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Analysis of nutrient concentration in the water of the Ouled Alkayem dam in the Wilaya of Mila and Design of a Floating device for combating eutrophication

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إهداء مع خالص الشكر والتقدير

إلى العزيز الذي حملت اسمه فخرا، إلى من كلّله الله بالهيبة والوقار
إلى من حصد الأشواك عن دربي، وزرع لي الراحة بدلًا منها.
إلى أبي، لم يحنِ ظهر أبي ما كان يحمله، لكنّ ليحملني من أجلي انحدب.
كنت أحجب عن نفسي مطالبها، فكان يكشف عمّا أشتهي الحُجُبَا.
شكرًا لك لأنك أبي.

إلى من علّمتني الأخلاق قبل أن أتعلّمها، إلى الجسر الصاعد بي إلى الجنّة،
إلى اليد الخفيّة التي أزاحت العقبات عن طريقي،
إلى من ظلّت دعواتها تحمل اسمي ليلًا ونهارًا،
أمي،
محبوبتي وملهمتي، إلى من وهبني الله نعمة وجودها
إلى مصدر قوتي، وأرضي الصلبة، وجدار قلبي المتين.

إلى إخوتي وأخواتي،
الذين إن ضاقت بي الدنيا، اتّسعت بخطواتهم،
وإن تعثّرت، كانوا أوّل من يرفعني بكلماتهم.

وإلى أساتذتي الكرام،
إلى من أضاءوا دربي بعلمهم، وزرعوا في عقلي بذور الفكر، وفي قلبي حب التعلّم.
إلى من كانوا قدوة في العلم ،أقدّم لكم أسمى آيات الشكر والامتنان.

شكرٌ للأستاذة **ليلى بعزيز**، على ما قدمته من مساعدة كان لها أثر طيب في مسيرتي.

وشكرٌ خاصٌ من القلب لأستاذتي **علية زينب** و**بومسنغ آمال**،
على ما قدّمتاه من دعم وتفانٍ. لقد كنتما أكثر من معلّمتين، كنتما نورًا في طريقي، وعونًا في لحظات التحدّي.
فلولا توجيهكم وإيمانكم بقدرتي، لما بلغت ما أنا عليه اليوم.

ها أنا اليوم،
أطوي صفحة التعب، وأسجّل في تاريخي فخرًا لا يُنسى.
لم أعد أتساءل عن ملامح الوصول ، فقد رأيتها في عينيّ.
تبدّدت غيوم التعب، وابتسم الأفق بعد عتمة الانتظار.
ها هي الخطى التي كانت تتعثّر أحيانً قد وجدت مستقرّها في قمّة الإنجاز.

وفي طيّات الطريق،
تنفّستُ سلامًا وفرحًا وامتنانًا.
وآخر دعوانا أنِ الحمدُ للهِ ربِّ العالمين.

Dedication

Abstract

Life would not be able to exist on Earth without water, as it is fundamental to all living organisms.

Every single organism on the planet needs water to sustain life and develop. To adhere to the increasing pressure towards the environment, preserving the quality of water resources is crucial, especially when it comes clarifying the problems of water pollution and eutrophication which causes excessive algae growth in water bodies.

This research aims to assess the reasons for algal bloom in the Oulad Kaïm Dam in Oued Athmania, Mila Province by evaluating the physical and chemical properties of the water in the dam. It also intends to study the impact of graphene and green clay to reduce algal bloom under test conditions.

Water samplings were conducted at the dam and brought to the lab for testing, which included the following physical and chemical aspects (Degrees of temperature Ph Conductivity Turbidity. Sulphates, Ammonium, Phosphates, Nitrites, Nitrates, and Silicon Concentration).

Graphene and green clay both proved to be effective in lowering the concentrations of these substances which helps limit algal proliferation and improves the quality of water nutritionally and structurally. The materials seem to be an effective environmentally sustainable method for treating surface waters impacted by eutrophication.

ملخص

الماء أساس الحياة، وبدونه لا يمكن تصور وجود أي شكل من أشكال الحياة على كوكب الأرض.

كل كائن حي على هذا الكوكب يحتاج إلى الماء للبقاء على قيد الحياة والنمو. ونظرًا للضغوط البيئية المتزايدة، فإن الحفاظ على جودة الموارد المائية أصبح أمرًا بالغ الأهمية، خاصةً في ظل التحديات المتعلقة بتلوث المياه وظاهرة الإثراء التي تؤدي إلى النمو المفرط للطحالب في المسطحات المائية (Eutrophication)الغذائي.

يهدف هذا البحث إلى تقييم أسباب تكاثر الطحالب في **سد أولاد قايم** بوادي العثمانية، ولاية ميلة، وذلك من خلال دراسة الخصائص الفيزيائية والكيميائية لمياه السد. كما يسعى إلى دراسة تأثير استخدام **الجرافين** و**الطين الأخضر** في الحد من هذا التكاثر تحت ظروف مخبرية .

تم أخذ عينات مياه من السد وتحليلها مخبريًا، وشملت التحاليل الجوانب الفيزيائية والكيميائية التالية التوصيل الكهربائي، التعكر، تركيز الكبريتات، الأمونيوم، الفوسفات، النتريت، (pH) درجة الحرارة، الرقم الهيدروجيني النترات، والسيليكون .

وقد أثبت كل من الجرافين والطين الأخضر فعاليتهما في تقليل تراكيز هذه المواد، مما ساعد في الحد من تكاثر الطحالب، وساهم في تحسين جودة المياه من الناحيتين التغذوية والبنيوية. وتُظهر هذه المواد واعدة كوسيلة بيئية مستدامة لمعالجة المياه السطحية المتأثرة بظاهرة الإثراء الغذائي .

Résumé

La vie ne pourrait pas exister sur Terre sans l'eau, car elle est fondamentale pour tous les organismes vivants.

Chaque organisme sur la planète a besoin d'eau pour survivre et se développer. Face à la pression croissante sur l'environnement, il est crucial de préserver la qualité des ressources en eau, en particulier en ce qui concerne les problèmes de pollution de l'eau et d'eutrophisation, qui entraînent une prolifération excessive d’algues dans les milieux aquatiques.

Cette recherche vise à évaluer les causes de la prolifération algale dans le barrage Oulad Kaïm, situé à Oued Athmania dans la wilaya de Mila, en étudiant les propriétés physiques et chimiques de l'eau du barrage. Elle a également pour objectif d'étudier l'impact du graphène et de l'argile verte pour réduire la prolifération algale dans des conditions expérimentales.

Des échantillons d'eau ont été prélevés au niveau du barrage et analysés en laboratoire, en tenant compte des paramètres physiques et chimiques suivants : température, pH, conductivité, turbidité, sulfates, ammonium, phosphates, nitrites, nitrates et concentration en silicium.

Le graphène et l'argile verte se sont révélés efficaces pour réduire les concentrations de ces substances, ce qui contribue à limiter la prolifération des algues et à améliorer la qualité de l'eau sur le plan nutritionnel et structurel. Ces matériaux semblent constituer une méthode durable et respectueuse de l'environnement pour le traitement des eaux de surface touchées par l'eutrophisation.

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Introduction

Introduction générale

Water is one of the most vital natural resources, especially in the socio-economic development of nations. This is even more critical in semi-arid and arid regions such as Algeria, where water scarcity significantly influences agriculture, industry, and daily life. Recognizing its strategic importance, the Algerian government has implemented a national policy focused on the construction of dams, aiming to optimize surface water use, meet the increasing demands for potable water, support agricultural irrigation, sustain industrial activities, and control flooding.

One notable hydraulic infrastructure project within this policy framework is the Ouled El Kaïm Dam, located in the district of Chelghoum Laïd, in Mila Province. This dam plays a vital role at the regional level by providing irrigation water, drinking water, and contributing to infrastructure development and socioeconomic growth.

However, despite its strategic importance, the Ouled El Kaïm Dam faces growing environmental challenges, most notably the proliferation of algae during the summer months. Algal blooms are more than just a nuisance—they pose serious threats to water quality, public health, and the operational efficiency of water supply systems, particularly for drinking water and agricultural use.

These blooms are often the result of eutrophication, a process driven by the accumulation of nutrients primarily nitrogen and phosphorus in stagnant water bodies, combined with rising temperatures. Addressing this issue requires a thorough understanding of its environmental drivers, ecological impacts, and technological solutions.

The aim of this research is to assess the state of eutrophication of the Ouled El Kaïm dam, identify its main causes, and explore innovative treatment methods. Particular attention is being paid to the use of advanced materials, notably graphene, recognized for its exceptional physico-chemical properties, and green clay, a natural material with interesting adsorbent properties. Both materials are being investigated as potential solutions for the sustainable improvement of water quality.

Structure of the Study

The research is structured into five main chapters:

- **Chapter 1 – General Concepts of Water**:

Introduces the types and roles of water in the environment, emphasizing its ecological and societal importance. This chapter also presents an overview of water pollution sources and classifications.

- **Chapter 2 – Eutrophication**:

Examines the eutrophication process in detail—its definition, primary causes, biological and environmental impacts, and the methods used to measure and monitor nutrient pollution in water bodies.

- **Chapter 3 – Graphene and clay**

Describes the characteristics and advantages of graphene for environmental applications, particularly in water treatment. The chapter also introduces the Agile project management methodology, as applied to scientific and technical research.

- **Chapter 4 – Materials and Methods**:

Outlines the procedures for water sampling and analysis. It details the physical, chemical, and biological parameters assessed, as well as the instruments and materials used during field and laboratory work.

- **Chapter 5 – Results and Discussion**:

Presents the data collected from the study, analyzes the impact of eutrophication on the dam’s water quality, and evaluates the effectiveness of graphene treatment. The findings are interpreted in the context of local environmental conditions and water management needs.

Bibliographic

Synthesis

Chapter I

General information about water and dam

Introduction

Water is a vital resource for life, economic development, and environmental sustainability. With increasing urbanization, climate change, and overuse, its sustainable management has become a global priority.

Dams play a strategic role by storing water, regulating river flow, supplying drinking water, supporting agriculture, generating hydroelectric power, and controlling floods.

However, beyond quantity, water quality is equally crucial. Dams influence the physical and chemical properties of water, which calls for strict monitoring to prevent eutrophication, pollution, and ecosystem degradation.

Therefore, the design, operation, and monitoring of dams must follow an integrated approach that ensures hydraulic safety, resource availability, and water quality

I.1.water

I.1.1. Definition of water

Pure water has the chemical formula H2O. Water, which makes up 71% of the Earth's surface and is readily observable in liquid form, is composed of 3% freshwater from different reservoirs and 97% saltwater. It can be found in lakes, rivers, streams, and oceans when it is liquid. Seas, lagoons, ponds, marshes, streams, canals, ditches, and the soil's interstitial zones that hold liquid water are additional examples of these.

The term "water" comes from the Latin aqua, according to its origin. Because water has played and still plays a part in the emergence and maintenance of life, its management is crucial to geopolitical issues. Water is vital to human health in addition to the water cycle and environmental preservation. Therefore, it's critical to avoid wasting water, look for leaks, practice responsible conduct, or gather rainwater [1].

Figure I.01 : Structure of the Water Molecule - H_2O

I.1.2. The different types of water in nature

I.1.2.1. Groundwater

Very deep underground aquifers typically have very high-quality water. In the same aquifer, their composition is rather constant. Compared to the waters of shallow aquifers, they are less susceptible to pollution. The majority of the time, dissolved oxygen is absent from groundwater. It can also contain undesirable elements including iron, manganese, ammonium, humic acid, carbon dioxide, and, less frequently, an overabundance of nitrates. Water production firms employ the following strategies, depending on the issues they face:

- Sand filtration to remove iron, manganese, and possibly ammonium;
- Disinfection to ensure bacteriological quality, including during transport to the consumer, sometimes over long distances;
- Removal of nitrates and pesticides through specific treatments;
- Aeration of the water to oxygenate it and remove carbon dioxide.

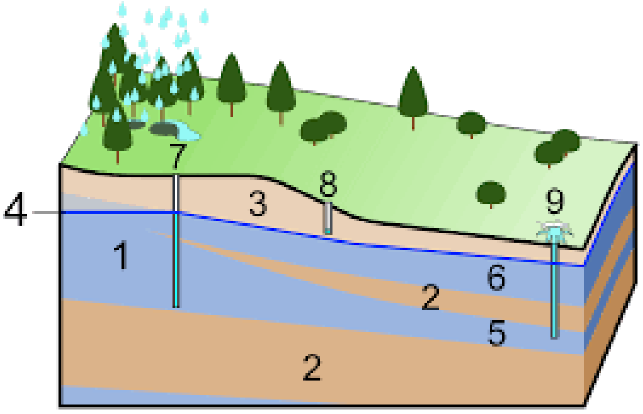


Figure I.02: Groundwater

I.1.2.2. Surface water

All of the water that flows or is stored on the continent's surface is included in this term. They are subjected to every type of pollution imaginable. As a result, these waters are contaminated. They contain soil microbes, suspended detritus, and garbage from homes and businesses.

They come from either surface runoff or deep aquifers where their emergence serves as a stream or river source. These waters congregate into a watercourse, which is distinguished by a high flow velocity and an ever-moving water-atmosphere contact surface.

Therefore, producing distribution water from surface water is a far more difficult undertaking for water production firms.

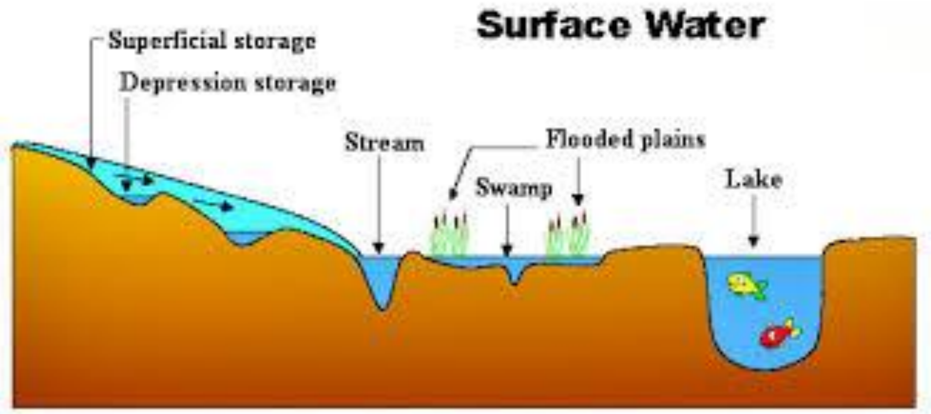


Figure I.03: Surface water

I.1.3. water in Algeria

Both the amount and quality of water are in danger. By 2025, Algeria will have a 1 billion m³ water shortage, even with the building of new dams and the use of desalination.

The hydrographic region of Constantinois, Seybouse, and Mellègue is the only area that appears to be exempt from the deficit by this horizon. This is despite the fact that it was in deficit by the year 2000 and was able to eradicate it because of the high regulatable volume supplied by the dams that were being built. The Beni Haroun dam, for instance, permits the control of a volume of 432 million m³.

Due to the shortage in the Algérois-Soummam Hodna and Oranie-Chott-Chergui regions, less water is being used for irrigation in order to give priority to the drinking water supply (A.E.P.) in these areas.

The regions of Chliff-Zahras and Algérois-Soummam-Hodna will have a significantly greater shortage. by 2025.

The conflict between needs and resources is an important and illuminating signal that directs our future water policy efforts to lessen the impact of the deficit. It is evident that although the amount of mobilizable water is declining, Northern Algeria is simultaneously facing a severe resource deficit at a time when needs are rising. This is because the water-capture locations are affected by a number of natural or man-made issues.

The primary technical issues influencing the amount and quality of water resources are examined in this study. These include eutrophication of reservoir waters, evaporation of reservoir lakes, leakage through dam foundations and banks, siltation of dams, and seawater intrusion into coastal aquifers.

I.1.4. Parameters of water quality

I.1.4.1. Physico-Chemical Parameters

I.1.4.1.1. The physical parameters

A. Temperature

Controlling temperature is crucial, particularly when industrial effluents are present. It is a crucial parameter for the systems' correct operation.

purifying to the degree that it can have a variety of certain effects: how soluble gasses and salts are. It is well known that a gas becomes less soluble as its temperature rises. When it comes to dissolved oxygen, this phenomenon is especially significant.

Additionally, the oxygen saturation concentration must drop with increasing water temperature. This resulted in a decrease in the oxygen reserve accessible to microorganisms involved in self-purification processes, which in turn affected biological purification through microbial multiplication.

B. Conductivity

It provides a sense of the water's salinity. Changes in the latter can affect sedimentation and biological treatment. A conductimeter is used to test the electrical conductivity of water in µS/cm or mS/cm (micro or milli Siemens per cm). It gauges how much electricity flows between two electrodes submerged in water.

C. Suspended Solids (SS)

Suspended solids are called very fine particles in suspension (sand, clay, organic goods, particles of polluting products, microbes,...) that provide a cloudy look in the water (turbidity) and oppose the entry of the light necessary for life aquatic. In overwhelming concentrations, they therefore constitute solid water contamination.

D. Dry volatile matter (DVM)

Suspended volatile matter is defined as that which is likely to volatilize when tested in a lab setting at 550°C. VSS, which make up between 70 and 80 percent of TSS, are typically regarded as suspended organic materials. The unit of VSS is mg/l.

E. Turbidity

is a metric that fluctuates based on humic acids (plant breakdown) or colloidal compounds (clays), but it also considers the relatively large amount of suspended matter of organic or mineral origin that obstructs the water.

I.1.4.1.2 The specifications of the chemical

A. The organic material

The portion of organic pollution that has not yet broken down—dead living matter or the waste products of living things—is known as organic matter (OM) and is found in water.

As a result, while in small amounts, they are naturally found in water. If there is more, it suggests pollution from runoff from farms, inadequately handled home wastewater discharges, etc. Both visible particle matter and dissolved organic matter can be present in water. Standardized methods such as COD and BOD5 can be used to quantify the organic pollution load.

B. Hydrogen potential, or pH

A key factor in biological treatment is pH. It conveys the wastewater's level of acidity or alkalinity. This parameter is very important:

- in biological activities, some of which necessitate extremely strict pH ranges of 6.5 to 8.5
- In physical and chemical characteristics (acidity, aggression);

C. BOD5, or biochemical oxygen demand over five days

is a measure of how much oxygen microorganisms need to oxidize (degrade) all of the organic matter in a water sample that has been kept at 20°C and in the dark for five days. The oxygen content of the water sample is first measured in order to calculate the BOD5. Five days later, we take this measurement again.

The difference between the two observed quantities is represented by BOD5. About 80% of all biodegradable pollutants is represented by the obtained value.

I.4.2. Parameters Related to Undesirable Substances

I.4.2.1.Nitrates

Measurement unit: mg/L NO_3

- The upper limit is 50 mg/L12.

- Origin: The biological oxidation of nitrogen forms found in the environment, especially as a result of overuse of agricultural fertilizers, is a common source of nitrates.
- Impact: Health issues, especially methemoglobinemia in babies, can result from excessive nitrate concentrations.

I.4.2.2.The Nitrites

- Measurement unit: mg/L NO_2
- Maximum limit: Although not stated clearly, their existence frequently serves as a sign of contamination.
- Origin: Ammonia's partial oxidation or nitrates' reduction are the sources of nitrites.
- Impact: The body may produce carcinogenic chemicals as a result of nitrites.

I.4.2.3. Fluor

- Unit of measurement: mg/L
- Maximum limit: 1.5 mg/L.
- Origin: Fluoride can be added to water for public health purposes (to prevent tooth cavities) or it can be found naturally
- Impact: Dental or skeletal fluorosis may result from an overabundance of fluoride [2] .

I.2. Dam

I.2.1.Définition

A dam is a barrier that stops or restricts the flow of surface water or underground streams. Reservoirs created by dams not only suppress floods but also provide water for activities such as irrigation, human consumption, industrial use, aquaculture, and navigability. Hydropower is often used in conjunction with dams to generate electricity.

A dam can also be used to collect or store water which can be evenly distributed between locations. Dams generally serve the primary purpose of retaining water, while other structures such as floodgates or levees (also known as dikes) are used to manage or prevent water flow into specific land regions.

I.2.2. History

Early dam building took place in Mesopotamia and the Middle East. Dams were used to control water levels, for Mesopotamia's weather affected the Tigris and Euphrates Rivers.

The earliest known dam is the Jawa Dam in Jordan, 100 kilometres (62 mi) northeast of the capital Amman. This gravity dam featured an originally 9-metre-high (30 ft) and 1 m-wide (3.3 ft) stone wall, supported by a 50 m-wide (160 ft) earthen rampart. The structure is dated to 3000 BC[3][4] . However, the oldest continuously operational dam is Lake Homs Dam, built in Syria between 1319-1304 BC [5] .

The Ancient Egyptian Sadd-el-Kafara Dam at Wadi Al-Garawi, about 25 km (16 mi) south of Cairo, was 102 m (335 ft) long at its base and 87 m (285 ft) wide. The structure was built around 2800 [6] or 2600 BC [7] as a diversion dam for flood control, but was destroyed by heavy rain during construction or shortly afterwards. [6][7] During the Twelfth Dynasty in the 19th century BC, the Pharaohs Senosert III, Amenemhat III, and Amenemhat IV dug a canal 16 km (9.9 mi) long linking the Fayum Depression to the Nile in Middle Egypt. Two dams called Ha-Uar running east–west were built to retain water during the annual flood and then release it to surrounding lands. The lake called Mer-wer or Lake Moeris covered 1,700 km^2 (660 sq mi) and is known today as Birket Qarun. [8]

Figure I.04: Sadd El-Kafara The Oldest Dam in The World.

I.2.3. Types of Dams

I.2.3.1.rigid dam

I.2.3.1.1.The dam for gravity

- It is the simplest and heaviest in stone or concrete.

- In relation to the dam, it is vertical, and in relation to the valley, it is sloped. It only sits on the floor.
- He thereby resists the water's pressure with all of his mass.

Figure I.05 : The dam for gravity **.**

I.2.3.1.2.The arch dam

It depends in part on rock barriers in concrete. It conveys the water pressure to the banks because of its curved design. Buttresses can also be used to support it.
It is vertical with regard to the valley and slanted with regard to the dam. In small valleys, it is frequently utilized. [9]

Figure I.06: The arch dam .

I.2.3.1.3.A buttress dam

Is a particular kind of dam that has a massive concrete wall held up by buttresses. Located downstream, these triangular buttresses contribute to the structure's lighter weight by conserving concrete. They increase the structure's stability by supporting the main wall, which keeps the water out. In broad valleys, buttress dams are frequently utilized.

Figure I.07: A buttress dam .

I.2.3.2. Embankment dams (flexible)

I.2.3.2.1. Earth dams

Earth dams can be constructed almost anywhere using locally available materials, without regard to height restrictions, and on inadequately sturdy foundations.
- Almost anywhere in the world, earthen dams can be constructed using locally available materials, without regard to height restrictions, and on inadequately sturdy foundations. When the foundation soil is composed of non-rocky materials, such the alluvial layers of valley bottoms, these are essentially the only ones that may be utilized.

The sealing mask and the structure's body can adjust to the foundation soil's movements (flexible dams).

The potential for advanced construction mechanization The presence of subterranean flow within the dam body and the inability to direct the flood discharge through the structure can cause the dam to deform in the case of a permeable foundation.

Figure I.08 : Earth dams.

I.2.3.2.2. Rockfill dams

Which can be constructed on rocky or non-rocky foundation soil as long as it is strong enough to prevent a rupture of the sealing layer due to settlement, are frequently utilized in isolated locations where cement is costly and supplies for an earth dam are unavailable.

Rockfill dams are not affected by the elements and are incredibly stable (no underpressure). One of its drawbacks is that they require a lot of materials—three to four times as much as a weight dam of the same capacity. As with earth dams, they are extremely susceptible to submersion by overflow. But there are a lot of leaks there. They are reasonably priced in comparison to concrete dams.

Figure I.09: Rockfill dams .

I.2.4. the main function of dams

I.2.4.1.Water retention

The dam prevents the water's natural flow. A reservoir is created when large amounts of water build up.

I.2.4.2.Water forced conduction

After the water is stored, valves are opened to allow the water to flow quickly into penstocks, which are lengthy metal pipes. The water is transported by these pipes downstream to the hydroelectric power plant.

In France, the majority of hydroelectric power plants are automated. Based on the need for electricity, each power plant begins operations on a predetermined schedule.

I.2.4.3.Production of electricity

The water's force rotates a turbine at the pipe's outlet in the power plant, which powers a generator. The alternator generates an alternating electric current using the energy from the turbine.

The height of the fall and the water flow determine the plant's power. This power will be higher the greater they are.

I.2.4.4.Tension adaptation

To make it easier to transmit the electric current generated by the alternator in very high and high voltage lines, a transformer increases the voltage of the current. [10]

I.3. source of water quality degradation in dams

The quality of surface water has declined as a result of population growth, agricultural development, and industrialization.

I.3.1.Degradation sources

I.3.1.1.Natural source

- **Soil erosion:** Watershed erosion can cause dams to silt up, lowering their capacity and changing the quality of the water in semi-arid regions or with little vegetation cover.

- **Climatic factors:** Weather patterns, like intense downpours, can affect the waterways' turbidity and solid load.

I.3.1.2.Human-caused Sources

- **Pollution from agriculture:** Agricultural pesticides and fertilizers can flow off into surface waters or seep into groundwater, which can lead to eutrophication.
- **Industrial pollution:** Water can get contaminated by chemicals released by companies, such as hydrocarbons.
- **Domestic pollution:** Water can also be contaminated by detergents, cosmetics, and untreated wastewater. [11]

I.3.1.3.consequences

- **Eutrophication:** The buildup of nitrogen and phosphorus causes algae to grow excessively, depleting oxygen and upsetting the environment.
- **Physical-chemical quality deterioration:** Water potabilization may be challenging due to changes in parameters like pH, COD, and nitrates.

Conclusion

Sustainable water management relies on a balanced approach between resource mobilization, protection of natural environments, and meeting human needs. As such, dams are essential infrastructures for ensuring water availability, particularly during periods of water stress. However, their effectiveness cannot be fully achieved without rigorous monitoring of water quality, which is essential for public health, agriculture, and ecosystems. Integrating quality parameters into dam management not only prevents pollution risks but also optimizes water use according to the requirements of each sector. Ultimately, the future of water resources depends on informed governance, based on the complementarity between quantity and quality.

Chapter II

Eutrophication

Introduction

Eutrophication of aquatic ecosystems is a sequence of biological processes triggered by an excessive input of nutrients, primarily nitrogen and phosphorus. It leads to complex reactions in freshwater, brackish, and marine environments. This phenomenon can develop gradually or occur suddenly.

The most noticeable effects include the proliferation of primary producers (such as aquatic plants, algae, and cyanobacteria), the emergence of toxic or anoxic conditions (absence of oxygen), and a decline in biodiversity.

To the general public, eutrophication often appears as a highly localized environmental issue, typically recognized through well-publicized events like green tides along the Breton coast.

However, the factors driving eutrophication are not limited to local influences. They operate across broader spatial and temporal scales. Nutrients reaching coastal waters can originate from upstream watersheds located several hundred kilometers away, being transported through river systems and eventually dispersed into the sea.

These eutrophication processes affect all aquatic ecosystems, although their manifestations and dynamics vary depending on the type of water body—whether freshwater, brackish, or saltwater. [12]

II.1.Definition

The OECD (Organisation for Economic Co-operation and Development) defines eutrophication as the "enrichment of water bodies with nutrients," leading to several adverse effects, such as increased production of algae and macrophytes, a decline in water quality, and other undesirable impacts that hinder various water uses.

Although eutrophication can occur naturally, it is significantly exacerbated by human activities. The two primary nutrients responsible for this phenomenon are nitrogen and phosphorus.

II.2. Origin of Nitrogen and Phosphorus Pollution

Nitrogen (N) and phosphorus (P) are two essential nutrients for aquatic life. Their availability, combined with other environmental factors, determines the extent of biomass growth. While these elements naturally occur in the environment in various forms—explained in the context of their biogeochemical cycles—an excessive concentration can lead to toxic and harmful effects, a phenomenon known as eutrophication.

The sources of nitrogen and phosphorus inputs in lakes and reservoirs can be categorized into two types: exogenous sources (external inputs such as agricultural runoff, wastewater, and atmospheric deposition) and endogenous sources (internal inputs, often resulting from sediment release within the water body itself).

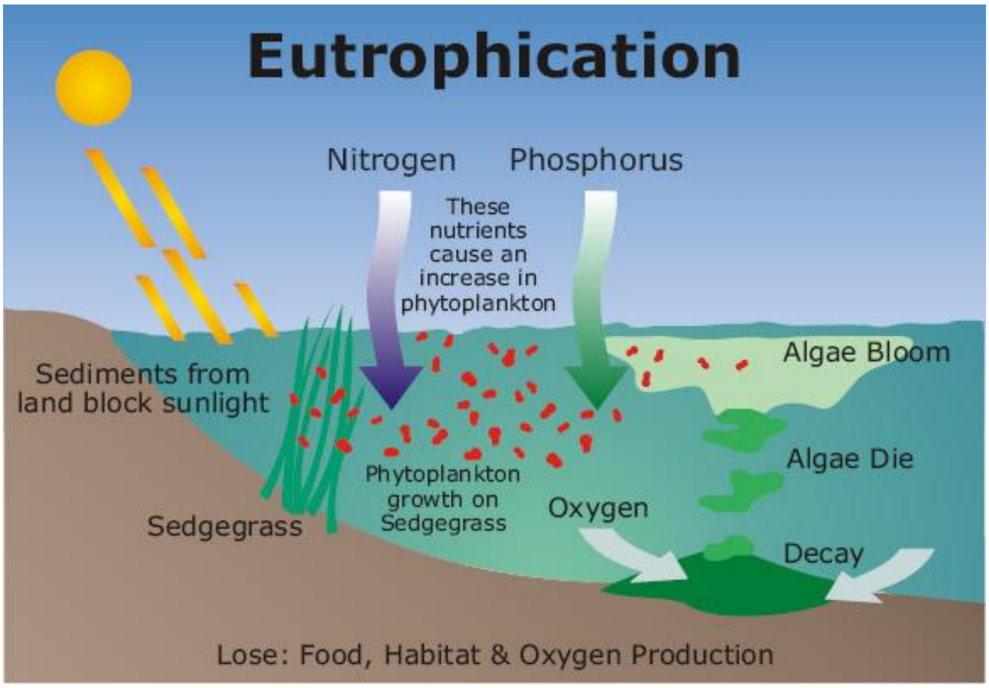


Figure II.10 : Phosphorus Pollution.

This figure illustrates the eutrophication process caused by nitrogen and phosphorus in an aquatic system. These nutrients stimulate the growth of phytoplankton, which is involved in metabolism. This allows aquatic ecosystems to regain a healthy environment, a healthy habitat, and oxygen production.

II.2.1 Forms and Transformations of Nitrogen (N) and Phosphorus (P) in the Environment

II.2.1.1 Nitrogen

In the absence of human activity, nitrogen in the environment primarily originates from microorganisms, such as cyanobacteria in water and certain soil bacteria, that convert atmospheric nitrogen gas (N_2) into ammonia (NH_3). Nitrogen constitutes approximately four-fifths of the Earth's atmosphere. Once fixed, it can be transformed into organic nitrogen by these organisms or released as ammonium ions (NH_4^+).

Under aerobic conditions, NH_4^+ can be oxidized into nitrites (NO_2^-) and then into nitrates (NO_3^-) through the process of nitrification. Plants are capable of assimilating nitrogen in the form of NH_4^+ or NO_3^-. When animals consume plants, they absorb organic nitrogen, which is later excreted through feces and quickly converted back into NH_3. In anaerobic environments, other microorganisms convert NO_3^- into NO_2^- and finally into N_2 gas — a process known as denitrification, completing the nitrogen cycle.

In soil, nitrogen in the form of nitrate is highly mobile and can leach into groundwater. Since denitrification cannot occur in aquifers due to the lack of organic matter, nitrate tends to accumulate and becomes a significant water pollutant.

II.2.1.2 Phosphorus

Most phosphorus originates from the weathering of phosphate rocks. Unlike nitrogen, phosphorus has no gaseous form; its principal mineral form is phosphate (PO_4^{3-}). Plants absorb phosphorus through their roots from the soil's interstitial solution, while the excess phosphorus becomes bound to soil particles and sediments.

Animals ingest phosphorus by feeding on plants and release the surplus as phosphate salts, which are quickly converted into phosphate ions. Ultimately, phosphorus is transported to the oceans, where it accumulates in marine sediments. Its return to land occurs only through geological processes such as the uplift of seabeds, making it an open cycle.

Fine sediments act as phosphorus sinks under normal oxidizing conditions. However, in reducing environments (e.g., oxygen-depleted conditions), these sediments can release large quantities of mineral phosphorus back into the water column, contributing to eutrophication. [13]

II.2.1.3. Disruption of the nutrient cycle in the absence of ecological Balance

The nutrient cycle can only function properly under conditions of ecological balance **(Figure II.2)** .

When nutrient inputs increase significantly (the potential sources will be discussed later in this section), the cycle becomes disrupted **(Figure II.3)** , leading to eutrophication. Dissolved substances and suspended matter are mineralized, consuming oxygen and releasing nutrient salts.

Algae benefit from the excess nutrients and proliferate at a rate that exceeds their consumption by animals, dispersion by currents, or decomposition by bacteria. This results in the accumulation of algal biomass, and the decomposition of these algae further depletes oxygen in the environment.

When oxygen concentrations become low, anaerobic bacteria begin to break down organic matter without using oxygen. The end products of this process—hydrogen sulfide (H_2S), ammonia (NH_4), and methane (CH_4)$^-$are toxic to many aquatic species.

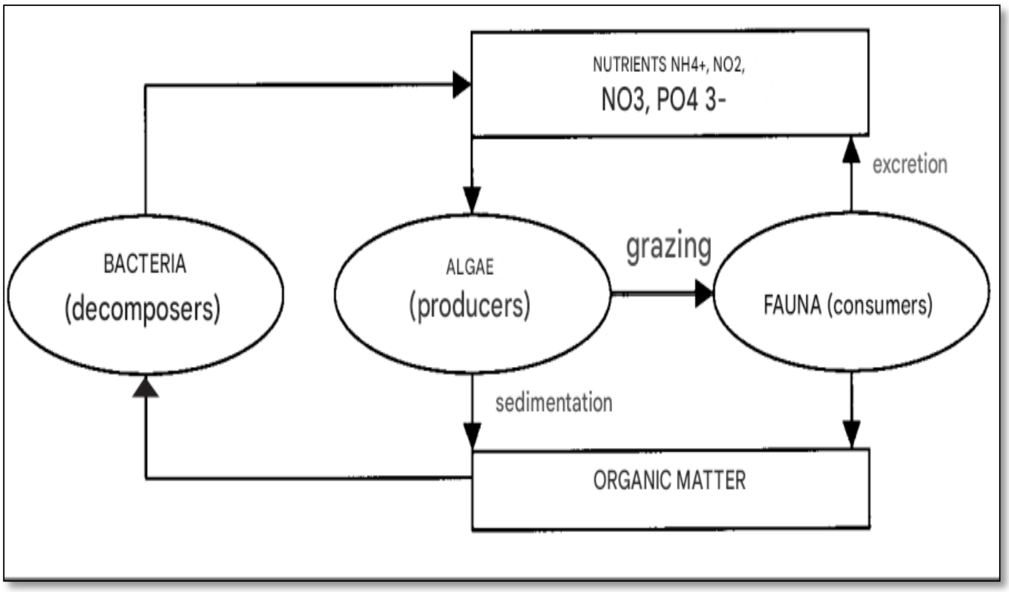


Figure II.11: Simplified nutrient cycle.

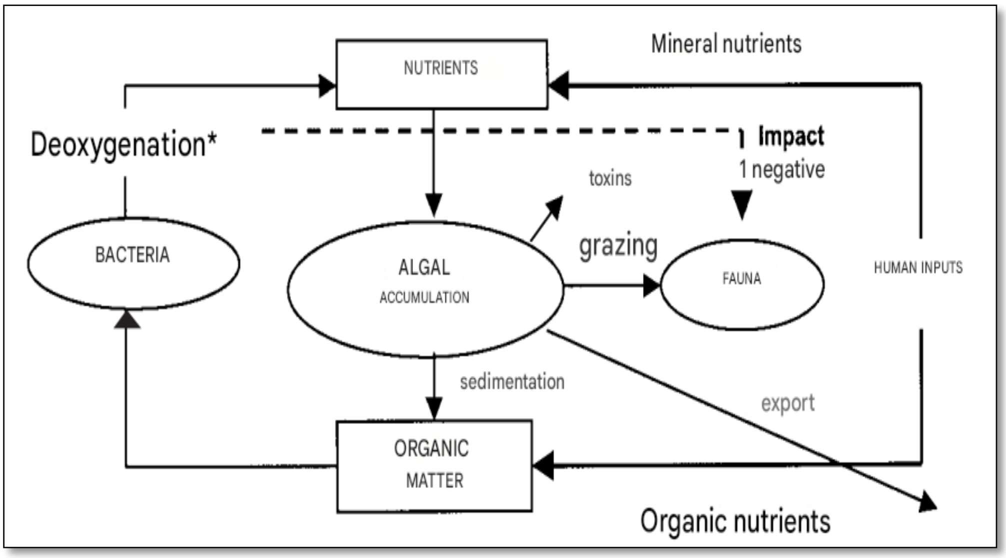


Figure II.12: Nutrient cycle, during excess intake.

II.3. Steps in the Eutrophication Process

1. The process begins with an overgrowth of aquatic plants, algae, phytoplankton, and photosynthetic bacteria (cyanobacteria). These organisms become so abundant that

aquatic herbivores cannot consume them all. A greenish film forms on the surface of the water, blocking sunlight and preventing it from reaching other aquatic plant species in the deeper layers of the lake.

2. As submerged vegetation can no longer perform photosynthesis due to lack of light, it eventually dies. These dead plants sink to the bottom of the lake, where they are decomposed by bacteria and other microorganisms.
3. The continuous accumulation of organic matter on the lakebed promotes bacterial proliferation. To decompose this organic material, bacteria consume increasing amounts of dissolved oxygen. As oxygen levels drop, aquatic animals begin to suffer. Reproduction ceases, and many species die due to hypoxic or anoxic conditions.

Even the bacteria may die off eventually from lack of oxygen. The remains of these organisms accumulate, forming a thick layer of organic sludge.

4. Over time, the buildup of sediment at the bottom of the lake leads to its progressive degradation. The lake gradually transforms into a marsh, then into a peat bog, and eventually into a meadow—a process known as natural lake succession.[14]

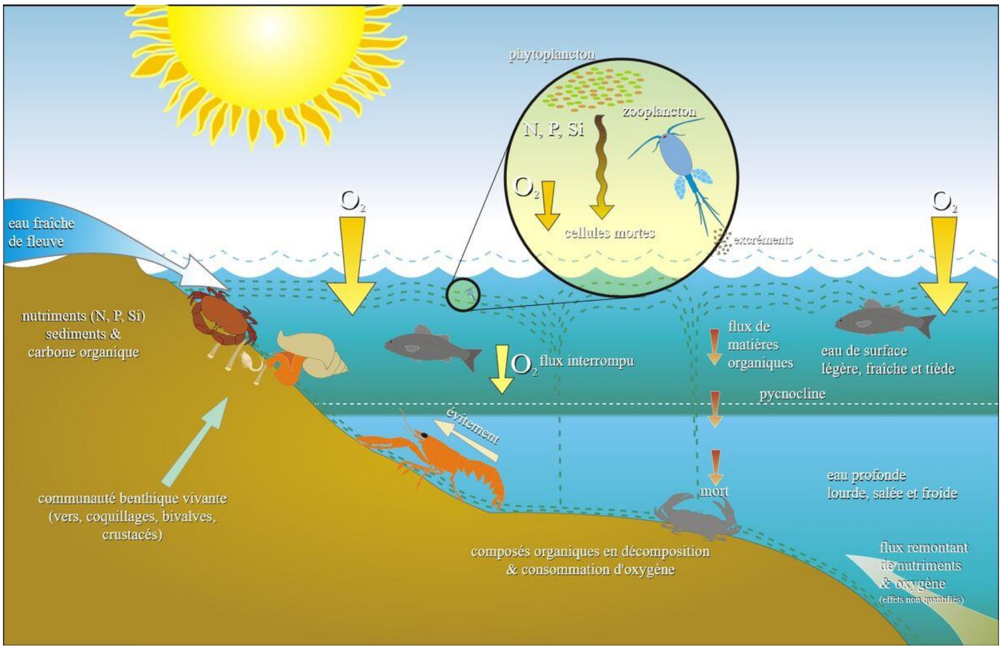


Figure II.13: Schema eutrophication.

II.4.The sources of nutrient inputs to nutrients to lakes and reservoirs

This table **(Table II.1)** presents the main sources of nutrient inputs to lakes and reservoirs, divided into two broad categories:

1. **Exogenous sources:** originating from outside the aquatic system, including point-source discharges (wastewater treatment plants, septic tanks) and diffuse sources (agricultural runoff, atmospheric deposition).

2. **Endogenous sources:** originating from within the lake, through underground infiltration or re-release of nutrient-rich sediments.

Table II.01: Sources of Nutrient Inputs to Lakes and Reservoirs.

Type	Source	Description
Exogenous	Point Sources	Wastewater treatment plants (WWTPs), septic tanks, and manure storage. Discharge treated or untreated effluents rich in nitrogen and phosphorus. Often exacerbated by stormwater overflows.
Exogenous	Diffuse Sources	Nutrient deposition from precipitation, dry atmospheric deposition, and runoff from agriculture and livestock activities. Mismanagement of fertilizers increases nutrient losses.
Endogenous	Groundwater Infiltration	Nutrient-rich groundwater (especially nitrates) resurges into lakes, particularly in agricultural areas. Generally low in phosphorus.
Endogenous	Sediment Release	Nutrients previously stored in sediments are recycled and may be released into the water column due to environmental changes like oxygen depletion.

II.5.Mechanism of eutrophication

The phenomenon of eutrophication, as described in the first part, is an excessive enrichment of water with nutrients, mainly phosphorus and nitrogen, which will promote the growth of plants, both algae and macrophytes.The term macrophyte designates large-sized algae, as opposed to opposition to large-sized algae microscopic like phytoplankton. This plant overgrowth can manifested by excessive amounts of phytoplankton (colored waters), or the presence of floating algae on the surface of the water and macrophytes on the shore and on the bottom.

The nocturnal respiration of phytoplankton or the degradation of plant matter by the microorganisms consume all both the oxygen in the water.Quite quickly, the depletion of dissolved oxygen in the waters have several harmful consequences: fish mortality, release of gases corrosive and other undesirable substances, and modification of pH values.[15]

II.6. Causes of Eutrophication: Nutrient Overload

II.6.1. The Direct Causes of the Phenomenon

This specific form of pollution is caused by an excessive input of nutrients and biodegradable organic matter, mainly resulting from human activities. These inputs primarily originate from phosphates found in detergents, nitrates from nitrogen-based fertilizers, and ammonia produced by the bacterial decomposition of organic effluents. The process manifests as follows:

- Biodegradable organic matter is decomposed by naturally occurring bacteria in the environment.
- The nutrient surplus leads to the rapid surface proliferation of certain aquatic plants, which, upon dying, further increase the amount of biodegradable organic matter in the ecosystem.

II.6.2. The indirect causes of eutrophication

The six main categories of polluters are: industry, agriculture, households, transportation, urbanization, and the armed forces. The discharge of wastewater into the natural environment is one of the primary sources of pollution affecting our waterways and, more broadly, the entire ecosystem. These discharges include:

- **Domestic wastewater**, which includes water from kitchens, bathrooms, and laundry, containing fats, soaps, detergents, and various household wastes;
- **Sewage from toilets**, containing fecal matter and urine;
- **Stormwater and drainage water**, which originate from precipitation or land runoff;

- **Agricultural wastewater**, particularly from livestock farming, where manure and slurry are rich in nitrogenous organic matter. Some compounds, such as nitrates, are highly soluble and can be leached into water bodies by runoff;
- **Atmospheric or runoff water**, resulting from atmospheric deposition (e.g., acid rain) and the leaching of pollutants from roads, railways, parking lots, and other impermeable surfaces.

II.7. Impacts of eutrophication on water exploitation

Eutrophication has various impacts on human water use.

- **Health risk**

Eutrophic water primarily presents a health risk to humans and animals:
risk related to nutrients or risk related to algal toxins

- **Difficulties in potabilization**

They may represent additional measures to be taken at the level of production drinking water

- **Biodiversity**

It is a significant threat to aquatic ecosystems.Biodiversity is declining, and many many species are dying.Overall, the death of fish is very significant.[16]

II.8. Indicators of eutrophication

The indicators of eutrophication manifest in compartments of the ecosystem concerned by the nutrient inputs in the water allows for characterize the state and/or level of eutrophication of an aquatic ecosystem

- **Phytoplankton can be considered an "objective" indicator**

Phytoplankton proliferations or blooms are closely related to nitrogen and phosphorus inputs.The levels of proliferation must be formalized through through counts.The chlorophylls that constitute indicators of biomasses phytoplanktonic are associated with routine variables...

- **Macrophytes**

They are also directly and indirectly related to the inputs of nitrogen and phosphorus. in the environment.The indirect relationship arises from the increase in turbidity related to the increase in phytoplankton densities.This latter leads to the decline of flowering plants at the expense of algae.The proliferation of green algae constitutes the relationship direct impact on the nitrogen and phosphorus inputs in the lagoons.The changes in the macrophyte biomasses, as nitrogen and phosphorus inputs increase, must be formalized.

- **The macrofauna**

Placed downstream of primary production in the trophic chain, benthic macrofauna is indirectly related to the inputs of nitrogen and phosphorus.The excess organic matter leads to a decrease in dissolved oxygen in the sediments which changes the living conditions for the animals.The excess of phytoplankton can also lead to the proliferation of benthic filter feeders.

- **The sediment**

It is indirectly related to the inputs of nitrogen and phosphorus because it constitutes the"conduit" for the eutrophying substances in the lagoon ecosystem.Phytoplankton and
macrophytes are recycled at its interface, consuming oxygen and releasing salts minerals .These latter partially enrich the sediment.This process makes the sediment an integrative compartment for the inputs of nitrogen and phosphorus in the environment.Also, the levels of concentration in organic matter, nitrogen, and phosphorus, must show a graduation.

- **The water column**

It includes a range of variables, some of which will reveal the causes and others the consequences of eutrophication.Nutrient salts are the causes, turbidity and chlorophyll are the consequences. chlorophylls represent the consequences.Finally, the total forms of nitrogen and phosphorus integrates the causes and consequences, as organic forms (plankton, detrital matter) ultimately constitute eutrophying materials due to efficient recycling at the interface
water-sediment.

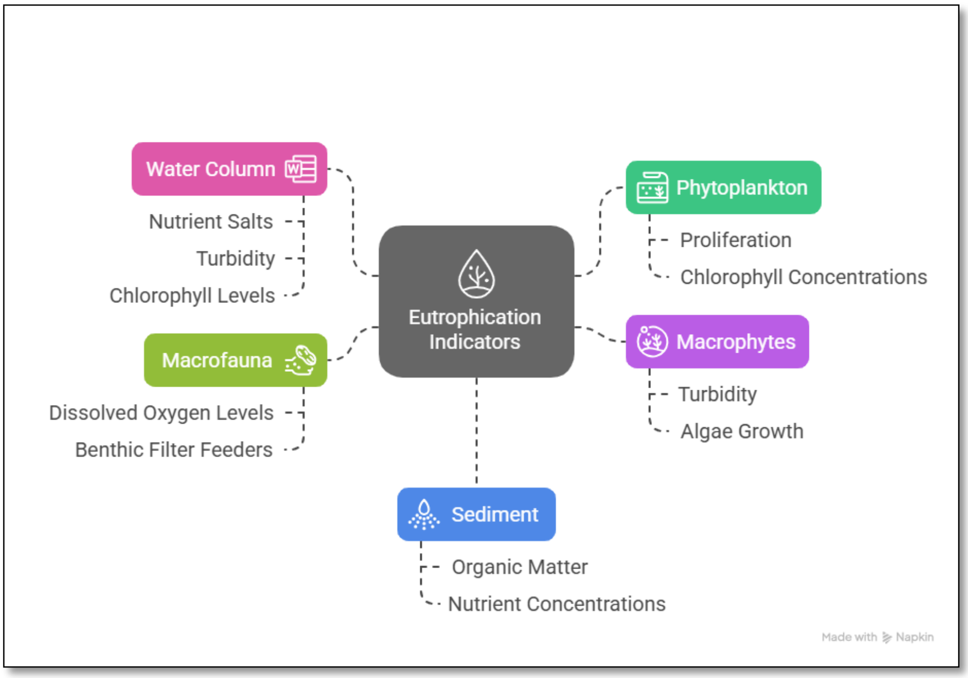


Figure II.14 : indicators of eutrophication in aquatic ecosystems

II.9. Means of Combating Eutrophication

Eutrophication is a widespread environmental problem affecting aquatic ecosystems worldwide. Awareness of this issue has grown in recent years, leading to the development of various mitigation techniques. These are primarily based on the principle of the **limiting factor**, aiming to reduce nutrient inputs either at the source or directly within lakes and reservoirs.

II.9.1. The Limiting Factor Principle

One of the most effective strategies to control accelerated eutrophication is to reduce the input of nutrients into the aquatic environment. The basic chemical requirements for photosynthesis can be summarized by the following conceptual equation:

$$CO_2 + NH_4^+ + PO_4^{3-} + H_2O + \text{Light} + \text{Trace elements} \longrightarrow \text{Algal biomass} + O_2$$

Theoretically, all variables in this equation can be managed. However, numerous lake restoration studies have shown that **limiting nutrient input**, particularly phosphorus, is the most effective measure for combating eutrophication.

II.9.2. Preventive Measures

Preventive measures focus on reducing nutrient inputs at their source, often targeting phosphorus due to its central role in algal growth. This reduction can be comprehensive—limiting all inputs—or selective, targeting only the dominant sources.

II.9.2.1. Reduction of Domestic Nutrient Inputs

The primary approach to reduce domestic nutrient inputs is through improved **wastewater treatment**. While many treatment plants are designed to remove suspended solids and some dissolved substances, they often fail to adequately remove nitrogen and phosphorus, which are released back into the environment. In sensitive ecosystems, advanced treatment processes to remove nitrogen and phosphorus are necessary to restore biological balance.

II.9.2.2. Reduction of Agricultural Nutrient Inputs

Agricultural activities are among the most significant diffuse sources of nutrient **pollution**:

- **Soil fertilization** involves using products rich in phosphorus, nitrogen, and potassium. The widespread detection of nitrates in water supplies has raised public concern. It is essential to promote better practices, such as calculating precise fertilizer requirements based on soil characteristics, crop type, and land-use history, thereby reducing excessive and unnecessary applications.
- **Livestock farming** produces nutrient-rich waste (e.g., manure, slurry), which, if mismanaged, can pollute surface and groundwater. These effluents contain **urea**, which decomposes into ammonia, a toxic compound for aquatic organisms. Preventing leakage and ensuring proper storage and treatment of these effluents is essential. Systematic monitoring of agricultural practices, alongside awareness programs for farmers, can help mitigate these impacts.

II.9.2.3. Tributary Treatment or Diversion

To reduce the inflow of nutrients into eutrophic lakes or reservoirs, pre-treatment or diversion of tributary waters is a viable solution. One such method involves the construction of pre-dams or pre-reservoirs to temporarily retain nutrient-rich inflows. These pre-reservoirs can act as bioreactors, allowing for nutrient uptake by algae and sedimentation before the water reaches the main reservoir.

This approach can also limit sedimentation in the main lake. Some projects have demonstrated that up to 96% of phosphorus can be removed through this technique.

II.9.3. Curative Control Measures

When rapid improvements in water quality are required, direct intervention in the water body can be considered. Although these treatments are typically less effective in the long term and primarily address the symptoms rather than the root causes, they can lead to immediate improvements. Several options are outlined below:

- **Nutrient Deactivation:** The direct introduction of agents such as iron salts or alum into the water can cause phosphorus to precipitate and become immobilized, rendering it unavailable to aquatic organisms. However, the temporary nature of this treatment and the potential toxicity to aquatic life are its main drawbacks.
- **Hypolimnetic Aeration:** Supplying oxygen to the deeper, hypolimnetic layers of a lake **(see Figure II.15),** without disturbing the thermocline, can help limit the release of phosphorus and other substances from the sediments.
- **Artificial Circulation:** Similar to hypolimnetic aeration, this method involves oxygenating the bottom layers of the lake. However, in this case, the aeration process is more vigorous, leading to the disruption of the thermocline and even causing complete mixing of the lake's water layers **(see Figure II.15)** .

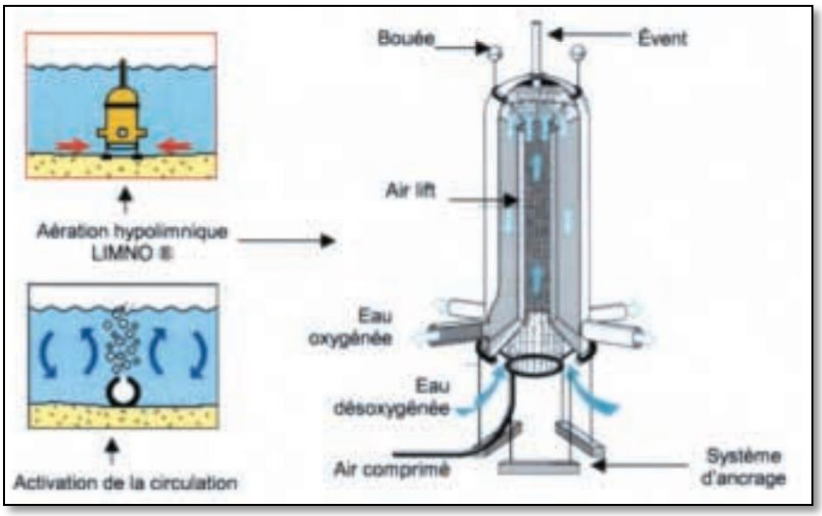


Figure II.15 : Water aeration techniques, by Aqua Technique [17]

- **Lower the water level :**The purpose of this technique is to expose the sediments to the atmosphere .This allows for the control of macrophytes and attached algae .One can accompany this measure with dredging or a covering of sediments .The problems related to this technique are the destruction of fragile organisms as well that the maintenance for a certain period a low water level, or even none at all.
- **Cover the sediments :** This covering can be done using a plastic tarp or a material particulate (fly ash) to limit the nutrient exchanges between the sediments and the water column and to reduce the development of macrophytes .The difficulties lie in the cost of the technique and the impact of materials particulate on living organisms.
- **Biological control :** The introduction new living species into a lake can help eliminate certain algae present in excessive numbers .Thus, fish can help control macrophytes and the manatee the water hyacinth water .The precautions to take are however important since the introduction of new species into a environment can have consequences on the other species.
- **Chemical control :** The use of certain chemicals allow the elimination of aquatic plants undesirable .Copper is an algicide . commonly used, and herbicides can also be used .The disadvantages are the costs, the nature temporary nature of the intervention and the risk poisoning of other organisms. [18]

Conclusion

Eutrophication represents a major environmental problem that highlights the impact of human activities on natural ecosystems.

While eutrophication can occur naturally, it is now significantly accelerated by domestic, industrial, and especially agricultural practices. Excessive nutrient inputs into aquatic environments lead to serious ecological imbalances, threatening biodiversity, water quality, and the overall health of ecosystems.

Addressing this challenge requires early intervention by reducing phosphorus and nitrogen inputs, combined with the implementation of effective remediation strategies where necessary. Combating eutrophication requires not only scientific and technical efforts, but also collective awareness and the adoption of integrated approaches to land and water resource management.

Chapter III

Graphene and Clay

Introduction

Graphene and clay represent two fundamentally distinct materials with significant technological and industrial applications. In 2004, physicists Andre Geim and Konstantin Novoselov isolated graphene, a two-dimensional carbon allotrope renowned for its exceptional mechanical strength, thermal conductivity, and electrical properties. While graphene production remains expensive, its revolutionary potential spans electronics, energy storage, nanotechnology, and advanced composites.

In contrast, clay a naturally abundant sedimentary material - exhibits unique absorption capacity and plasticity, making it valuable for construction, biomedical applications, agricultural practices, and cosmetic formulations.

Contemporary materials science shows growing interest in graphene-clay hybrids, as their synergistic combination offers promising solutions for sustainable development challenges. This interdisciplinary research avenue explores how these dissimilar materials can complement each other's properties when integrated into novel functional materials.

III.1. graphene

Graphene is a new material that was first isolated in 2004 by A. Geim and K. Novoselov [19], with exceptional properties, it currently finds applications in all fields: electronics, medical, energy, aerospace, nanotechnology etc.

Pure graphene is still very expensive and there are only a few companies that monopolize the global production of graphene, mainly in China and the USA. Current industrial techniques are still quite complex, which is why research aims to simplify and generalize production by new methods.

The functionalization of (graphene, reduced graphene oxide or reduced graphene oxide) is done either by non-covalent route or by covalent route leads to composites with very interesting properties which also find new applications in all fields.

I.1 III.1.1. Definition

Graphene consists of a single layer of carbon atoms arranged in a ‘two-dimensional honeycomb lattice’ . In its natural state, multiple graphene sheets stack together to form ‘graphite’—the material found in pencil leads. When rolled into a cylindrical structure, graphene transforms into ‘carbon nanotubes’. This distinctive atomic configuration endows graphene with exceptional strength, electrical conductivity, and thermal properties, positioning it as a groundbreaking material for advanced research.

Its potential applications are vast, particularly in next-generation electronics and energy storage systems, driving innovation across multiple scientific and industrial domains.

III.1.2. History

The first mention of graphene dates back to its theorisation in 1947 by the physicist P.R. Wallace of McGill University in a paper on graphite [20].

Subsequently, many groups will try to obtain evidence of its existence which had long been thought impossible although it is now a “case study” in the calculation of electronic tape structure.

It was not until advances in transmission electron microscopy (1933, the first MET microscope to surpass optical microscopes) that the first graphene images were observed. In 1948, G. Ruess and F. Vogt provided the first graphene images of a few layers using an MET microscope [21].

The first single-layer graphene isolation and characterization is attributed to the team of Andre Geim and Konstantin Novoselov at the University of Manchester in England in 2004 [22]. The National Graphene Institute was built in Manchester and completed in 2015.

III.1.3. Structure of graphene

The term multilayer graphene (≤ 10) is used by the scientific community to refer to a stacking of several layers of graphene bound to each other by Van der Waals forces Van der Waals with inter-planar distances of 3.35 Å.

Graphene represents a plane of carbon atoms carbon, which is a hexagonal 2D structure with sp2 hybridization leading to the formation of three cr bonds (responsible for the rigidity and mechanical properties of the Graphene) and a 1t bond (responsible for electronic conduction) [23]. **(see figure III.16)** .

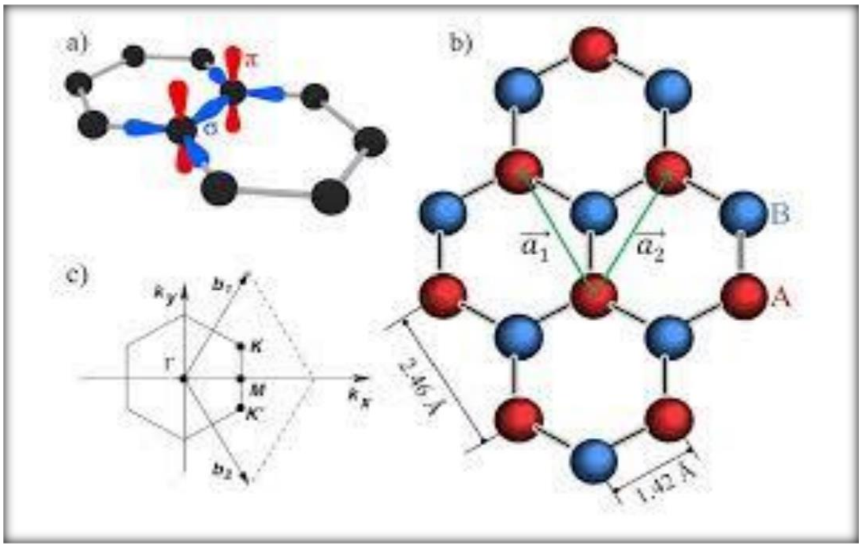


Figure III.16: Schematic representations of the graphene structure.

III.1.4. properties of graphene

Graphene possesses remarkable properties that distinguish it from other carbon-based materials like nanotubes and graphite. Unlike these materials which often contain structural defects, graphene maintains exceptional purity in its atomic structure [24]. Among its defining characteristics are: **(see table III.02)**

Table III.02 : Exceptional Properties of Graphene.

Property	Description	Underlying Cause
Electrical Conductivity	Extremely high, enabling rapid and efficient electron transport	Two-dimensional structure with delocalized π-electrons
Thermal Conductivity	Exceptional, surpassing that of copper or diamond	Highly ordered crystal lattice with minimal defects
Mechanical Strength	Extremely strong approximately 200 times stronger than steel	Stable honeycomb lattice of sp^2-hybridized carbon atoms
High Transparency	Absorbs only ~2.3% of visible light despite being a single atom thick	Ultra-thin monolayer of carbon atoms

Gas Impermeability	Even the smallest gas molecules (e.g., helium) cannot pass through a single graphene layer	Densely packed atomic arrangement without pores

These unique properties stem from graphene's perfect two-dimensional honeycomb lattice structure, which remains largely defect-free compared to other carbon allotropes. This structural perfection is responsible for many of graphene's extraordinary physical and chemical properties that have revolutionized materials science.

III.1.4. 1. optical properties of graphene

A graphene monolayer has, experimentally, a transmittance of 97.7% in the visible area, a 2.3% opacity. Theoretically, the transmittance optics T is completely in agreement with the experimental result, it is defined by the following equation:

$$T= (1+ \frac{1}{2\pi\alpha})^{-2} = 97,7\% \qquad (1\ )$$

Or α is the fine structure constant

$$\alpha= \frac{2\pi e^2}{hc} = \frac{1}{137} \qquad (2)$$

; is the electronic charge, C The speed of light and h la Planck constant [25]

The optical properties of graphene are more fascinating than the electronic properties from which they derive.

On the one hand, the physics of the system means that light absorption over a wide energy range can be described in terms of fundamental constants. Measurements have shown that graphene attenuates visible light by around 2.3%, a substantial reduction for a single atomic layer of material. [24]

III.1.4. 2.The mechanical strength properties of graphene

The first measurements of graphene’s mechanical properties were published in 2008. While graphene initially gained attention for its exceptional electronic properties, it also exhibits outstanding mechanical strength.

These remarkable characteristics arise from the strong covalent bonds formed between adjacent carbon atoms within its two-dimensional lattice.

Graphene demonstrates a breaking strength of approximately 40 $N\cdot m^{-1}$, making it about 100 times stronger than steel. In addition to its strength, graphene is also notable for its exceptional elasticity, with a Young’s modulus of around 0.5 TPa, allowing it to be flexed and then return to its original shape without damage.

III.1.4. 3.The properties of thermal conductivity

Graphene is recognized as a two-dimensional crystal with a thermal conductivity that exceeds even that of diamond. The absence of interlayer interactions allows its thermal conductivity to reach values as high as 5000 $W\cdot m^{-1}\cdot K^{-1}$.

Recent studies have demonstrated that a graphene monolayer exfoliated onto a silicon substrate can maintain a thermal conductivity higher than that of copper, which is one of the best-known thermal conductors. These findings highlight graphene’s exceptional ability to conduct heat, making it a promising material for the control and optimization of thermal flux in advanced thermal management systems. [24]

III.1.5. Methods of manufacturing graphene

Several techniques have been developed for the synthesis of graphene. Two main approaches are commonly used:

1. The "bottom-up" method, which involves synthesizing graphene sheets from organic or inorganic precursors, typically through chemical vapor deposition (CVD) or related techniques.
2. The "top-down" method, which consists of extracting graphene from bulk materials such as graphite or carbon nanotubes, typically through exfoliation or chemical treatments.

These two approaches differ in their scalability, cost, and quality of the graphene produced. **(See figure III.17)** .

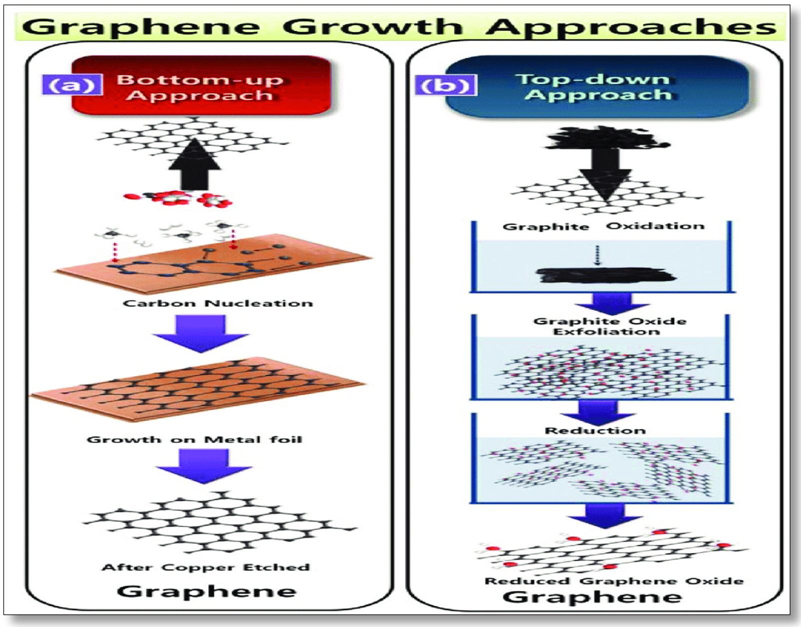


Figure III.17: Bottom-up and top-down techniques.

III.1.5. 1.Chemical exfoliation

The chemical route is an alternative that has developed strongly to produce grapheme at the industrial and low-cost scale using graphite [26]. Oxide production steps of grapheme reduced from graphite, are summarized in the following diagram:

The chemical route has emerged as a strong alternative for producing graphene on an industrial scale and at low cost, using graphite as the starting material [26].

The key steps involved in the production of reduced graphene oxide (rGO) from graphite via the chemical route are summarized in the following diagram: **(see figure III.18 and table III.03)**

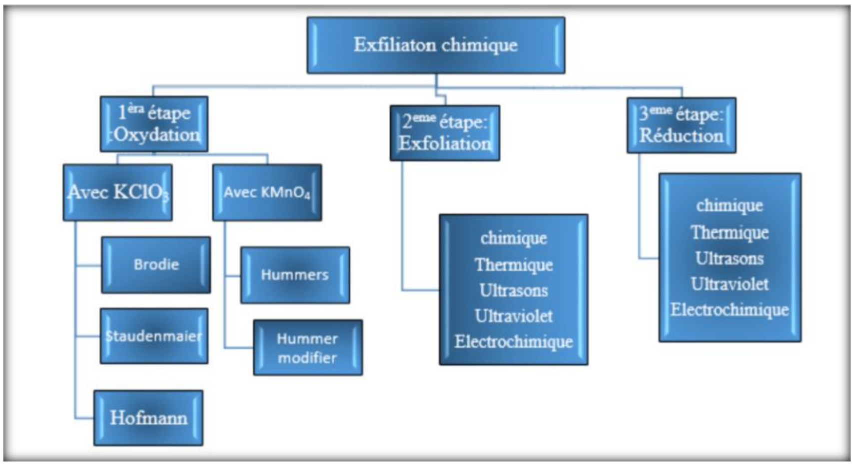


Figure III.18: the three techniques of chemical graphite exfoliation

Table III.03: Chemical Route for Producing Reduced Graphene Oxide from Graphite.

Step	Description
1. Raw Material: Graphite	Natural graphite is used as the starting material due to its layered structure.
2. Oxidation to Graphene Oxide	Graphite is oxidized using strong acids and oxidizing agents (e.g., H_2SO_4, $KMnO_4$) to form GO.
3. Exfoliation	The oxidized graphite (graphene oxide) is exfoliated into single or few-layer sheets, often via sonication or stirring.
4. Reduction	Graphene oxide is chemically, thermally, or electrochemically reduced to remove oxygen groups, yielding reduced graphene oxide (rGO).
5. Post-treatment & Drying	The reduced material is washed, filtered, and dried to obtain rGO powder suitable for applications.

- **The first step:**

Graphene oxide is typically synthesized by oxidizing graphite using acid and oxidizing agents. The main methods for graphite oxidation were developed by Brodie, Staudenmaier, and Hummers, each involving different degrees of oxidation. Brodie and Staudenmaier employed a mixture of nitric acid and potassium chlorate, while Hummers proposed a method using a combination of sulfuric acid, sodium nitrate, and potassium permanganate.

These treatments introduce various oxygen-containing functional groups—such as hydroxyl, epoxy, carbonyl, and carboxyl groups—on the surface of the graphene sheets, which disrupt the sp^2-hybridized carbon network.

This chemical modification increases the interlayer spacing of graphite from approximately 3.4 Å to about 9.5 Å. **(see figure III.19)**

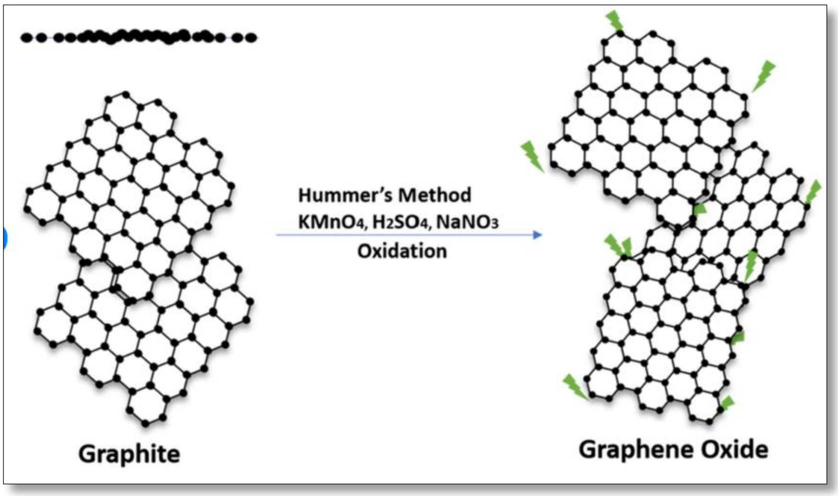


Figure III.19 : Hummer's process for oxidation of graphite to form graphene oxide [27]

- **The second step:**

Consists of separating the graphene oxide (GO) sheets by exfoliation (chemical, thermal, ultrasound, electrochemical... etc.).

Graphene oxide (GO) contains oxygen functional groups such as groups: hydroxyl (-OH); carbonyl (C=O); carboxyl (O-C=O) and epoxides (C-O-C). **(see figure III.20).**

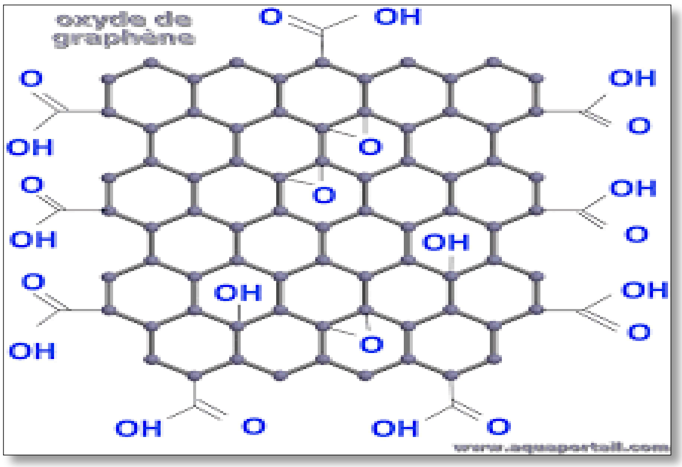


Figure III.20 : Structure of Graphene oxide.

- **The third stage:**

The reduction of graphene oxide (GO) involves decreasing its oxygen content through various techniques, such as chemical, thermal, photochemical, microbial, or microwave-assisted methods.

The resulting material, known as reduced graphene oxide (rGO), typically retains some residual oxygen-containing functional groups, resulting in inferior electrical, mechanical, thermal, and optical properties compared to pristine graphene.

The carbon-to-oxygen ratio and overall composition of rGO depend on the reducing agent employed. Among the most common are hydrazine, which is more effective in aqueous environments due to its stability, and sodium borohydride ($NaBH_4$), which may undergo hydrolysis and lose efficiency in water-based systems.

III.1.5. 2.Electrochemical exfoliation

The electrochemical exfoliation of a graphite electrode is performed using an aqueous ionic solution (electrolyte) such as KOH, $(NH_4)_2SO_4$, Na_2SO_4, etc., in order to produce graphene layers while eliminating oxidizing or reducing agents. The exfoliation mechanism proposed by Khaled Parvez is as follows [28]:

1. The application of a polarization voltage leads to the electrochemical reduction of water at the cathode, generating hydroxyl (•OH) and oxygen (•O) radicals. These reactive species oxidize the edges and/or grain boundaries of graphite.
2. Oxidation at the edges and grain boundaries results in depolarization and expansion of the graphite layers, thereby facilitating the intercalation of sulfate ions (SO_4^{2-}) into the graphitic structure. During this process, water molecules may co-intercalate with the sulfate anions.
3. The reduction of SO_4^{2-} ions, along with the self-oxidation of water, produces gaseous species such as SO_2, O_2, and others. This strong gas evolution, observed during the process, exerts sufficient force to overcome the weak van der Waals forces between graphite layers, thus enabling their separation.

III.1.6. The graphene oxide

Graphene oxide (GO) is a widely studied material due to its amphiphilic structure, high surface area, and chemical reactivity.

Composed of a honeycomb carbon lattice with polar oxygen functional groups, it is both easily functionalized and dispersible in polar solvents. GO can be reduced to rGO through various chemical or thermal methods, making it a versatile precursor for advanced material applications.

III.1.7.Reduced graphene oxide

Reduced graphene oxide (rGO) is a compound obtained by reducing graphene oxide, with the aim of producing a material whose physicochemical properties are close to those of graphene.

This reduction process is intended to remove the oxygen-containing functional groups initially present in the structure. Several methods can be employed for this purpose, including chemical, thermal, and electrochemical approaches. Among these, chemical reduction is the most widely used method.

III.1.8.Main differences between GO and rGO

Graphene oxide (GO) and reduced graphene oxide (rGO) are two forms of graphene derivatives that differ significantly in their chemical structure and resulting properties. These differences impact their behavior, performance, and suitability for various applications.

1. Oxygen content: As previously mentioned, GO has a high oxygen content due to the presence of oxygen functionalities, while rGO has less oxygen functionalities.

2. Hydrophilic/hydrophobic nature: GO is highly hydrophilic, while rGO is hydrophobic.

3. Conductivity: The presence of oxygen functionality in GO makes it less conductive than rGO, which has a lower resistance path.

4. Applications: GO has applications in areas such as energy storage, detection and catalysis, while rGO is used in electronics, photonics and optoelectronics.

III.1.9.applications of grapheme

The remarkable properties of graphene continue to captivate researchers and industries worldwide. Thanks to its exceptional electrical conductivity, mechanical strength, and large surface area, graphene holds the potential to revolutionize various sectors, including electronics, energy storage, power generation, batteries, sensors, and more

- **Mechanical applications**

  Graphene is the strongest known material in the world and can be used to enhance the mechanical strength of other substances.

  Numerous studies have demonstrated that adding even a small amount of graphene to plastics, metals, or other materials can significantly increase their strength or make them lighter, since less material is needed to achieve the same level of durability. These graphene-enhanced composite materials have promising applications in aerospace, construction, mobile devices, and many other fields.

- **Thermal applications**

  Graphene is the most heat conductor found to date. As graphene is also durable and lightweight, this means that it is an excellent material for solutions manufacturing of heat diffusion, such as heat sinks or heat dissipation films.

  This could be useful both in microelectronics (for example to make LED lighting more efficient and sustainable) and also in larger applications - for example thermal films for mobile devices. Huawei’s latest smartphones, for example, have adopted graphene-based thermal films.

- **Energy storage**

  Graphene being the thinnest material in the world, it also has a surface/ extremely high volume. This makes graphene a very promising material for in batteries and supercapacitors. Graphene can enable batteries and supercapacitors (and even fuel cells) to store more energy - and recharge also faster.

- **Coatings, sensors, electronics and others**

Graphene holds great promise for a wide range of additional applications, including corrosion-resistant coatings and paints, high-performance and precise sensors, faster and more efficient electronics, flexible displays, advanced solar panels, rapid DNA sequencing, targeted drug delivery, and more.

As a revolutionary nanomaterial, graphene represents a fundamental building block with the potential to benefit virtually every industry. Only time will reveal the full extent of its impact or whether alternative emerging materials may prove to be more suitable for specific applications. **(See figure III.21).**

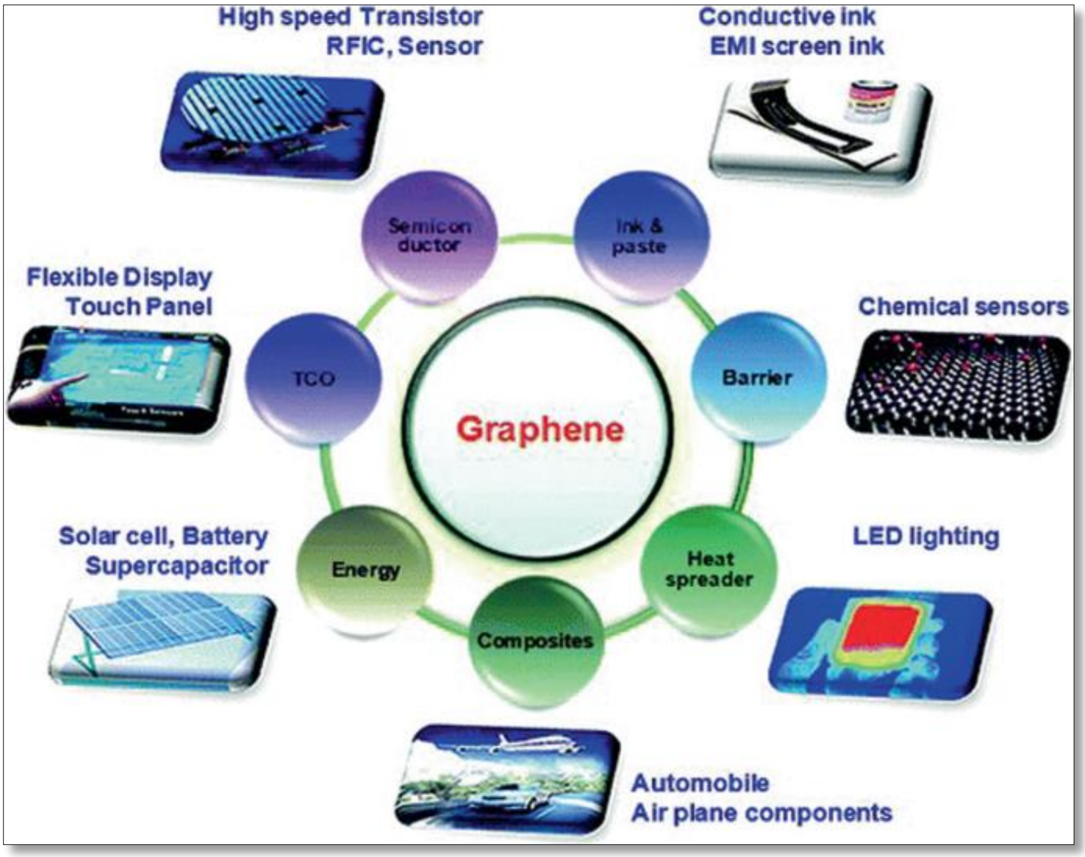


Figure III.21: Overview of graphene applications [24]

III.1.10. Use of Reduced Graphene Oxide (rGO) in Water Treatment

1. Desalination Using rGO-Based Membranes

Reduced graphene oxide (rGO)-based membranes demonstrate remarkable efficiency in seawater desalination. Studies have shown that these membranes can achieve salt rejection rates comparable to those of commercial nanofiltration membranes, while offering enhanced water permeability. This improvement is often attributed to structural modifications such as the incorporation of nanopores.

2. Removal of Pollutants (Heavy Metals and Dyes)

rGO is well known for its high adsorption capacity for a wide range of pollutants, including organic dyes like methylene blue and heavy metals such as mercury (Hg(II)). The incorporation of metal nanoparticles or metal oxides into rGO-based composites further enhances the adsorption efficiency.

3. Degradation of Micropollutants via Peracetic Acid (PAA) Activation

rGO can activate peracetic acid (PAA) through direct electron transfer, facilitating the rapid degradation of various micropollutants in complex aqueous environments. This method offers high efficiency while maintaining low toxicity.

III. 2. clay

III. 2.1.Introduction

Clay is a type of natural soil, characterized as an extremely fine-textured, earthy material that is plastic when wet and impermeable when dry.

It plays a vital role in various applications, such as the adsorption of degraded hazardous organic compounds, the manufacturing of pharmaceuticals, and the purification of contaminated water. To enhance its adsorption capacity, clay can be activated through heat treatment or chemical modification.

III.2.2. Definition of clay

Clay is a naturally occurring fine-grained sedimentary material composed predominantly of hydrated aluminum silicates, often in the form of phyllosilicate minerals. These minerals have a layered or fibrous structure, giving clay its characteristic plasticity when wet and hardness or impermeability when dry. Clay particles are typically less than 2 micrometers in size [29].

Because of its high surface area, adsorptive properties, and chemical reactivity, clay is widely used in applications such as ceramics, construction, pharmaceuticals, water purification, and environmental remediation [30]..

III.2.3. Origin of clays

III.2.3.1 Inheritance and alteration

Clay minerals, which result from the weathering of rocks, may either remain at the site of formation (residual clays, e.g., flint clays, decalcification clays) or be transported over long distances (e.g., deep-sea or ocean-bottom clays).

The type of clay minerals formed depends on both the nature of the parent rock and the prevailing climate conditions.

- In cold climates, weathering is minimal, and the resulting clay minerals (such as illite and chlorite) closely resemble those found in the original rock; they are considered inherited minerals.

- In hot and humid climates, advanced hydrolysis occurs: kaolinite forms in well-drained environments, while smectites develop in poorly drained (confined) environments.
- In temperate and humid climates, weathering is moderate and leads to the formation of interstratified clays, as well as degraded illites and chlorites, and vermiculite [31].

III.2.3.2 Neoformations in confined environments

The fibrous clays are formed in calcareous crusts, in areas with a dry season climate, in highly saline evaporitic environments:

- neoformation of sepiolite by ion concentration by evaporation (current lake basin of Sommières, Ghassoul in Morocco).

Some clay minerals are formed outside the soil from ions in solution.

- glaucoy neoformation (ferritic illite) in coastal vessels.
- neoformation of the "deep seabed red clays" (ferric smectites from calcareous and siliceous vases and volcanic ash).

III.2.3.3 Transformation of clay minerals

Newly formed or inherited minerals can evolve to reach a new state of equilibrium with their environment.

These transformations are generally classified as degradation, involving the elimination of ions, or eigmatization, involving the incorporation of additional ions. These transformations can occur during alteration (alteration) and diagenesis. **(See figure III.22).**

Figure III.22: Origin of clay.

III.2.4. green clay

Green clay refers to a group of natural clay minerals that are typically green in color due to their mineral composition, particularly the presence of iron. These clays are found in various geological environments and have a wide range of applications, including environmental, medical, and industrial uses.

Green clay is a natural sedimentary rock that belongs to the phyllosilicate family. It is notably rich in mineral salts and is composed primarily of aluminum silicate and hydrated magnesium .

The characteristic green color is mainly attributed to the presence of iron oxides, while the many other minerals that complete its composition are present as trace elements. **(See figure III.23)**.

Figure III.23: green clay.

III.2.5. Structure of clay minerals

Clays possess a complex structure that can be described at several hierarchical levels:

- Layers of elements
- Elementary sheets
- Elementary particles
- Crystallites or tactoids

Clay minerals are primarily characterized by a layered structure, which is why they are classified as phyllosilicates. These layers are composed of two main structural units: the tetrahedral layer (denoted T or Te) and the octahedral layer (denoted O or Oc), whose vertices are occupied by oxygen (O^{2-}) and hydroxyl (OH^{-}) ions **(Figure III.24).** The negative charges of these ions generate repulsive forces that are balanced by the insertion of cations within the structure, ensuring its electrostatic stability.

The structural representation of clay minerals can be schematically described as a unit composed of a layer and an interlayer space. Typically, each layer is formed by two types of sheets (or "diapers"), depending on the type of phyllosilicate involved [32].

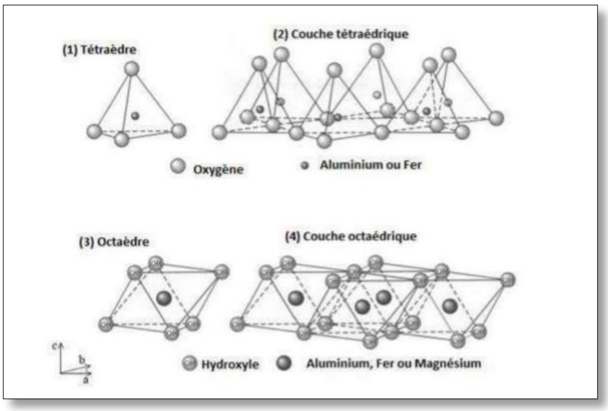


Figure III.24: Representations of a tetrahedron (1) and an octahedron (3), types of arrangement

III.2.6. The main types of clay

Clays are a group of phyllo-silicate minerals characterized by their structure in sheets. The main types of clays are: **(see table III.04).**

Table III.04 : Main Types of Clay and Their Characteristics. [33]

Clay Type	Dominant Mineral	Structure	Key Properties	Common Applications
Kaolinite	Kaolinite	1:1 (one tetrahedral + one octahedral sheet)	Non-swelling, low cation exchange capacity (CEC), good thermal stability	Ceramics, paper coating, pharmaceuticals
Smectite	Montmorillonite	2:1 (two tetrahedral + one octahedral sheet)	Swelling, high CEC, high water retention	Drilling mud, sealants, nanocomposites, water purification
Illite	Illite	2:1 (non-expanding)	Moderate CEC, low swelling, potassium-rich	Soils, ceramics, shale formations
Chlorite	Chlorite	2:1:1 (2:1 layers + brucite-like layer)	Stable, moderate swelling, moderate CEC	Metamorphic rocks, soil science
Vermiculite	Vermiculite	2:1 (expanding)	High CEC, moderate swelling, good thermal stability	Insulation, horticulture, soil conditioning
Sepiolite / Palygorskite	Fibrous clay minerals	Chain-like (not layered like phyllosilicates)	High porosity, good sorption capacity	Cat litter, industrial absorbents, pharmaceuticals

III.2.7. The use of clay

Throughout history, clay has been a widely available natural resource. It is distinguished by its remarkable physical and chemical properties ranging from plasticity to adsorption and ion exchange which make it valuable in fields such as construction, healthcare, and even advanced technologies.

III.2.7.1. Industrial and Construction Applications

III.2.7.1.1. Building Materials

1. **Clay**: Clay is a fundamental material used in the production of bricks, ceramics, and tiles. These materials undergo a firing process, often mixed with other components, to enhance their mechanical strength.
2. **Innovative Cement (LC3)**: By combining clay with limestone or clinker, a low-carbon cement known as LC3 (Limestone Calcined Clay Cement) is produced. This formulation significantly reduces CO_2 emissions in construction.
3. **Light Ceramics**: Expanded clay can also serve as lightweight aggregates in concrete, providing effective insulation and reducing the overall weight of structures [34].

III.2.7.1.2. Industrial Applications

- **Paint and Paper**: Clay, especially polymer clay, is used to improve the texture of ceramics and provide a smoother finish in paints.
- **Rubber and Plastics**: Clay is added as a filler to improve workability and performance, particularly in hard-to-mold areas.
- **Zeolites**: Certain clays act as precursors in zeolite synthesis and serve as catalysts in chemical reactions to accelerate industrial processes.

III.2.7.2. Medical, Cosmetic, and Culinary Applications

III.2.7.2.1. Treatment and Health Care

- **Therapeutic Properties**: Clay is used in poultices, masks, and powders for its anti-inflammatory, healing, and absorbent effects.
- **Detoxification**: Clay can bind to toxins and heavy metals, aiding detoxification. However, overuse may pose health risks.
- **Culinary Use**: In some cultures, edible clay is consumed to relieve gastric disorders, supplement minerals, or fulfill ritualistic or religious practices.

III.2.7.2.2. Cosmetics and Pharmaceuticals

- Clay serves as **an active ingredient in** a wide range of products, including:
- Cleansing masks
- Toothpastes
- Body powders
- Medicinal products (e.g., bandages and gastric tablets) [35]

III.2.7.3. Environmental and Agricultural Applications

III.2.7.3.1. Environmental Protection

- **Adsorbent**: Clay can trap pollutants such as heavy metals and organic compounds in both soil and water.
- **Barrier Layer**: Used as sealing liners in landfills to prevent pollutant percolation.
- **Waste Management**: Clays stabilize or encapsulate hazardous waste to reduce environmental risk.
- **Controlled Release Systems**: Clays regulate the release of fertilizers and pesticides, minimizing leaching and pollution.

III.2.7.3.2. Agriculture

- **Soil Amendment**: Clay improves soil structure and enhances water and nutrient retention.
- **Chemical Absorption**: Reduces the volatilization and leaching of agricultural chemicals.
- **Fertilizer Support**: Acts as a matrix for nutrient retention and controlled delivery [36].

III.2.7.4. Innovations, New Applications, and Others

- **Nanocomposites**: Incorporating clay nanoparticles into polymers creates lightweight, strong, and durable materials for use in automotive, aerospace, advanced packaging, and high-performance engineering.
- **Energy**: Clay is being explored as a component in batteries, supercapacitors, and **solar cells**, offering promising options for energy storage and conversion.
- **Sustainable Development**: The reuse of waste clay from quarries, industry, or construction supports the development of eco-friendly building materials, contributing to circular economy practices by reducing waste [37].

III.2.8. Use of Green Clay in Water Treatment

Green clay is a natural material recognized for its adsorptive, filtering, and disinfectant properties, making it an effective, economical, and versatile solution for enhancing water quality. It can be incorporated into a wide range of water treatment systems, from household filtration units to large-scale industrial installations.

III.2.8.1. Main Applications

1. Adsorption of Heavy Metals

Natural green clay, particularly when used in filtration columns, has proven effective in removing heavy metal contaminants such as hexavalent chromium (Cr^{6+}). It also demonstrates good regenerative capacity, making it a promising material for the treatment of industrial wastewater.

2. **Removal of Organic Dyes and Pollutants**

Both natural and modified clays (e.g., ceramic-based composites) exhibit strong adsorption capabilities for industrial dyes such as malachite green and methylene green. Under optimized conditions, removal efficiencies can exceed 99%, highlighting their potential for advanced wastewater treatment.

3. **Water Disinfection**

Thanks to their physicochemical properties, clays—either in their natural form or functionalized—can eliminate a wide variety of pathogenic bacteria and organic micropollutants. This makes them valuable for both biological disinfection and chemical contaminant removal, contributing significantly to overall water purification.

Conclusion

As previously discussed, the exploration of graphene–clay composites has opened new avenues in the field of materials engineering. Modern advanced devices increasingly rely on multi-scale architectures, with graphene integrated for its exceptional mechanical strength, thermal conductivity, and electronic properties.

On the other hand, clay due to its natural abundance, low cost, and functional versatility remains indispensable across a wide range of industrial sectors.

When combined, these two materials have the potential to unlock remarkable innovations in nanocomposites, flexible electronics, smart coatings, and energy-related applications.

The continued development of such hybrid technologies could transform multiple industries by making them more efficient, sustainable, and better equipped to meet emerging global challenges.

Experimental Part

Chapter IV

Methods and Materials

Part 01: Presentation of the Study Area

IV.1. Location and presentation of the Wilaya de Mila

IV.1.1. Geographical and administrative situation La wilaya de Mila

Is located in northeastern Algeria, at an altitude of 464 km and a distance of 400 km from the capital Algiers [38]. Its total area is 3480.54 km2, which represents 0.14% of the country's total area. It is the result of the administrative division of 1984 and consists of 32 municipalities [39]. It has 1,006,199 inhabitants in 2023 [40]

The 6 Province limit Mila's Province **(Figure IV.25):**

- Northwest by the Province of Jijel.
- To the northeast by the Province of Skikda.
- East of the Province of Constantine.
- West by the Province of Setif.
- To the southeast by the Province of Oum-El Bouaghi and Batna [38].

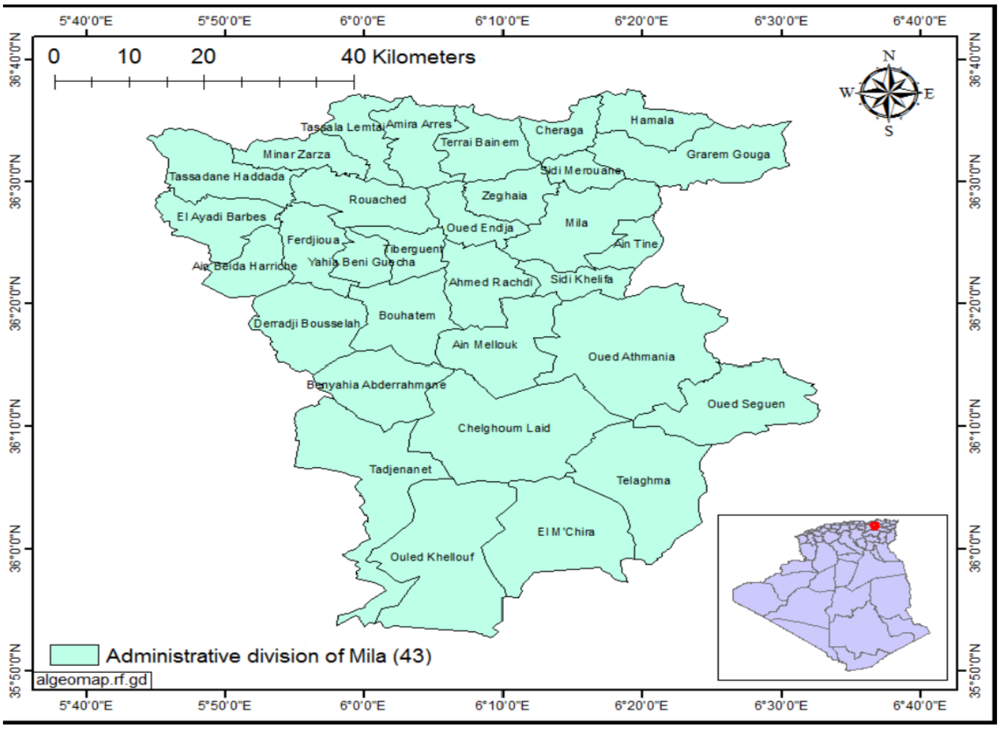


Figure IV.25 : Geographical location and boundaries of the Mila Province.[41]

The total population of the wilaya is estimated as:

- Area: 3480, 54 km 2.
- Population: 1, 006,199 hab.
- Communes: 32.
- Province Code: 43.
- Province since: 1984.
- Density: 220 hab/km.

IV.1.2.Edaphic situation

IV.1.2.1.Pedology

In terms of soil, all the soils of the Province de Mila are brown forest soils (brownish soils), rich in potassium, low in phosphorus and with a high content of limestone. The specific features of these soils also include:

- High water retention with maximum capacity.
- The presence of withdrawal slits during dry periods [42].

IV.1.2.2.The relief

The study area is divided into three morphological sets, representing the relief of the Province of Mila.

- To the north, a set of high mountains, characterized by very high altitudes and excessively marked slopes such as: Djebel M'cid Aicha and Sidi Driss;
- To the south, a set of high plains (plains and hills) such as: Djebel Osman and Grouz;
- In the centre, a complex combining hills and foothills valleys or even some high slopes
- Djebel Akhal, Chettaba and Kheneg of the East, and Djebel Boucherf and Oukissene by OuesT [38]

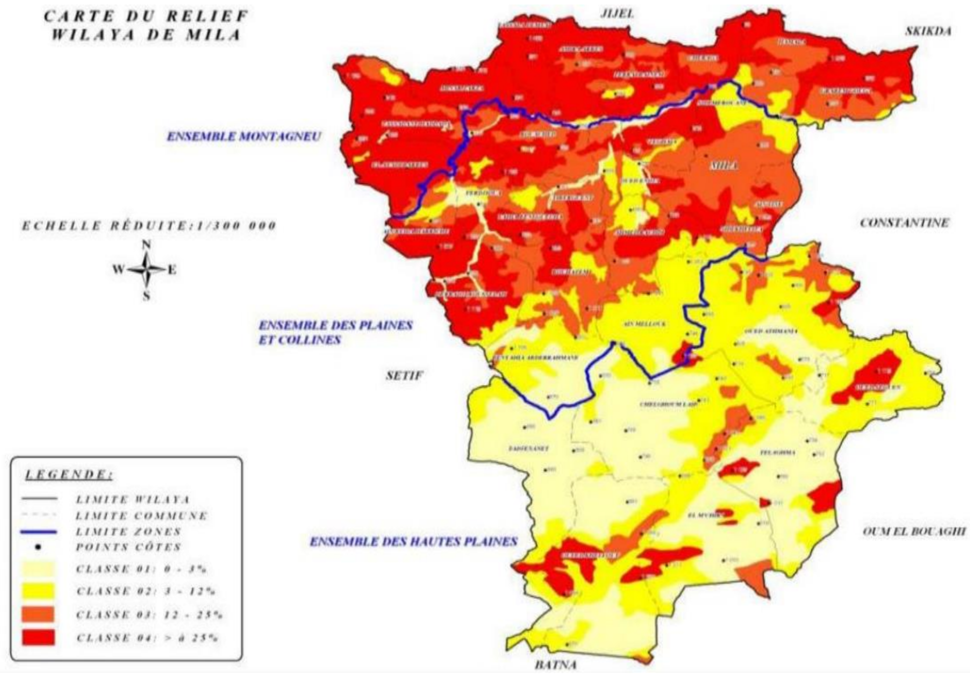


Figure IV.26 : Map of the relief of the Province of Mila [38]

IV.1.2.3.River system

In the Province of Mila, water resources include surface and groundwater. The latter are in the absence of recent and reliable hydrogeological studies and still poorly known. The few existing data concerning them indicate that they are a priori weaker than the first [38].

a. Groundwater

Groundwater is located below ground level and fills either the cracks in the bedrock or the pores present in granular media such as sands and gravel. It is not clustered like a stream or river, but flows deep into the geological formations that form the underground space [43]. The Province de Mila, which is composed of small streams feeding important rivers such as oued Radjas, Oued El-Kébir and Ouedi El-Rhumel, crosses the high plains region (from east to west). In addition, it has important tributaries such as the Méhari River, the Tajenanet River and the Athmania River [44].

b. Surface waters

Surface waters are waters circulating or stored on the surface of continents. They may be from groundwater that is a source of runoff (rivers, streams, dams, puddles, seagrasses) [45]. The Beni-Haroun dam basin is considered one of the most important watersheds in Algeria. The coherence of this hydrographic unit allows a global Organization of water quality management or restoration [46].

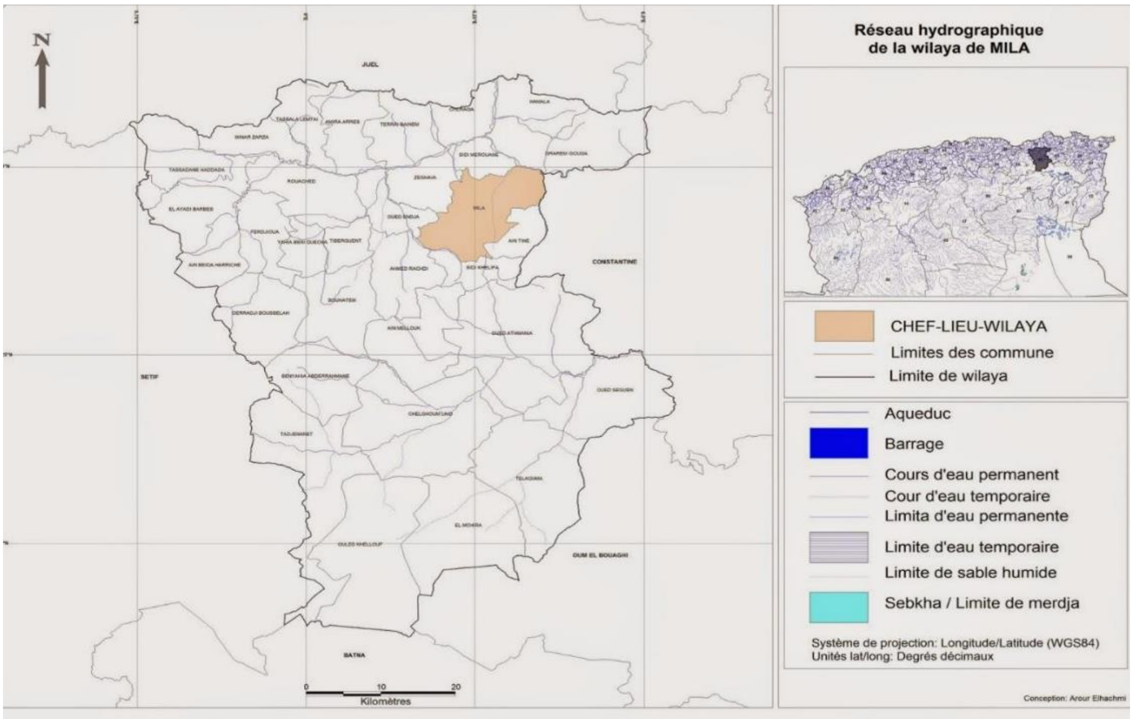


Figure IV.27: Mila Province hydrological network [47].

IV.1.3.Climate situation

The Province of Mila is governed by three microclimates, modelled on the arrangement of the three major morphological ensembles.

- Humid: for the mountainous reliefs of the north and the middle part that extends from Bouhatem to Ain Tine;
- Semi-arid to sub-humid: for the middle part of the Province ;
- Semi-Arid: for the High Plains [38].

IV.1.3.1.Temperature

Temperature is the level of heat or cold in a place or air. The recording thermometer is used to measure temperature (in degrees Celsius) at 1.5 m above ground level, in shade and sheltered from wind. The air is temperate according to time of day, altitude and seasons. It plays an essential role in the influence of climate and water balance by influencing evaporation and evapotranspiration [48] .

Table IV.05: Temperature parameter over the study region period (2010-2023) [49].

parameter	jan	feb	mar	apr	may	jun	jul	aug	sep	oct	nov	dec
MINI (C°)	5	4.7	6.5	8.8	11.7	16.3	20.6	20.2	15.8	13.6	9.4	5.8
MAX (C°)	13.5	13.8	16.2	20.3	14.1	30.7	34.8	34.5	29.3	23.9	17.4	13.6
MED (C°)	8.9	9	11.3	14.5	17.7	23.4	28.6	26.3	22.3	18.7	13.2	9.7

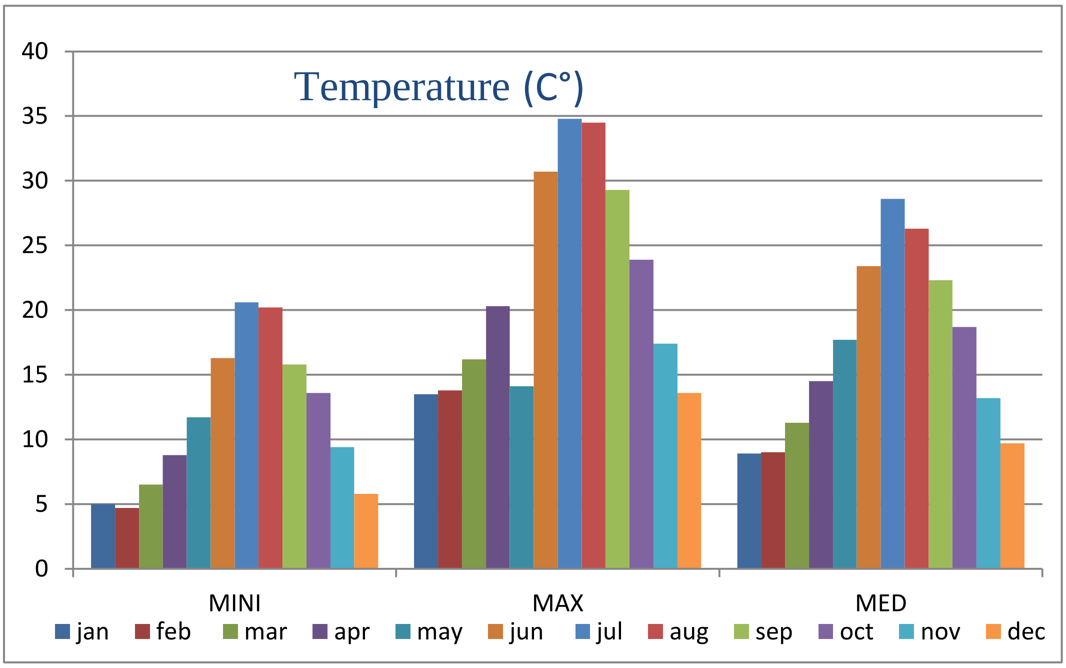


Figure IV.28: Temperature variation over the period (2010-2023) in the Western region [49].

According to Table 01, the monthly temperatures of the study area reach their low point in February with a value of about 4.7 C , while the maximum value is observed in July with a value of 34.8 C during the period (2010-2023).

IV.1.3.2.Precipitation

Precipitation is all kinds of water falling from the sky, whether liquid or solid [50]. The distribution of species in biogeographic areas is influenced by annual rainfall [51].

Table IV.06: average precipitation (mm) over the period (2010-2023) [49] .

parameter	jan	feb	mar	apr	may	jun	jul	aug	sep	oct	nov	dec
Precipitation (mm)	83	99	96	55	51	25	7	24	32	58	70	73

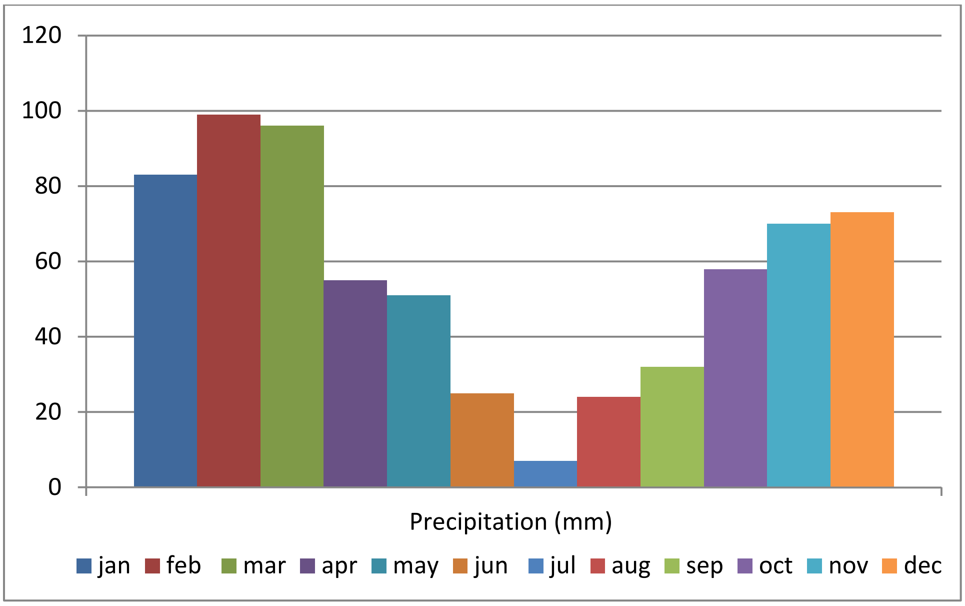


Figure IV.29: average precipitation (mm) over the period (2010-2023) in the region of study [49] .

Based on the analysis of information collected from Mila's weather station, it is observed that the study area receives about 673 mm of rain each year. However, the distribution of this tranche is uneven, as shown in **(Table IV.06)**. Rainfall is highest between February and March. July is the driest month.

IV.1.3.3.Pluvio-Thermal or Ombro-Thermal diagram

This diagram distinguishes between dry and wet periods in a given region. It is established according to the method of Gaussen and Begnouls, which defines a dry period as a period during which the total precipitation for the month in question is less than or equal to twice the temperature ($P \leq 2T$) [52].

Table IV.07: Precipitation and temperature variation over the period (2010-2023) in the study area [49].

parameter	**jan**	**feb**	**mar**	**apr**	**may**	**jun**	**jul**	**aug**	**sep**	**oct**	**nov**	**dec**
PP (mm)	83	99	96	55	51	25	7	24	32	58	70	73
T (C°)	8.9	9	11.3	14.5	17.7	23.4	28.6	26.3	22.3	18.7	13.2	9.7

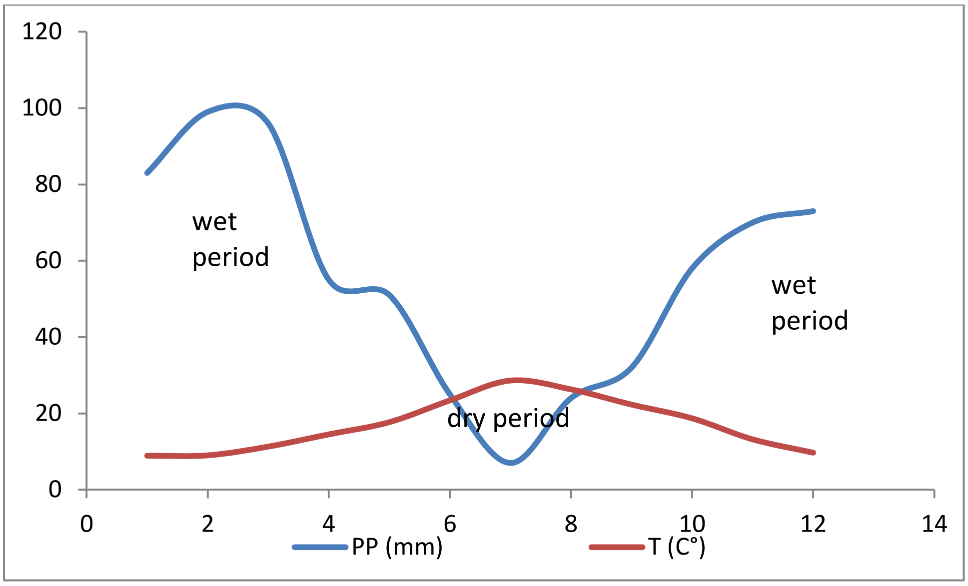


Figure IV.30: Pluviothermal or Ombrothermic diagram over the period (2010-2023) [49].

Based on the analysis of the Ombrothermique digram **(Figure IV.30)** based on temperature and precipitation data from the Ain Tine weather station, two periods can be identified:

- A wet season from October to the end of May.
- A dry and warm season, from late May to late September.

IV.1.3.4. Humidity

Humidity is a very important parameter for the study of evaporation losses in a dam [53] .

Table IV.08: Average Moisture Levels over the period (2010-2023) in the region[49].

parameter	**jan**	**feb**	**mar**	**apr**	**may**	**jun**	**jul**	**aug**	**sep**	**oct**	**nov**	**dec**
Humidity (%)	74	76	72	70	63	54	43	49	64	66	73	76

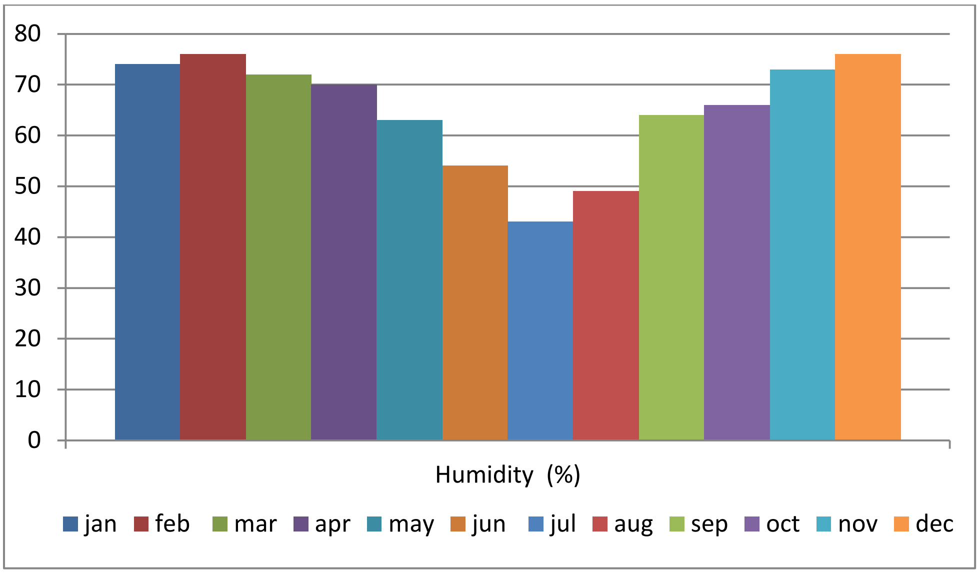


Figure IV.31 : Change in average humidity over the period (2010-2023) [49].

In (**Figure IV.31)**, it was found that the humidity level in the study area can reach 76% in December and February, while the minimum value is 43% in July.

IV.1.3.5. Wind

Wind is a very important climatic factor, as it plays a fundamental role in the transport, propagation and release of pollutants of different sizes due to its direction and strength characteristics [54].

Table IV.09: Average Wind Force Variation over the Region's Period (2010-2023) of study [49].

parameter	**jan**	**feb**	**mar**	**apr**	**may**	**jun**	**jul**	**aug**	**sep**	**oct**	**nov**	**dec**
Wind (m/s)	21	22	18	18	17	16	17	21	22	20	22	20

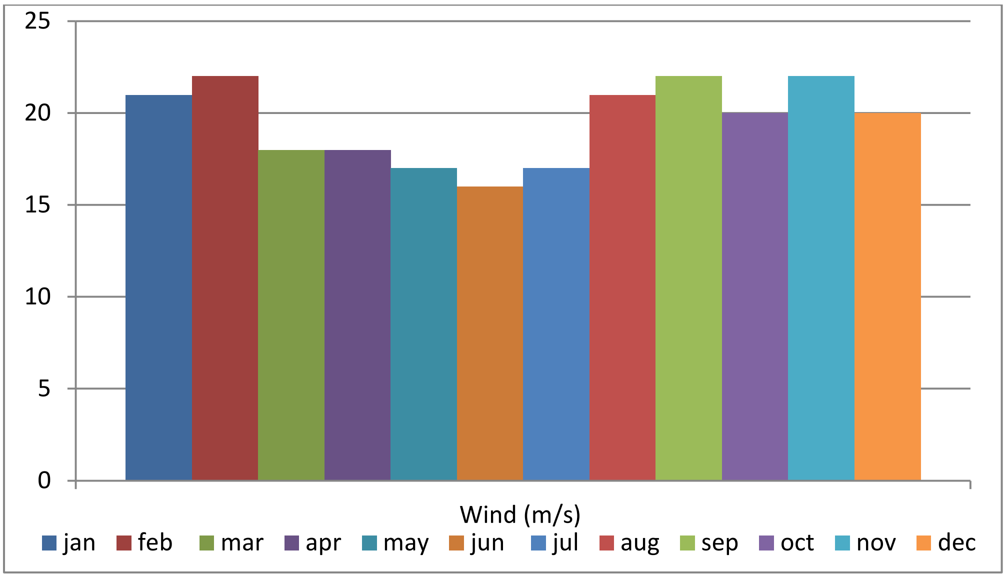


Figure IV.32: Change in average wind strength over the period (2010-2023) [49].

The wind data recorded in the weather station of Mila for the period from 2010 to 2023, the wind speed reaches its maximum in November with 23 m/s and its minimum in June with a force of 16 m/s. However, It was noted that wind speeds are approximately homogeneous during the other months.

IV.2.Presentation of study areas

IV.2.1.Situation of Oued Athmania

Oued Athmania is a commune in the Province of Mila in Algeria. In 2009, it had 45,039 inhabitants, 24,810 of whom lived within the city walls. The city is located halfway between Mila and Constantine and is watered by the river of the same name.

Home to the ancient baths of Pompeianus, the thermal site was an important crossing point for the Romans. Small town founded in the colonial era, it was a notable center of the region, served by its station connected to Constantine. Since the 20th century, Oued Athmania has been home to an important hydraulic dam supplying water to the surrounding communities.

IV.2.1.Situation of the dam Ouled El Kaim

It is a transfer dam of Beni Haroun, it will be used to fuel 05 wilayas of Eastern Algeria. The length of the dike is 600 m, with a storage capacity of 33.6 cubic hectometers. The Ouled El Kaim located on the upstream part of the great basin of Kebir – Rhumel, is drained on its northern part by Oued Kaim which takes its origin on the south flank of Djebel Lakhal (the source of Ras El MA) at the cote 1030 m. It receives on its banks some small streams before they flow in Rhumel

Figure IV.33: The municipality of Oued Athmania

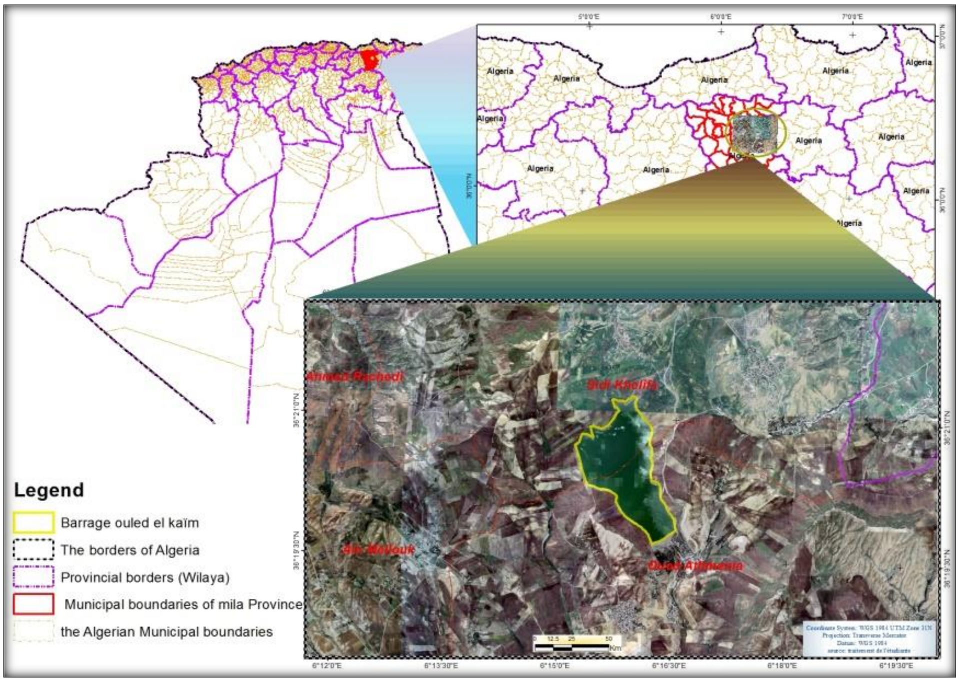


Figure IV.34: the dam of ouled el kaim

Part 02: Materials and Methods

IV.1.Sampling

The physico-chemical analyses of the water in Oulad Kaïm Dam, located in the Wilaya of Mila, were carried out as part of this experimental study, which aims to assess water quality and identify the causes of algal bloom.

IV.1.1.Sampling Technique

Water sampling is a delicate and essential step in the analytical process. The collected samples must be homogeneous, representative of the aquatic environment, and obtained without altering their physico-chemical properties.

A total of 50 water samples were collected from various and widely distributed points across the dam. This was done to ensure a comprehensive and accurate assessment that reflects the spatial diversity of the dam’s water characteristics. Sampling points were carefully selected to cover different zones, including surface and deeper areas, as well as locations near potential inflows or pollution sources.

Before sampling, plastic bottles were thoroughly cleaned from the inside to remove any residues that might affect the analysis.

Each bottle was labeled with detailed information including the date, time, and location of the sample collection.

At the sampling site, the bottles were first rinsed with distilled water, followed by rinsing with the water to be analyzed, in order to avoid any interference or changes in the original properties of the samples.

IV.2.Physical-chemical analysis

IV.2.1.On ground

Field Physical analyses (PH, TDS, temperature, salinity, conductivity) are measured on places to avoid changes in the characteristics of these parameters.

Figure IV.35 : multiparameter electrochemical analyser .

Figure IV.36 : Measurement of physical water properties

IV.2.2.In the laboratory

IV.2.2.1.Phosphate dosage (PO^{-3}_4)

- **Principle**

In the presence of an acidic medium and ammonium molybdate, the ortho phosphates form a phosphomolybdic complex which, reduced by exoraic acid, has a coloration blue that can be measured by spectrophotometry. Some organic elements may be hydrolyzed during the establishment of staining, which is accelerated by the use of a catalyst, the double tartrate of antimony and potassium.

- **Solution and products used**

• Ammonium molybdate solution

• Ascorbic acid solution (dissolve 0.34 g of potassium antimony(III) oxalyrate, K(SbO)C H O, in 250 ml of distilled water while heating if necessary) .

• Potassium oxytartarate and antimony solution

• Sulphuric acid solution (add little by little, with caution, 140 ml of sulfuric acid (density = 1.84) " for analysis " in 900 ml of distilled water. Let cool and store in a glass bottle)

Figure IV.37 : Phosphate régents.

- **Mode of operation**

- Prepare the mixture of reagents: put 25 ml of ammonium molybdate solution, add 62.5 ml of sulphuric acid, 25 ml of ascorbic acid and 12.5 ml of potassium oxytartarate and of antimony.
- In beakers, put 25 ml of each sample and add 2.5 ml of reagent mixture, wait 5 min.
- Perform the spectrometer readings at 885 nm.
-

IV.2.2.2.Ammonium (NH_4^-)

- **Principle**

Ammonium concentration in water can be determined by measuring the activity ion of ammonia under precise experimental conditions of ion concentration and of pH.

- **Solution and products used**

Reagent 01: phenol-nitroprussiate solution

- For 500 ml of reagent: dissolve 17.5 g phenol and 200 mg sodium nitroprusside in distilled water and make up to 500 ml.

Reagent 02: alkaline solution of hypochlorite

- For 500 ml of reagent: dissolve 140 g trisodium citrate and 11 g soda in about 400 ml of distilled water, then add a volume of sodium hypochlorite solution corresponding to 1.4 g of chlorine and make up to 500 ml.

Figure 38 : régents ammonium.

- **Mode of operation**

- Take 50 ml of sample directly into the reaction flask.
- Add 1.5 ml of reagent 1, plug and shake to homogenize well.
- Add immediately 1.5 ml of reagent 2 and shake again.
- Place immediately away from light overnight at room temperature.
- Perform the spectrometer readings at 630 nm

Figure IV.39 : Dosage ammonium.

IV.2.2.3.Silicon ($SI(OH)_4^-$)

- **Principle**

The method used is to create a compound between ammonium molybdate and monomer or dimer forms of ortho-silicic acid. Subsequently, the metol transforms this composed into a blue complex, which can be evaluated using spectrophotometry.

- **Reagents and solutions used**

• **Reagent 01:** Molybdate

- For 500 ml of reagent: dissolve 4 g of ammonium para molybdate into fine powder in about 300 ml of distilled water, add 12 ml of concentrated hydrochloric acid (d=1.18), Mix and make up to 500 ml with distilled water.

Figure IV.40 : Silicon régents 1.

• **Reagent 02:** Reducing

This reducing reagent is obtained by successively mixing the above reagents in The following order and proportions:

- 50 ml of metol-sulphite solution.
- 30 ml of oxalic acid solution (agitate 50 g oxalic acid for analysis, $C_2H_2O_4.2\ H_2O$, with 500 ml of distilled water. Let settle and take the supernatant).
- 30 ml of 50% sulphuric acid(Add, with caution and mixing as you go, 250 ml concentrated sulphuric acid (d = 1.84) of quality 'for analysis' at 250 ml of distilled water)

Top up with distilled water to obtain 150 ml of solution. This solution should be be prepared immediately prior to use and is not durable.

Figure IV.41 : Silicon dosing reagents 2.

- **Mode of operation**

- Pipette into beakers 5 ml of reagent 1, add 12.5 ml of each sample, plug and mix and wait 10 min.
- Then add 7.5 ml of reagent 2 and mix again and wait 02 h and do the readings to the spectrometer at 810 nm wavelength

IV.2.2.4.Nitrite (NO_2^-)

- **Principle**

Nitrite ions react in an acidic medium (pH=1.9) with the sulfonamide to form the di-azonium salt (diazotization) which forms with N-(1-naphthyl)-ethylenediamine-dichlorohydrate a red azo dye.

- **Reagents and solutions used**

Reagent 1: sulfanilamide solution

- To prepare 500 ml of reagent: dilute 50 ml of concentrated hydrochloric acid (d=1.18 **Concentration:** 37% , very low pH (less than 1)) in about 300 ml of distilled water.
- Dissolve 5 g of sulfanilamide in this solution and make up to 500 ml.

Reagent 2: N-naphthyl-ethylenediamine solution

- Dissolve 0.5 g of N-(1-naphthyl) ethylenediamine dihydrochloride in 500 distilled water (NED).

Figure IV.42 : Reagents for nitrite and nitrate.

- **Mode of operation**

-Introduce 10 ml of each sample into beakers, add 0.2 ml of 1,

Mix and let stand for up to 8 minutes.

- Add 0.2 ml of reagent 2 and mix again and wait 10 min-02 h, and make the readings to the spectrometer at 543 nm.

Figure IV.43 : Dosage Nitrate.

IV.2.2.5.Nitrate (NO_3^-)

- **Principle**

In the presence of sodium salicylate, nitrates give sodium paranitrosonylate coloured yellow and susceptible to colorimetric dosage.

- **Reagents and solutions used**

• **Reagent 1:** sulfanilamide solution

- To prepare 500 ml of reagent: dilute 50 ml of concentrated hydrochloric acid (d=1.18 **Concentration:** 37% , very low pH (less than 1)) in about 300 ml of distilled water.
- Dissolve 5 g of sulfanilamide in this solution and make up to 500 ml.

• **Reagent 2:** N-naphthyl-ethylenediamine solution

- Dissolve 0.5 g of N-(1-naphthyl) ethylenediamine dihydrochloride in 500 distilled water (NED).

➢ **Mode of operation**

- Pass 25 ml of water to be analysed one by one from each sample inside the column containing Cadmium, then add 0.5 ml of reagent 1, mix and let stand 8 min at most.
- Add 0.5 ml of reagent 2 and mix again and wait 10 min-02 h, and make the readings to the spectrometer at 543 nm.

Figure IV.44 : column.

IV.2.2.6.Sulfate (SO_4^-)

➢ **Principle**

Sulphates are precipitated in a hydrochloric medium as barium sulfate. The stabilises the precipitate obtained by using a Tween 20 solution. Suspensions are measured homogeneous using a spectrometer.

➢ **Reagents and solutions used**

• 1/10 hydrochloric acid solution(d=1.18 **Concentration:** 37% , very low pH (less than 1)).

- 20 to 25% Tween solution.
- Barium chloride solution.

Mode of operation

- Prepare barium chloride solution +Tween 20: dilute 10g barium chloride in 20 ml of Tween 20% and make up to 100 ml with distilled water.
- Put 12.5ml of water to analyze, add 0.25ml of hydrochloric acid to 1/10 and 1.25ml solution of barium chloride + Tween 20.
- Prepare in the same conditions a control by replacing the water to be analysed with water distilled.
- Shake and let stand 15 min. Stir again and make the spectrometer readings at 650 nm wavelength.

Figure IV.45 : spectrophotometer.

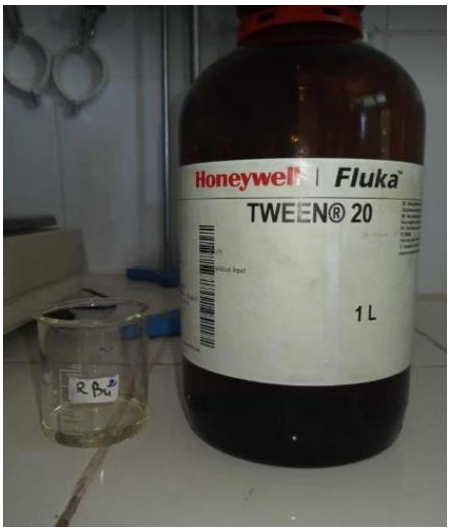


Figure IV.46 : Tween 20%.

IV.3.Graphene

IV.3.1.Protocol for the use of graphene oxide to remove nutrients

- **Necessary equipment**
  - Graphene oxide (GO) in powder or aqueous dispersion
  - Water to be treated (containing common nutrients phosphates or nitrates)
  - Magnetic stirrer or mechanical mixer
- Preparation of graphene oxide
  - pH meter
  - Membrane filter (0.22 µm or less) or centrifuge
  - Precision balance
  - Reactuits to adjust the pH (HCl hydrochloric acid (d=1.18 **Concentration:** 37% , very low pH (less than 1) or NaOH soda)

Step 1: Preparation of graphene oxide

1. Dispersion of graphene oxide

- If you are using graphene oxide powder, disperse it in distilled or dionized water to obtain a homogeneous suspension. A typical concentration is 0.1 to 1
- Shake vigorously for 30 minutes using a magnetic stirrer or ultrasonicator to ensure uniform dispersion

Figure IV.47 : Weigh grapheme.

Figure IV.48 : Mixing Graphene .

2. pH adjustment (optional)

- Measure the pH of GO suspension. For optimal nutrient adsorption, adjust pH to a suitable value:

- For “phosphates” , a slightly acidic pH (5-6) is optimal.
- For “nitrates” , a neutral to slightly basic pH (7-8) is preferred.
- Use dilute hydrochloric acid (HCI (d=1.18 **Concentration:** 37% , very low pH (less than 1)) or soda (NaOH) to adjust the pH.

Figure IV.49 : pH adjustment.

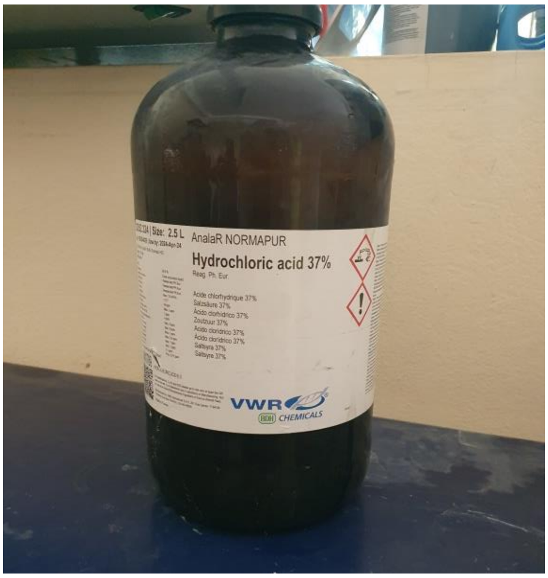


Figure IV.50: hydrochloric acid (HCI).

Step 2: Nutrient adsorption

1. Determination of graphene oxide

- Add the GO suspension to the water to be treated. The recommended dose is usually 10 to 100 mg GO per litre of water, depending on nutrient concentration.

- For example, for an initial concentration of 10 mg/l, phosphates, start with 50 mg/L. of GO,

Figure IV.51: Addition of graphene.

2.mixing and contact time

- Shake the mixture with a magnetic shaker or mechanical mixer for 1 to 2 hours. this time allows the oxide and graphene to adsorb nutrients

Figure IV.52 : mixing.

3.monitoring the ph

- During adsorption monitor and adjust the pH if necessary to maintain optimal conditions

Figure IV.53 : Adjust PH after shaking.

Step 3: Separation of graphene oxide

1. Filtration

- Filter the mixture through a 0.22 µm membrane filter to separate the nutrient-charged graphene oxide from the treated water.

- If you do not have a membrane filter, you can use a high speed centrifuge (10,000 to 15,000 rpm for 10-15 minutes) to separate the GO.

Figure IV.54 : centrifuge.

2. Recovery of treated water

- Filtered or centrifuged water is now free of the nutrients adsorbed by the graphene oxide.

Step 4: Analysis of results

1. Measurement of residual nutrients

- Analyze the treated water to measure the residual concentration of nutrients (phosphates, nitrates, etc.) using colorimetric test kits or a spectrophotometer.
- Compare the results with baseline concentrations to assess the efficacy of the sorption.

2. Optimization

- If the efficiency is insufficient, adjust the GO dosage, contact time or pH to Improve outcomes.

Mode of operation

- Prepare graphene oxide solution: put 25 mg of graphene oxide to 500 ml in distilled water. Shake vigorously for 30 minutes
- Put 50ml of water to analyze, add 2.5ml of graphene oxide
- Shake for 1 to 2 hours
- Adjust the pH again and make the spectrometer readings

IV.4.CLAY

IV.4.1.Protocol for the use of clay to remove nutrients

Step 1: Prepare the clay

1.Cleaning

- Sieve the green clay to remove impurities (pebbles, organic debris, etc.).
- Grind clay to a fine powder (grain size less than 0.5 mm).

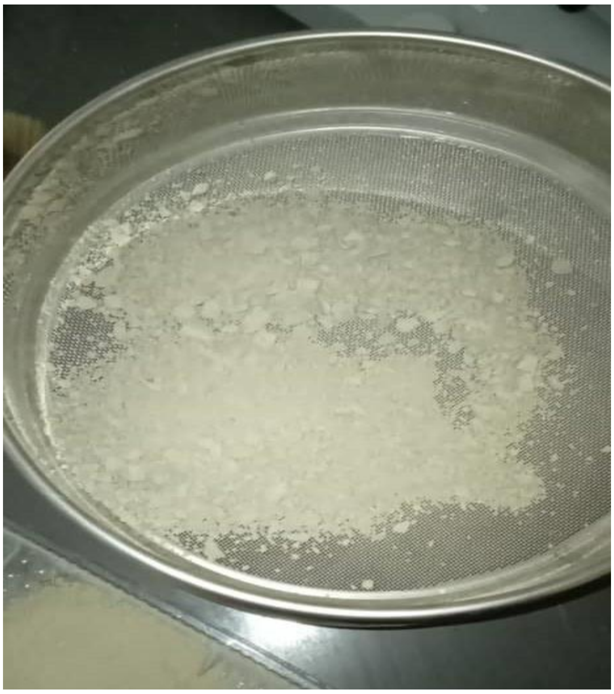


Figure IV.55 : Sieve the green clay .

2.Drying

- Dry clay in the open air or in an oven at 50-60°C for 24 hours to remove residual moisture.

Step 2: Acid treatment (chemical activation)

1. Preparation of the acid solution

- Dilute; hydrochloric acid (HCl (d=1.18 **Concentration:** 37% , very low pH (less than 1))) or sulphuric acid (H SO) in distilled water to obtain a concentration of 0.5 to 1 M (for example, 40 ml of HCl concentrated in 1 litre water gives a solution ~1 M).

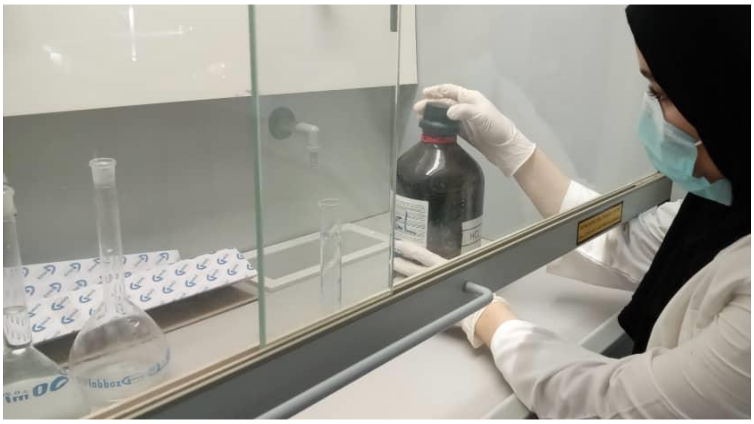


Figure IV.56 : Preparation of the acid solution.

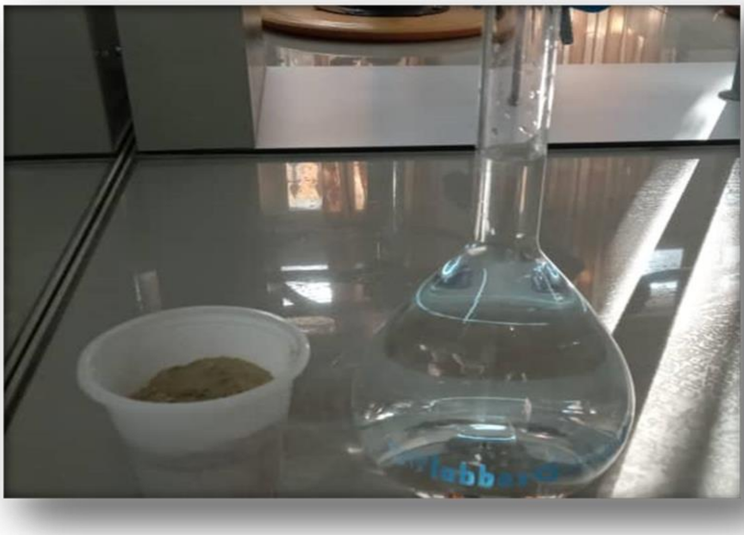


Figure IV.57 : acid solution and green clay .

2. Clay-acid mixture

- In an acid-resistant container, mix 100 g of dry clay with 500 ml of the prepared acid solution.

- Shake vigorously using a magnetic stirrer or mechanical mixer for 2 to 4 hours at room temperature.

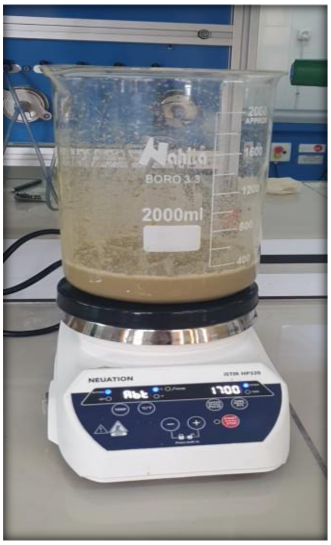


Figure IV.58: Clay-acid mixture.

3. Rest

- Let the mixture sit for 12 to 24 hours to allow the acid to react clay and open its pores.

4. Filtration and rinsing

- Filter the mixture with a fine sieve or filter to separate the clay from the solution Acid.
- Rinse the clay thoroughly with distilled water until the pH of the filtrate is neutral (pH ~7). This removes acid residue.

Figure IV.59: Filter the mixture.

Step 3: Salt treatment (optional to improve nutrient adsorption)

1. **Preparation of the saline**

- Prepare a 5-10% saline solution (for example, 50 to 100 g of NaCl or CaCl in 1 litre of distilled water).

2. Clay-salt mixture

- Immerse the acid activated clay in saline.
- Shake for 1 to 2 hours at room temperature.

3. Rest

- Let stand for 12 hours to allow ion exchange.

4. Filtration and rinsing

- Filter the clay and rinse lightly with distilled water to remove excess salt.

Step 4: Drying activated clay

1. Drying:

- Spread activated clay on a clean surface and dry it in the open air or in an oven 50-60°C for 24 hours.

2. Fine grinding (optional)

- Grind the dried clay into a fine powder to increase its specific surface and improve its adsorption efficiency.

Step 5: Use of activated clay

1. Dosage

- Use 1 to 10 g of activated clay per litre of water to be treated, depending on the concentration of nutrients to be removed.

2. Mixing and contact

- Add the clay to the water and shake vigorously for 10-15 minutes.
- Let stand for 1 to 2 hours to allow the nutrients to adsorb.

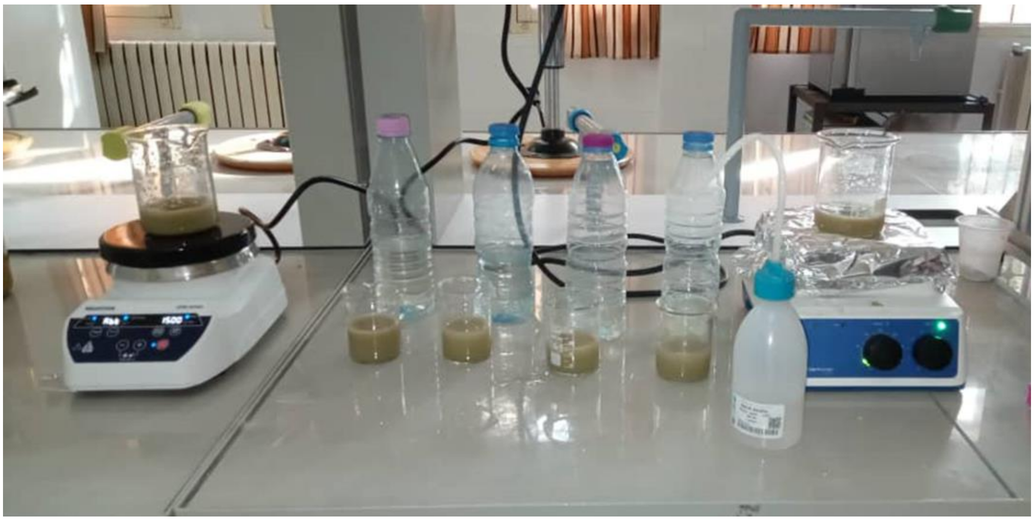


Figure IV.60: Water to be treated and clay .

3. Filtration

- Filter water to remove clay and adsorbed nutrients.

Step 6: Clay regeneration (optional)

1. Recovery

- Recover used clay after filtration.

2. Cleaning

- Wash the clay with distilled water to remove adsorbed nutrients.

3. Reactivation

- Repeat the acid and/or salt treatment to reactivate clay

Precautions

- Wear personal protective equipment (gloves, goggles, mask) during acid handling.
- Work in a well-ventilated area to avoid the inhalation of acid vapours.
- Test the effectiveness of activated clay on small volumes of water before using it on a large scale.

Chapter V

Results and discussion

This study aims to identify and apply appropriate hydraulic and environmental solutions to mitigate algal proliferation in the Oulad Ghaïem Dam, located in the municipality of Oued Athmania, Mila Province. The following section presents the principal results obtained from the physicochemical and biological analyses carried out.

V.1. Results &Interpretation before using graphene and clay

V.1.1.phosphate

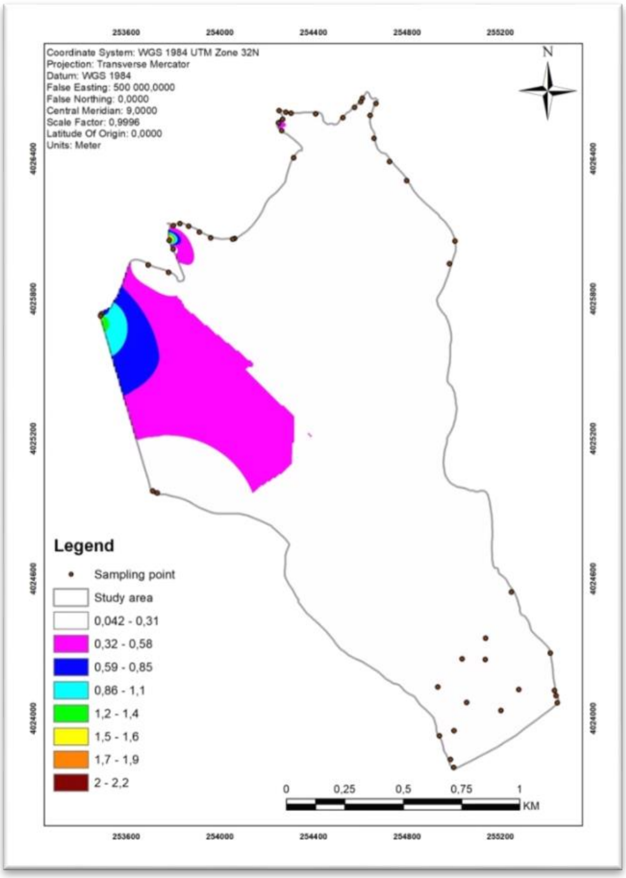


Figure V.61 : The map presents a analysis of phosphate concentration(mg/L).

V.1.1.1.Interpretation

This map provides a spatial overview of phosphate concentrations (ranging from 0.042 to 2.2 mg/L) in the Oulad Kaïm Dam, using a gradient of eight color classes.

The highest concentrations, shown in dark red and brown, are concentrated in the northwestern inflow zone, suggesting potential contamination from anthropogenic sources, such as agricultural runoff, urban wastewater, or point-source discharges.

The systematic and well-distributed sampling points support high-quality spatial interpolation and enhance confidence in the data.

The southern and eastern zones exhibit lower phosphate levels or data gaps, indicating either reduced human impact, better natural dilution, or areas requiring further investigation.

Elevated phosphate levels are a known trigger for eutrophication, posing risks such as algal blooms, oxygen depletion, and decline in water quality and aquatic biodiversity.

This spatial analysis is an essential decision-support tool for environmental management, helping identify pollution hotspots and informing targeted intervention strategies to mitigate phosphate loading and protect the dam’s ecological health

V.1.2.nitrate

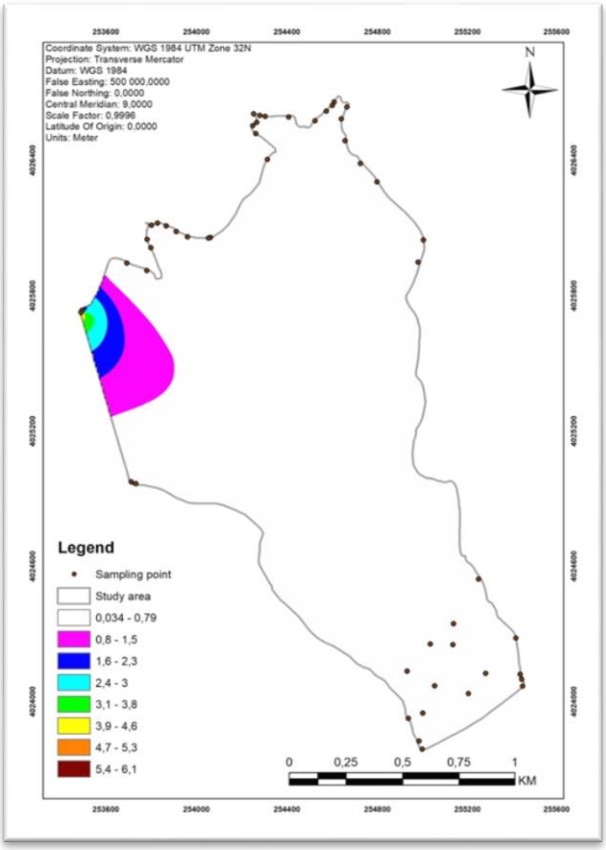


Figure V.62 : The map presents a analysis of nitrate concentration(mg/L).

V.1.2.1.Interpretation

The presented map illustrates the spatial distribution of nitrate (NO_3^-) concentrations in the Oulad Khaïem Dam, located in the Oued El Athmania region.

Nitrate concentrations are categorized into eight distinct classes, ranging from 0.034 to 6.1 mg/L, and are visually depicted using a color gradient. The highest concentration zones (5.4 – 6.1 mg/L, shown in dark brown) are observed in the northwestern sector of the study area, particularly near the reservoir’s inlet. These elevated levels are likely associated with upstream inputs, notably agricultural runoff — a common source of nitrate contamination due to the leaching of nitrogen-based fertilizers into surface waters.

In contrast, the southern and eastern regions of the reservoir exhibit predominantly low nitrate concentrations or, in some areas, undetectable values. This pattern may indicate minimal anthropogenic impact or the presence of natural attenuation processes such as denitrification or dilution.

The map is supported by a dense and uniformly distributed network of sampling points, which enhances the reliability of the spatial interpolation and ensures an accurate representation of nitrate variability across the site.

From an environmental standpoint, elevated nitrate concentrations in freshwater systems can promote eutrophication, which threatens aquatic ecosystems and may compromise drinking water quality if concentrations exceed recommended limits. According to World Health Organization (WHO) guidelines, the maximum permissible concentration for nitrates in drinking water is 50 mg/L. The values observed in this study remain well below that threshold, suggesting no immediate health risk but still warranting ongoing monitoring.

Overall, this spatial analysis serves as a critical tool for water resource managers and environmental planners. It enables the identification of high-risk areas and supports the development of targeted mitigation strategies aimed at controlling nitrate pollution and safeguarding long-term water quality.

V.1.3.nitrite

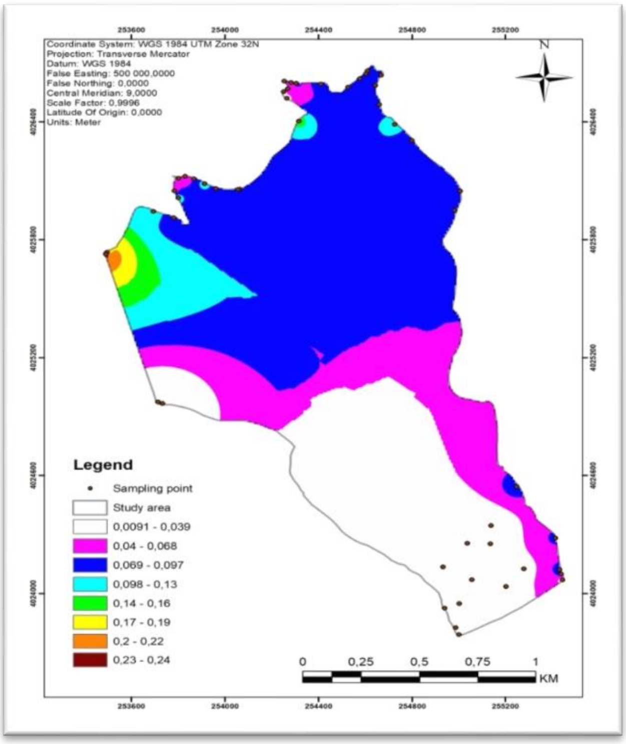


Figure V.63 : The map presents a analysis of nitrite concentration(mg/L).

V.1.3.1.Interpretation

The map displays the spatial distribution of nitrite (NO_2^-) concentrations in the Oulad Khaïem Dam (Oued El Athmania region), with values ranging from 0.0091 to 0.24 mg/L across nine color-coded classes. Most of the reservoir—especially the central and northeastern areas—shows moderate levels (0.069–0.097 mg/L), while higher concentrations (0.2–0.24 mg/L) are confined to small zones in the northwest, likely reflecting localized pollution sources such as agricultural runoff or wastewater discharge.

As a reactive intermediate in the nitrogen cycle, nitrite often signals recent organic pollution or microbial imbalances (e.g. inhibited nitrification). Although generally moderate, levels above 0.1 mg/L may pose health risks, particularly for infants, due to their effect on oxygen transport in the blood.

Supported by a dense sampling network, this spatial analysis enables early detection of water quality degradation and informs targeted strategies to control nitrite pollution and maintain ecological and drinking water safety.

V.1.4.Ammonium

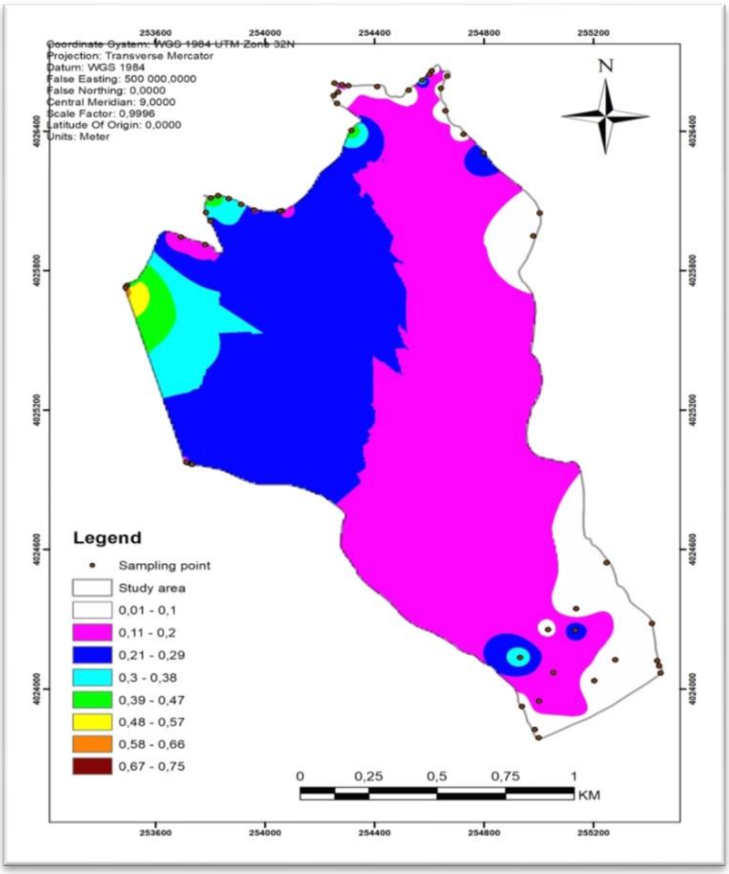


Figure V.64: The map presents a analysis of ammonium concentration(mg/L).

V.1.4.1.Interpretation

Spatial Distribution of Ammonium (NH_4^+) Concentrations in the Oulad Kaïm Dam Oued El Athmania Region

The map presents the spatial distribution of ammonium (NH_4^+) concentrations in the Oulad Kaïm Dam (Oued El Athmania region), with values ranging from 0.01 to 0.75 mg/L across nine color-coded classes. Moderate concentrations (0.11–0.2 mg/L) dominate the southeastern and central areas, while the highest levels (up to 0.75 mg/L) appear in localized zones, particularly in the south-central, western, and northwestern parts of the reservoir.

These elevated concentrations likely stem from agricultural runoff, sewage inputs, or organic matter decomposition under low-oxygen conditions. Ammonium, a byproduct of organic matter breakdown, often signals recent pollution and disrupted nitrification.

Although not directly regulated by WHO, levels above 0.5 mg/L are considered indicators of deteriorating water quality. The dense sampling network enhances the accuracy of the analysis, making the map a valuable tool for detecting early signs of contamination, guiding water quality management, and supporting ecosystem protection strategies.

V.1.5.Sulfate

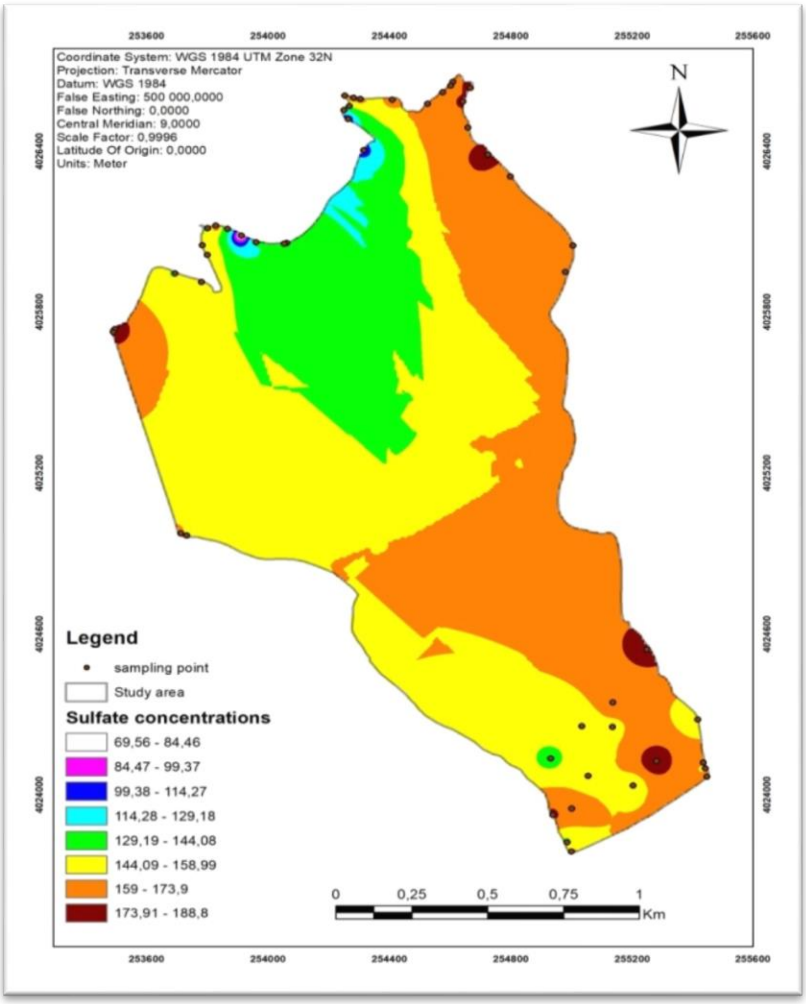


Figure V.65: The map presents a analysis of sulfate concentration(mg/L).

V.1.5.1.Interpretation

Spatial Distribution of Sulfate (SO_4^{2-}) Concentrations in the Oulad Kaim Dam – Oued El Athmania Region

The map shows the spatial distribution of sulfate (SO_4^{2-}) concentrations in the Ouled Kaïm Dam, with values ranging from 69.56 to 188.8 mg/L, divided into eight color-coded classes. Most of the reservoir, particularly in the east and southeast, exhibits moderately high levels (144.09–158.99 mg/L), while the highest concentrations (up to 188.8 mg/L) are confined to localized areas in the southeastern corner—possibly indicating pollution hotspots or areas with limited water renewal.

Lower sulfate levels (69.56–99.37 mg/L) are found in the northwest, suggesting reduced human impact or cleaner water conditions. Sulfates may originate from natural mineral dissolution or human activities like agriculture and industry.

Although generally non-toxic, high sulfate levels can affect water taste and cause digestive discomfort if concentrations exceed 250 mg/L. A well-distributed sampling network ensures reliable spatial analysis, helping environmental managers detect sulfate accumulation early and implement targeted water quality strategies to protect ecosystem and human health.

V.1.6.Silicate

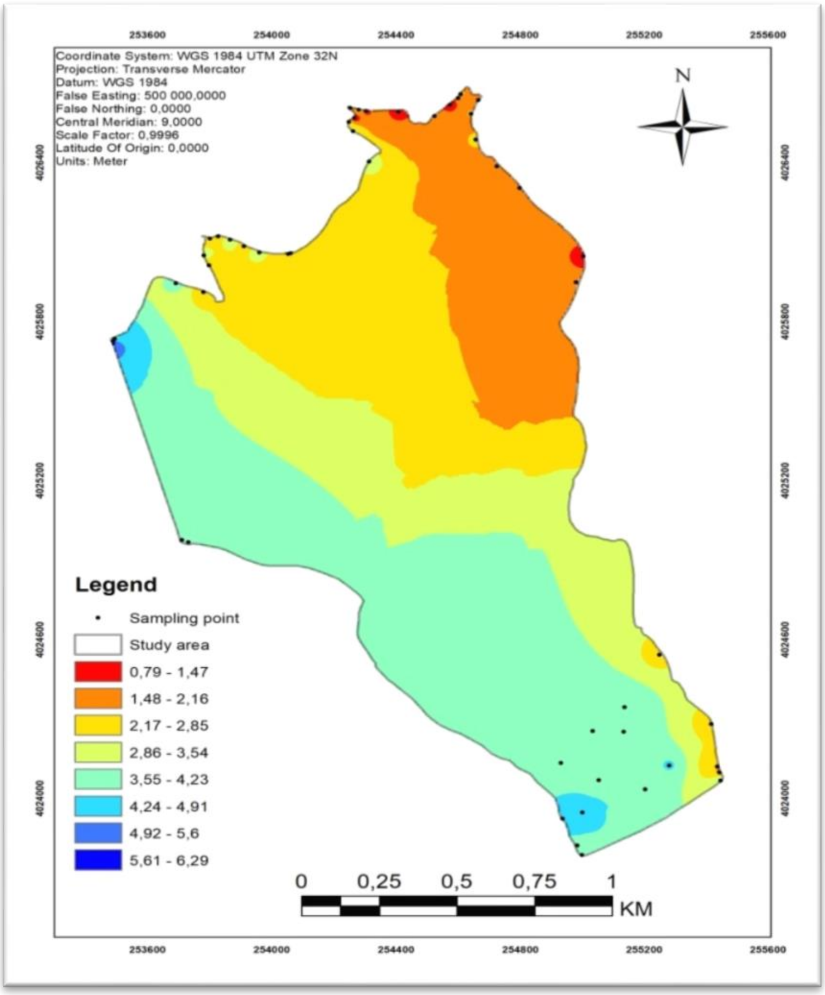


Figure V.66: The map presents a analysis of silicate concentration (mg/L).

V.1.6.1.Interpretation

Spatial Distribution of Silicate (SiO_4^{4-}) Concentrations in the Oulad Kaim Dam – Oued El Athmania Region

The map shows the spatial distribution of silicate (SiO_4^{4-}) concentrations in the Ouled Kaïm Dam, with values ranging from 0.79 to 6.29 mg/L across eight color-coded classes. Lower concentrations (0.79–2.85 mg/L), found mainly in the central and northeastern zones, may result from limited geological input or high biological uptake by diatoms.

In contrast, higher concentrations (4.92–6.29 mg/L) occur in the southern and southwestern areas, likely due to mineral weathering, runoff, or reduced biological consumption.

Silicate, while non-toxic, is a key nutrient for diatoms and thus plays an important ecological role. Its distribution reflects both geochemical conditions and biological activity within the reservoir. The dense sampling network ensures reliable spatial analysis, supporting effective environmental monitoring and management of nutrient dynamics in freshwater ecosystems.

V.2.Results after using graphene

V.2.1.Phosphate (PO^{-3}_4)

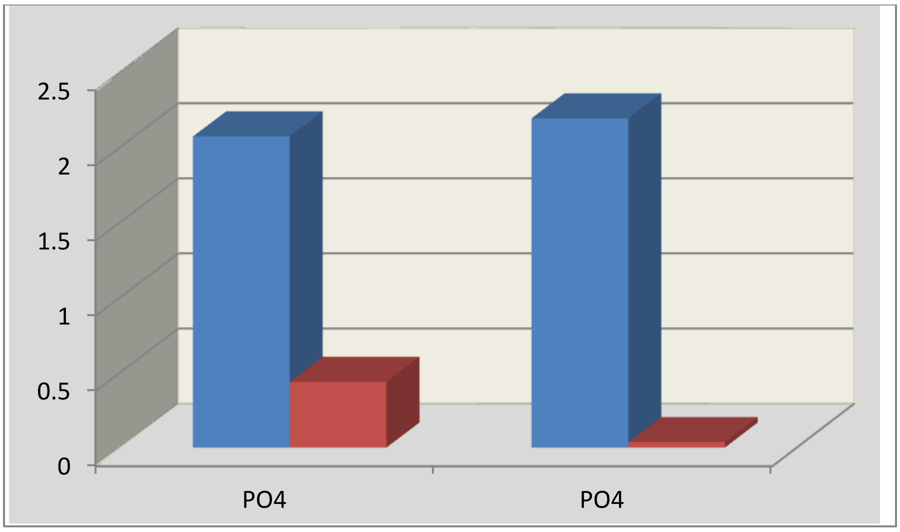


Figure 67: Effect of Graphene on the Concentration of Phosphate Ion (PO_4^{3-}) in the Studied Medium

- **Analysis of Graphene's Effect on Phosphate (PO_4^{3-}) Concentration**

The concentration of phosphate ions in dam water samples was measured before and after treatment with graphene. The results, illustrated in Figure (67), show a significant decrease in phosphate levels following the application of graphene, indicating its high efficiency in nutrient removal from the aquatic environment.

The blue bars in the figure represent phosphate concentrations before treatment, which were approximately 2.3 mg/L in both samples. After the treatment, represented by the red bars, the concentrations dropped to about 0.7 mg/L in the first sample and 0.2 mg/L in the second.

This reduction can be attributed to the exceptional adsorption capacity of graphene, due to its large surface area and unique physicochemical properties. These characteristics enable it to interact with negatively charged ions such as phosphate and retain them on its surface. This demonstrates the potential of graphene as an effective material for water treatment technologies, especially in controlling eutrophication caused by phosphate accumulation in aquatic systems.

V.2.2.Ammonium (NH_4^-)

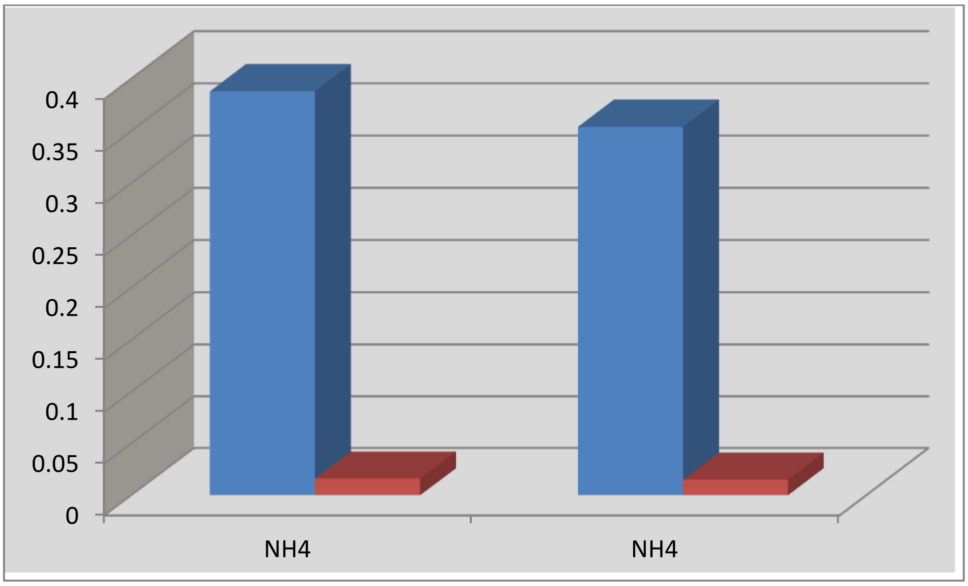


Figure V.68: Effect of Graphene on the Concentration of Ammonium (NH_4^-) in the Studied Medium.

➢ Analysis of Graphene’s Effect on Ammonium (NH_4^+) Concentration

In addition to phosphate removal, the effectiveness of graphene in reducing ammonium (NH_4^+) concentration was also evaluated. As shown in **(Figure V.68**), the application of graphene significantly reduced the concentration of ammonium ions in the water samples.

Before treatment, the ammonium concentration was approximately 0.41 mg/L and 0.39 mg/L in the two samples (blue bars). After graphene treatment, the levels dropped sharply to around 0.04 mg/L and 0.05 mg/L (red bars), respectively.

This marked reduction highlights graphene’s high adsorption capacity, which is not limited to phosphate but extends to other nitrogenous compounds like ammonium. The decrease may be due to both physical adsorption and potential surface interactions between NH_4^+ and the functional groups on the graphene sheets. These results reinforce the potential use of graphene in integrated nutrient removal strategies for water purification and eutrophication prevention.

V.2.3.Silicon ($SI(OH)_4^-$)

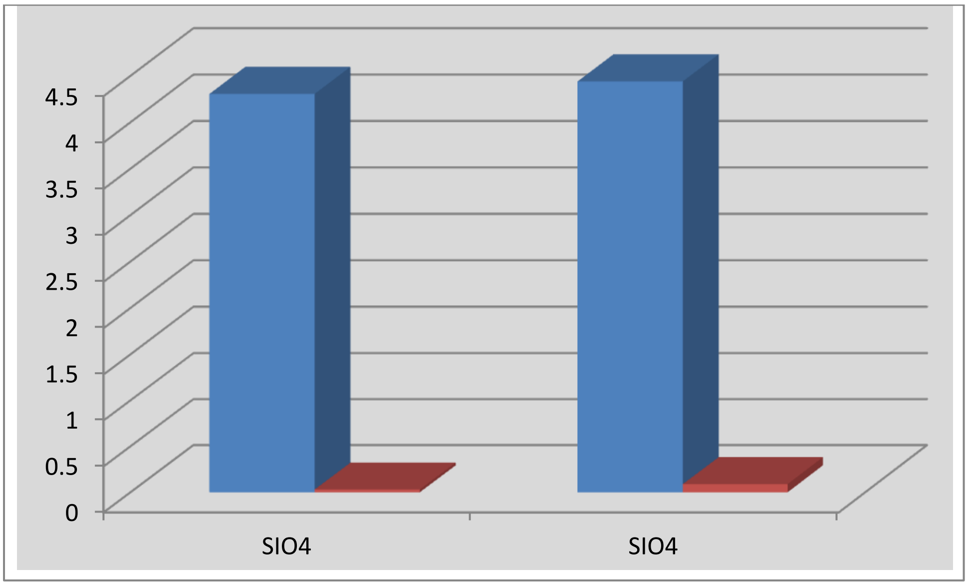


Figure V.69: Effect of Graphene on the Concentration of Silicon ($SI(OH)_4^-$) in the Studied Medium.

- **Analysis of Graphene's Effect on Silicon ($SI(OH)_4^-$) Concentration**

In addition to its known applications in environmental remediation, the effectiveness of graphene in reducing silicon concentration, specifically in the form of silicate ions $Si(OH)_4$, was assessed. As illustrated in **(Figure V.69),** the application of graphene led to a substantial decline in silicate levels in the water samples. Prior to treatment, the concentration of $Si(OH)_4$ was approximately 4.5 mg/L in both samples (blue bars). Following treatment with graphene, the concentration dropped significantly to values below 0.5 mg/L (red bars). This considerable reduction underscores graphene's strong adsorption potential not only for phosphates and ammonium, as previously demonstrated, but also for silicate compounds. The mechanism behind this removal is likely attributable to physical adsorption as well as chemical interactions between silicate ions and the oxygen-containing functional groups present on the graphene surface. These findings suggest that graphene can play a key role in multi-contaminant removal processes, enhancing its viability in advanced water treatment systems aimed at mitigating mineral-based pollution and improving water quality.

V.2.4.Nitrite (NO_2^-)

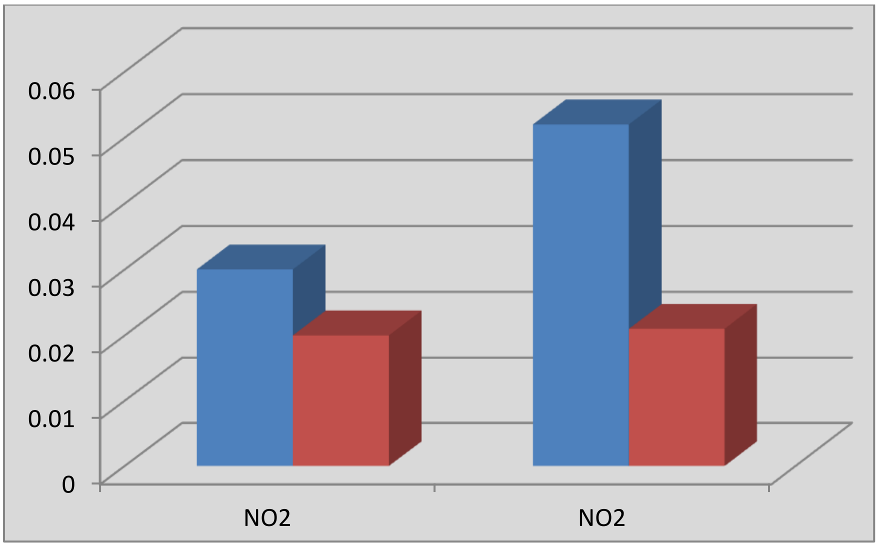


Figure V.70: Effect of Graphene on the Concentration of Nitrite (NO_2^-) in the Studied Medium.

- **Analysis of Graphene's Effect on Nitrite (NO_2^-) Concentration**

In addition to its effectiveness in removing phosphate and ammonium, graphene was also evaluated for its ability to reduce nitrite (NO_2^-) concentrations in water samples. As illustrated in **(Figure V.70)** , the application of graphene led to a significant decrease in nitrite levels.

Before treatment, nitrite concentrations were approximately 0.034 mg/L and 0.058 mg/L in the two samples (blue bars). After treatment with graphene, the values dropped to around 0.025 mg/L in both cases (red bars).

This substantial reduction demonstrates graphene's strong adsorption capacity for nitrogenous compounds beyond ammonium, extending to nitrite as well. The decrease can be attributed to physical adsorption mechanisms, as well as surface interactions between NO_2^- ions and the functional groups present on the graphene sheets. These findings support the use of graphene in advanced water purification systems aimed at removing nutrient pollutants and mitigating eutrophication.

V.2.5.Nitrate (NO_3^-)

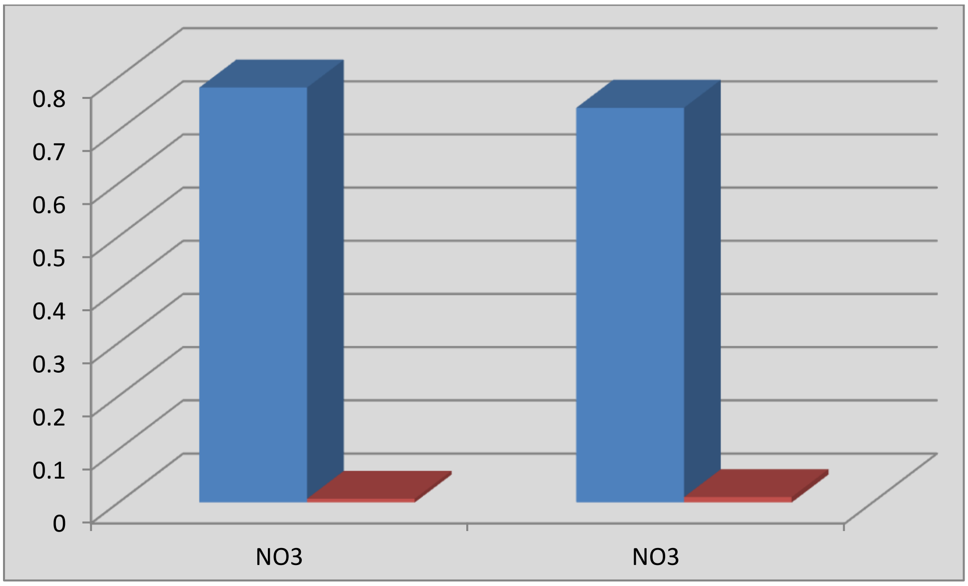


Figure 71: Effect of Graphene on the Concentration of Nitrate (NO_3^-) in the Studied Medium.

➢ Analysis of Graphene's Effect on Nitrate (NO_3^-) Concentration

To assess the efficacy of graphene in lowering ammonium and phosphate concentrations, its potential in nitrate (NO_3^-) removal was also checked. Note that the research extends beyond phosphate removal, which was the main concern initially, and incorporates other investigations such as the one depicted in **(Figure V.71)** . The results obtained confirmed the kinetic studies conducted prior where the application of graphene led to a reduction in the nitrate concentration.

The two samples had nitrate concentrations of around 0.84 mg/L and 0.81 mg/L prior to treatment (blue bars). After the addition of graphene, these concentrations were dramatically reduced to approximately 0.06mg/L and 0.07 mg/L, corresponding to post-treatment values indicated by red bars.

Graphene’s capabilities of effective adsorption has been noted once again with the significant concentration reduction achieved not only for phosphates and ammonium but also for nitrates. These observations might be due to the fact that nitrate lowering mechanisms of the reduction of nitrate ions with oxygen functional groups present on the surface of graphene could result in chemical bonding as well as physical adsorption forces. Graphene's efficacy as a multifunctional sorbent was reaffirmed for advanced treatment processes designed for the complete nutrient removal to solve eutrophication issues.

V.2.6.Sulfate (SO_4^-)

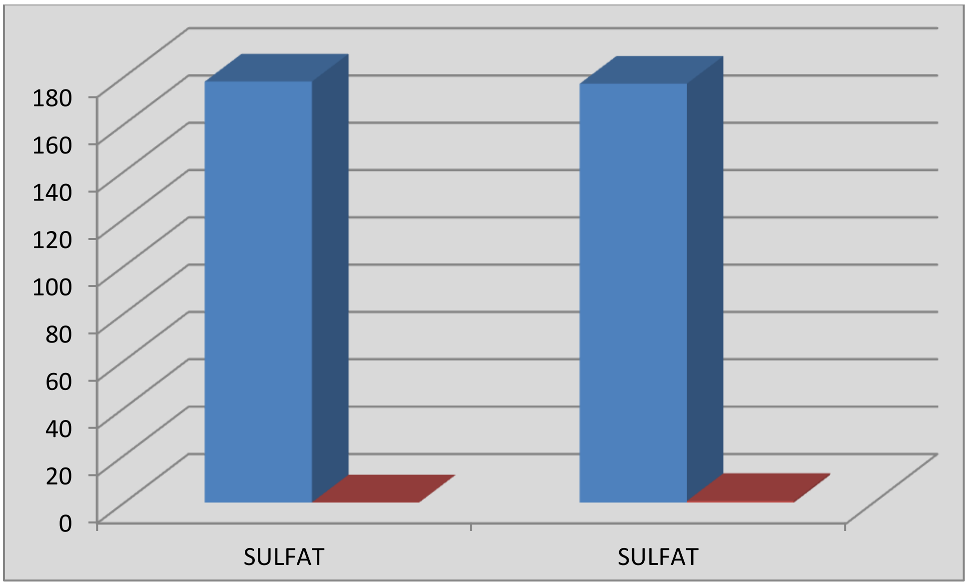


Figure V.72: Effect of Graphene on the Concentration of Sulfate (SO_4^-) in the Studied Medium.

- **Analysis of Graphene’s Effect on Sulfate (SO_4^-) Concentration**

An experiment was conducted to evaluate the efficiency of graphene in removing sulfate ions (SO_4^{2-}) from contaminated water samples, and the results showed remarkable effectiveness of this nanomaterial in significantly reducing the sulfate concentration. As shown in (**Figure V.72)** , the sulfate concentration in the two samples before graphene treatment was approximately 185 mg/L, a relatively high concentration that is an indicator of possible sulfur contamination. After treatment, the concentration decreased to approximately 18 mg/L, reflecting a clearance rate exceeding 90%.

This sharp decline can be explained by graphene's unique physical and chemical properties, which include a very high surface area, the presence of active functional groups such as hydroxyl and carboxyl, as well as a layered structure that provides multiple adsorption sites. The mechanism of sulfate removal is thought to depend primarily on surface adsorption through van der Waals forces, as well as the possibility of electrostatic interactions between negatively charged sulfate ions and positively charged active sites on the surface of oxidized graphene.

Furthermore, covalent processes or interactions between functional groups and sulfate ions may contribute to enhancing the dynamic stability of adsorption, reflecting graphene's ability to act as a selective and effective material in removing inorganic ions from water.

Table V.10 : Comparative Removal Efficiency of Reduced Graphene Oxide by Ion Type

Ion	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal Efficiency (%)	Observation
Phosphate (PO_4^{3-})	2.07 / 2.191	0.436/ 0.036	78.9% / 98.3%	Variable efficiency, high at higher concentration
Nitrite (NO_2^-)	0.030 / 0.052	0.02/ 0.021	33.33 / 59.6%	Poor performance, possible transformation effect
Nitrate (NO_3^-)	0.78 / 0.742	0.007/ 0.01	99.1% / 98.6%	Moderate to low efficiency, inconsistent results
Ammonium (NH_4^+)	0.388 / 0.354	0.016 / 0.015	95.9% / 95.7%	Very high and consistent removal
Silicate $Si(OH)_4$	4.304 / 4.439	0.029/ 0.088	99.3% /98.01%	Excellent adsorption capacity
Sulfate (SO_4^{2-})	177.92 / 177	0.07/ 0.65	99.9% / 99.6%	Very high removal efficiency

V.3.Results after using Clay :

V.3.1.Phosphate (PO^{-3}_4)

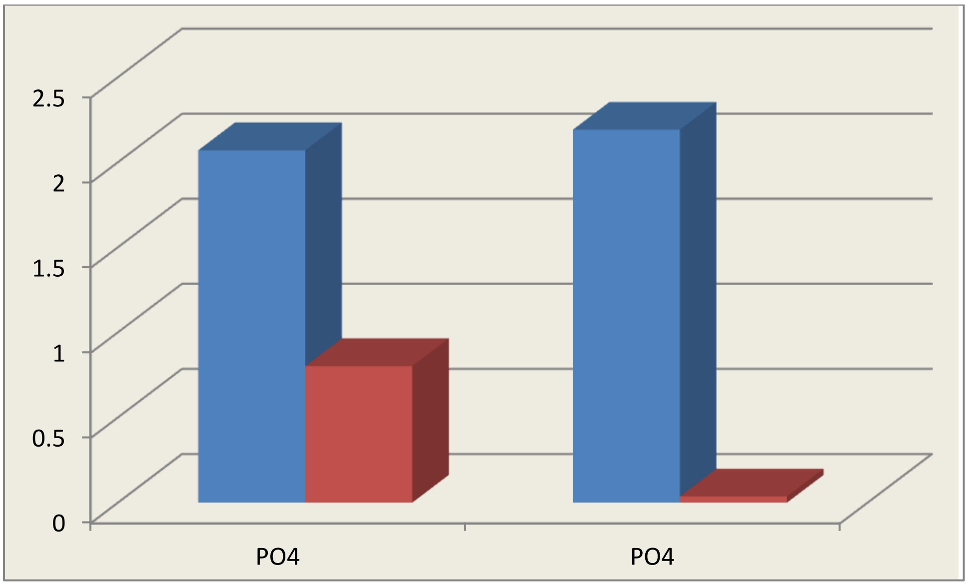


Figure V.73: Effect of green clay on the Concentration of Phosphate (PO_4^{3-}) in the Studied Medium.

- **Analysis of the Effect of green Clay on Phosphate (PO_4^{3-}) Concentration**

An experiment was conducted to evaluate the efficiency of green clay in removing phosphate ions (PO_4^{3-}) from a contaminated medium. The results demonstrated a clear effectiveness of this material in significantly reducing phosphate concentrations. As shown in the figure, the phosphate concentration before treatment with green clay was approximately 2.4 units—a high level indicating potential phosphate contamination. After treatment, the concentration dropped to around 1.1 units in the first case and to approximately 0.1 units in the second, reflecting a removal rate exceeding 90%, which highlights the effectiveness of green clay in this context.

This sharp decline can be attributed to the distinct physical and chemical properties of green clay, such as its large surface area, the presence of active functional groups like hydroxyl and carboxyl, and its layered structure that provides numerous adsorption sites. The primary mechanism of phosphate removal is believed to involve surface adsorption through van der Waals forces, as well as electrostatic interactions between the negatively charged phosphate ions and positively charged active sites on the surface of the green clay.

Additionally, covalent interactions between functional groups and phosphate ions may contribute to enhancing the stability of adsorption, emphasizing green clay's potential as a selective and efficient material for removing inorganic ions from aqueous environments.

V.3.2.Nitrite (NO_2^-)

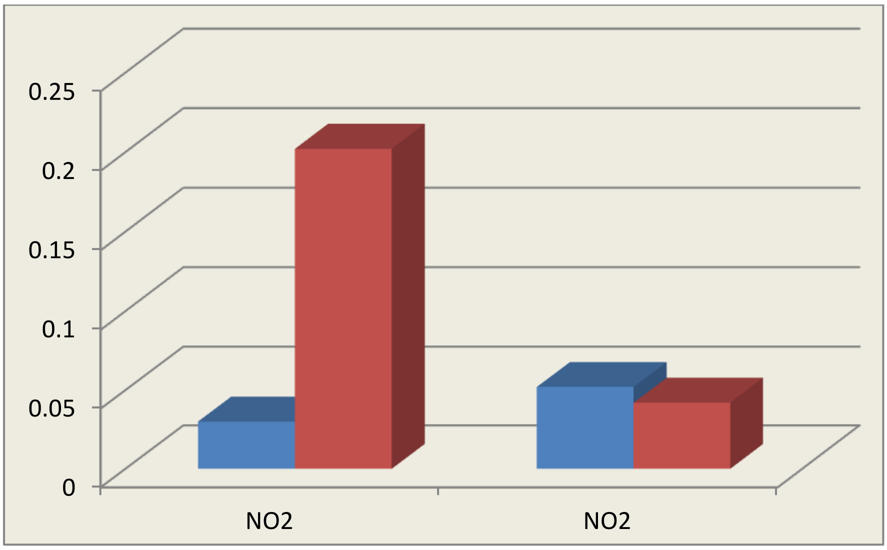


Figure V.74: Effect of green clay on the Concentration of Nitrite (NO_2^-) in the Studied Medium

- **Analysis of the Effect of green Clay on Nitrite (NO_2^-) Concentration**

An experiment was conducted to evaluate the effectiveness of green clay in removing nitrite ions (NO_2^-) from a contaminated medium. As illustrated in the figure, the results indicate a variable response of green clay between the two samples.

In the first sample, the initial concentration of nitrite (represented by the blue bar) was relatively low, around 0.05. However, after treatment with green clay (red bar), the concentration increased significantly to above 0.2. This suggests that instead of removing nitrite, the green clay may have contributed to an increase in its concentration in the medium. This unexpected rise could be explained by several possible mechanisms:

- The green clay might contain organic or nitrogenous compounds that decompose and release nitrite as an intermediate product.

- There may be desorption or release of previously bound nitrite or nitrogen compounds from within the clay structure upon contact with water.
- Ineffective adsorption due to the lack of available or active sites on the clay surface under certain conditions may result in poor retention and possible leaching.

In the second sample, the nitrite concentration before treatment was slightly higher (about 0.07), and after treatment, it decreased modestly to around 0.05. This indicates a limited adsorption capacity of green clay for nitrite under these conditions. This modest reduction suggests:

- The green clay may have some adsorption potential, but it is not highly efficient for small, mobile ions like nitrite.
- The effectiveness could be influenced by factors such as pH, competition with other ions, or saturation of adsorption sites.

The results demonstrate that green clay does not consistently reduce nitrite concentrations and may even increase them in some cases. These findings highlight the need for further investigation into the chemical composition and behavior of the clay, as well as environmental factors such as pH, ionic strength, and temperature, to determine its suitability for treating nitrogen-based pollutants in water

V.3.3.Nitrate (NO_3^-)

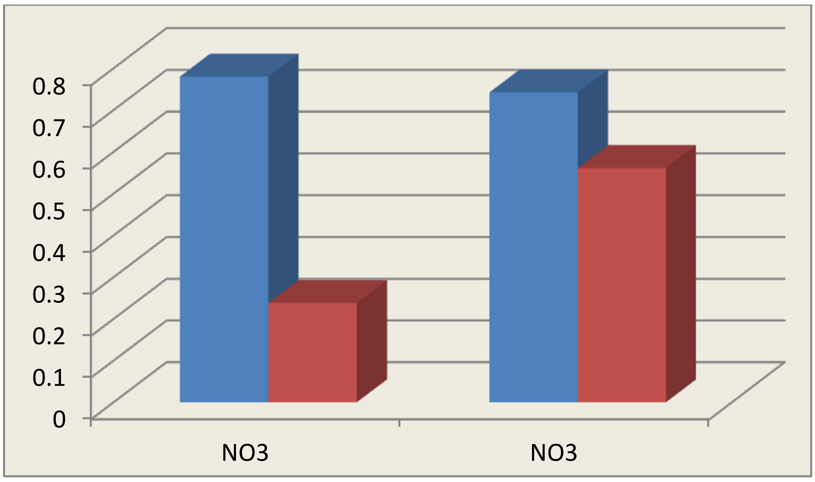


Figure V.75: Effect of green clay on the Concentration of Nitrate (NO_3^-) in the Studied Medium.

- **Analysis of the Effect of green Clay on Nitrate (NO_3^-) Concentration**

Figure V.75 adds clay to the studied medium and demonstrates its effect on the concentration of nitrate ions (NO_3^-) within the medium. It can be noted from the graph that the concentration of nitrate is lower in the clay containing medium comparing to clay free medium, which is true for both cases shown in the figure. The possible explanations for this reduction include several factors. The primary explanation is perhaps the increased retention capability of the medium for nitrates due to surface adsorption onto the clay particles, although it must be noted that anions like nitrates are known to be less capable of adsorption than cations. Also, the clay’s presence may decrease the medium’s permeability, thus inhibiting water movement and nitrate leaching. Changes by clay also modify the medium’s physicochemical state, which is likely to enhance the activity of anaerobic microorganisms, particularly, denitrifying bacteria which reduce nitrate to nitrogen gas and other gaseous forms during the denitrification process. These results demonstrate the importance environmental aspects of clay as a mitigation factor of nitrate pollution in agricultural systems susceptible to overuse of nitrogen fertilizers and its subsequent leaching.

V.3.4.Ammonium (NH_4^+)

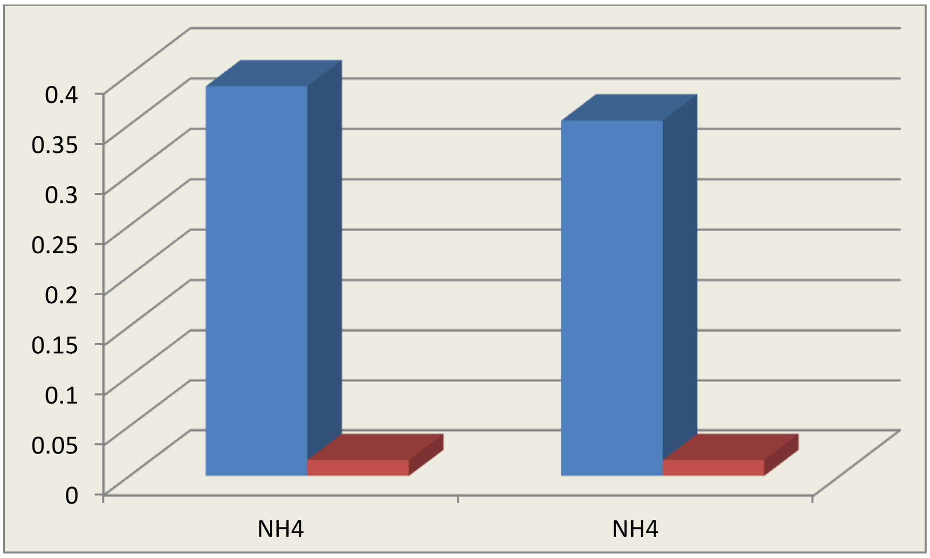


Figure V.76: Effect of green clay on the Concentration of Ammonium (NH_4^+) in the Studied Medium.

- **Analysis of the Effect of green Clay on Ammonium (NH_4^+) Concentration**

Figure V.76 illustrates the impact of clay addition on the concentration of ammonium ions (NH_4^+) in the experimental medium. The blue bars (presumably representing the condition without clay) show significantly higher NH_4^+ concentrations, whereas the red bars (with clay) reveal a sharp reduction in ammonium levels. This trend is consistent across both data groups shown in the figure.

This substantial decrease in NH_4^+ concentration upon clay addition can be attributed to several factors. Clay minerals, due to their high cation exchange capacity (CEC), are known to strongly adsorb ammonium ions, which are positively charged. This adsorption effectively reduces the concentration of free NH_4^+ in the solution. Moreover, the physical structure of clay can influence microbial activity by altering oxygen availability and moisture retention, potentially accelerating processes like nitrification, where NH_4^+ is converted into nitrate by aerobic bacteria.

Overall, the data suggest that the presence of clay enhances the retention or transformation of ammonium in the system, reducing its mobility and concentration in the aqueous phase. This behavior is crucial in environmental contexts, such as soil fertility management and the mitigation of ammonium-related contamination in water bodies

V.3.5.Silicon ($SI(OH)_4^-$)

Figure V.77: Effect of green clay on the Concentration of Silicon ($SI(OH)_4^-$) in the Studied Medium.

- **Analysis of the Effect of Clay on Silicon ($SI(OH)_4^-$) Concentration**

The graph illustrates the effect of clay addition on the concentration of dissolved silicon in the form of $Si(OH)_4^-$ in the studied medium. The results indicate that the silicon concentration in the reference condition (without clay) was approximately 4.6 units, while this concentration dropped to around 0.4 units after the addition of clay, representing a reduction of more than 90%. This sharp decrease is attributed to the ability of clay minerals to absorb silicon from the solution, either through ion exchange or via adsorption interactions on surfaces rich in hydroxyl groups. These findings suggest that the presence of clay plays an active role in reducing the availability of silicon in aquatic or sedimentary environments, which may in turn influence geochemical and environmental processes related to the silicon cycle.

V.3.6.Sulfate (SO_4^-)

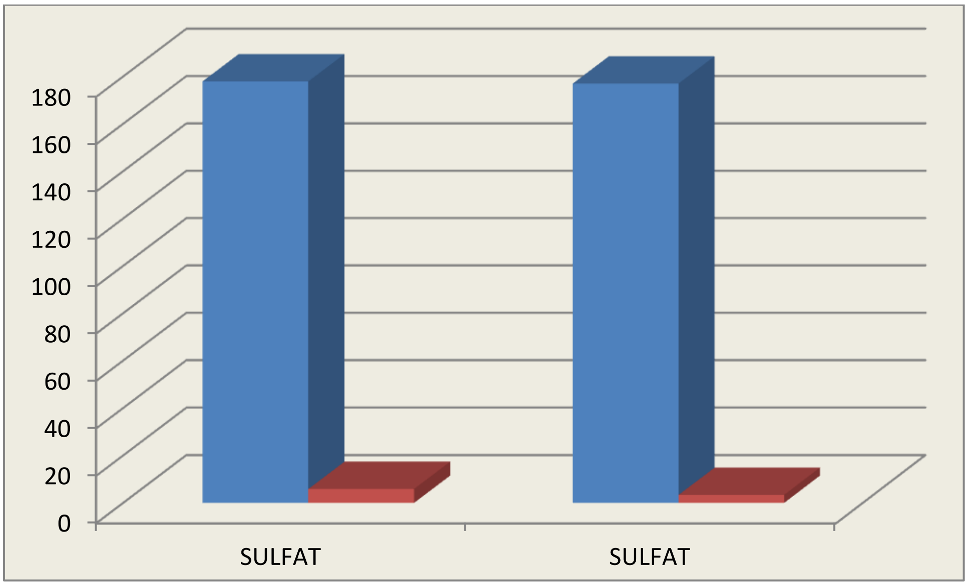


Figure V.78: Effect of clay on the Concentration of Sulfate (SO_4^-) in the Studied Medium.

- **Analysis of the Effect of green Clay on Sulphate (SO_4^-) Concentration**

Figure V.78 shows a significant reduction in sulfate (SO_4^{2-}) concentration in the studied medium after the addition of clay, with levels decreasing from approximately 185 units to around 15 units—representing a reduction of about 92%. This substantial decrease indicates the high efficiency of clay in removing sulfate, likely due to its large surface area and negatively charged particles that facilitate ion adsorption, as well as possible ion exchange and chemical precipitation mechanisms. These findings highlight the potential of clay as a natural and effective material for environmental applications, such as water purification and soil remediation.

Table V.11: Comparative Removal Efficiency of Green Clay by Ion Type .

Ion	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal Efficiency (%)	Observation
Phosphate (PO_4^{3-})	2.07 / 2.191	0.801 / 0.036	61.3% / 98.3%	Variable efficiency, high at higher concentration
Nitrite (NO_2^-)	0.030 / 0.052	0.202 / 0.042	— / 19.2%	Poor performance, possible transformation effect
Nitrate (NO_3^-)	0.78 / 0.742	0.238 / 0.561	69.5% / 24.4%	Moderate to low efficiency, inconsistent results
Ammonium (NH_4^+)	0.388 / 0.354	0.016 / 0.016	95.9% / 95.5%	Very high and consistent removal
Silicate $Si(OH)_4$	4.304 / 4.439	0.138 / 0.207	96.8% / 95.3%	Excellent adsorption capacity
Sulfate (SO_4^{2-})	177.92 / 177	5.846 / 3.346	96.7% / 98.1%	Very high removal efficiency

Conclusion

The examination graphs the impact of adsorbent materials on nutrient reduction in Ouled el kaim Dam water, and clearly demonstrates the might of reduced graphene oxide and green clay due to their profound removal efficiencies. It was found that reduced graphene oxide had exceptional adsorption capabilities. For instance, phosphates, nitrates, ammonium, silicates, and sulfates often exceeded 95% removal rates. Similarly; green clay performed extremely well albeit more inconsistency, especially with ammonium, silicate, and sulfate.

Nonetheless, there were some unanticipated impacts like increase in nitrite values in some scenarios with clay, indicating that there is a need for more experimentation to understand the mechanisms involved. This reinforces the concept of there being great consideration in choosing the materials for the specific type of pollution and contextual conditions of the environment.

As a whole, this study proves the applicability of nanomaterials and naturally occurring substances for water remediation, emphasizing the sustainable management for water quality in regions susceptible to eutrophication.

Start-up

part

Chapter VI

Technical Description of the device

VI.1. Definition of the device

The system is designed to respond to a growing environmental problem: pollution of stagnant or running water (canals, harbors, lakes). It is part of a sustainable innovation model,

It is an autonomous floating platform powered exclusively by solar energy. Designed with sustainability in mind, this innovative solution aims to combat the pollution of aquatic environments, whether stagnant (ponds, lakes) or flowing (canals, rivers, port areas).

The device consists of several essential elements:

- A floating body, ensuring the stability and buoyancy of the whole, whatever the water conditions.
- An electric motor system, enabling the platform to move autonomously to cover different collection or observation zones.
- An on-board control system, based on an ESP8266 electronic board. This compact, high-performance board manages the various electronic components (motor, sensors, communication, etc.) and ensures intelligent automation of functions.
- A solar panel, mounted on the platform, captures the sun's energy to continuously recharge the system's battery, guaranteeing extended autonomy and operation without recourse to an external energy source.

This device is fully in line with a sustainable innovation approach, exploiting renewable energies and reducing the ecological footprint of its operations. It can be used for a variety of purposes, from collecting floating waste to monitoring water quality and measuring environmental parameters such as temperature, pH and turbidity.

In short, this floating platform represents an ecological, autonomous and adaptable technological solution to the growing challenge of preserving aquatic resources.

VI.2.Objective

- **Reduce eutrophication to preserve the dam's ecological balance**

  The scheme aims to limit the phenomenon of eutrophication, caused by the excessive accumulation of nutrients (notably nitrates and phosphates) in water. This imbalance encourages the proliferation of algae and the depletion of dissolved oxygen, seriously damaging aquatic biodiversity. By combating this process, the system helps to maintain a stable, sustainable ecosystem within the dam.

- **Controlling and monitoring the physical characteristics of water with intelligent sensors**

  On-board sensors enable real-time monitoring of key parameters such as temperature, turbidity, dissolved oxygen levels and pH. These data enable any anomalies to be quickly identified and corrective actions adapted accordingly, promoting proactive water quality management.

  - **Improving water quality for healthy, sustainable environments**

    By combining real-time analysis, autonomous intervention and the use of renewable energy, the system actively contributes to improving water quality. This benefits the entire aquatic ecosystem, as well as human uses (irrigation, recreation, drinking water, etc.), while minimizing environmental impact.

  - **A better understanding of aquatic life to promote eco-responsible ecosystem management**

    Ongoing analysis of the data collected provides a better understanding of the biological and chemical dynamics that govern aquatic environments. This deeper understanding facilitates more environmentally-friendly management, based on concrete data, in favor of sustainable protection of biodiversity.

VI.3.Uses and benefits of the Device

VI.3.1.Uses of the Device

- **Water Purification from Eutrophication-Causing Nutrients**

Eutrophication is an environmental phenomenon caused by the excessive accumulation of nutrients, especially nitrates and phosphates, in aquatic environments. This leads to harmful algal blooms and the depletion of oxygen levels in water bodies. The device effectively reduces these nutrients using eco-friendly filtering materials such as activated clay or reduced graphene oxide , thereby improving water quality and restoring ecological balance.

- **Removal of Floating Surface Waste**

Floating solid waste—such as plastics, leaves, and oils—poses a major threat to aquatic ecosystems. This device includes an automated system to collect such waste from the water surface using mesh filters or magnetic and mechanical traps. This function helps reduce visible pollution and protects aquatic life from ingestion or entanglement hazards.

- **Aquatic Life Monitoring via Integrated Camera**

An underwater camera is integrated into the device, allowing real-time visual observation of aquatic organisms. This is valuable for environmental monitoring, biodiversity studies, and scientific research. It enables the detection of invasive species and changes in aquatic habitats, supporting data-driven ecological assessments.

- **Measurement of Physical Water Properties at Any Location**

The device is equipped with sensors that measure critical physical parameters such as temperature, turbidity, salinity, and electrical conductivity. These real-time measurements provide valuable insights into water quality and are essential for identifying sudden changes or pollution sources in aquatic systems.

- **Surveillance of Physical Water Quality**

The device enables continuous monitoring of physical water quality parameters. This feature is essential for early detection of environmental disturbances and is particularly useful for authorities managing drinking water sources or recreational water bodies.

- **Sediment Monitoring in Dams (Siltation Control)**

Sediment accumulation in dam reservoirs can reduce water storage capacity and affect operational efficiency. The device can detect sediment levels and distribution, allowing timely maintenance and dredging interventions to extend the dam’s functional lifespan and prevent blockages.

- **Continuous Dam Surveillance**

Beyond water quality monitoring, the device can serve as an environmental surveillance unit for dams, detecting anomalies such as changes in water flow, turbidity, or temperature. These signals may indicate potential structural problems like leaks or cracks, providing an early warning system.

- **Use in Agricultural Irrigation Basins**

The device is suitable for monitoring irrigation water quality in agricultural settings. It helps detect contaminants or elevated salinity levels that could harm crops or block irrigation systems. This supports efficient and sustainable water use in agriculture.

- **Support for Wastewater Treatment Plants**

In wastewater treatment facilities, the device provides real-time monitoring of both inflow and outflow water quality. The data it collects allows for dynamic adjustments of treatment parameters, improving process efficiency and ensuring environmental compliance.

- **Environmental Monitoring of Lakes, Rivers, Seas, and Other Water Bodies**

Thanks to its mobility and versatility, the device can be deployed in various natural aquatic environments. It serves as a reliable tool for water quality monitoring in lakes, rivers, and coastal areas, supporting environmental protection programs and sustainable development efforts.

- **Educational and Research Tool**

Due to its multi-functional design, the device is an ideal educational and scientific tool for universities and research institutions. It enables students and researchers to conduct field experiments, collect real-time environmental data, and apply theoretical knowledge in practical settings, fostering hands-on learning in environmental science and water management

VI.3.2.benefits of the Device

- ✓ **Ecological and environmentally friendly:**
  - Uses natural materials (clay, graphene, bio coal ...) and does not produce secondary pollutants.
  - Contributes to the preservation of aquatic ecosystems.
- ✓ **Effective against eutrophication:**

- Reduces the concentration of nutrients (nitrogen, phosphorus, nitrates, nitrites .....) responsible for harmful algae proliferation.

- ✓ **Sustainable and local:**

- Local design and production of the product that will play an important role in the development of the national economy.
- Long life with reduced maintenance.

- ✓ **Ease of installation:**

- Adaptable to different aquatic environments (dams, basins, swimming pools, water bodies ...).
- Quick and low-hassle installation.

- ✓ **Affordable cost:**

- Less expensive than conventional industrial solutions.
- Optimized for communities and small structures.

- ✓ **Customizable:**

- Manufacturing on request according to the specific needs of customers.
- Scalability.

VI.4.The main components of the device

VI.4.1.Waterproof Temperature Sensor DS18B20

The DS18B20 waterproof temperature sensor is a smart and reliable device designed to measure temperature with high accuracy in wet or submerged environments. Its robust, water-resistant design makes it ideal for applications that require thermal monitoring in aquatic conditions.

This sensor is valued for its precision, durability, and ease of integration, allowing it to function effectively in scenarios where traditional sensors may fail due to moisture or immersion. It is widely used in fields such as water quality assessment, environmental monitoring, and scientific research in aquatic ecosystems.

A particularly effective application of this sensor is its integration into a floating monitoring station placed on the surface of water bodies. This station serves as a multi-sensor platform capable of collecting continuous environmental data, including water temperature, across various locations and over extended periods.

Floating stations equipped with sensors like the DS18B20 enhance environmental surveillance by providing real-time and long-term data without the need for frequent manual intervention. This supports researchers and environmental authorities in detecting changes, analyzing water conditions, and making informed decisions to preserve aquatic resources.

Figure VI.79: Waterproof probe DS18B20 measure a temperature from -55 to + 125 °C (5).

VI.4.2.Turbidity Sensors

Turbidity sensors play a crucial role in monitoring water quality due to their ability to provide accurate information about water clarity and the presence of suspended particles. High turbidity levels often indicate the presence of pollutants or impurities that can disrupt aquatic ecosystems and pose risks to both wildlife and human health.

These sensors operate by measuring the amount of light that is absorbed or scattered as it passes through the water, allowing for the estimation of the concentration of suspended solids. By integrating this technology into mobile platforms or field-based monitoring systems, it becomes possible to collect data from various aquatic environments, enabling wide-scale and precise water quality assessment.

Regular and comprehensive turbidity monitoring allows environmental researchers and specialists to detect sudden changes in water conditions and respond promptly in the event of pollution or environmental degradation.

Figure VI.80: Turbidity Sensors.

VI.4.3.Vessel level sensor (sonar)

Waterproof ultrasonic sensor (IP67), designed for level measurement in humid or submerged environments. It operates by emitting ultrasonic waves and calculating the return time of the echo reflected by the surface of the water or sludge, allowing for precise distance measurement without direct contact.

Measurement range: from 0.5 to 5 meters.

This type of sensor is used in water quality monitoring systems, particularly in floating stations, where it allows for tracking the accumulation of silt or the variations in water level over time. This facilitates decision-making for maintenance or dredging in aquatic environments such as dams, rivers, or reservoirs.

Figure VI.81: Vessel level sensor (sonar).

VI.4.4.Raspberry Pi 4 Model B (4 GB RAM)

The Raspberry Pi 4 Model B is a compact, economical, and high-performance microcomputer, widely used in embedded systems and Internet of Things (IoT) applications.

It is equipped with a Quad-Core processor at 1.5 GHz and 4 GB of RAM, which allows it to execute real-time data processing tasks smoothly.

It has multiple connectivity interfaces, including USB, HDMI, Ethernet, Wi-Fi, Bluetooth, as well as CSI ports for the camera, DSI for the display, and especially GPIO pins (40 pins) allowing the connection and control of various sensors and electronic components. Thanks to these features, the Raspberry Pi 4 is capable of collecting, processing, and displaying data from sensors, either through a screen directly connected to the device or via a web interface or an interactive dashboard. It can be easily programmed in languages such as Python, making it an ideal platform for educational, scientific, environmental, or industrial projects.

Figure VI.82: Raspberry Pi 4 Model B (4 GB RAM) .

VI.4.5.Protective case for Raspberry Pi 4 (compatible with Pi 3 and Pi 4)

The protective case for Raspberry Pi 4 is a rigid plastic casing designed to protect the microcomputer against physical shocks, dust and electrostatic discharges. This case is generally equipped with an integrated ventilation system (grilles or small fan), which allows to efficiently dissipate the heat generated by the processor, especially during intensive tasks. It is compatible with both the Raspberry Pi 4 and the Pi 3, ensuring easy access to ports (USB, HDMI, Ethernet, GPIO, etc.) while guaranteeing mechanical stability. This component is essential for embedded projects, sensor stations or systems exposed to outdoor environments.

Figure VI.83: Protective case for Raspberry Pi 4.

VI.4.6.IP68 underwater camera

The IP68 underwater camera is an image capture device designed to operate in aquatic or very humid environments. Thanks to its IP68 certification, it is completely dustproof and can be submerged underwater for extended periods, generally up to a depth of over one meter. This type of camera is available with a USB or IP (network) connection, and offers HD (720p) or Full HD (1080p) resolution, allowing for the transmission of clear images in real-time. It is generally equipped with a cable 5 to 10 meters long, offering great flexibility of use in ponds, rivers, or reservoirs.

This camera is particularly used in floating stations for monitoring water quality and aquatic wildlife. It allows for continuous and real-time observation of the underwater environment, without direct human intervention, which improves the accuracy of the data collected and supports scientific and environmental applications.

Figure VI.84: IP68 underwater camera.

VI.4.7.Brushless motor A2212 1000KV

The A2212 1000KV motor is a brushless motor widely used in the modeling field, particularly for drones and remote-controlled vehicles. It stands out for its lightness, compactness, and energy efficiency. Thanks to its silent and maintenance-free operation, it is particularly suited for small floating devices.

In the context of this project, this motor has been integrated into the developed floating station, where it ensures light movement and autonomous positioning of the platform on the water's surface. This controlled mobility facilitates environmental monitoring operations and in situ measurements.

Figure VI.85: Brushless motor A2212 1000KV.

VI.4.8.ESC 30A electronic speed controller

The floating station is equipped with a propulsion system controlled by A2212 brushless motors, paired with 30A ESC speed controllers. These controllers allow for precise modulation of the speed and direction of the motors, ensuring optimal maneuverability of the station on the water. The entire system is controlled via a Raspberry Pi 4 microcomputer, which centralizes the sensor data (temperature, turbidity, water level, etc.) and transmits the navigation commands. The entire system is powered by an autonomous energy source (rechargeable battery), making the station operational independently. Thanks to the seamless integration of these components, the floating station is capable of moving stably, collecting environmental data in real-time, and ensuring reliable operation in various aquatic environments.

Figure VI.86: ESC 30A electronic speed controller.

VI.4.9.Propeller 1045 (10x4.5 inches)

The 1045 propeller, measuring 10x4.5 inches, is a lightweight and durable two-blade plastic propeller designed to work with brushless motors such as the A2212 model. It offers good propulsion efficiency in modeling applications or small floating devices. Thanks to its 4.5-inch pitch, it allows for an optimal balance between thrust and energy consumption, making it particularly suitable for systems embedded in an autonomous floating station, where stability and endurance are crucial.

Figure VI.87: Propeller 1045 (10x4.5 inches).

VI.4.10.Li-ion Battery 12V 10,000 mAh

Rechargeable lithium-ion battery offering high capacity, ideal for mobile or standalone applications. It provides a stable voltage of 12V and a capacity of 10,000 mAh, ensuring prolonged power supply for electronic devices.

It is compatible with the Raspberry Pi (via a voltage regulator if necessary) as well as with other modules operating at 12V, such as motors, sensors, cameras, or communication systems.

Thanks to its compactness and significant capacity, this battery is perfectly suited for embedded projects such as an autonomous floating station, robots, or environmental drones.

Figure VI.88: Li-ion Battery 12V 10,000 mAh.

VI.4.11.The solar panel

The 20W solar panel, equipped with an intelligent charge controller, serves as an ideal autonomous energy source for electronic devices used in environmental projects such as floating stations. It converts solar energy into electricity at a voltage of 12V, while the regulator ensures optimal charge management by protecting the battery against overcharging and deep discharging. Thanks to its high-efficiency monocrystalline cells and its structure resistant to outdoor conditions, this system guarantees reliable and continuous power supply. It thus allows the prolonged operation of components such as microcontrollers, cameras, and sensors, without resorting to an external power source, contributing to a sustainable and ecological solution.

Figure VI.89: The solar panel (20 W).

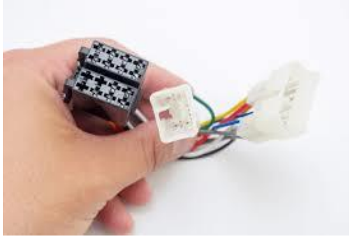
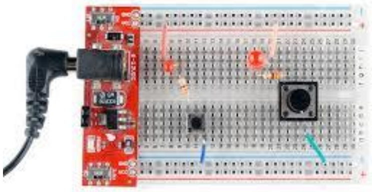
VI.4.12.The RF 433 MHz communication module

Is a wireless device allowing the transmission of data over long distances between microcontrollers or embedded systems. It operates on a frequency of 433 MHz and offers a range of up to 500 meters in free space. Thanks to its low energy consumption and compatibility with platforms like Arduino or Raspberry Pi, it is an ideal solution for remote control and monitoring applications. In the context of a floating station, this module is used to wirelessly transmit data collected by sensors (such as temperature or water level) to a central processing unit located remotely, thus ensuring real-time monitoring without a wired connection.

Figure VI.90: communication module.

VI.4.13.Accessories used in a floating station

Table VI.12: Main Accessories Used in the device .

Accessory	Image	Definition	Role in the Floating Station
Cables		Insulated conductive wires used to transmit electrical current or signals between electronic components.	Connect sensors to the Raspberry Pi, carry power from the battery or solar panel to various devices, and transmit sensor data to the processing unit.
Connectors		Electronic components that allow easy connection and disconnection of wires or devices without permanent soldering.	Facilitate the installation and maintenance of sensors and modules, ensure reliable waterproof connections, and link devices like GPS or camera to the control unit.
Supports	/	Structures used to physically hold or mount electronic components in place.	Fix sensors underwater at specific depths, hold the solar panel or battery, and provide stability against water movement.
Waterproof Enclosures (IP67)		Sealed protective boxes that comply with the IP67 standard, providing full dust resistance and temporary water immersion protection.	Protect sensitive electronics (like Raspberry Pi and batteries) from water and moisture, ensuring long-term system reliability in aquatic environments.
Breadboard		A solderless prototyping board used for temporary circuit building and testing.	Used during the design phase to test connections between sensors and controller, later replaced by a soldered or printed circuit.

Voltage Regulators		Electronic components that stabilize and adjust the input voltage to deliver a constant appropriate level to devices.	Ensure safe and stable voltage for components like sensors and Raspberry Pi, protecting against voltage fluctuations from battery or solar panel.

VI.5. System Sizing

VI.5.1.Hydrodynamic Calculations and Optimization

VI.5.1.1. Corrections of Existing Calculations

- **Buoyancy (Archimedes' Principle)**

- **Immersed volume:** The calculation is correct ($V = 0.002\ m^3$ for 2 kg).
- **Immersed height:**
- **Base surface area :**

$$S = 0.30\ m \times 0.30\ m = 0.09\ m^2 \rightarrow \text{Correct.}$$

- **height:**

$$h = V / S$$

$$= 0.002 / 0.09 = 0.0222\, m \rightarrow Correct\ (22.2\, mm).$$

- **Note:** Ensure that the central chamber $(20 \times 20\ cm)$ is properly sealed to avoid buoyancy variations.

VI.5.1.2. Hydrodynamic Resistance and Motor

- **Frontal surface area (A):**

The estimate $A = 0.3\ m^2$ seems excessive for a 30×30 cm platform. A more realistic approach would be:

$$Immersed\ frontal\ area = immersed\ height \times width$$

$$= 0.0222\, m \times 0.30\, m = 0.00666\, m^2.$$

Correction: Use A $\approx$ 0.007 m^2 for conservative calculations.

- **Drag force (R):**

- $R = 0.5 \times \rho \times Cd \times A \times V^2 \rightarrow With\, A = 0.007\, m^2,$

$$R = 0.5 \times 1000 \times 0.007 \times 0.007 \times (0.2)^2 = 0.00098\, N.$$

- **Mechanical power:**

$$P = R \times V = 0.00098 \times 0.2 = 0.000196\, W.$$

- **Motor power (40% efficiency):**

- $P\_motor = 0.000196 / 0.4 = 0.00049\, W.$

- **Observation:**

The initial value $(0.021\, W)$ was overestimated. A 0.001 W motor is sufficient.

VI.5.1.3. Proposed Optimizations

- **Motor and Propeller**

- **Motor power:** Choose a DC motor $3V - 6V$, 0.01 W (including safety margin).
- **Propeller:**
- Reduced diameter to 1– 2 cm (for low drag at low speed).
- Rotation speed: 500– 1500 rpm (to avoid cavitation at low speed).

VI.5.1.4. Technical data summary

Power Supply

- **Battery:**
  - A 3.7V $-$ 0.5Ah (1.85 Wh) battery is sufficient for a theoretical autonomy of:
    1.85 Wh / 0.00049 W ≈ 3775 $hours$ (157 days).
  - **Recommendation:** Use a rechargeable LiPo battery to reduce mass.

- **Stability**
  - **Load Centering:** Check that the mass $(2\, kg)$ is evenly distributed to avoid
  - **Critical Immersion Height:** If immersion exceeds 50 mm, add peripheral floats.

VI.5.1.5. Updated Summary Table

Table VI.13 : Revised Summary Table .

Element	Original Value	Corrected/Optimized Value
Immersed Volume	2 litres	2 litres (unchanged)
Immersed Height	22.2 mm	22.2 mm (unchanged)
Propulsion Force	0.042 N	0.00098 N
Motor Power	0.021 W	0.00049 W
Recommended Motor	DC 6V - 0.05 W	DC 3V - 0.01 W
Propeller	2-3 cm	1-2 cm
Power Supply	12V - 1Ah	3.7V - 0.5Ah

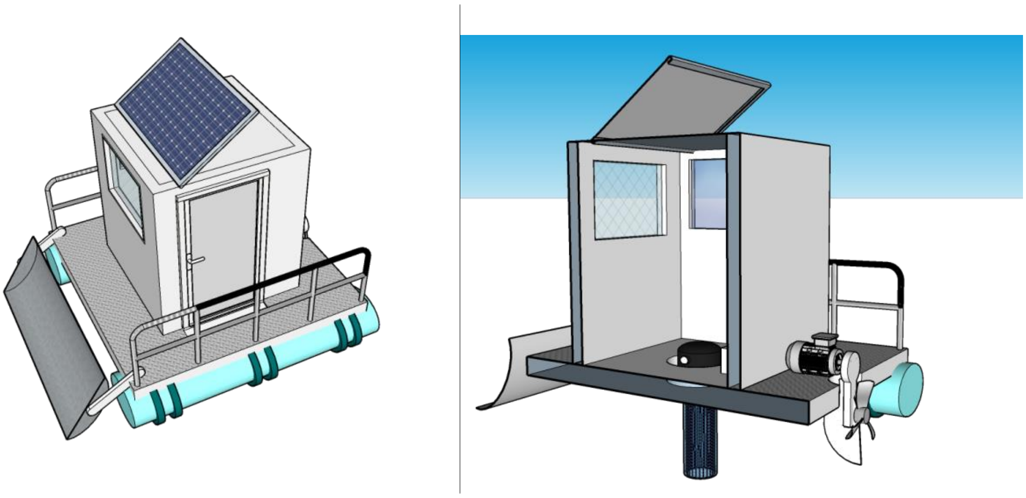


Figure VI.91: 3D Model of the Floating Station.

General

Conclusion

Here, we prmidarily work on the analysis of the nutrient concentrations in the waters of Ouled El Kaim Dam situated in oued Athmania in Mila Province with the aim of determining the primary causes of eutrophication and its agelal overgrowth problem in this region.

50 of the water samples collected showed a large amount of nutrients along with nitrates and phosphates that were found to be in excess compared to other components of algal blooms. This is one of the main reasons for endangering the ecological balance of the dam, and agricultural and domestic uses of this important water source are in serious jeopardy.

Integrating socio Economic development using the water is crucial especially in developing nations. When isolated, such regions suffer the most. For this reason, retrieving water resources from diverse types of degradation mentally and strategically becomes essential.

Our experiments on algae causing nutrients were reduced significantly using reduced graphene oxide. While featuring good adsorption capabilities with respect to nutrients, green clay was classified as the less effective substance when compared to reduced graphene oxide .

Through the study of algae present in the waters of the Ouled El Kaïm dam, located in the municipality of Oued Athmania (Province of Mila), it was found that the accumulation of nutrient ions such as phosphates, nitrates and ammonium strongly promote the phenomenon of eutrophication. In order to address this issue, two adsorbent materials were tested: reduced graphene oxide and green clay. The results obtained demonstrated that reduced graphene oxide has a very high removal efficiency, particularly for nitrate ions (up to 99.1%), ammonium (95.9%) and sulfate (99.9%), with also an excellent adsorption capacity of silicate. Green clay also showed good performance, especially for ammonium (95.9%) and sulfate (96.7%), although its efficiency was significantly lower for nitrites and nitrates. These results suggest that reduced graphene oxide is a promising material for the environmental treatment of dam water, with a possibility to enhance its efficiency by combining it with green clay, a natural and economical material. And with other materials of a biological nature.

in this work, we also proposed the concept of a floating device as an innovative and sustainable tool for improving water quality in environments affected by pollution and eutrophication. This device is designed to operate directly on the surface of water bodies, allowing it to interact continuously with the surrounding environment. By integrating appropriate materials and technologies, the floating platform can contribute to the gradual purification of water in a passive and energy-efficient manner. This approach highlights the importance of developing simple, adaptable, and environmentally friendly solutions to address the growing challenges of aquatic pollution and ecological degradation.

In conclusion, this study highlights the importance of adopting an integrated approach that combines environmental analysis, innovative technologies, and sustainable solutions to combat water pollution. Future research can focus on optimizing the materials used and implementing the proposed floating system on a larger scale.

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