements of the application.

III.7. Characterizing factors of adsorbents

Not all substances are equally capable of adsorption. The adsorption capacity of a pollutant depends on:[24]

- The binding energy of the adsorbate;
- The structure and size of the molecules: a high molecular weight reduces diffusion and therefore adsorbate fixation;
- Its solubility: the less soluble a substance is, the better it will be adsorbed.
- Its concentration.

CHAPTER IV

General information on zinc oxide

Chapter IV

General information on zinc oxide

IV.1.Introduction

Zinc oxide (ZnO) or zinc white is one of the most widely used chemical compounds today. This material is used in the manufacture of glass, ceramics, foodstuffs and cosmetics. In this chapter, we will provide a brief bibliographical review of the various physicochemical properties of this material.

IV.2 Definition

Zinc oxide is a chemical compound consisting of the oxygen atom (O) located in row 2 and column 6 of the periodic table (VI A), and the zinc atom (Zn) in row 4 and column 10 of the periodic table (II B), with the chemical formula (ZnO) [14].

It can occur naturally in the form of ‘zincite’ (Figure IV.1) but can also be synthesized chemically. It is a non-toxic (II-VI) binary material with a large direct gap (3.37 eV) and a high exciton binding energy (60 meV) at room temperature. It is transparent in the visible and near infrared. It has a range of characteristics that enable it to be used in a wide variety of applications. For example, thanks to its very interesting photoluminescence and cathodoluminescence properties, it is used as a piezoelectric material, as well as a variety of other applications.

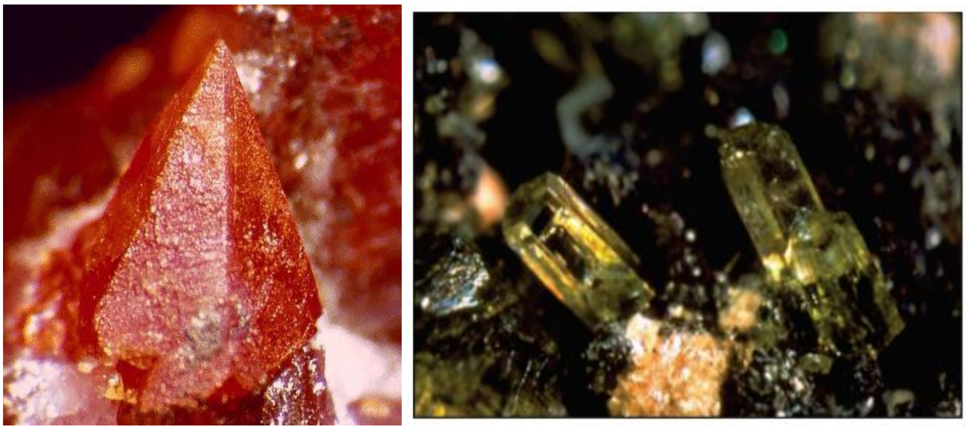


Figure IV.1: Zinc oxide (ZnO) in natural form

IV.3.The chemical properties of ZnO

Pure ZnO is a white powder, but in nature it occurs as zincite (a rare mineral), which generally contains manganese and other impurities that give it a yellow to red colour.

Crystalline zinc oxide exhibits thermo chromic properties, whereby it undergoes a color change from white to yellow when heated in air and returns to white upon cooling. This color change is attributed to a minor loss of oxygen from the surrounding environment at elevated temperatures, which results in the formation of the non-stoichiometric Zn 1 + x O.

Zinc oxide is an amphoteric oxide. Zinc oxide is almost insoluble in water, but soluble in most acids, including hydrochloric acid.

$$ZnO + 2\,HCl \rightarrow ZnCl_2 + H_2O$$

Solid zinc oxide also dissolves in alkalis to give zincates.

$$ZnO + 2NaOH + H_2O \rightarrow Na_2[Zn\,(OH)_4]$$

ZnO reacts slowly with fatty acids in oils to produce the corresponding carboxylates, such as oleate or stearate. Upon mixing ZnO with a strong aqueous solution of zinc chloride, a cement-like product is formed. This product is best described as a zinc hydroxyl chloride [10]. This cement was employed in the field of dentistry.

Furthermore, ZnO forms a cement-like material when treated with phosphoric acid. Related materials are used in dentistry. A significant constituent of zinc phosphate cement produced by this process is the compound $Zn_3\,(PO_4)_2{\cdot}4H_2O$, commonly referred to as "spirit."

Zinc oxide is derived from zinc sulphide through a chemical transformation. This transformation is carried out by an exothermic reaction, such that once initiated, the operation continues without any external heat input between 800 and 1000 °C.

$$ZnO + ZnS + \frac{3}{2}O_2 \longrightarrow ZnO + SO_2$$

IV.4.Physical properties of ZnO [16]

The physical properties of zinc oxide with a hexagonal structure are listed in the following table:

TableIV.1: Physical properties of zinc oxide with a hexagonal structure

Proprieties	**Value**
Mesh parameters at 300K a_0 c_0 c_0/a_0	0,325 nm 0,521 nm 1,602(1,633 for the structure Ideal hexagonal)
Density	5.606g.cm^{-3}
a is stable at 300K	wurtzite
Melting point	1975°C
Thermal conductivity	1-1,2W.m^{-1}.K^{-1}
Coefficient of linear expansion(/°C)	a_0:6,510^{-6},c_0:3,010^{-6}
Static dielectric constant	8,656
Refractive index	2,008-2,029
Energy of the band gap	3,37 eV
Concentration of intrinsic carriers	<106cm^{-3}
Exciton binding energy	60meV
Effective mass of the electron	0,24 m_0
Hall electron mobility at 300 K for n-type low conductivity	200cm^2.V^{-1}.s^{-1}
Effective mass of the hole	0,59 m_0
Hall mobility of holes at 300 K for p-type low conductivity	5-50cm^2.V^{-1}.s^{-1}

IV.5.The catalytic properties of ZnO

The composition and surface characteristics of a substance determine its ability to act as a catalyst in a certain system. The effectiveness of zinc oxide is determined by its manufacturing process. Zinc oxide is used as a gas trap and as a chemical sensor (H_2S, CO_2, H_2, CH_4). It can function as a photochemical catalyst for a variety of reactions when suspended in water, including the conversion of oxygen to ozone, the conversion of ammonia to nitrate, the reduction of methylene blue, the creation of hydrogen peroxide and the oxidation of phenols.[26]

IV.6.The use of ZnO as an adsorbent and as a catalyst:

In the chemical industries, ZnO is used both as an adsorbent and as a catalyst due to its unique properties**.**[27]

IV.6.1. As an adsorbent

ZnO is effective at adsorbing various organic and inorganic pollutants found in water and air. Its large specific surface area and ability to form chemical bonds with contaminants make it an ideal material for purification.

IV.6.1.1.Water purification:

ZnO can be used to remove various contaminants from water, such as heavy metals, organic dyes and volatile organic compounds. It works by adsorbing these pollutants on its surface, effectively trapping them and purifying the water.

IV.6.1.2. Gaz treatment:

ZnO is also effective at adsorbing certain harmful gases present in the air, such as sulphur dioxide (SO_2), ammonia (NH_3) and volatile organic compounds (VOCs). This property is often exploited in air purification and industrial waste gas treatment systems.

IV.6.1.3. Catalysis:

ZnO can be used as a support for catalysts in various chemical reactions. Depending on its structure and surface properties, it can improve the catalytic efficiency of active materials, facilitating reactions such as the selective catalytic reduction (SCR) of nitrogen oxides (NOx) or the synthesis of valuable chemicals.

IV.6.1.4. Filtration:

ZnO can be used as a filter material to remove suspended particles and contaminants from liquids and gases. Its adsorption properties enable it to effectively retain these impurities, thus improving the quality of the fluid treated.

IV.6.1.5. Biomedical applications:

In the biomedical field, ZnO is sometimes used as an adsorbent to remove toxins and pathogens from various biological fluids. It can also be incorporated into medical devices for its antibacterial properties and adsorption capacities.

IV.6.2. As a catalyst:

ZnO is often used in chemical reactions such as the synthesis of organic chemicals and the decomposition of harmful compounds. Its ability to catalyse specific chemical reactions by accelerating the reactions while remaining unchanged at the end of the process makes it a valuable catalyst in many industrial applications.

IV.6.2.1. Dehydrogenation reactions:

ZnO can be used as a catalyst in dehydrogenation reactions, where it promotes the removal of hydrogen atoms from organic molecules to form unsaturated compounds. For example, it can catalyse the dehydrogenation of methanol to form formaldehyde.

IV.6.2.2. Oxidation reactions:

ZnO is also used in oxidation reactions, where it facilitates the addition of oxygen atoms to organic or inorganic compounds. It can be used in reactions such as the oxidation of alcohol to aldehyde or carboxylic acid, or in reactions to remove organic pollutants from air or water.

IV.6.2.3. Chemical synthesis reactions:

ZnO can be used as a catalyst in various chemical synthesis reactions, such as the synthesis of organic and inorganic chemicals. It is often used as a support for catalytic metals, such as copper, cobalt or nickel, which are deposited on its surface to improve its catalytic activity.

IV.6.2.4. Reduction reactions:

ZnO can also be involved in reduction reactions, where it facilitates the loss of oxygen atoms or the addition of hydrogen atoms to compounds. For example, it can be used in the selective catalytic reduction (SCR) of nitrogen oxides (NOx) in vehicle exhaust gases to reduce pollutant emissions.

IV.6.2.5. Heterogeneous catalysis:

ZnO is often used as a heterogeneous catalyst, which means that the chemical reaction takes place on its surface while the catalyst remains in solid form. This configuration allows easy recovery of the catalyst and can be used in continuous catalysis processes.

These applications demonstrate the versatility of ZnO as a catalyst in a range of chemical reactions important to the chemical, petrochemical and environmental industries. Its use can help improve the efficiency of industrial processes while reducing costs and environmental impact.

As such, ZnO is a versatile material with important applications as an adsorbent for purification and as a catalyst for accelerating chemical reactions.

Experimental part

CHAPTER V

Materials & methods

Chapter V

Materials &methods

V.1. Introduction

This study was conducted at SONATRACH's research and development center. This section presents the analytical techniques and experimental protocol employed. These include X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (FTIR), and particle size analysis.

Subsequently, the experimental protocols employed for mercury adsorption experiments on zinc oxide will be delineated in detail.

V.2. Equipment

The instruments used in our study are shown below:

a. Analytical balance, METTLER TOEDO brand, precision 0.01 mg (Figure. V.1)

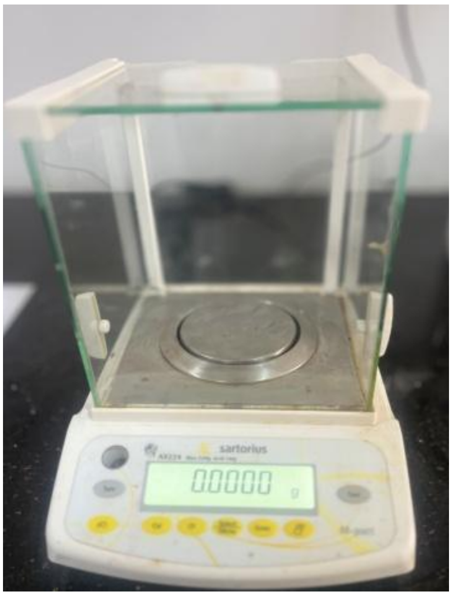


Figure.V.1 : Analytical balance.

b. Multi-stage magnetic stirrer plate (Figure. V.2)

Figure. V.2: Multi-stage magnetic stirrer plate

c. pH meter Hach HQ40d brand(Figure. V.3)

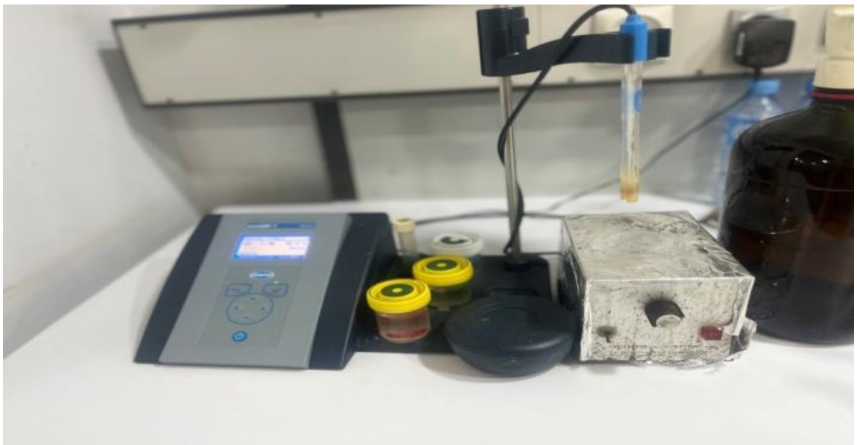


Figure. V.3:pH meter

d. Heating plate CORNING Stirrer/Hot plate (Figure.V.4)

Figure.V.4: Heating plate Corning

e. Mercury vapor monitor brandVm 3000 / 254 LabAnalyzer (Figure.V.5)

Figure.V.5: Mercuryvapormonitor

f. Scanning electron microscopy (SEM) FEIQUANTA 650 (Figure.V.6)

Figure.V.6: Scanning electron microscopy (SEM)

g. Bruker "D8 Advance" X-ray diffraction with LynxEye detector (Figure. V.7)

Figure.V.7:X-ray diffraction

h. LA 950 laser granulometer (Figure. V.8)

Figure.V.8: granulometer

i. SAFAS MONACA Spectrum Two infrared spectroscopy (FTIR) (Figure.V.9)

Figure.V.9 Infrared spectroscopy (FTIR)

Chemical reagents

The chemical reagents that have been used in this experiment are as follows:

Table V.1: The chemical reagents that have been used

Chemical reagents	Chemical formula	Molar mass (g/mol)	Purity (%)
Zinc oxide	ZnO	81,38	99,99
Hydrochloric acid	HCl	36 ,46	38
Potassium bromide / potassium bromate	$KBr/KBrO_3$	119/167	99/99,5
Sodium hydroxide	$NaOH$	39,997	98
Tin chloride(II)	$SnCl_2$	189,6	99
Nitric acid	HNO_3	63,012 8	70

V.3. Analysis methods

a. Scanning electron microscope (SEM)

This technique was employed to gain insight into the morphology of certain phases at a scale of a few micrometers. The microscope utilized was a FEIQUANTA 650 equipped with a field emission gun. The sample was deposited on a pellet containing carbon. The acceleration voltage was adjusted between 0.5 and 30 kV, depending on image quality, magnification up to x 150,000, and resolution of 1.6 nm at 20 kV. The observation is performed using secondary electron detection.

b. Infrared spectroscopy (FTIR)

Infrared spectroscopy is a physical method of structural analysis. It determines the nature of interatomic bonds in a molecule and identifies functional groups. IR absorption spectra were recorded using a SAFAS MONACA Impact FTIR spectrometer on a press-pasted sample of zinc oxide (ZnO) in potassium bromide (KBr) at a ratio of 2 mg product to 300 mg KBr. The recording is conducted within the wave number range between 4000 and 600 cm^{-1}.

Among the techniques employed in the analysis of solid samples, that of pelletizing with potassium bromide (KBr) is the most prevalent. This technique is advantageous as it eliminates the potential for the introduction of additional infrared (IR) bands due to potassium bromide.

c. X-ray diffraction (XRD)

X-ray diffraction (XRD) is a technique that identifies the nature of the crystalline and amorphous phases present in a solid. However, in order for visible diffraction lines to form, it is necessary for several crystalline lattices to be present one after the other. In the event that the number of meshes constituting the crystallites is relatively low, the diffraction lines will appear broad. In certain instances, this property can be employed to ascertain the dimensions of crystallites.

d. Laser particle size analyzer type LA 950

The sample was analyzed using a LA 950 Laser granulometer (Fig.V.8) with OPEXCEL, design calculation software, which is a kit comprising the following components:

- ➢ The laser particle size analyzer, or LA 950, is composed of an array of essential elements, including a laser source generator, two distinct analysis options (one for wet samples and another for dry samples), a light convergence faceplate, 87 detectors (sensors), and an electronic interface board.
- ➢ Two samplers (wet and dry) were utilized.

▪ The instrument offers a granulometric range extending from 0.01 microns to 3000 microns.

▪ The dry process has a particle size range of 0.1 microns to 3000 microns.

e. Mercury vapor manitorVm 3000 / 254 LabAnalyzer

The LabAnalyzer is the perfect solution for quantitative determination of mercury in aqueous samples and sample digests in the laboratory.

In contrast to a typical multi-element AAS the LabAnalyzer 254 is specially designed for elemental mercury. This allows top performance in analytical applications. The use of a specially developed highly stable mercury lamp in connection with thermostat-controlled UV sensors results in a detection limit of a few ppt of mercury.

V.4 Study of mercury Hg adsorption on zinc oxide ZnO :

V.4.1. Experimental protocol

All experiments were carried out in batch mode, contacting a mass m of zinc oxide according to the study parameters with a solution of Hg of initial concentration C_i=30 µg/l. The mixture was then subjected to magnetic stirring at regular speed. For the time required to reach equilibrium.

The pH of the aqueous solution is adjusted by adding nitric acid HNO_3 and sodium hydroxide Na OH solution.

V.4.2. Influence of adsorption operating conditions on mercury removal

The investigation of the impact of experimental parameters on the adsorption efficiency of metal ions represents a pivotal stage in the optimization of the adsorption process. It has been demonstrated that the efficiency of the adsorption process is highly contingent upon the physicochemical characteristics of the solution, particularly the solid/liquid ratio, time, pH, and temperature.

V.4.2.1.The Effect of the Solid/Liquid Ratio

To investigate the impact of the solid/liquid ratio on the adsorption of Hg2+ ions, experiments were conducted with ratios of (0.25, 0.5, 0.75, 1 and 2 g/l), an optimal pH, and an initial concentration of 30 µg/l at room temperature.

V.4.2.2.The Effect of Contact Time

The adsorption experiment was conducted over a period of two hours with an initial concentration of 30 µg/l, a free pH, and a zinc oxide dose of 1 g/l at room temperature.

The mixture was agitated at a moderate speed. Tests were conducted at various contact times (0, 30, 60, 90, and 120 minutes).

IV.4.2.3.The Effect of pH

In any adsorption study, pH is an important factor that can influence the adsorbent, the adsorbate, and the adsorption mechanism. It is therefore logical to ascertain the adsorption efficiency at different pH levels.

The impact of pH on the adsorption of Hg^{2+} ions by zinc oxide (ZnO) was investigated over a pH range of 1 to 11, with an initial concentration of 30 µg/L and a ratio (S/L) of 1 g/L ZnO at room temperature.

V.4.2.4.The Effect of Temperature

To investigate the influence of temperature on the adsorption of mercury ions by zinc oxide (ZnO), adsorption tests were carried out at different temperatures (25 ºC, 30 ºC, 40 ºC, 50 ºC and 60 ºC). The remaining conditions are identical to those previously described.

CHAPTER VI

Characterization of zinc oxide

Chapter VI

Characterization of zinc oxide

VI.1. Introduction

In this chapter we present the various analytical techniques (X-ray diffraction, scanning electron microscopy, Fourier transform spectroscopy and granulometry) used to identify our material, its structure and textural properties (pore sizes, chemical composition, etc.)

VI.2.X-ray diffraction

The analysis by X-ray diffraction of zinc oxide ZnO, provided us with the diffractogram shown in Figure VI.1, it can be concluded that the sample is composed of zinc oxide type zincite.

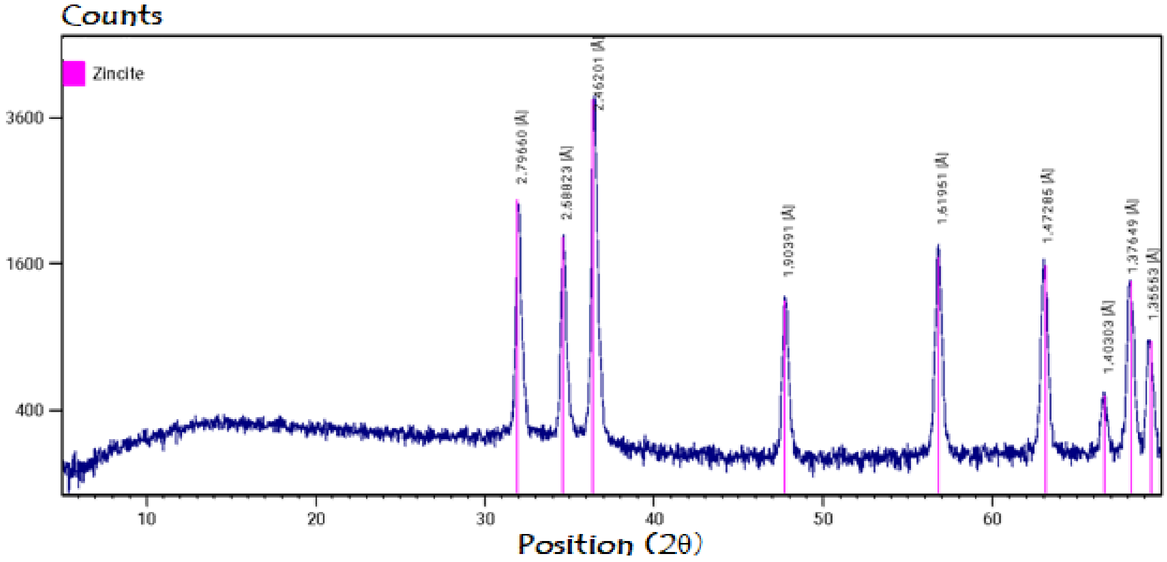


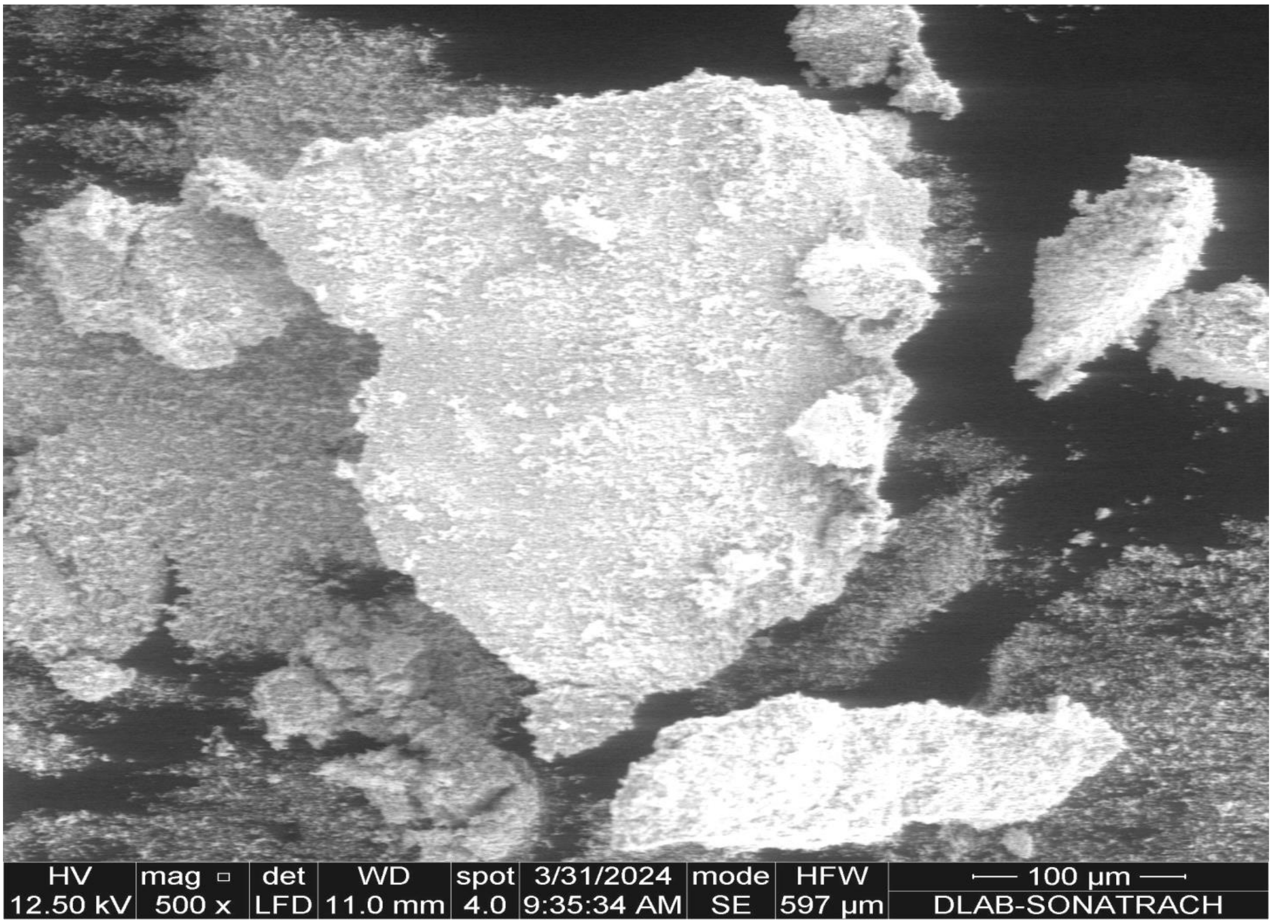
Figure VI.1 : diffractogram of zinc oxide (ZnO)

The purpose of this analysis is to specify the structure of the layers and measure the lattice parameters. The crystalline structure and orientation of the ZnO layers are studied by X-ray diffraction (XRD), which is presented in Figure Five diffraction peaks can be seen located at 2θ° = 34.35°, 36.2°, 47.5°, 62.96° and 67.99° corresponding to the (0002),(1011) ,(1012), (1013) and (1122) planes respectively. These positions are identical to those reported on the JCPDS sheet for ZnO (JCPDS 36-1451 card). X-ray diffraction analysis of ZnO shows that the layer studied is polycrystalline and has retained a hexagonal Wurtzite-type structure (JCPDS

36-1451 card). In addition, no additional diffraction peaks related to other impurity phases were observed, indicating that the synthesized layer has a high crystalline quality.

VI.3. Study of morphology of zinc oxide by scanning electron microscopy (SEM)

The morphology of zinc oxide is determined by scanning electron microscopy, as demonstrated in (Figure VI.2). The shape and dimension of zinc oxide can be described as angular and between 100 and 500 nanometers in size.



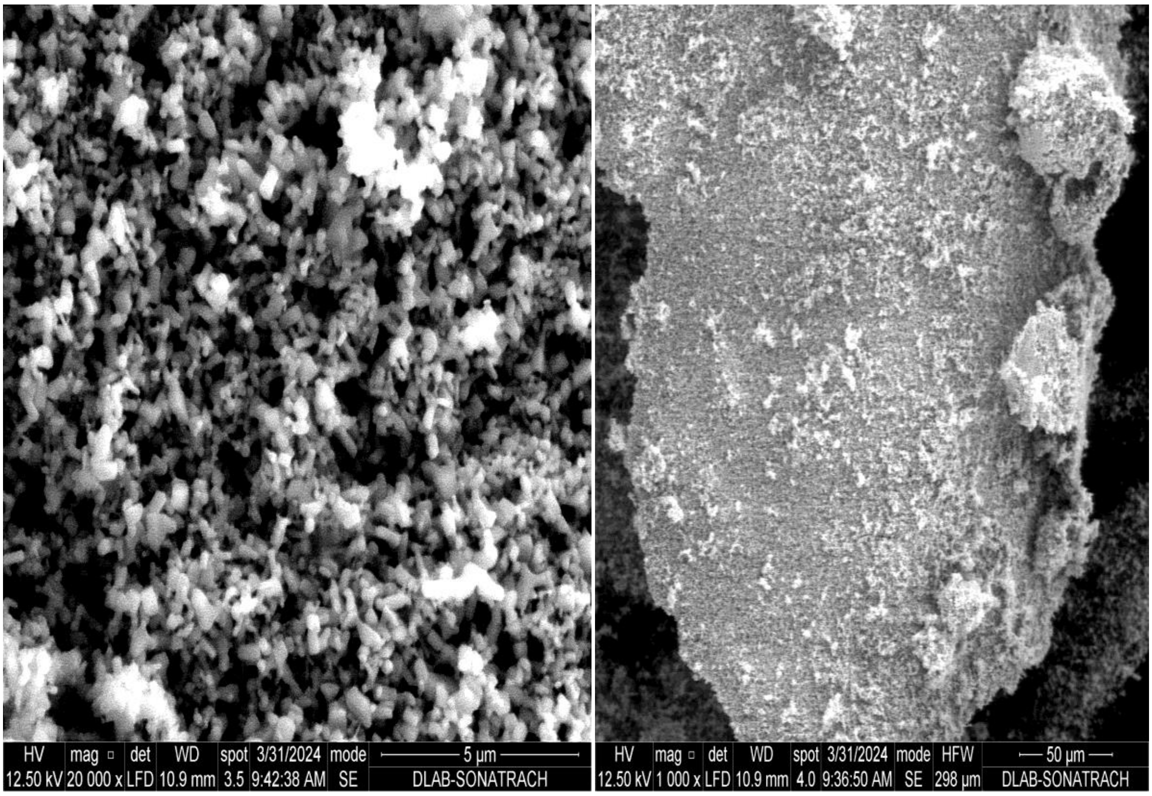


Figure .VI.2: Scanning electron microscopy of zinc oxide ZnO

The zinc and oxygen atoms occupy only 40% of the volume of the crystal, leaving empty spaces with a radius of 0.95 Å. It is possible that, under certain conditions, excess zinc atoms can lodge in these interstitial spaces. This feature helps to explain certain specific properties of zinc oxide related to the phenomena of semi-conductivity, photoconductivity and luminescence, as well as catalytic and chemical properties [28]. Zinc oxide is available in rectangular and hexagonal forms and is between 100 nm and 500 nm in size.

VI.4. Fourier transform infrared spectroscopy (FTIR) study

Our sample of ZnO nanoparticles were characterized by Fourier transform infrared (FTIR), as illustrated in Figure VI.3

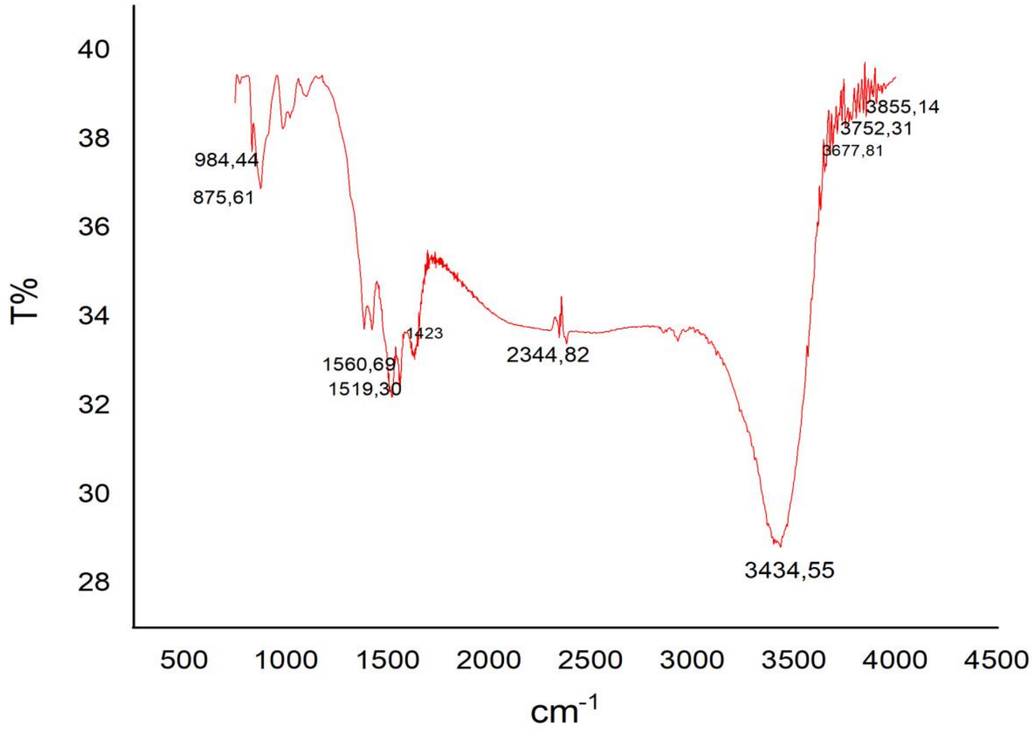
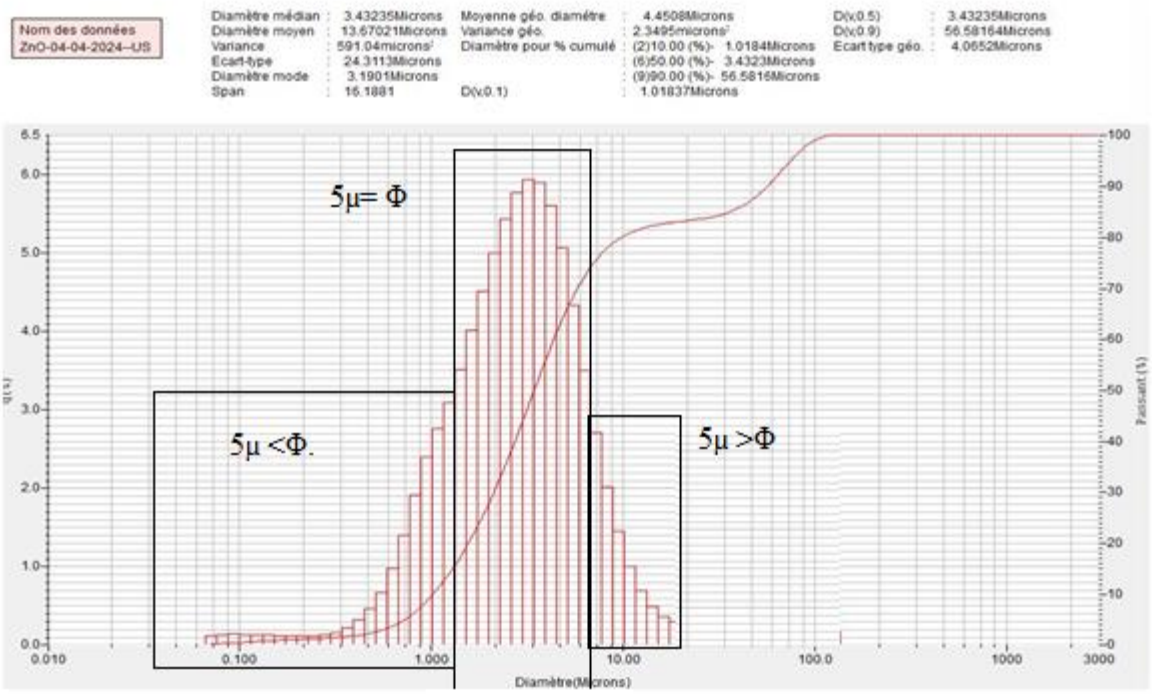


Figure .VI.3. : Spectroscopy (FTIR)

Adsorption bands in the region <1000 cm^{-1} represent interatomic vibrations. The Figure VI.3 confirms that the ZnO nano particles had adsorption peaks at 3438, 2918, 2367, 1634, 1446, 1033, 876 and 701 cm^{-1}. The peaks at around 1033 cm^{-1} were characteristic peaks (absorption) of the Zn-O bonding. Meanwhile, peaks at 1033, 876 and 701 cm^{-1} confirm the presence of Zn-O in the sample [29]. The adsorption peaks at around 1446 cm^{-1} represent C=C stretching, while the peak at 3600 cm^{-1} indicates the stretching vibrations of OH. The presence of C-O is indicated by a peak at 2367 cm^{-1}. Adsorption peaks can also be observed at3428 cm^{-1}, which then diminish gradually [30][31]. The interference pattern illustrated in the FTIR spectra clearly demonstrates the adsorption peaks of Zn-O at 1033 cm^{-1}, which authenticated the presence of ZnO.

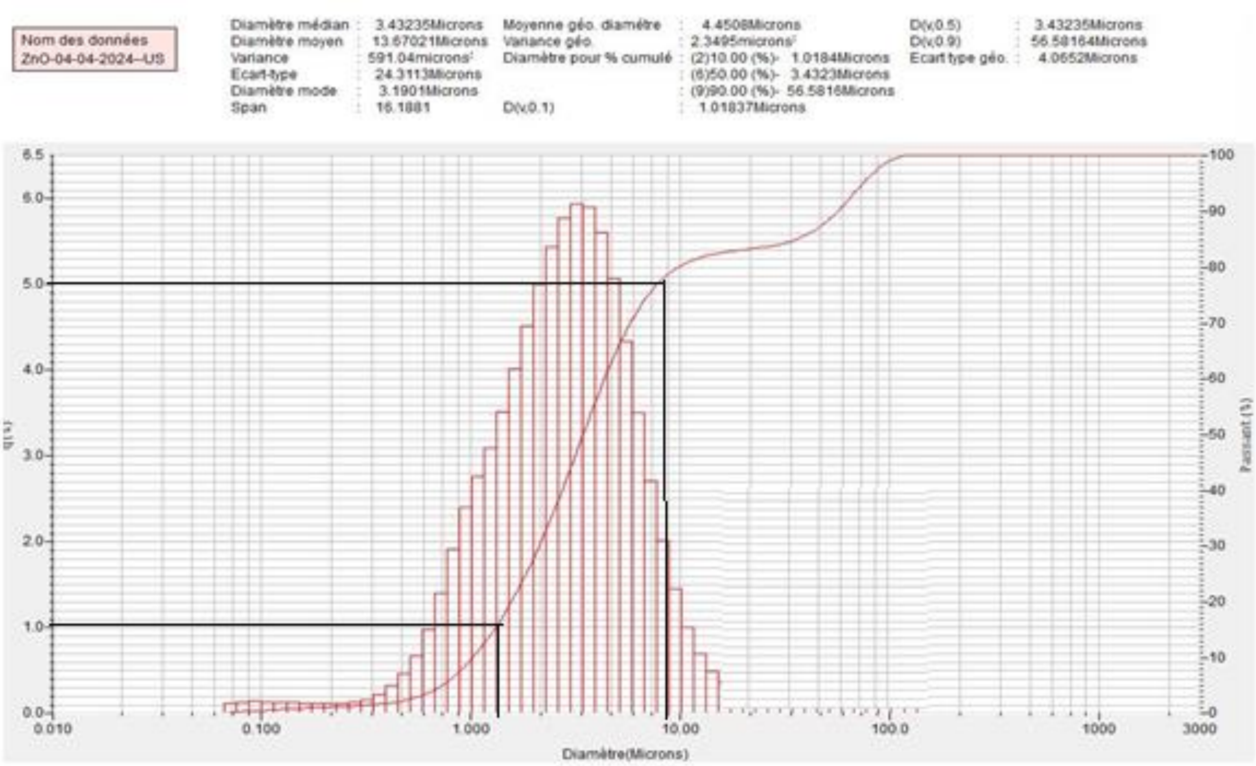
VI.5. Determination of the grain size of zinc oxide

The results of measuring the grain size distribution of zinc oxide using this technique are shown in Figure VI.4.



Diamètre médian : 3.43235Microns
Diamètre moyen : 13.67021Microns
Variance : 591.04microns²
Ecart-type : 24.3113Microns
Diamètre mode : 3.1901Microns
Span : 16.1881
Moyenne géo. diamètre : 4.4508Microns
Variance géo. : 2.3495microns²
Diamètre pour % cumulé : (2)10.00 (%)- 1.0184Microns
: (6)50.00 (%)- 3.4323Microns
: (9)90.00 (%)- 56.5816Microns
D(v,0.1) : 1.01837Microns
D(v,0.5) : 3.43235Microns
D(v,0.9) : 56.58164Microns
Ecart type géo. : 4.0652Microns

Figure .VI.4 : granulometric Gaussian distribution of zinc oxide



Diamètre médian : 3.43235Microns
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D(v,0.5) : 3.43235Microns
D(v,0.9) : 56.58164Microns
Ecart type géo. : 4.0652Microns

Figure.VI.5: granulometric cumulative distribution of zinc oxide

The particle size of the adsorbent therefore has a significant impact on the rate of cation transfer from the solution to the adsorbent [32-33]. Consequently, the particle size was optimized by utilizing a range of grains (Figure VI.4). By varying the grain size of the kaolin, it can be observed that the optimal yield is achieved when the kaolin grains have a diameter of $150 \leq \Phi$.

CHAPTER VII

Study of the elimination of Hg^{2+} ions by adsorption on Zinc oxide ZnO

Chapter VII

Study of the elimination of Hg^{2+} ions by adsorption on Zinc oxide ZnO

VII.1. Introduction

This experimental study is divided into three main parts. The first part of the study examines the influence of certain physico-chemical parameters on the adsorption of mercury based compounds with zinc oxide (ZnO) used as an adsorbent. Parameters such as pH, equilibrium time, the solid/liquid ratio, concentration and temperature are considered in this first part in order to determine the favorable conditions for the adsorption phenomenon.

The second phase of the investigation involved the application of isotherm models to the data sets derived from the preceding experiment. The adsorption capacity, the heterogeneity of the material surface, and its affinity for the Hg^{2+} ion are determined.

In the final section, a kinetic study was conducted to test various models, including first-order, second-order.

VII.2. Parametric study

VII.2.1. The effect of pH

In order to identify the optimal pH value that would maximize the retention of Hg^{2+} ions on zinc oxide, we initiated the experiment with a starting concentration of 30 µg/l and an S/L ratio of 1 g/l.

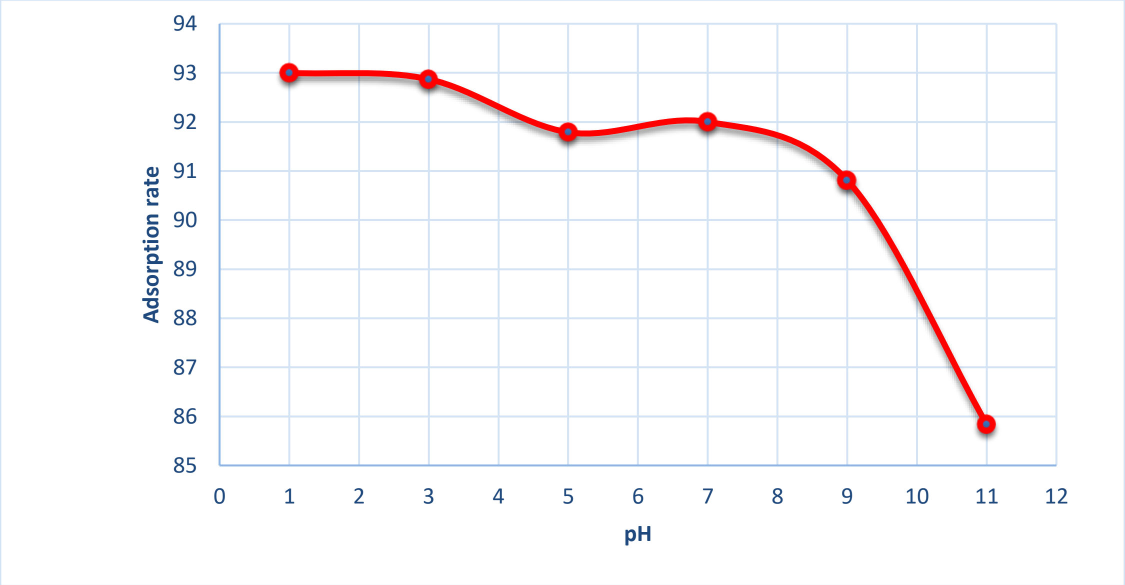

Figure. VII.1 : Effect of pH on the adsorption rate of Hg^{2+} ions on zinc oxide ZnO [C_0=30 µg/l, (S/L)=1 g/l and T=25 ^{0}C]

The adsorption capacity was determined as a function of pH and the graph shows that the maximum adsorption capacity is in an acid medium. According to the experimental data, the amount adsorbed is about 93%, which corresponds to a pH = 1. The adsorption rate is relatively low for a pH between 1 and 7. Above pH=7, the adsorption percentage decreases sharply.

This phenomenon is explained by the exploitable chemical properties of zinc compounds.

The pH chosen for the other experiments was pH = 6.3, which corresponds to an adsorption capacity of 92%. This choice was made to minimize the interaction between hydrochloric acid and traces of hydrocarbons in the effluent. The presence of these hydrocarbons can alter the pH of the solution. In an acidic environment, corrosion phenomena can occur, so we preferred to work with a pH of around 6.3, which corresponds to an inert environment.

VII.2.2. Effect of contact time

The influence of contact time was studied to determine the amount of Hg^{2+} fixed from the time of contact until thermodynamic equilibrium was reached. In order to see the effect of the contact time on the adsorption of mercury on the adsorbent, the adsorbent was contacted for time intervals [0-120 min], with an initial adsorbate concentration of 30 µg/l, at a solution pH of 6.3, at room temperature, with a ratio (S/L) = 1 g. The results obtained are shown in Figure VII.2. The results obtained are shown in Figure VII.2.

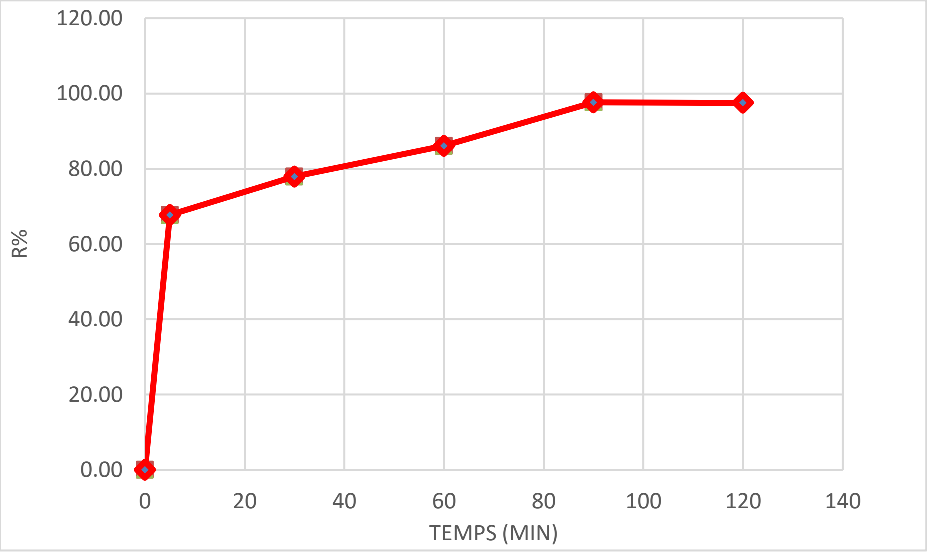

Figure. VII.2: Effect of contact time on the adsorption rate of Hg^{2+} ions on zinc oxide ZnO [C_0=30 µg/l, pH=6,3 , (S/L)=1 g/l and T=25 ^{0}C]

The results obtained are presented in Figure VII.2. Based on the experimental results, a correlation has been established between the adsorption rate of mercury-based compounds on zinc oxide. It can be observed that the adsorption rate increases with contact time, reaching a maximum value of approximately 98% after 90 minutes. Thereafter, the adsorption rate remains constant, which under these conditions corresponds to a maximum adsorption power.

For a solution containing 30 µg/l of mercury compounds, in order to reduce the time required for the study, it is preferable to investigate the influence of the adsorbent concentration as a function of the cycle time.

VII.2.3. Effect of solid/liquid

In order to determine the optimum adsorption mass, we proceeded with the following operating conditions: an S/L ratio of (0.25, 1, 0.5, 2, 2.5 g) is brought into contact with 100 ml of Hg^{2+} solution with a concentration of 30 µg/l and after 120 minutes stirring the solution is filtered.

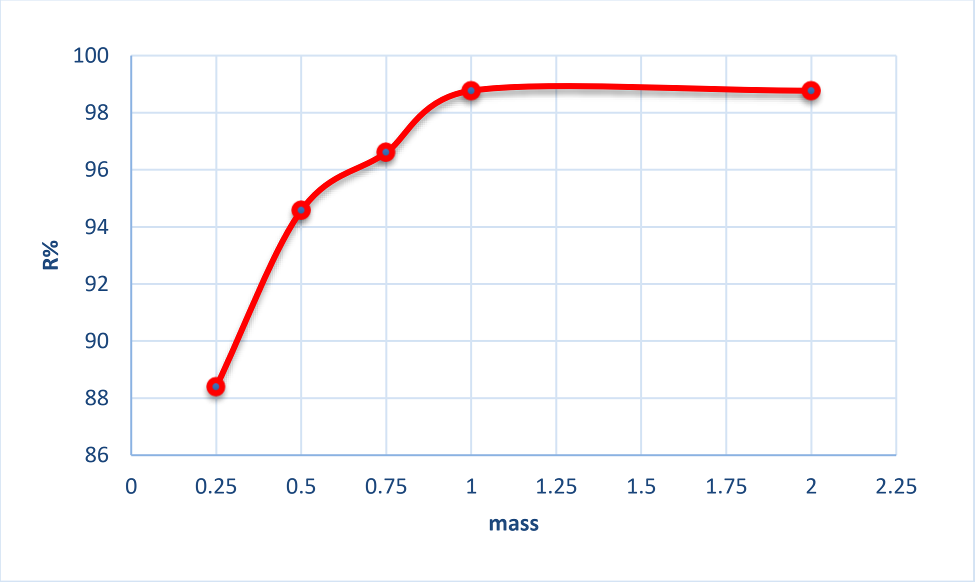

Figure.VII.3: Effect of Solid/liquid on the adsorption rate of Hg^{2+} ions on zinc oxide ZnO [C_0=30 µg/l, pH=6,3 and t=2h]

The influence of the quantity of adsorbent as a function of the quantity adsorbed of the mercury compounds was investigated for the operating mode, which involves bringing the adsorbent into contact with the solution to be studied. The experimental conditions were a C_0= 30 µg/l, pH= 6.3 and T=25C^0.

The results of the experiment, as shown in Figure VII.3, indicate that the adsorption of the adsorbent increases with the quantity absorbed until it reaches a mass of 1 g, which corresponds to the maximum adsorption capacity. This is evidenced by the fact that for 1 g of zinc oxide (ZnO) as an adsorbent, practically all the mercury compounds present in the wastewater were absorbed. This value can be translated on an industrial scale to define the quantity of adsorbent required for a flow of wastewater with a maximum cycle time.

Based on the chemical properties of zinc oxide, it can be confirmed that the active adsorption centers are located on the zinc atoms, where there may be complications between zinc and mercury ions. This is the reason why the quantity of adsorbent is contingent upon the quantity of mercury compounds present in the wastewater.

VII.2.4. Effect of temperature

Adsorption is a process that can be exothermic or endothermic. To this end, we studied the impact of temperature on the adsorption of Hg^{2+} ions onto zinc oxide ZnO. We adopted the same experimental protocol. The suspensions were stirred using a hot plate for 2 hours at the following temperatures: 25, 30, 40, 50 and 60°C. Figure VI.4 shows the results obtained.

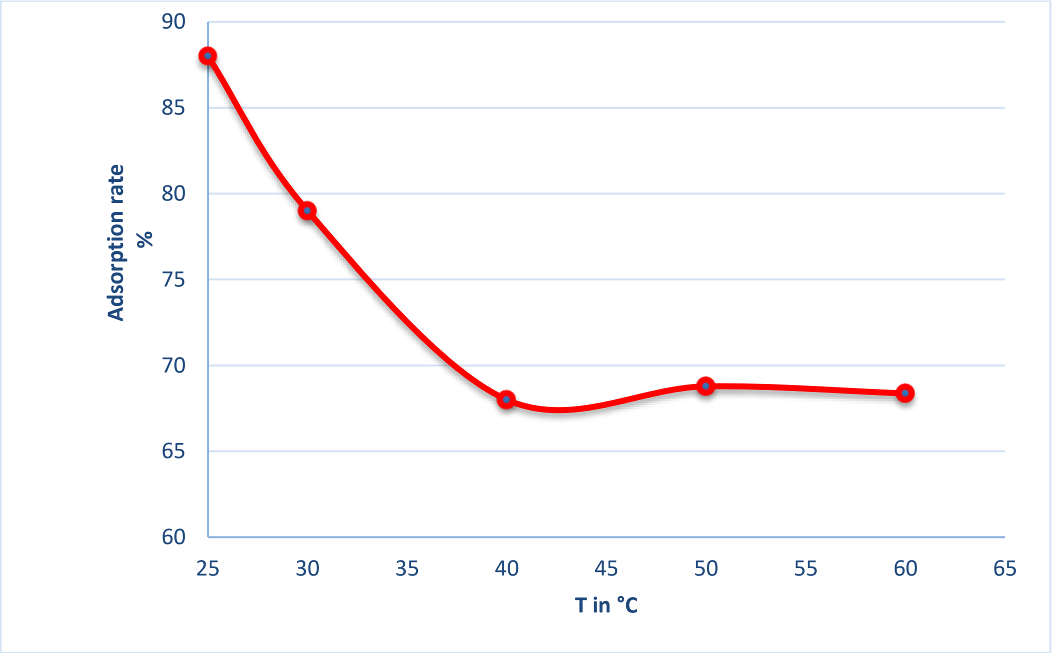

Figure.VII.4: Effect of Temperature on the adsorption rate of Hg^{2+} ions on zinc oxide ZnO [C_0=30 µg/l, pH=6,3, (S/L)=1 g and t=2h]

The graph illustrates a decline in adsorption power with increasing temperature, which is consistent with the thermodynamic premise that the process is exothermic. At 40°C, the adsorption power is constant, indicating that at this temperature,. This implies that the system is in a state of saturation.

The temperature was selected based on a study conducted to optimize the energy input to the process. [34, 35].

VII.2.5. Effect of concentration

The influence of the concentration of the products to be adsorbed was carried out under the following conditions C_0 = 30 µg/l, pH= 6,3, S/L=1g/l ,T=25°C for 2h.

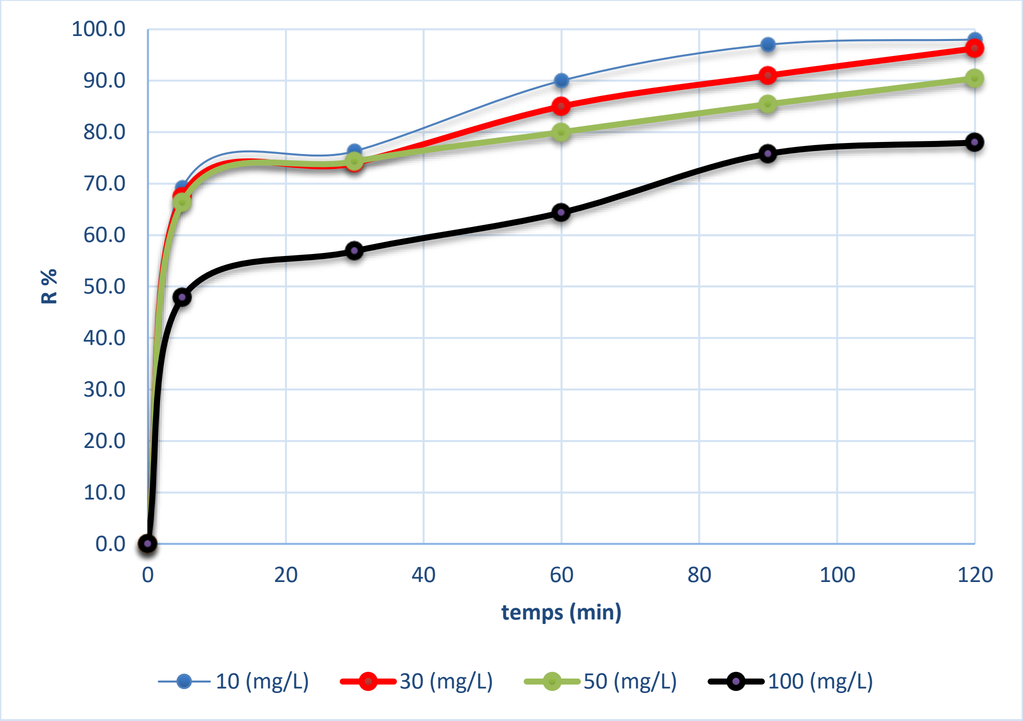

Figure.VII.5: Effect of concentration on the adsorption rate of Hg^{2+} ions on zinc oxide (ZnO) [C=10,30,50 and 100 µg/l, pH=6,3, (S/L)=1 g/l and t=2h]

The initial observation from the results is that all the functions exhibit a similar appearance. However, it can be seen that the adsorption power for all the samples remains constant up to a time of approximately 10 minutes. Thereafter, a change in adsorption power can be observed, which is a function of the concentration of mercury compounds that have been adsorbed. The low adsorption corresponds to the maximum content of mercury compounds, and as the concentration of mercury compounds in the solution decreases, the adsorption power increases, with the highest power corresponding to the maximum concentration of mercury compounds. It can be posited that at a time of less than 10 minutes, the rate of adsorption is at its maximum, while at 20 minutes, the rate of adsorption is relatively slow.

In light of the aforementioned experiments and operational parameters, it is recommended that an optimization study be conducted based on the experimental data in order to identify the optimal operational parameters. Given the constraints of time, we defined the optimal parameters for each experiment and selected a solution of C_0=30 µg/l of mercury compounds with 1 g of adsorbent and T = 25 °C for a duration of 2 h.

VII.3. Adsorption isotherm

VII.3.1. Study of the adsorption equilibrium

To study the adsorption isotherms of mercury by zinc oxide (ZnO), it was agreed to carry out tests in which 100 ml of different concentrations of mercury-based compounds (10, 30, 50 and 100µg/l) were brought into contact with a mass of 1g of zincoxide at room temperature.

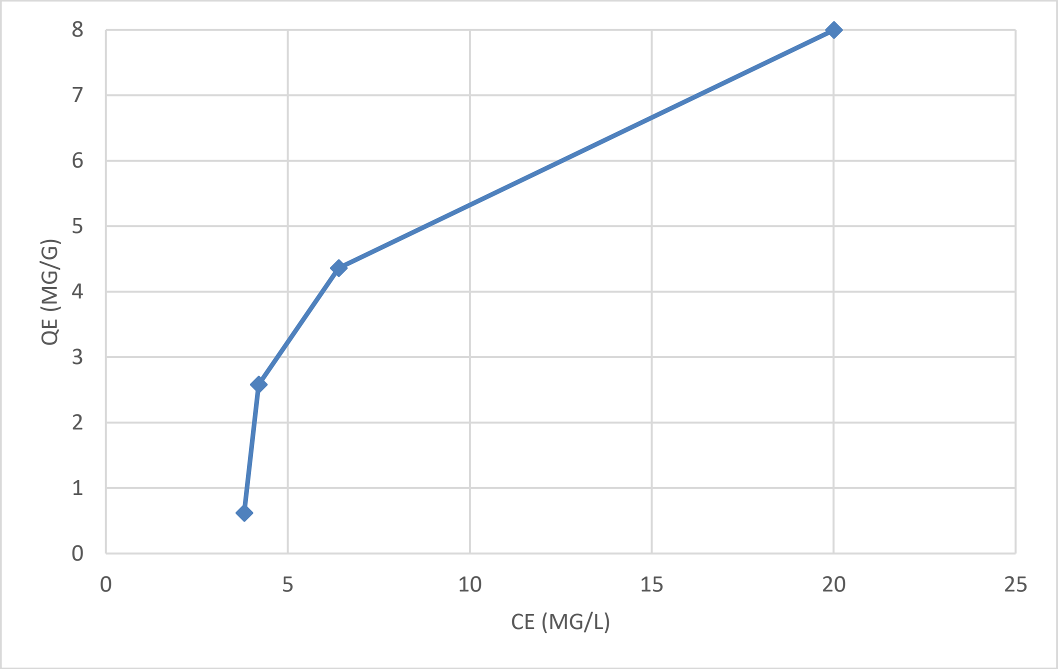

Figure.VII.6: Equilibrium isotherm for adsorption rate of Hg^{2+} ions on zinc oxide ZnO [C=10, 30,50and 100 µg/l, pH=6,3, (S/L)=1 g/l andt=2h]

As illustrated in Figure VII.6, the isotherm shape is classified as L-type according to the Giles et al. [36] classification, with the concavity facing downward. This reflects the decrease in free sites as adsorption progresses. This type of isotherm is typically observed in the adsorption of ionic solutes, where there is minimal competition with solvent molecules for the adsorption sites.

VII.3.2. Applications of adsorption isotherm

Many theoretical adsorption models have been developed to describe adsorption isotherms, which are important for describing the interaction between the adsorbate and the adsorbent surface. To this end, we have used various models described in the literature

a) Langmuir isotherm

The application of Langmuir's isotherm to the experimental measurements obtained is shown by plotting $\frac{1}{qe}$ as a function of $\frac{1}{Ce}$.

The equation for the Langmuir isotherm is often expressed as follows:

$$\frac{1}{qe} = \frac{1}{K_l qmax} * \frac{1}{Ce} + \frac{1}{qmax}$$

Where:

q_e : Equilibrium adsorption density (amount of adsorbate adsorbed per gram of adsorbent at equilibrium)

q_{max}: Maximum adsorption capacity

Ce : Equilibrium concentration of the adsorbate in the bulk solution

K_l : Langmuir adsorption constant

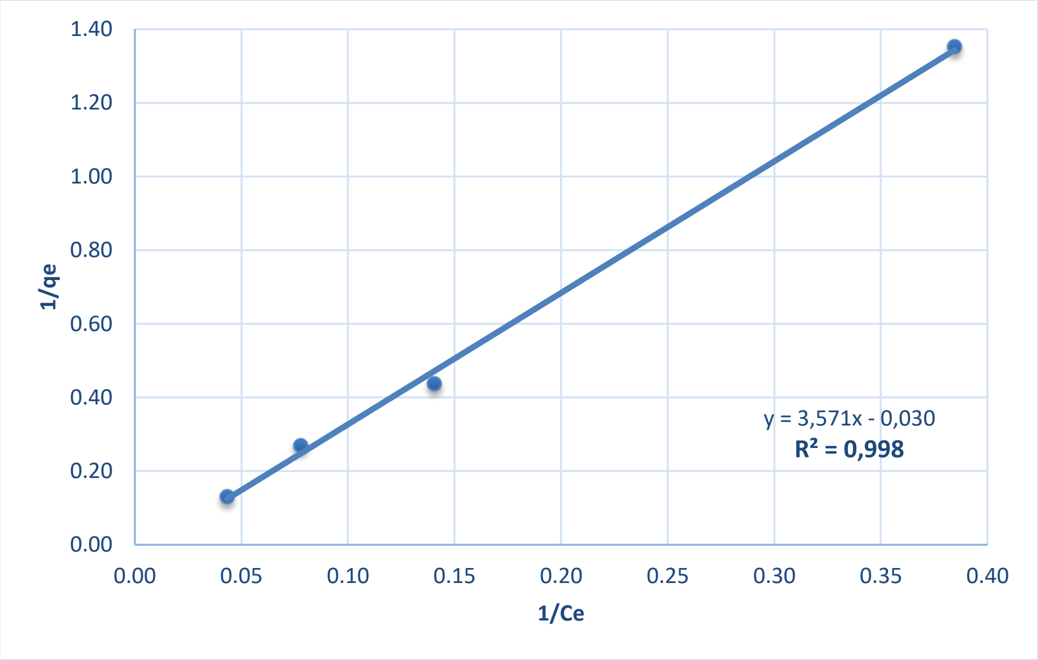

Figure.VII.7: Langmuir isotherm for adsorption of Hg^{2+} ions on zinc oxide ZnO [C=10,30,50 and 100 µg/l, pH=6,3, (S/L)=1 g/l and t=2h]

b) Freundlich isotherm

If we plot log qe as a function of log Ce, we obtain a straight line with slope 1/n and intercept$logK_F$.

The equation for the Freundlich isotherm is often expressed as follows:

$$logq_e = logK_F + \frac{1}{n} logC_e$$

Where:

q_e : Equilibrium adsorption density (amount of adsorbate adsorbed per gram of adsorbent at equilibrium)

Ce : Equilibrium concentration of the adsorbate in the bulk solution

K_f : Equilibrium adsorption constant

n: Dimensionless constant related to the number of adsorption sites and the interaction energy

The Freundlich isotherm is a frequently employed model for systems where adsorption increases without reaching clear saturation. Its utility extends to a number of fields, including water purification, mixture separation and solid surface characterization.

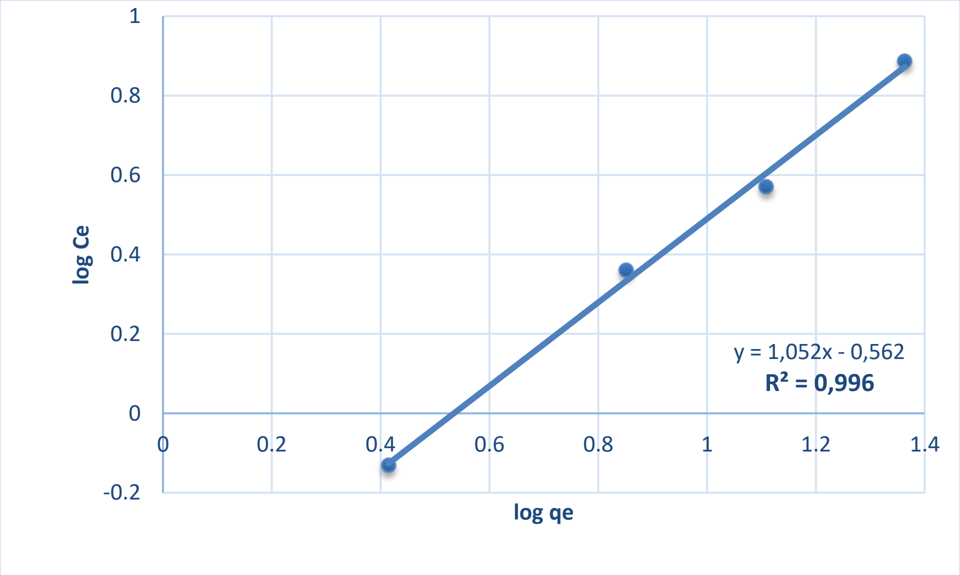

Figure.VII.8: Freundlich isotherm for adsorption of Hg^{2+} ions on zinc oxide ZnO [C=10,30,50 and 100 µg/l, pH=6,3, (S/L)=1 g/l and t=2h]

c) Temkin isotherm

The curve of qe versus LnCe (Figure VII.8.) allows the isotherm constants of $b_T$and K_T to be determined from the slope and intercept, respectively.

The equation of the Temkin isotherm used:

$$qe = \frac{RT}{bT} lnKt + \left(\frac{RT}{bT}\right)\mathrm{lnCe}$$

Where:

q_e : Equilibrium adsorption density (amount of adsorbate adsorbed per gram of adsorbent at equilibrium)

Ce : Equilibrium concentration of the adsorbate

K_t :Temkin isotherm constant (l/g)

b : Temkin constant(J/mol)

T :absolutetemperature (K)

R : Gas constant (8.314 J/mol K)

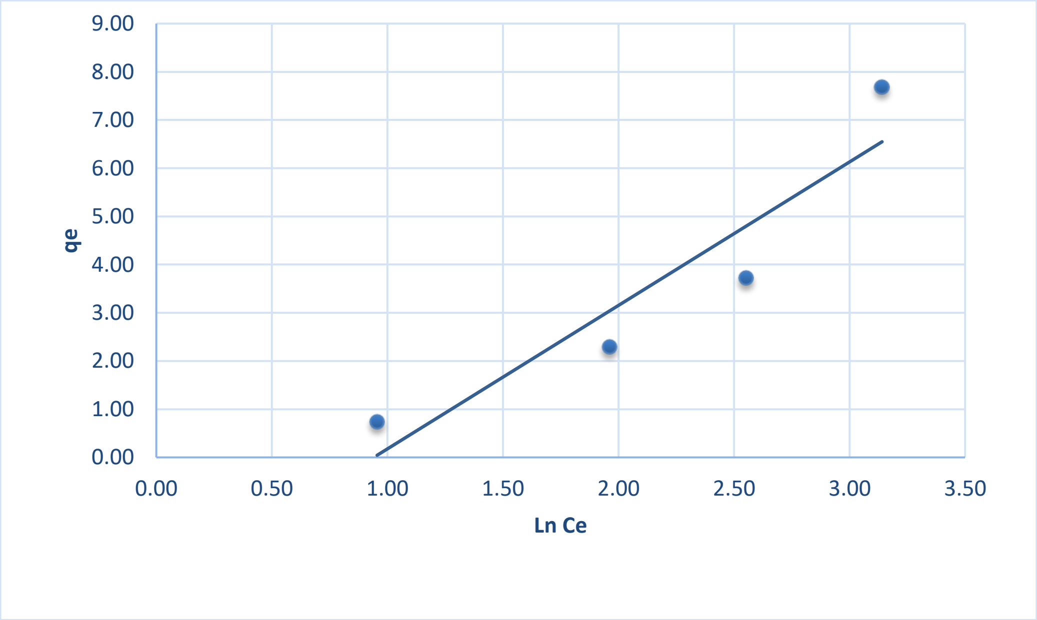

Figure.VII.9 : Temkin isotherm for adsorption of Hg^{2+} ions on zinc oxide ZnO [C=10,30,50 et 100 µg/l, pH=6,3, (S/L)=1 g/l and t=2h]

The values of the Langmuir, Freundlich and Temkin parameters are summarized in Table VII.1.

Table VII.1: Parameters of the isotherms tested for the adsorption of Hg^{2+} ions on zinc oxide ZnO.

Model	Parameter	
Langmuir	Equation	$\frac{1}{qe} = \frac{1}{Klqmax} * \frac{1}{Ce} + \frac{1}{qmax}$
	q_m(mg/g)	0,2800336
	K_1 (l/mg)	0,00840101
	R^2	0,998
Freundlich	Equation	$logq_e = logK_F + \frac{1}{n} logC_e$
	K_F	1,754
	n	1,052
	R^2	0,996
Temkin	Equation	$qe = \frac{RT}{bt} lnKt + \left(\frac{RT}{bT}\right)\ln Ce$
	b_T(J/mol)	826.67
	K_T (l/mg)	0.392
	R^2	0,867

From the results in Table VII.1 we can deduce that:

- The Langmuir model leads to a good correlation of the adsorption isotherm with a good correlation coefficient R^2= 0,998.

  The Langmuir equation $\frac{1}{qe} = \frac{1}{Klqmax} * \frac{1}{Ce} + \frac{1}{qmax}$was translated into a mathematical equation of the first degree.The results presented on the graph with abscissa $\frac{1}{Ce}$and ordinate $\frac{1}{qe}$correspond to an equation of the first degree, which confirms the Langmuir isotherm equation.

- The Freundlich model is also close to the previous one; the correlation coefficient R^2= 0.996. The value of 1/n is low, implying a low adsorption intensity.
- Temkin's model has a correlation coefficient of R^2=0.867, and the heat of adsorption is low, indicating that adsorption is exothermic.

VII.4.Study of adsorption kinetics

The adsorption kinetics of Hg^{2+} ions on zinc oxide ZnO at different initial concentrations is shown in Figure VII.9.

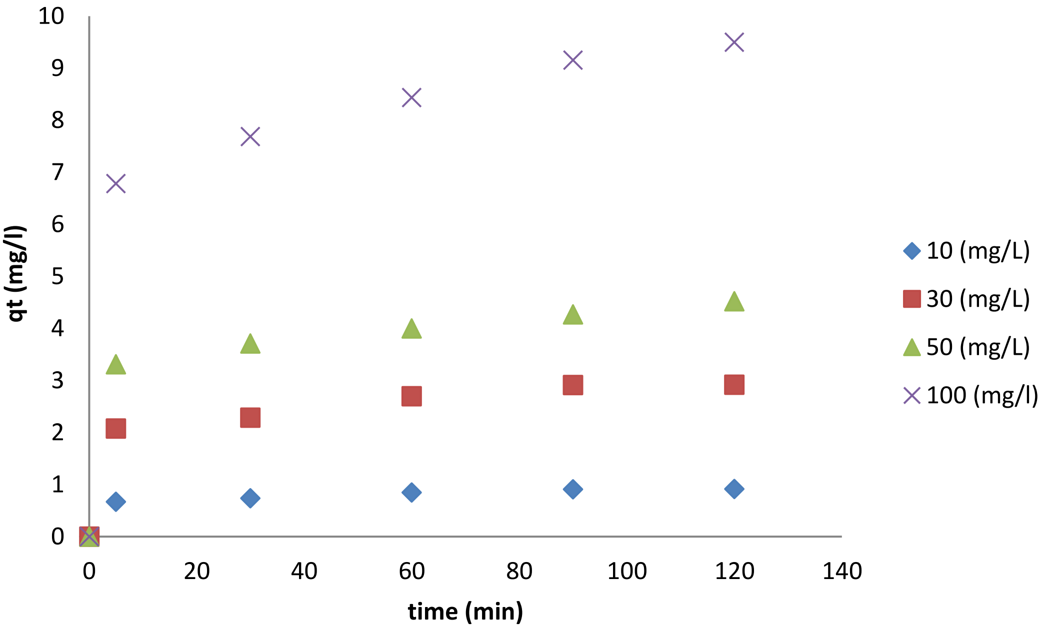

Figure. VII.10 Evolution of the adsorbed quantity of Hg^{2+} ions as a function of time at different initial concentrations on zinc oxide ZnO [pH =6.3, t=2h, T = 25 °C and (S/L) = 1g/l].

VII.4.1. Pseudo first order kinetic model

From the graphical illustration of the variation of log(qe-qt) as a function of time shown in Figure VII.10, we can determine K1 and qe at the different initial concentrations studied.

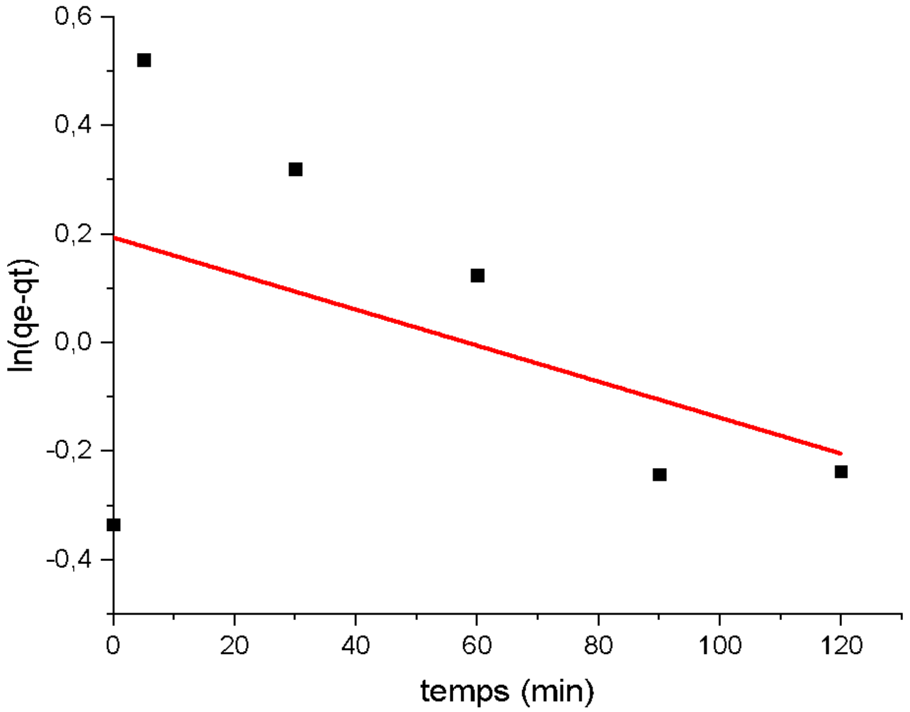

Figure.VII.11 : pseudo first-order kinetics of Hg^{2+} ion adsorption as a function of time at different initial concentrations on zinc oxide ZnO [pH =6.3, T = 25 °C et (S/L) = 1 g/l].

VII.4.1. Pseudo-second order kinetic model

From the graphical illustration of the variation of t/qt as a function of time shown in Figure VII.11, we can determine K2 and qe at the different initial concentrations studied.

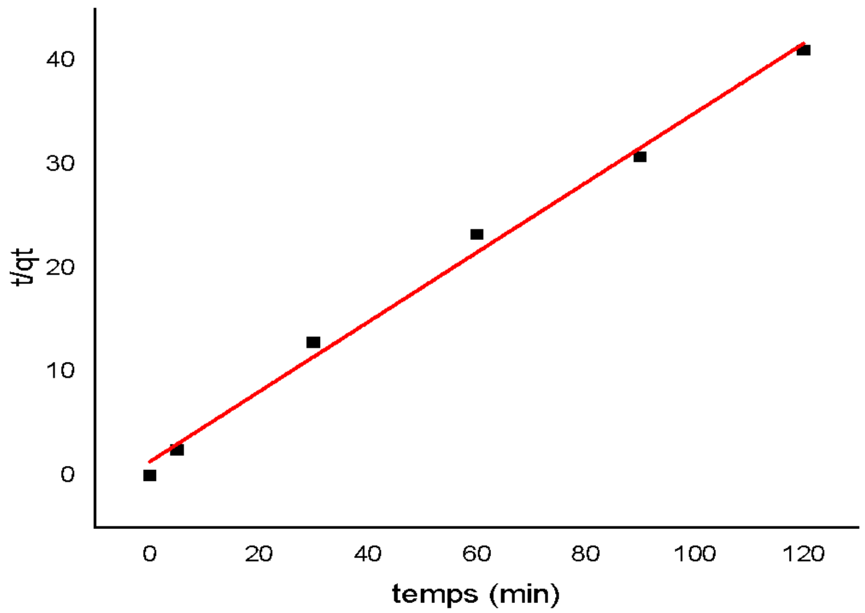

Figure.VII.12 : pseudo-second-order kinetics of Hg^{2+} ion adsorption as a function of time at different initial concentrations on zinc oxide ZnO [pH =6.3, T = 25 °C et (S/L) = 1 g/l].

Pseudo first-order and pseudo second-order kinetic models were employed to analyze experimental data pertaining to the adsorption of Hg^{2+} ions onto zinc oxide (ZnO). The results indicate that the reaction is of second order for the different initial concentrations, as evidenced by a comparison of the correlation coefficients. Similarly, the values of qe calculated by this model, which are in close agreement with those obtained experimentally, indicate that the pseudo-second order model is the most appropriate for determining the order of the adsorption kinetics of Hg^{2+} ions on ZnO.

CONCLUSION

Conclusion

The adsorption of Hg^{2+} ions on zinc oxide, by optimizing certain physico-chemical parameters, has a significant influence on the phenomenon. The different experiments carried out (XRD, FTIR, SEM), which led to the identification of the ZnO phase.

The study of the influence of physico-chemical parameters (pH, contact time, S/L ratio, initial concentration of mercury in solution and temperature) on the adsorption capacity of mercury on zinc oxide (ZnO) showed that:

- Adsorption is favorable in an acidic medium ($pH = 1\ to\ 3$).
- The adsorption equilibrium is reached after 2 hours.
- Adsorption is best at an S/L ratio of 1 g/l.
- Adsorption efficiency increases with decreasing initial lead concentration.
- The elimination rate is maximal at room temperature.

Adsorption of Hg^{2+} ions on zinc oxide ZnO has been shown to eliminate mercury at a rate around 98% of the initial load, with relatively fast kinetics.

The adsorption isotherm for Hg2+ ions on zinc oxide is of type L according to Gill's classification, and the experimental results were compared with the Langmuir, Freundlich and Temkin models. According to the regression coefficients of the plots, the adsorption isotherms are well described by the Langmuir model. In order to specify the order of the reaction, we studied the adsorption kinetics of Hg^{2+} ions on zinc oxide (ZnO) by applying two kinetic models, the first-order Lagergren model and the second-order Lagergren model, by comparing the regression coefficients of the curves. We found that the kinetics of the adsorption reaction is second-order, and the thermodynamic study showed that the adsorption of zinc oxide (ZnO) on Hg^{2+} is exothermic and spontaneous, and is accompanied by a reduction in disorder.

To investigate the efficacy of zinc oxide (ZnO) in the recovery of Hg ions from a pH-adjusted industrial effluent. The results showed the possibility of effective treatment of mercury-loaded effluents, with high removal rates of 93% for effluents at free pH.

Overall, these results demonstrate the interesting adsorption capacity of zinc oxide (ZnO) towards Hg^{2+} ions, which can play an important role in the removal of heavy metals.

REFERENCES

References

[1] United Nations Environment Program, « Second session of the intergovernmental negotiating committee to prepare a global legally binding instrument on mercury (INC2) », Chiba, Japan, 2011.

[2] INERIS - Mercure et dérivés du mercure. Fiche de données toxicologiques etenvironnementalesdes substances dangereuses. (2000)

[3] J. F. Thomassin, S. Touzé, et P. Baranger, « Le mercure et ses composés. Comportement dans les sols, les eaux et les boues de sédiments », BRGM/RP51890-FR. Orléans, France: Bureau de RecherchesGéologiques et Minières, 2003.

[4] Cossa D., Thibaud Y., Romeo M., Gnassi-Barelli M., - Le mercure en milieumarin: bio géochimie etécotoxicologie. EdIfremer, Rap.Sci. Tech.(1990).

[5] Cappon C. - Mercury and selenium content and chemical form in vegetablecrops grown on sludge amended soil. Arch. Environ. Contam. Toxicol, (1981)

[6] Bruce M. Sass, Mona A. Salem, and Lawrence A. Smith Battelle MERCURY USAGE AND ALTERNATIVES IN THE ELECTRICAL AND ELECTRONICS INDUSTRIES Columbus, Ohio 43201 (January1994).

[7] N. Bouziane, Elimination du 2-mercaptobenzothiazole par voie photochimique et par adsorption sur la bentonite et le charbon actif en poudre, Mémoire de Magister En Chimie, Université Mentouri de Constantine. (2007)

[8]UllrichS.M.,TantonT.W.,AbdrashitovaS.A.(2001)Mercuryintheaquaticen vironment. Etude bibliographique.

[9] Porcella, D. B. (1994) - Mercury in the environment: biogeochemistry. *In* Mercury as aGlobalPollutant.Watras.C.J.andJ.W.Huckabee(Eds),AnnArbor:LewisPublishers.

[10] T. Monteiro, C. Boemare, M.J. Soares, E. Rita, E. Alves, Photoluminescence and Damage Recovery Studies in Fe-implanted ZnO Single Crystals,Journal. Appl. Phys, 2003.

[11] N.BOUGDAH, «Etude de l'adsorption de micropolluants organiques sur le Bentonite,» 2007.

[12] J. P. Chen, M. Lin, Surface charge and metal ion adsorption on H-type activated carbon: Experimental observation and modeling simulation by the surface complex formation approach, Carbon. 39 (2001)

[13] N. Sedira, Etude de l’adsorption des métaux lourds sur un charbon actif issu de noyaux de dattes)2012\2013

[14] Design of solution-grown ZnO nanostructures. Chapter book in Lecture Notes on Nanoscale Science and Technology volume. 7, Towards Functional Nanostructures, Z.M. Wang (Ed.), springer books, 2009.

[15]J.M.Davidson, C.H.Lawrie, and K. Sohail. Kinetics of The Absorption of HydrogenSulfidebyHighPurityandDopedHighSurfaceAreaZincOxide,Ind.Eng.Chem.Res,34,1995

[16] F. Mouzaia, D. Djouadi, A. Chelouche, L. Hammiche, and T. Touam, "Particularities of pure and Al-doped ZnO nanostructures aerogels elaborated in supercritical isopropanol," Arab Journal of Basic and Applied Sciences, vol. 27

[17]Fiani, Adsorption de polluants gazeux sur des filtres à charbon actif, Modélisation des échanges couplés de matière et de chaleur, INPG-EMSE. Saint-Etienne. France. (2000).

[18] J. P. Chen, M. Lin, Surface charge and metal ion adsorption on H-type activated carbon: Experimental observation and modeling simulation by the surface complex formation approach, Carbon. 39 (2001)

[19]D. Mohan, K.P. Singh, Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste, Water Research. 36 (2002)

[20]Barrer, Zeolites and clay minerals as sorbents and molecular sieves, Academic Press. 1978.

[21] Fiani, Adsorption de polluants gazeux sur des filtres à charbon actif, Modélisation des échanges couplés de matière et de chaleur, INPG-EMSE. Saint-Etienne. France. (2000).

[22] Barrer, Zeolites and clay minerals as sorbents and molecular sieves, Academic Press. 1978.

[23] Industrial alumina chemicals, ACS Monograph. 184

[24] L. Robert, F. Dardel, Adsorption J 2730, Traité Génie des procédés. (1988).

[25] COULSON, John, RICHARDSON, Jack. Chemical Engineering. 2nd Edition. 1979.

[26]R.Zamiri, A. Lemos, A. Reblo, H.A. Ahangar, J. Ferreira, Effects of rare-earth (Er, La and Yb) doping on morphology and structure properties of ZnO nanostructures prepared by wet chemical method, Ceramics International, 40 (2014)

[27]W. Shen, J. Wang, Q. Wang, Y. Duan, Y. Zeng, Structural and optical properties of ZnO films on Si substrates using a γ-Al2O3 buffer layer, Journal of Physics D: Applied Physics, 39 (2006)

[28] A. Moustaghfir : élaboration et caractérisation de couches minces d'oxyde de zinc.Application à la photoprotection du polycarbonate. Thèse de doctorat à l'université BLAISE Pascal,(Novembre 2004).

[29] Ditta MA, Farrukh MA, Ali S, Younas N. X-ray peak profiling, opticalparameters and catalyticproperties of pure and CdSdopedZnO–NiOnanocomposites. Russ J Appl Chem. 2017;90(1):151–159

[30]Rahemi A, Rouhaghdam A, Nazari M. N-Doped ZnO-CuO nanocomposite prepared by one-step ultrasonic spray pyrolysis and its photocatalytic activity. Chem Phys Lett.2018;705:19–22

[31]Bhuyan T, Mishra K, Khanuja M, Prasad R, Varma A. Biosynthesis of zinc oxide nanoparticlesfromAzadirachtaindica for antibacterial and photocatalytic applications. Mater SciSemicond Proc. 2015;32:55–61. doi:10.1016/j.mssp.2014.12.053

[35]Thomas Raynaud. Influence de l'acide borique sur la solubilité des oxydes (Ni et Zn) dans les conditions du circuit primaire d'un réacteur à eau sous pression. Génie chimique. Université Paul Sabatier - Toulouse III, 2023

[36] C.H. Giles, T.H. Mac Ewan, S.N. Nakhwa, D.J. Smith, Journal of Chemical Society 93 (1960)