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Option: **Applied chemistry**

THEME

Study of Diatomite adsorption capacity of sig (Mascara): application in the abatement of the pollutant Rhodamine B

END OF STUDY DISSERTATION

For obtaining a Master's Degree in Chemistry

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Dedecace

Dedicate this final year project to:

To my dear **mom** and **dad,** who never stopped praying for me, supporting me, and helping me achieve my goals.

To my **siblings,**To my sister **Fatiha**

To my friend and colleague **Doua**

To everyone I love

And I dedicate it to **myself,** the girl who ended a chapter that lasted for 17 years.

To you

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To my dear **stock** and **stock**, who, thanks to them and their sacrifices,

allowed me to live this day.

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To You, **the Reader**.

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Abstract

The present work is a continuation of the research carried out by previous researchers and a modest contribution to the many attempts made by environmental scientists to eliminate toxic pollutants.

We chose diatomite from among all the natural resources because it is abundant in Algeria from Mascara (SIG), is cheaper, and has physico-chemical properties that allow its use in several applications.

Our study focused on the optimization of diatomite (Kieselguhr) for the adsorption of Rhodamine B (a pollutant).
Several properties of the diatomite were determined using characterization techniques such as X-ray fluorescence (XRF), X-ray diffraction (XRD), FTIR, and UV-vis. Two treatments were applied to the diatomite to increase its capacity to adsorb Rhodamine B: a thermal treatment in which we increased the temperature of the diatomite to several temperatures (75°C, 100°C, 150°C, and 200°C) and a chemical treatment (treatment with a mixture of H_3PO_4 and HCl). The results obtained by the two treatments showed good visible and invisible results, such as UV-vis and FTIR analyses, and the diatomite changed color from white to violet, indicating its adsorption to Rhodamine B.

Keywords: diatomite, characterization techniques, adsorption, Rhodamine B, treatments.

Résumé

Le présent travail est une continuation des recherches effectuées par les chercheurs précédents et une modeste contribution aux nombreuses tentatives faites par les scientifiques de l'environnement pour éliminer les polluants toxiques.

Nous avons choisi la diatomite parmi toutes les ressources naturelles parce qu'elle est abondante en Algérie de la Mascara (SIG), qu'elle est moins chère, et qu'elle possède des propriétés physico-chimiques qui permettent l'utilisation dans plusieurs applications.
Notre étude a porté sur l'optimisation de la diatomite (Kieselguhr) pour l'adsorption de la Rhodamine B (un polluant).

Plusieurs propriétés de la diatomite ont été déterminées à l'aide de techniques de caractérisation telles que la fluorescence X (XRF), la diffraction des rayons X (XRD),

le FTIR, et l'UV-vis.
Deux traitements ont été appliqués à la diatomite pour augmenter sa capacité à adsorber la Rhodamine B, un traitement thermique dans lequel nous avons augmenté la température de la diatomite à plusieurs températures (75°C, 100°C, 150°C, 200°C), et un traitement chimique (traitement avec un mélange de H_3PO_4 et HCl).
Les résultats obtenus par les deux traitements ont montré bons résultats visibles et invisibles, tels que les analyses UV-vis et FTIR et la diatomite a changé de couleur du blanc au violet, indiquant son adsorption à la Rhodamine B.

Mots-clés: diatomite, techniques de caractérisation, adsorption, Rhodamine B, traitements.

ملخص

يعد العمل الحالي استمرارًا للأبحاث التي قام بها الباحثون السابقون ومساهمة متواضعة في المحاولات العديدة التي يقوم بها علماء البيئة للقضاء على الملوثات السامة.

وقع إختيارنا على الدياتوميت من بين جميع الموارد الطبيعية الممتزة لوفرته في الجزائر معسكر (السيج) ويعد اقل تكلفة وذو خصائص فيزيوكيميائية ساعدت على إستعماله في عدة تطبيقات.

ركزت دراستنا على تثمين وزيادة قدرة الدياتوميت (كيسلغوهر) في إمتصاص الرودامين ب (ملوث).

تم تحديد العديد من خصائص الدياتوميت باستخدام تقنيات التوصيف مثل فلورية الأشعة السينية، وإنحراف الأشعة السينية، والأشعة الطيفية تحت الحمراء والأشعة فوق البنفسجية.

تم تطبيق معالجتين على الدياتوميت لزيادة قدرته على إمتزاز الرودامين ب، معالجة حرارية قمنا فيها بزيادة درجة حرارة الدياتوميت إلى عدة درجات (75 درجة مئوية، 100 درجة مئوية، 150 درجة مئوية، 200 درجة مئوية)، ومعالجة كيميائية (معالجة بمزيج من حمض الفوسفوريك H_3PO_4 وحمض الهيدروكلوريك HCl) .

وفي ظل النتائج التي تم الحصول عليها من المعالجتين أظهرت نتائج مرئية ولامرئية جيدة كتحاليل الاشعة الفوق البنفسجية والاشعة الطيفية تحت الحمراء وكذلك تغير لون الدياتوميت من الأبيض الى البنفسجي مما يدل على إمتزازه للرودامين ب.

الكلمات الرئيسية: الدياتوميت، تقنيات التوصيف، الإمتزاز، الرودامين ب، المعالجات.

LIST OF SYMBOLS

Symbol	Meaning	Unit
A	Absorbance	Without unit
a_s	Sips equilibrium consta	(L/mg)1/ns
C	Concentration of absorbent substance	mg/L
C_e	Equilibrium solution concentration	mg/L
C_t	Concentration of solution at time t	mg/L
C_0	Initial concentration of the solution	mg/L
K_f	Freundlich constant	$mg^{1-1/n}$/Ln/g
K_L	Langmuir constant	L/mg
K_t	Toth constant	L/mg
n_s	Sips model constant	Without unit
q_e	Quantity adsorbed at equilibrium	mg/g
q_m	Maximum coverage of the monolayer	mg/g
R^2	Coefficient of determination	Without unit
T	Temperature	K
t’	Toth model constant	Without unit
V	Volume of solution	mL
λ	Wavelength	nm
λ_{max}	Maximum wavelength	nm
EC	Effective concentraction	mg/L
LC	Lethal concentration	mg/L
t	Contact time	min
V_a	Volume of acid solution	mL
M_m	Mass molar	g/mol
d	Density	g/ml
Z	Effective Nuclear Charge	Without unit

LIST OF ABBREVIATIONS

Abbreviations	Meaning
DE	Diatomite
XRF	X-ray fluorescence spectrometry
XRD	X-ray diffraction spectrometry
UV	Ultraviolet
Vis	Visible
FTIR	Fourier transfor infrared
PH	Potential of hydrogen
SiO_2	Silicon dioxide
Al	Aluminum
Fr	Iron
Ca	Calcium
Na	sodium
Mg	Magnesium
SEM	Scanning Electron Microscopy
BET	Brunauer-Emmett-Teller
Na_2SiO_2	Sodium silicate
$SiCl_4$	Silica tetra chloride
SiO	Silicon monoxide
OH	Hydroxyl
H_3PO_4	Phosphoric acid
PH_{PZC}	PH where the net charge is zero
HCl	Hydrochloric
$C_{28}H_{31}ClN_2O_3$	Rhodamine B
CBZ	Carbamazepine
BE	Benzocaine
DCF	Diclofenac
IBU	Ibuprofen sodium salt
ACR	Acridine
BZ8	Dioxybenzone
TRI	Triallat
TCS	triclosan
ODZ	Oxadiazon
E2	β-Estradiol
EE2	17α-Ethinylestradiol
EEME	Mestranol
P4	Progesterone
BHT	Butylated
CAF	Caffeine

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General introduction

General introduction

Nowadays, water pollution has given rise to serious environmental problems. Among the different contaminants affecting the aquatic ecosystems, dyes belong to one of the larger and most important groups generally discharged in wastewaters from industrial and agricultural sectors, which present considerable toxicity to human beings and living organisms. Hence, the depollution of water from dyes has become of high priority concern. In response, several methods have been studied to assess their applicability and removal efficiency.[1]

Among these methods, adsorption especially onto activated carbon has been considered as the most effective and widely used one.

Nevertheless, due to the expensive price and difficult regeneration process of activated carbons, worldwide attention has been focused on finding out alternative adsorbents such as Diatomite. [1]

Diatomites of marine origin, whose source of silica were products of erosion of the surrounding dry land, are most characteristic for epicontinental basins of the Paleogene. Diatomites form beds in the form of layers up to 80 – 100 m thick and large lenses in sandy and sand-opoka formations. Deposits of diatomites of this type are characterized by large reserves and relatively high quality.[2]

The diatomite provides a wide variety of uses in sustainable development and environment such as purification of drinking water, filtration, insulation, adsorption, manufacture of antibiotics, catalysis, and as an additive in cement.

Algeria is considered to have rich area of natural DE, but these deposits are still little exploited, since the most important exploitation is mainly concentrated on the site of Sig in western Algeria.[1]

The present contribution aims to first highlight the physicochemical, mineralogical and textural properties of a natural diatomite from the Mascaraian deposit (SIG) using various methods: X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), Ultraviolet (UV/Visible) spectrophotometry and Furrier transform infrared spectroscopy (FTIR).

In our search warrant, we relied on the bibliographic and experimental chapter.

1) A bibliographic part, which is to subdivide:

- ✓ Chapter I: General information on diatomite and micropollutants
- ✓ Chapter II: Characterization techniques and principle of adsorption

2) An experimental part :

- ✓ Chapter III: Materials and methods
- ✓ Chapter IV: A Results and Discussion Party.

3) Finally, we finished our search with a general conclusion.

Part 01:

Bibliographic part

Chapter I:

General information on diatomite and micropollutants

In recent years, Algerian laboratories have been interested in looking for an alternative to active carbon, where diatomet has been selected to characterize it as a physiochemical characteristic, including adsorption, which helps to eliminate aquatic pollutants, such as poisoning colors for living and natural beings, so we have studied diatomet as a adsorbent and Rhodamine B as a contaminant.

I.1 General information on diatomite

I.1.1Definition:

Diatomaceous earth, also known as ***diatomite*** or kieselguhr, is a sedimentary rock formed by the accumulation of diatom shells in aquatic environments. Diatoms are unicellular algae with a siliceous shell and outer membrane.[3]

Diatomite can be white, yellowish, light gray, dark gray, or occasionally brownish gray diatomite is known for its exceptional adsorption capacity due to its high surface area and porosity, making it useful for various industrial and environmental applications.[4]

Numerous environmental conditions, including the presence of dissolved silicon, the availability of phosphorus and nitrogen, pH, salinity, and light, all affect the proliferation of diatoms.[5]

Figure 1: Photo of diatomite from the sig mine[6]

I.1.2The main diatomite deposits in Algeria:

Numerous diatomite deposits can be found in Algeria, especially in the northwest of the nation. Tahalait near Sig, Ouillis near Mostaganem, Chlef, Mohammadia, Ain Larabaa, and Hammam Bouhadjar are the most significant of these deposits. The layers in these deposits range in thickness from 20 to 50 meters.[7]

Algeria's Sig diatomite is found in the Mascara Province, which is situated in the country's northwest. Sig is located northwest of Mount Touakas and roughly 29 kilometers south of the Gulf of Arzew, divided by the Sig plains. Sig is well-known for its lush, dam-irrigated terrain. It is also a major location for mineral extraction, especially diatomite mining.[8]

- ✓ **Tahalait near Sig:**

Based on the quaternary formations and marine deposits from the Greater Miocene, we may determine the geological structure of Sig Tahalait. This plant, which is situated in the south, is thought to have 10 million tons of exploitable deposits.

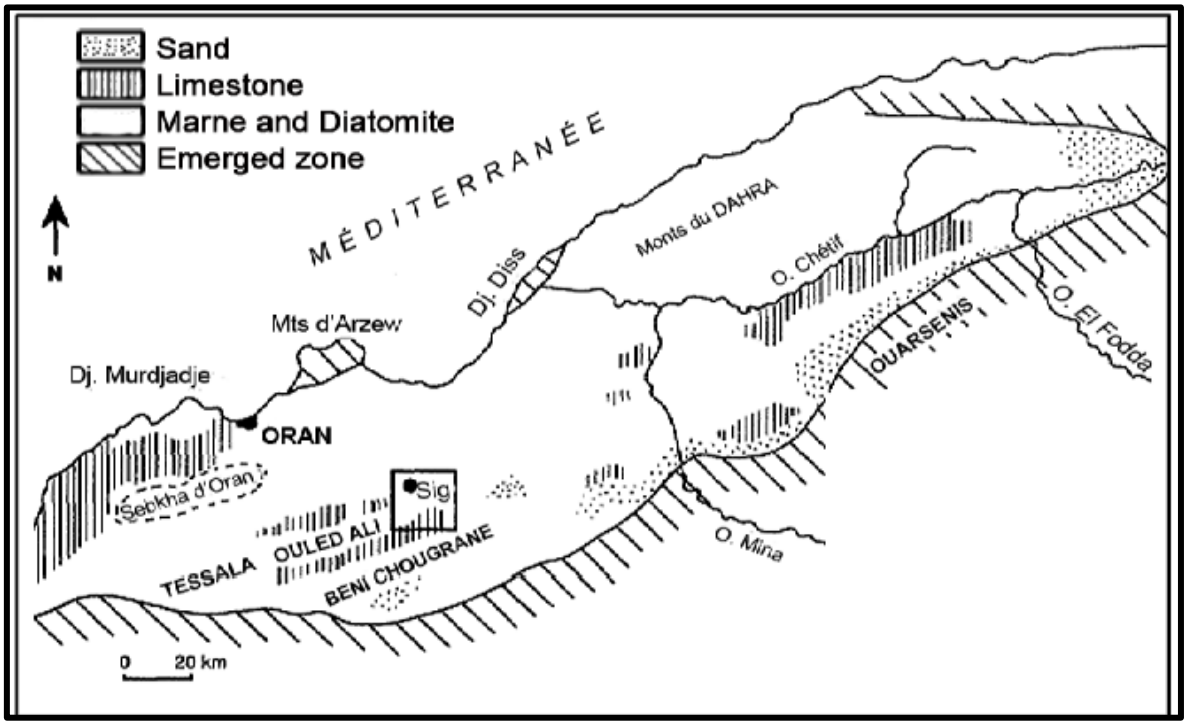


Figure 2: Geographical localization of the layer of diatomite[9]

I.1.3 Silica:

In nature, it exists in two different forms: freestanding and amorphous or crystalline. Silica is an inorganic substance, found in mixtures of silicon dioxide (SiO_2), present in a variety of minerals and bonded to other atoms (Al, Fr, Ca, Na, Mg, K, etc.). Silica makes up 60.6% of the Earth's crust and is found in various forms, including diatomaceous earth, quartz, and calcined ore. Currently, silicon (SiO_2) is mostly obtained from two sources: synthetic silicon and natural silicon. The former is produced by extracting certain stone materials in diatomaceous earth, while the latter consists of a number of key components, including dioxide (SiO_2), sodium silicate (Na_2SiO_3), and silica tetrachloride ($SiCl_4$).[10]

I.1.4 Structure of diatomite:

Diatomite's structure consists of both macroporous and mesoporous elements, with no discernible microporous structures. Silica or hydrated silica combined with mineral oxide impurities (oxides of alkali metals, alkaline earth metals, iron (Fe) , and aluminum (Al)) makes up the majority of the skeleton of diatomite. Clays such as kaolin, bentonite, and others may be present in these diatomite skeletons. The genesis and origin of diatom deposits are frequently associated with the kind and amount of mineral contaminants.[11]

The quantity of complete skeletons and their sizable fragments varies greatly across diatomites, ranging in diameter from less than 1 mm to more than 1 mm, with 10–200 m being the typical size. Generally speaking, the volume mass of a piece does not surpass 1, and for the best kinds (Dzhradzorskoe and Masel'skoe deposits) it equals 500–700 and even 250–300 kg m^3. [12]

The range of the real density is 2 to 2.66 g cm^3, or glassy to the most prevalent crystalline forms (-quartz).

The qualities of diatomites and the bedding's character are closely related to the circumstances surrounding their formation. Marine sediment contains the biggest diatomite deposits.

Diatomite is a structure that contains up to 80–90% voids and diatoms in a wide range of shapes and sizes, usually 10-200 mm.[2], [13]

Table I.1 shows the chemical composition in % of the few diatomites exploited worldwide.[14]

Table I.1: Chemical composition in % of the few diatomites exploited in the world.[14]

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	***CaO***	***MgO***	**losses**
China	82.9	5.75	1.41	0.69	0.06	0.06	0.24	0.21	7.93
Turkish	76.5	7.25	3.85	0.5	0.45	0.85	-	-	0.43
Egypt	83.6	4.24	1.07	-	-	-	6.17	-	4.86
Algeria	72.1	5.3	3.8	0.37	0.65	0.54	7.2	2.6	7.44
Jordan	72.5	11.42	5.81	-	7.21	0.96	1.48	0.25	0.64
Mexico	70.38	13.52	3.37	-	0.17	0.3	0.66	0.42	11.18
Guangdong	90.1	-	0.3	0.4	-	-	0.5	0.2	8.5
Shengzhou, Zhejiang Province, China	65	17.50	4.8	-	0.5	-	1.1	-	11.1
China	62.8	9.7	11.4	-	7.3	-	-	-	8.8
Morocco	72	7.3	4.3	-	1.8	1.2	10	1	2.4
Suizhou. China	71.35	13.26	5.5	0.08	6.7	0.11	1.94	0.15	0.91
Caldiran. Lake Van basin. Eastern Antolia. Turkey	96.7	11.5	0.65	0.65	0.8	1.4	-	-	15.3
Shengzhou. China	89.6	2.5	1.8	-	1.5	-	0.1	-	4.5

I.1.5 Diatomite Surface:

About 90% of the surface of the raw diatomite is silica. It's made from silicon oxide (SiO_2). This natural surface of diatomite contains mainly SiO silicon monoxide. Each silicon atom is bound to oxygen atoms.

The surface of silica is usually covered with OH hydroxyl groups, which play a crucial role in silica's adsorption characteristics.

There are three categories of silanols. These are isolated, giminal and close-knit silanol groups, as illustrated in the figures below.

In isolated silanol groups, the silicon atom is attached to the mass by three jumps. As for the fourth silanol, it has an isolated hydroxyl group that cannot interact with another nearby Silanol group (Figure3).

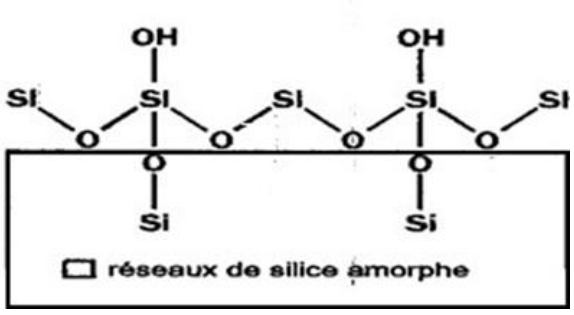


Figure 3: Structure of isolated silanol groups

Geminal silanol groups or two silanol groups are bonded to the same silicon atom

as shown in the figure below (Figure 4).

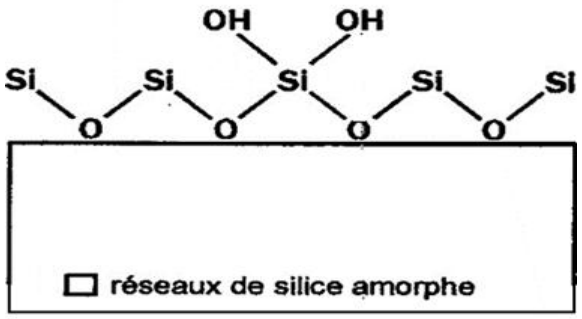


Figure 4: Structure of geminal silanol groups

Finally, two adjacent silicon atoms carry the vicinal silanol groups, as illustrated in the figure below (Figure 5).

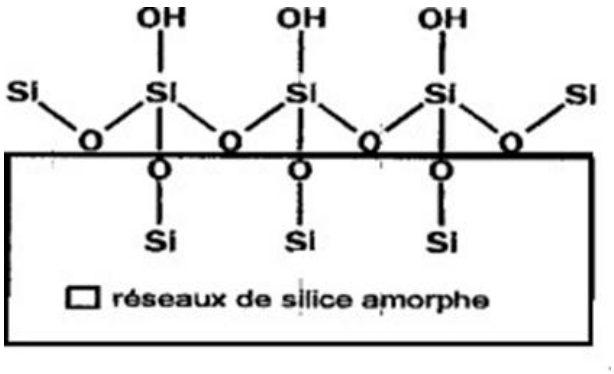


Figure 5: Structure of vicinal silanol groups

It should be mentioned that because these silanol groups can form hydrogen bonds with water, they are in charge of the silica's hydrophilic surface. Highly hydrophilic surfaces can be produced by increasing the number of silanol groups, and vice versa. Stated differently, isolated silanols thus dominate the surface that has become dehydrated.

The number of free silanols reduces as the degree of hydration rises because of an increase in binding rate .[15]

Silanols isolated and tied by H to the surface of the diatomite are bound to physically adsorbed water at room temperature. Hydroxyl silicon can dissociate into $Si\text{-}O^-$ and H^+ resulting in a negatively charged surface. Therefore, diatomite has negative electrophoretic mobility, adsorption and cation exchange properties (for example, metal cations or dyes).

The diatomite is electropositive by protonation when the pH is lower than pH_{PZC} (pH where the net charge is zero). Therefore, diatomite can have excellent adsorption capacity on cations and anions by altering the pH of the solution.

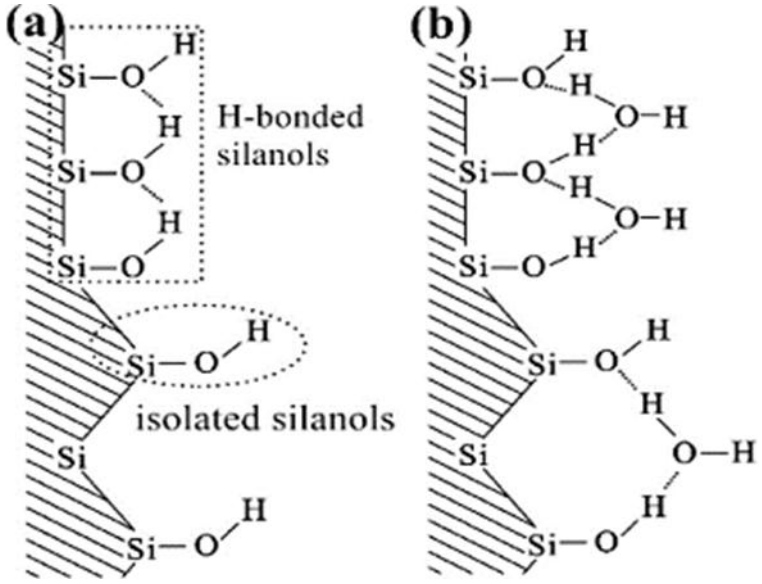


Figure 6: Hydroxyl structure on the surface of diatomite:(a) isolated,(b) bound to water physically adsorbed.[16]

Diatomite's unique physical and chemical features make it an effective adsorbent for removing heavy metals from water[17]. Adsorbates and adsorbents often interact near the water's surface. To remove heavy metals from water, diatomite requires surface modification due to its limited electronegative hydroxyl groups.

Heavy metals are prevalent in the water. Diatomite can be modified by many techniques, including calcination, acidification, and organic functionalization (organic).

Isolated silanol groups (-SiOH), the free double silanol group (--i$(OH)_2$), and -Si-OSi bridges with oxygen atoms are separated on the silica surface .[18] (Figure 6).

A large number of silanol groups (-OH) are also found on the surface of diatomite.

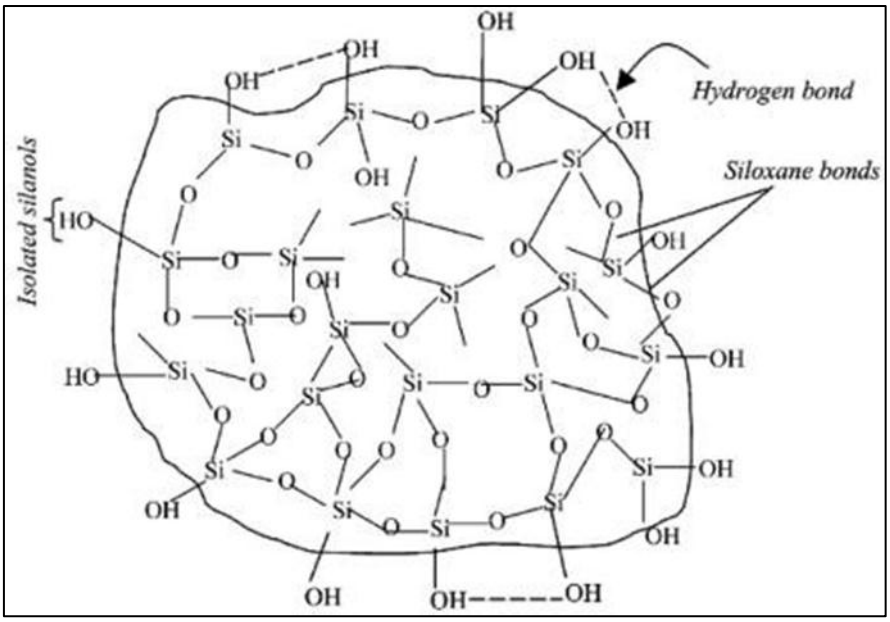


Figure 7: Different types of bonds on the surface of silica

Silanol (-OH) groups ionize in aqueous solution and gain or lose protons depending on the pH. At low pH, the diatomite is positively charged due to proton gain by the -OH group (reaction 1).

On the other hand, the surface loses protons and charges negatively at a high pH (reaction 2).

$$\equiv Si - OH + H^+ \rightarrow \equiv Si - OH_2^+ \qquad (\overrightarrow{R_1})$$

$$\equiv Si - OH + OH^- \rightarrow \equiv Si - O^- + H_2O \qquad (\overrightarrow{R_2})$$

At low pH, hydrogen ions (H^+) compete with cations (metal ions) and chemical groups on the diatomite surface, resulting in the primary adsorption process[16].

I.1.6. Properties of diatomite:

Diatomaceous earth has several distinctive properties that make it valuable for a variety of industrial, agricultural, and commercial applications.

Some of the main properties of diatomaceous earth are Porosity and permeability:

Characteristics: Diatomaceous earth is very porous, containing a network of microscopic pores and voids.

Significance: This property makes diatomaceous earth an excellent filtering material, effectively filtering liquids and gases.[19]

Porosity also contributes to its use as an absorbent material.

- ✓ ***High surface area***: Diatomaceous earth has a high surface area due to the complex structure of diatom frustrations .

Significance: The high surface area enhances the adsorption capacity of diatomaceous earth, making it useful for water purification, adsorption of pollutants, and as a carrier for catalysts.

- ✓ ***Adsorptive properties:*** Diatomaceous earth has high adsorption properties.

Significance: This property is used in applications where absorption of liquids is essential, such as cat litter, runoff absorbents, and filtration processes.

- ✓ ***Low Density:*** Diatomaceous earth has a low density.

Significance: Because of its low density, it is used in the construction industry as a lightweight aggregate and as a component of lightweight concrete.

- ✓ ***Abrasive Properties***: Diatomaceous earth can have abrasive properties.[19]

Significance: In some formulations, diatomaceous earth is used as a mild abrasive in products such as toothpaste, polishes, and facial cleansers.

- ✓ ***Insulating properties:*** Diatomaceous earth exhibits insulating properties.

Significance: This property makes diatomaceous earth suitable for the manufacture of thermal insulators, refractory materials, and refractories.

- ✓ ***Chemical stability:*** Diatomaceous earth is generally chemically stable.

Significance: This stability makes diatomaceous earth suitable for use in a variety of chemical processes, including filtration of corrosive liquids.

- ✓ ***Biological inertness:*** Diatomaceous earth is biologically inert.

Significance: The inert nature of diatomaceous earth makes it safe for use in food and beverage processing, pharmaceuticals, cosmetics, and other applications.

- ✓ ***High silica content:*** Diatomaceous earth is composed primarily of silica.

Significance: The high silica content contributes to the hardness and durability of diatomaceous earth. It is also an important factor in the filtering and adsorption capabilities of diatomaceous earth.

- ✓ ***Frictional Properties:*** Diatomaceous earth can exhibit low friction properties.

Significance: This property is relevant to certain industrial applications, such as a component in the manufacture of non-slip coatings and materials.

- ✓ ***pH Stability:*** Diatomaceous earth is generally pH stable.

Significance: The pH stability of diatomaceous earth is advantageous in applications where it is important to maintain a specific pH level , such as in water treatment processes.[19]

I.1.7. Applications and uses areas:

Removes impurities and contaminants and contributes to the purification of drinking water.

- ✓ **Food and beverage processing:**

Applications: Diatomaceous earth is used in the food and beverage industry to filter sugar, oil, beer, wine, and other beverages during processing.

- ✓ **Plastics and Rubber Industry:**

Applications: Diatomaceous earth is used as a filler in the manufacture of plastics and rubber improve mechanical properties and reduce costs.

- ✓ **Geology and Environmental:**

Applications: Analysis of diatomaceous earth deposits and diatom fossils are used in geological and environmental studies to understand past environmental conditions and changes.

- ✓ **Renewable Energy:**

Applications: Diatomaceous earth is being considered for energy storage and battery technology applications due to its unique porous structure and high surface area.

The versatility of diatomaceous earth and its ability to meet a variety of industrial needs contribute to its widespread use in a wide variety of applications across many different sectors.

Specific types of diatomaceous earth and their processing can be tailored to meet the requirements of particular applications.[19]

I.1.8. Types of diatomite:

Diatomite comes in many varieties depending on a number of variables, including composition, purity, and place of origin.

-***Typical varieties of diatomite consist of:*** Marine diatomite is derived from marine habitats such as seas and oceans.

It is composed of diatoms that have adapted to saltwater circumstances and may have a higher salt content than freshwater diatomite.

-***Freshwater diatomite:*** Usually found in lacustrine or fluvial deposits, this type of diatom is adapted to freshwater conditions and is formed in freshwater settings including lakes, rivers, and ponds.

-***High Purity diatomite:*** Because of its composition and high percentage of pure silica, this type is valuable for a variety of industrial applications. [19]

I.1.9. Treatment of diatomite:

Diatomite is treated using a variety of methods to change its structure for specific uses. Diatomite can be treated through calcination, acid treatment, alkali leaching, and nano-silica decorating.These treatments seek to change the pore structure of diatomite, making it appropriate for applications such as medication delivery systems and industrial wastewater treatment.[20]

a) **Chemical Treatment:** chemical treatment entails using chemicals to change a material's chemical makeup and physical characteristics. Chemical heat treatment is applied to metals and alloys to modify their mechanical and physical characteristics by means of regulated chemical processes.

By exposing the material to particular chemical treatments like carburizing, nitriding, and case hardening, this procedure seeks to improve properties like hardness, strength, and ductility.[21]

Chemical treatment is widely used and essential in many different sectors, especially in surface modification and water treatment procedures.

b) **Thermal Treatment**: Using heat to change a material's chemical, biological, or physical characteristics is known as thermal treatment. It includes heat-based breakdown and destruction procedures like gasification, pyrolysis, and incineration.

The application of thermal treatment is diverse and crucial in various fields, including waste management, metallurgy, and food processing.[22]

I.2.Micropollutants

I.2.1. Definition of a micropollutant:

Micropollutants are unwanted substances that may be detected in the environment at extremely low quantities (µg/L or even ng/L).

Human activity, including industrial operations, agricultural techniques, and daily activities, contributes to its existence.

Even at low concentrations, it can have harmful impacts on living creatures because to toxicity, persistence, and /or bioaccumulation.[23]

I.2.2. The toxicity of a micropollutants:

The toxicity of a micropollutants varies with the individual chemicals and amounts. According to research, micropollutants such as 1-chloro-2,4 dinitrobenzene, arsenic, and azinphos-methyl are very hazardous to aquatic creatures such as water fleas, marine microalgae, and zebrafish.

These compounds, which are widely utilized in sectors such as paint production and agriculture, pose serious threats to aquatic life and ecosystems.[24]

Furthermore, research has revealed that organic micropollutants can harm zebrafish eggs, aquatic invertebrates, and algae.

The wide spectrum of micropollutants, which includes Bisphenol A, Ciprofloxacin, Metoprolol, and Sulfamethoxazole, emphasizes the importance of complete assessment and monitoring of these compounds due to their potential negative impacts on water quality and aquatic life.[25]

Figure 8 presents the obtained results of the toxicological assessment and classification of

water samples to toxicological classes.[26]

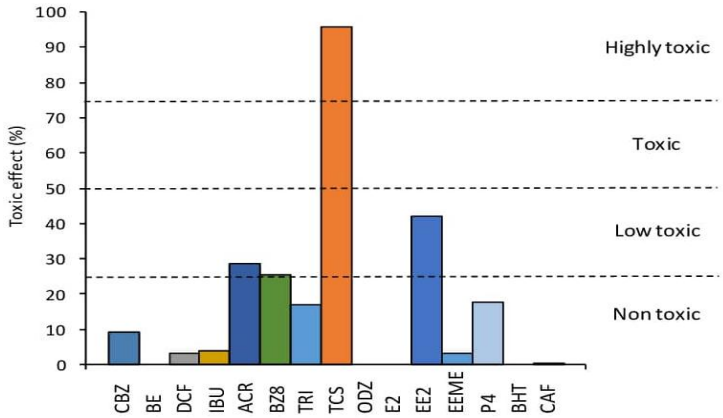


Figure 8: Toxicity of micropollutant water solutions.

I.3.Generainformation on Rhodamine B:

I.3.1. Definition of Rhodamine B:

Because of its unique properties, Rhodamine B is a fluorescent xanthene dye that dissolves in water and has a wide range of applications appears as reddish-violet powder or green crystals.[27]

It is used in water as a tracer dye to determine flow rates and directions, especially in environmental research.

Because this dye fluoresces, it can be easily and affordably detected using instruments like fluorometers.

In biology, Rhodamine B is a fluorescent staining dye that is frequently used. It is commonly used to illustrate acid-fast organisms, such mycobacterium, in conjunction with auramine O.

It is also utilized in biotechnology for applications such as fluorescence microscopy,and flow cytometry.

Rhodamine B finds use in paper printing, colored glass, and textiles because of its fluorescence properties, tunability, and stability.

However, Rhodamine B should be treated with caution as it can be hazardous, especially to the eyes, and it has the potential to cause cancer. Tight safety protocols need to be adhered.[28]

Figure 9: Rhodamine B powder.[29]

I.3.2. Caractirisation and properties of Rhodamine B:

Rhodamine B is a chemical compound with a molecular formula of $C_{28}H_{31}ClN_2O_3$ and

a molecular weight of 479.02 g/mol, appearing as a solid at 20°C.[27]

Additionally, Rhodamine B can exist in equilibrium between two forms: an "open" fluorescent form dominant in acidic conditions and a "closed" no fluorescent Spiro lactone form colorless in basic conditions.

The compound's solubility in water varies by manufacturer, reported as 8 g/L and ~15 g/L, while its solubility in alcohol, likely ethanol, is reported as 15 g/L.

Rhodamine B's fluorescence intensity decreases with increasing temperature, and it is known for its stability and fluorescence properties, making it valuable in various industries and biotechnological processes like fluorescence microscopy and flow cytometry.[30]

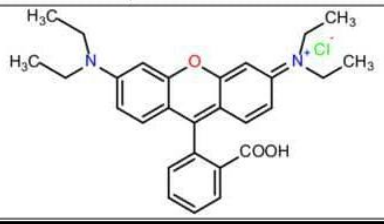
Common name	Rhodamine B
Chemical name	[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride
Chemical formula	$C_{28}H_{31}ClN_2O_3$
Molecular weight	479.017 g/mol
Adsorption maximum	545 nm
Class	Triphenylmethane
Appearance	Basic Violet 10; Brilliant Pink B
Molecular structure	

Figure 10: General properties of Rhodamine B.[31]

I.3.3. Toxicity of Rhodamine B:

Rhodamine B exhibits varying toxicity depending on concentration ; at concentrations above 10 mg/L, Rhodamine B is considered moderately toxic (80 > GI% > 50),at concentrations of 10 mg/L and 25 mg/L it is moderately toxic and at higher concentrations it becomes highly toxic.[32]

In addition, ecotoxicity studies in dicate that Rhodamine B can harm aquatic organisms, with effective and lethal concentrations (EC50 and LC50) that cause 50% toxicity ranging from

14 to 24 mg/L.[27]

Chapter II:

Characterization techniques and principle of adsorption

Chapter II: Characterization techniques and principle of adsorption

Characterization techniques are used to study and analyze the adsorption process, as well as the properties of adsorbent materials and adsorbates.

These techniques provide valuable information about the surface area, pore size distribution, surface chemistry, and adsorption capacity of materials. Some common adsorption characterization techniques include: UV-vis, FTIR, XRF, XRD.

II.1. Characterization techniques

II.1.2.X-ray diffraction (XRD):

X-ray diffraction is one of the most useful and widely used techniques for identifying the structural properties of materials.[33]

Any crystallized body can be analyzed by DRX, so this technique identifies the purity.[34]

And the nature of the crystalline phases presents in a solid. However, several crystalline mesh must be succeeded to form visible diffraction strips. If the number of mesh forming the crystallites is low, the diffraction strips will appear wide. This property allows in some cases to determine the size of the crystallites.

X-ray diffraction analysis of the prepared phase was performed using a D8 advance diffractometer (Brukeraxs).

The anti-cathode is copper (CuKα ray) with a graphite rear monochrome (tension 40 kV, courant 40 mA). Its principle is based on the selective reflection of X-rays by a crystal, using Bragg's law:

$$\boldsymbol{\lambda = 2d \sin \theta}$$

with:

λ: The wavelength of the incident beam (λ=1.5406).

d: The interreticular distance between the diffracting planes.

θ: The angle between the incidence beam and the diffracting plants.

The angle range (2θ) is between 2 and 80°. The set of measurements of the diffracted

intensities during a scan in θ is an X-ray diffraction spectrum.[33]

This equation can be used to determine the equitant of the different families of planes in the material analyze 0 imperfections in the periodicity can limit the extent of the domains diffracting in phase.

The coherent domain can be determined from Sherrer's (1918) equation:

$$d_{hkl} = \theta\lambda \cos l_{hkl} K'$$

With:

d_{hkl}**:** the length of the consistent domain in the hkl direction.

L_{hkl}**:** the half-height width of the reflection strip in question (radian).

***K'*:** a constant dependent on the device used.

λ : the wavelength of the radiation.

θ : the diffraction angle.[35]

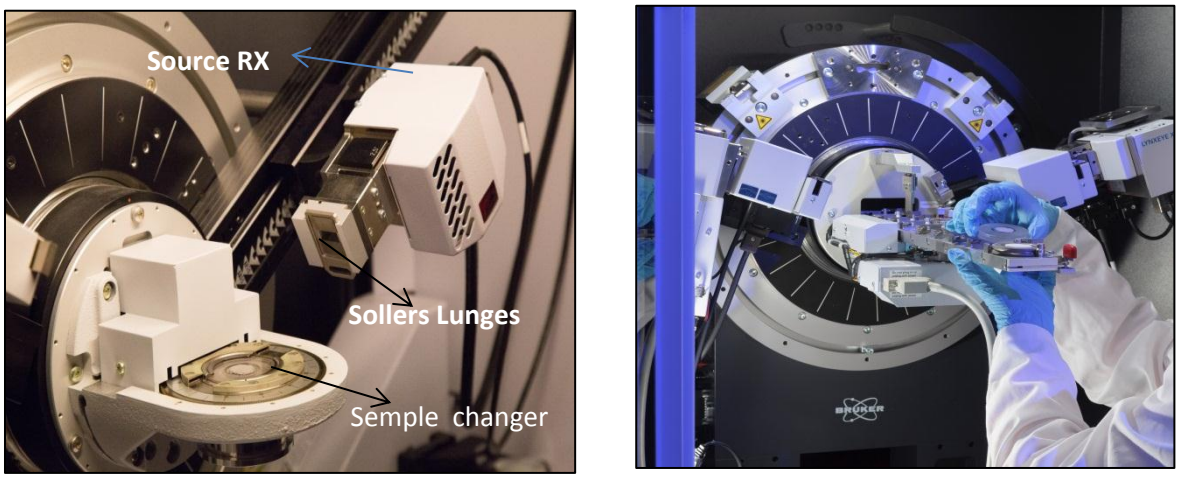


Figure 11: Apparatus in DRX-Bragg Brentano configuration.[36], [37]

II.1.3.X-Ray Fluorescence (XRF):

X-ray fluorescence spectrometry is a technique for performing non-destructive chemical analyses on rocks, minerals, sediments, and fluids.[38]

It is based on the interaction of high-energy X-rays with atoms in a sample, which results in the emission of distinctive fluorescence X-rays specific to each element.

The released X-rays are then detected and examined to identify the sample's elemental makeup. XRF operates on the concepts of ionization, electron transitions, and the emission of characteristic radiation when inner electrons are displaced and outer electrons fill the ensuing vacancies. This approach is widely utilized in many sectors such metallurgy, forensics, environmental analysis, and mining for the qualitative and quantitative examination of material composition.[23]

- **Interaction of X-rays with a Substance:**

When X-rays irradiate to a substance, some of the X-rays pass through the substance, and some are absorbed in the substance. The absorbed X-rays interact within the substance in atomic level and cause various phenomena such as scattering and releasing photons, electrons, and fluorescent X-rays (Figure 13).

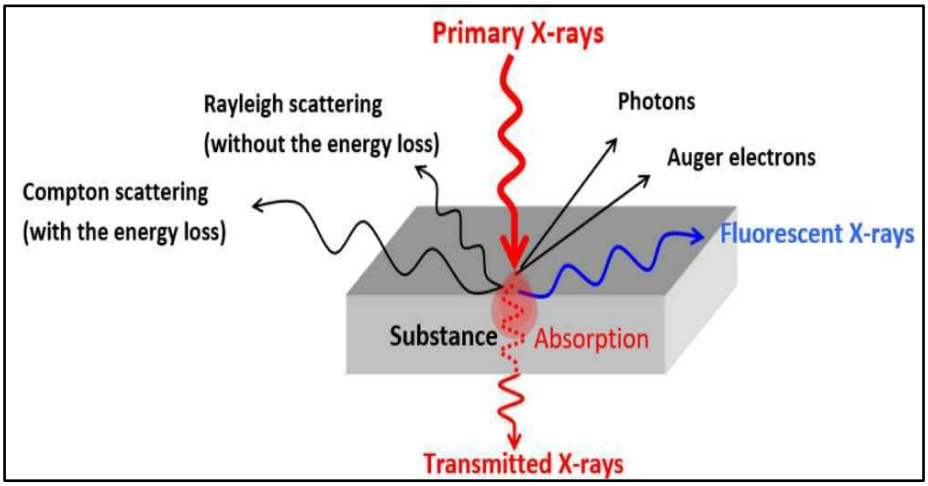


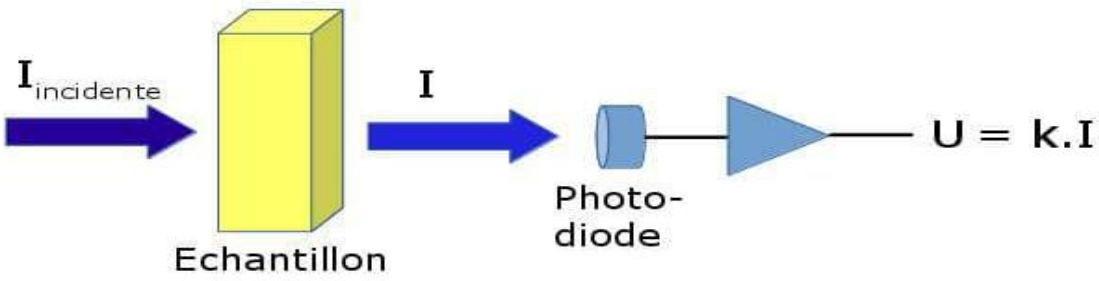
Figure 12: Interaction of X-rays with a substance.[39]

For routine X-ray fluorescence analysis, powdered sample material is fused to a glass disc. Therefore, the powered samples (grain sizes < 62 µm), as well as two Fluxana-samples are dried at ~100 °C, weighed, and melted on different heaters at temperatures between 400-1150 °C. The melt is then quenched to a glass disc and analyzed. We analyze major elements (wt% oxide) and some trace elements (ppm).[40]

Figure 13: X fluorescence spectrometer.[40]

II.1.4.UV-visible spectrophotometry:

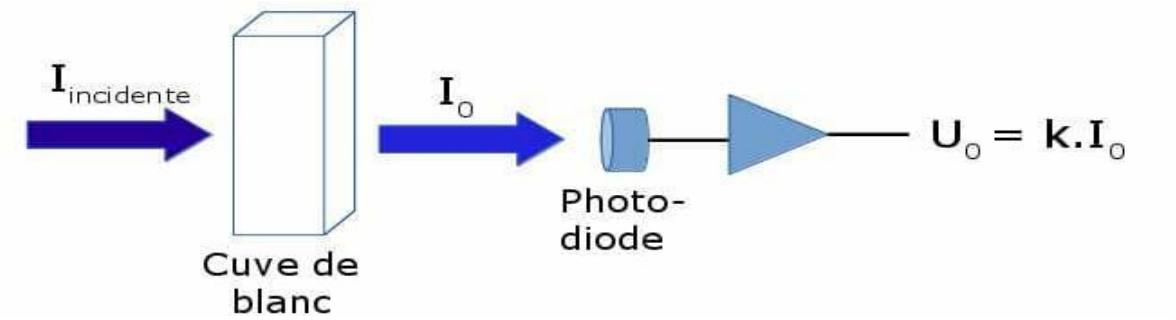
In UV-visible spectrophotometry, a quasi-monochromatic light beam is irradiated onto the sample to be analyzed and the light intensity I transmitted through the sample is measured.



This technique is widely used in chemistry. Samples are placed in solution and placed in cuvettes.[41]

They appear transparent, but both the cuvette and the solvent absorb some of the incident light. To obtain only the measured value of the sample, the effects of the cuvette and the solvent must be "subtracted".

So, we now pass the light beam through the same cell containing only the solvent and make a "white" measurement:



This measurement is always taken before the sample measurement.

(Do not allow too much time between the two measurements to minimize instrument drift errors).[41]

The light intensity 10 of the beam passing through this "blank" is greater than **I**

The absorbance of a sample is defined by the following relationship:

$$\boldsymbol{A = \log(\frac{I_0}{I})}$$

As shown in the figure, light intensity is usually converted to an electrical voltage using a photodiode (light sensor) and subsequent electronic circuitry. The absorbance is from the measured voltage:

$$\boldsymbol{A = \log(\frac{U_0}{U})}$$

II.1.5. Furrier transform infrared spectroscopy (FTIR):

This method of analysis by accumulation in a reasonable time of a large number of spectrums is based on the absorption of radiation. It allows for the identification of the chemical groups present in the prepared adsorbents. The name «forrier transformed» is based on the name of the mathematical operation that processes information collected as a spectrum. The data acquisition is controlled by software to determine the resolution and the number of spectrum accumulations (scans).[42].

The spectrum is recorded in transmission mode. The samples are prepared by mixing homogeneously in a mortar a minimal amount of the solid to be analyzed at the rate of 1mg of powder dispersed in 200 mg of KBr. The mixture has subsequently undergone high-pressure compression to obtain a very thin and sufficiently transparent material for the radiation (of 2/10 cm thickness). The final measurements are invested in these tablets, which will have been gently fixed in sample bearings positioned in front of the light beam of the analyzer.[42]

Two infrared spectrophotometers were used, namely one of the RS/1 (UNICAM) brand and another of the «Perkin Elmer» Bruker Equinox 55 type with a DTGS (Deutérium Tri-Sulfur Glyceride) detector. Spectra are recorded in the range of infrared medium wave numbers, ranging from 400 to 4000 cm^{-1}.

However, it is useful to take a brief look at a technique similar to IRTF, including diffuse reflection mode infrared transformed furry spectroscopy (DRIFT). In fact, this technique can exacerbate the surface response, so it is especially useful in the case of an adsorbent study. It was suggested in a previous study.[43] This analysis technique could be more appropriate than transmission spectroscopy (TIRT) for powder samples because it provides a quick means for analysis without any possible interference during sample preparation, just as it would be suitable for the study of, among other things, the hydroxyl region of silica or silicate minerals. In our work, we used DRIFT tests to confirm species on the studied surfaces from 400 to 4000 cm^{-1}, compared to the IRTF analysis. The samples were just placed in the powdered state in a medium inside the analysis chamber without the addition of KBr. Although spectra were not shown in this work due to the similarity of the results and beyond the detection areas of the functional groups sought. [42]

II.1.6. Brunauer-Emmett-Teller (BET) analysis :

Brunauer-Emmett-Teller (BET) analysis is a method used to determine the specific surface area of solid materials by measuring gas adsorption. It involves the physical adsorption of inert gases like nitrogen or krypton onto a solid sample, allowing for the calculation of surface area in square meters per gram (m2/g).[44]

BET analysis is crucial for characterizing various materials, including catalysts, pharmaceuticals, and nanomaterials, providing insights into reactivity and adsorption capabilities. [45]

This technique, developed in 1938, extends Langmuir theory to multilayer adsorption, enabling precise surface area determination and pore size analysis.[46]

Figure 14: BET Surface Area Analyzer.[47]

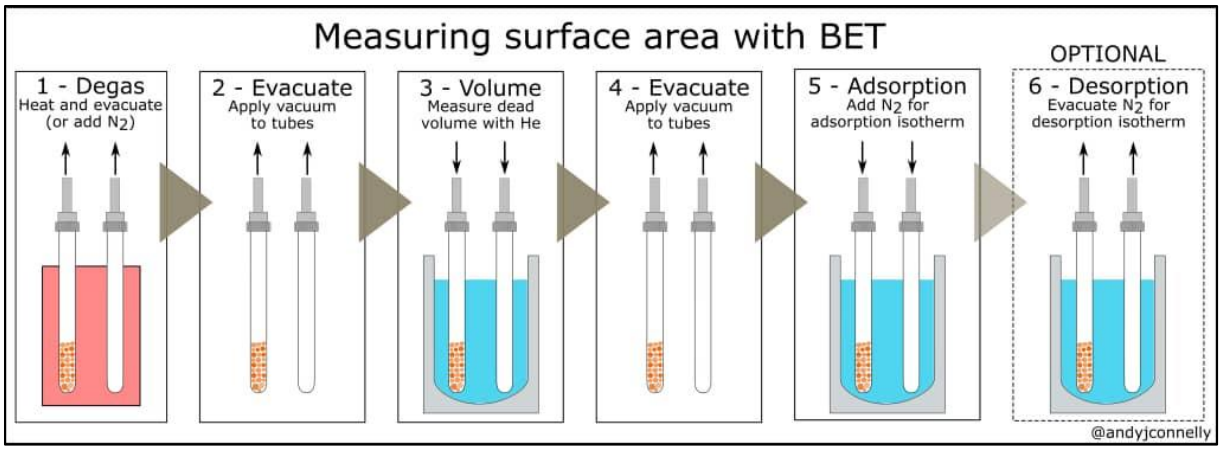


Figure 15 : Measuring surface area with BET.[48]

II.1.7. Scanning Electron Microscopy (SEM) analysis:

SEM analysis stands for Scanning Electron Microscopy analysis, a technique that utilizes a focused electron beam to scan a sample's surface, producing high-resolution images revealing topography and composition.[49]

This method is crucial in various industries like electronics, forensics, and materials science, offering detailed insights into microstructures, chemical compositions, and coatings of samples.[50]

SEM is non-destructive and provides 3D imaging, making it a powerful tool for understanding the surface characteristics of diverse materials.[50]

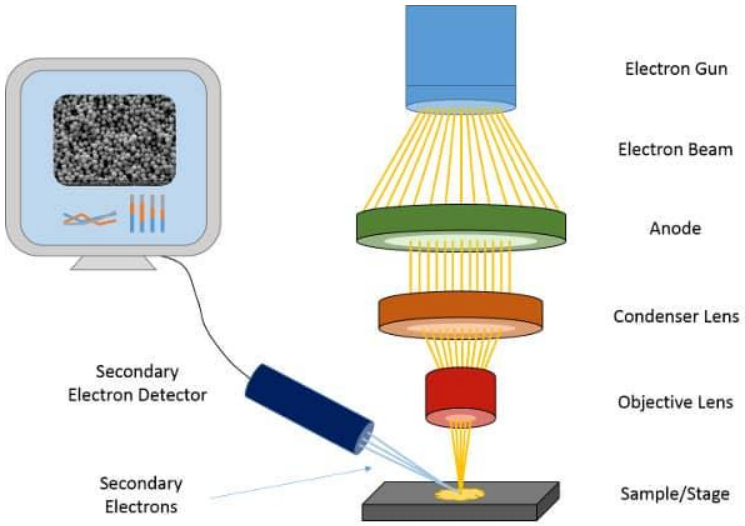


Figure 16:Schematic image of SEM components. [51]

Figure 17 : SEM instrument by Hitachi.[51]

II.1.8. Zero charge point pH:

The Point of Zero Charge (PZC) is the pH at which the net surface charge of an adsorbent is zero, crucial in adsorption studies .[52]

It's determined by the balance of positive and negative charges on a material's surface. Below the PZC, surfaces are positively charged, attracting anions, while above, they're negatively charged, attracting cations. PZC plays a vital role in environmental science, affecting adsorption of harmful ions and colloidal stability. Experimental methods like titrations are used to determine PZC accurately.[52], [53]

II.2. Adsorption

II.2.1. Definition of adsorption:

Adsorption is a surface phenomenon by which atoms, ions, or molecules (adsorbat) are attached to a solid surface (adsorbent) from a gas, liquid, or solid solution phase.[54]**.** This process creates a film of the adsorbent on the surface of the absorbent. This process differs from absorption, in which a fluid (the absorbed) is dissolved in a liquid or penetrates a solid (the absorbent). Adsorption is a surface phenomenon, while absorption involves the entire volume of the material, although adsorptions often precede absorptions.[55] The term sorption encompasses both processes, while desorption is the opposite.

However, the atoms on the surface of the adsorbent are not entirely surrounded by other atoms of the absorbent and can therefore attract adsorpts. The exact nature of the bond depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of the weak forces of van der Waals) or chimisorption, characteristic of covalent bonds. It can also occur due to electrostatic attraction.[56]

The adsorption of an adsorbent should be described in two aspects: adsorbing capacity and affinity.

The adsorption capacity is limited by the potential space of an adsorbent available for the adsorption of a given adsorbat, whereas the affinity of adsorption depends on the forces of attraction between the adsorbat and the adserbent.[57]

Adsorption is present in many natural, physical, biological, and chemical systems and is widely used in industrial applications such as heterogeneous catalysts **,** activated charcoal, the capture and use of residual heat to supply cold water for air conditioning and other process needs (adsorption coolers), synthetic resins, the increased storage capacity of derived carbon, and water purification.[14]

II.2.2. Types of adsorption:

Based on the force of interaction between the adsorbate and the adsorbent, there are two types of adsorption. [58]

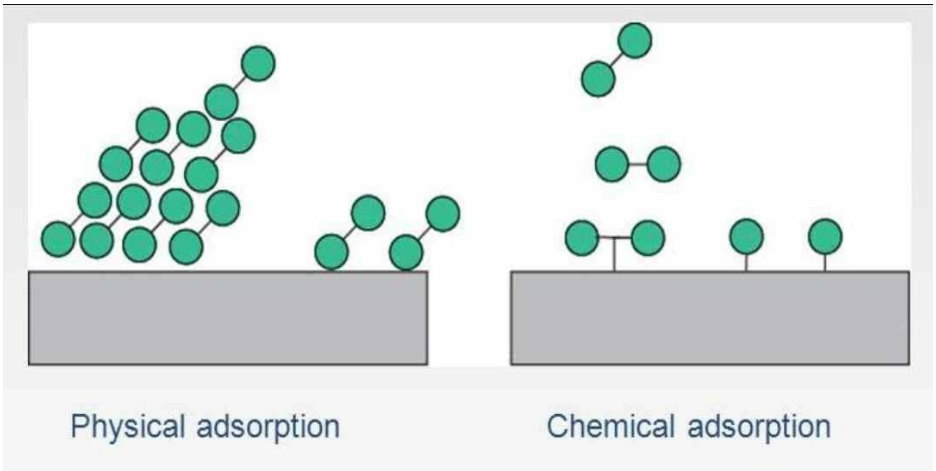


Figure 18: Types of adsorption.[58]

II.2.2.1. Chemical adsorption:

- ✓ One type of adsorption in which the surface and the adsorbate undergo a chemical reaction is called chemical adsorption. Chemisorption is another name for chemical adsorption.
- ✓ The procedure is particular in that it only takes place in the event that a chemical link forms between the both adsorbate and adsorbent.
- ✓ The essence of the procedure is irreversible.
- ✓ Chemical bonds form between the molecules of the gas and the surface of the adsorbent during chemical adsorption.
- ✓ When the temperature is low, chemical adsorption is slow.
- ✓ Additionally, it happens more frequently as pressure.
- ✓ A specific amount of energy is needed to activate chemical adsorption.
- ✓ Surface area and chemical adsorption rate are intimately correlated. When surface area increases, so does the surface area.[58]

II.2.2.2. Physical adsorption:

- ✓ A type of adsorption known as physical adsorption occurs when hydrophobic contacts, electrostatic forces, van der Waals forces, and hydrogen bonds bind the target material to a chip. Physisorption is another name for physical adsorption.
- ✓ Since any gas can be adsorbed onto the surface, there is no specificity.
- ✓ Physical adsorption is temperature- and pressure-dependent and reversible in nature.
- ✓ Weak van der Waal forces are used in physical adsorption.
- ✓ A rise in temperature causes physical adsorption to increase, and a fall in temperature causes the rate of physical adsorption to decrease.
- ✓ Energy is not needed for the activation of physical adsorption.
- ✓ An increase in surface area causes the rate of physical adsorption to rise.[58]

II.2.3. Differences between physisorption and chemisorption :

Differentiating between the two types of adsorption is not always easy.

Table II: Differences between physical and chemical adsorption.

Properties	Physical adsorption	Chemical adsorption
Adsorption energy	5 à 10 Kcal/mol	20 à 100 Kcal.mol^{-1}
Type of bond	Physical (Van der Waals)	Chemical
Desorption	More or less perfect	Difficult
Kinetics	Very fast	Slow
Surface condition	Multilayer	Monolayer

II.2.4. Adsorption mechanism:

The adsorption phenomenon involves two main parameters: adsorbate and adsorbent. [59]

Inside the adsorbent, the particles are surrounded by some kind of atoms or molecules and so all the forces acting between them are mutually balanced.[60]

The adsorbent surface's outer atoms are not. Adsorbent molecules can be attracted as they are completely surrounded by other atoms. Adsorption occurs when adsorbent atoms on the surface are not in the same environment as those in the bulk of the solution.

The surface molecules have higher energy than those in the bulk, resulting in residual attractive forces .[61]

The attractive force per unit surface area, known as surface energy, is responsible for the adsorption of metal ions on the adsorbent surface. To improve adsorption efficiency, increase the adsorbent surface area per unit mass at a specific pressure and temperature.[62]

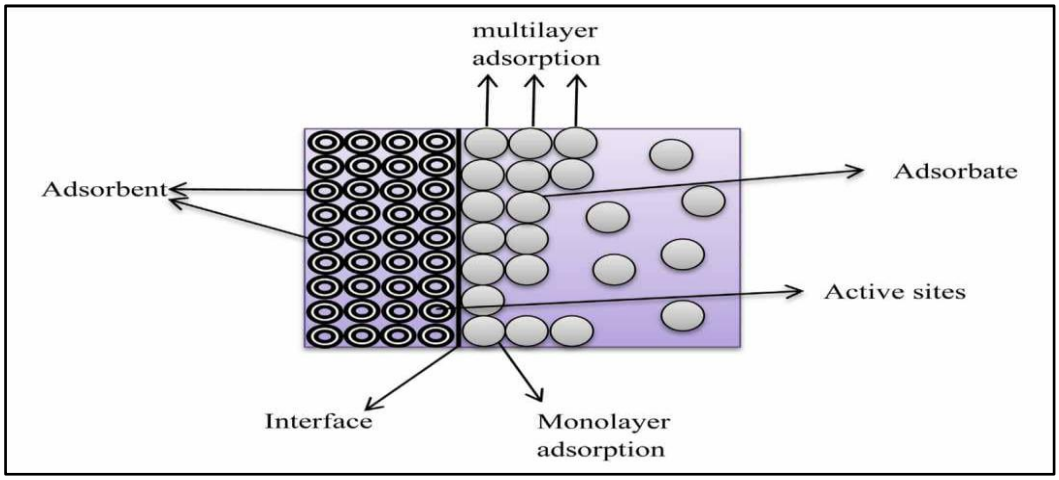


Figure 19: Schematic diagram of the adsorption process.[61]

II.2.5. Modeling adsorption isotherms:

The migration of pollutants in aqueous media and the subsequent development of containment measures have led to the use of adsorption, among other techniques.[14]

A good understanding and interpretation of adsorption isotherms is essential for the overall improvement of adsorption mechanism pathways and efficient adsorption system design .[63]

Recently, linear regression analysis has been one of the most widely used tools for defining the most suitable adsorption models, as it quantifies the adsorbate distribution, analyzes the adsorption system, and verifies the consistency of the theoretical assumptions of the adsorption isotherm model.

In parallel with the development of computer technology, the use of non-linear isotherm modeling has become widespread.

II.2.5.1. Langmuir model:

Langmuir adsorption, which was primarily designed to describe gas and solid-phase adsorption, is also used to quantify and contrast the adsorption capacities of different adsorbents. [64]

The Langmuir isotherm accounts for surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium).

Adsorption is proportional to the fraction of the adsorbent surface that is open, while desorption is proportional to the fraction of the adsorbent surface that is covered.[65]

The Langmuir equation can be written in the following linear form:

$$q_e = q_m \frac{K_l C_e}{1 + K_l C_e}$$

With

C_e**:** Equilibrium adsorbate concentration (mg. L^{-1}).

K_L: Langmuir constant ($L.mg^{-1}$).

q_m**:** Maximum adsorption capacity (mg. g^{-1}).

q_e**:** Quantity of solute adsorbed per unit mass of adsorbent at equilibrium (mg. g^{-1}).

II.2.5.2. Freundlich model:

The Freundlich isotherm is applicable to adsorption processes that occur on heterogeneous surfaces.[66] This isotherm gives an expression that defines the heterogeneity of the surface and the exponential distribution of active sites and their energies .[66]

The linear form of the Freundlich isotherm is given by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \cdot \ln C_e$$

With

K_f **:** Adsorption capacity (L/mg).

$1/n$**:** Adsorption intensity; this also indicates the relative energy distribution and heterogeneity of the adsorption sites.

C_e**:** Equilibrium adsorbate concentration (mg. g-1).

II.2.5.3. Sips model:

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms and is given the following general expression:

$$q_e = \frac{q_m a_s C_e^{\frac{1}{ns}}}{1 + a_s C_e^{\frac{1}{ns}}}$$

With

q_e**:** The quantity adsorbed at equilibrium (mg/g).

q_m**:** The maximum quantity adsorbed to form a monolayer (mg/g).

C_e**:** The equilibrium concentration (mg/L).

a_s**:** Sips equilibrium constant $(L/mg)^{1/ns.}$

***ns*:** The Sips model constant.

This model is suitable for predicting adsorption on heterogeneous surfaces, thus avoiding the limitation of increasing adsorbate concentration normally associated with the Freundlich model .

Consequently, at low adsorbate concentrations, this model reduces to the Freundlich model, but at high adsorbate concentrations, it predicts the Langmuir model (monolayer adsorption). The parameters of the Sips isothermal model are pH, temperature, and concentration-dependent [64], [67], and the isothermal constants differ by linearization and non-linear regression .

II.2.5.4. Toth model:

The toth isotherm is an empirical modification of the Langmuir equation with the aim of reducing the error between experimental data and the predicted value of equilibrium data .[68]

This model is very useful for describing heterogeneous adsorption systems that satisfy both the lower and upper limits of adsorbate concentration.[14]

The toth isotherm model is expressed as follows:

$$q_e = q_m \frac{K_t C_e}{(1 + (K_t C_e)^{t'})^{\frac{1}{t}}}$$

with

q_e**:** the quantity adsorbed at equilibrium (mg/g).

q_m**:** the maximum amount adsorbed to form a monolayer (mg/g).

C_e**:** the concentration of the solution at equilibrium (mg/L).

k_t (L/mg) and t'**:** Toth model constants.

The parameter values of the Toth model can be evaluated by the nonlinear curve fitting method using Sigma plot software.

This isothermal model has been applied to model several multilayer and heterogeneous adsorption systems.[14]

II.2.6. Factors Influencing Adsorption:

The main factors influencing the adsorption process a large number of parameters are likely to have an influence on the adsorption process of the solute in the liquid phase:

- The nature of the adsorbent [69]:
  - Specific surface area.
  - The density and nature of the functional group on its surface.
  - Pore size distribution.
- The nature of the adsorbate[70] :
  - Its molecular mass.
  - Polarity.
  - Solubility.
  - Molecule size.
  - The nature of the functional groups (acidic or basic).
- Operating conditions [71]:
  - The concentration of adsorbent and adsorbate.
  - Contact time between adsorbent and adsorbate.
  - Stirring speed.
  - Solution temperature.
  - pH of the medium.

Part 02:

Experimental part

Chapter III:

Materials and methods

III.Materials and methods

In this chapter, we did experimental research at the university laboratories (INES), where we studied the diatomite of the Sig using several characterization techniques, such as XRF, XRD, UV/visible, and FTIR.

We then relied on experimental protocols, where we treated diatomite by exposing it to heat (thermal treatment) and chemical treatment by adding acid in order to increase diatomite adsorption capacity for Rhodamine B.

- In our study, diatomite represents the adsorbent, and Rhodamine B is the adsorbate.

1.The products use:

				
Diatomite (SIG)	**Distilled water**	**Rhodamine B**	**Hydrochloric acid (HCl)**	**Phosphoric acid (H_3PO_4)**

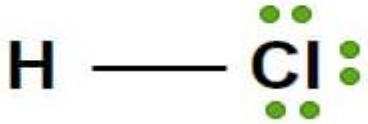
Figure 20: The products use

1.1. Definition and properties of HCl:

Hydrochloric acid (HCl) is an inorganic, colorless, highly corrosive liquid that is the aqueous solution of hydrogen chloride gas. It has a distinctive pungent odor and is a strong acid.[72], [73]

Here is a concise table summarizing the key physical and chemical properties of hydrochloric acid (HCl):

Table III.1 : physical and chemical properties of hydrochloric acid (HCl)[72]

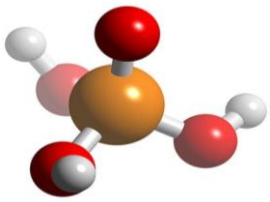
Property	**Description / Value**
Structure	
Molar mass	36.458 g/mol
Acidity	Extremely strong acid; dissociates in water to release hydrogen ions (H+) and chloride ions (Cl-)
Corrosiveness	Highly corrosive to metals, organic materials, and some plastics; requires careful handling
Solubility	Highly soluble in water and polar solvents
Reducing Agent	Acts as a strong reducing agent in certain reactions by donating electrons to other substances
Fumes	Concentrated HCl exposed to air produces white, pungent fumes of hydrogen chloride gas; irritating to eyes and respiratory system, necessitating proper ventilation
Appearance	Colorless, transparent liquid
Odor	Pungent
Boiling point	Depends on concentration
Precipitation Reactions	Used to confirm presence of specific ions in solution by forming insoluble metal chloride salts when added to solutions containing metal cations
Melting point	Depends on concentration

1.2. Definition and properties of H_3PO_4:

Phosphoric acid is (H_3PO_4) is a crucial inorganic compound, colorless, and odorless, primarily found in an aqueous solution with an 85% concentration. It is a weak acid that can exhibit both acidic and basic properties depending on its concentration. Phosphoric acid reacts with sodium hydroxide to form various salts like Na_2HPO_4, NaH_2PO_4, and Na_3PO_4. Its pH varies from highly acidic to slightly basic based on concentration.[74]

Here is a concise table summarizing the key physical and chemical properties of (H_3PO_4):

Table III.2: physical and chemical properties of (H_3PO_4).[75]

Property	**Description**
Chemical Formula	H_3PO_4
Molar Mass	97.99 g/mol
Melting Point	42.4 °C (108.3 °F)
Boiling Point	407 °C (765 °F)
Acidity	Weak acid with varying pH from 1.08 to 7.00 based on concentration; can exhibit both acidic and basic properties
Salts	Forms various phosphates like calcium phosphate, ammonium phosphate, and sodium phosphate; used in fertilizers and industrial applications
Structure	

2.Materials use:

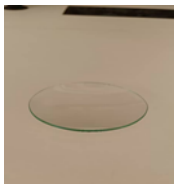
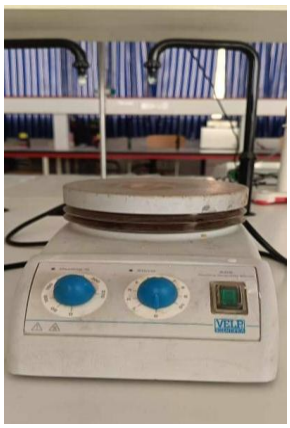
				
Spatula	**Buchner flask**	**Funnel**	**Desiccator**	**Filter paper**
				
Crucible	**Buchner funnel**	**Watch class**	**Rubber bung**	**Silver paper**
				
Measuring cylinder(100 ml, 25 ml)	**Beakers (100ml,250ml)**	**Volumetric flask (100 ml ,500 ml, 1L)**	**Vial with cap**	**Magnetic bar**

Figure 21: Materials use

3.Equipment:

			
Drying oven	**Magnetic hotplate stirrer**	**Multistirrer**	**X fluorescence spectrometer (S8 TIGER).**

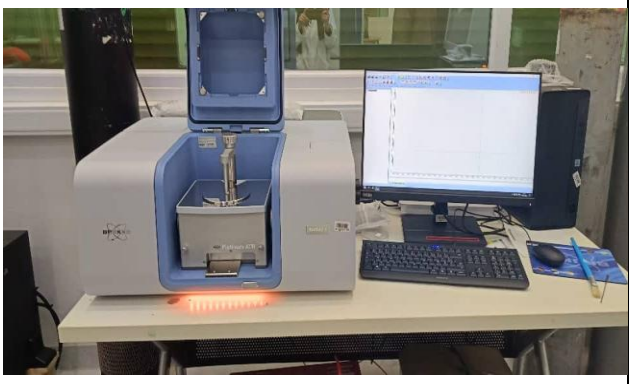
		
Furrier transform infrared spectroscopy (FTIR)(BRUKER)	**Analytical balance**	**X-ray diffraction (XRD)** (SmartLab)
		
Spectrophotometer UV-visible (OPTIZEN 2120UV)	**fume hood**	

Figure 22: Equipment.

III.1. Operating mode:

III.1.1. Thermal treatment:

- Ten grams of diatomite powder were weighed for four samples.
- Each sample was placed in the heating oven at a temperature of 75°C, 100°C, 150°C, and 200°C.
- The samples were left in the drying oven for 18 hours.
- The samples were then removed from the drying oven and placed in sealed containers.

			
Weight of diatomite	**Drying**	**Cooling**	**Preservation in vial with cap**

Figure 23 : Thermal treatment protocol

III.1.2. Chemical Treatment:

Before preparing the acidic solution, we calculate the volume of the two acids H_3PO and HCl:

$$V_0 = \frac{V_a \times M_m \times \frac{N}{Z}}{\% d \times 10}$$

V_a: Volume of acid solution

V_0: Volume of acid

M_m : Mass molar (g/mol)

d: Density (g/ml)

N: Normality

Z: Effective Nuclear Charge

%: Purity

- The acidic solution was prepared. A volume of 11.15 ml of H_3PO_4 and 43.769 ml of HCl were taken, each placed separately in a 100 ml graduated flask.
- Then, the two solutions were emptied into a 1 L graduated flask, and it was filled with distilled water to the calibration line.
- 10 grams of diatomite powder was added to 100 ml of the prepared acid solution in a beaker.
- The mixture was stirred for two and a half hours.
- The mixture was filtered using a vacuum filtration process, and the solid remains of the filtration were placed in a drying oven until dry.
- They were removed from the drying oven, weighed, and then each one was placed in an airtight container.

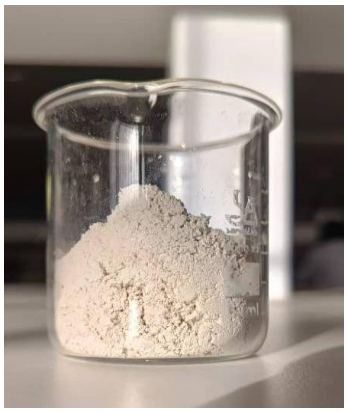
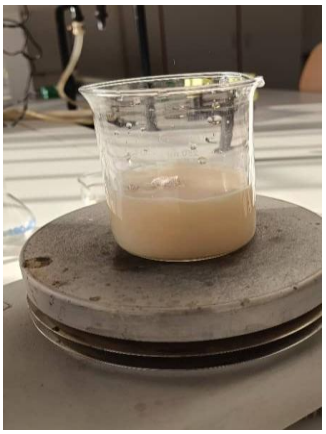
		
10g Diatomite	**Acidic solution (PH_3O_4+HCl)**	**stirrer**
		
vacuum filtration	**Drying**	**Preservation in vial with cap**

Figure 24 : Chemical treatment protocol.

III.1.3. Experimental protocol for Rhodamine B adsorption:

- Four samples of 0.5 g of diatomite powder were weighed. The samples were then treated thermally at a temperature of 200°C and four other samples of 0.5 g of diatomite powder were treated chemically.
- A solution of Rhodamine B (the stock solution) was prepared.
- 0.239 g of Rhodamine B powder was taken and placed in a 500ml graduated flask.
- The flask was then filled with distilled water to the measuring line.

Twice, four diluted solutions of the stock solution were prepared. The solutions were diluted twice, 3 times, 4 times and 5 times.

- To obtain the concentrations of the prepared solutions, we used the following dilution equation:

$$C_1V_1 = C_2V_2$$

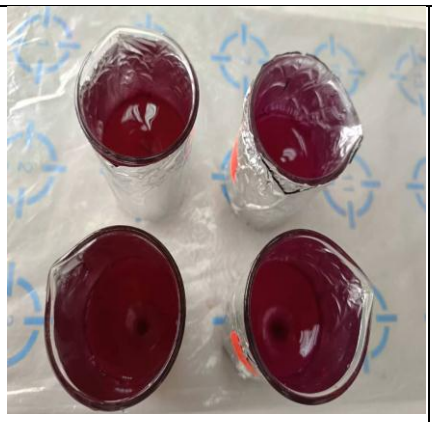
C_1: Concentration of the stock solution (mol/l).

C_2: Concentration of the daughter solution (mol/l).

V_1: Volume of the stock solution to take (ml)

V_2: Volume of the daughter solution (ml)

- Each 0.5 g of the weighed samples of diatomite powder heat-treated at 200°C was placed in 50 ml of diluted solutions (each 0.5 g in 50 ml of the solution diluted 2 times, 3 times, 4 times, and 5 times).
- The same process was then repeated for the other four weighed samples of chemically treated diatomite powder.
- The eight samples were covered and left on the stirrer for 3 hours.
- The eight samples were filtered, and the vacuum filtration products were placed in closed containers protected from light.

		
Rhodamine B (the stock solution)	**The stirrer for 3 hours**	**Vacuum filtration**

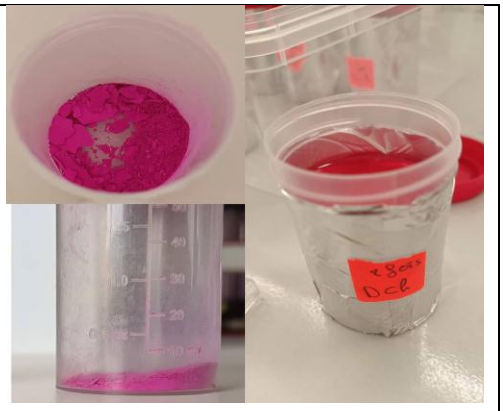
	
Drying	**Save filtration products**

Figure 25: Experimental protocol for Rhodamine B adsorption.

III.2. Characterization methods

Among the characterization analyses that can be applied to diatomite, we have done the following:

The chemical compositions of the diatomite were determined by X-ray fluorescence spectroscopy (XRF) (S8 TIGER).

X-ray powder diffraction data (XRD) were acquired with a «SmartLab» analyzer.

The Fourier infrared transform (FTIR) spectra were obtained from (BRUKER) spectrometer.

Using an ultraviolet (UV-visible) spectroscopy (OPTIZEN 2120UV) spectrometer, the concentrations and absorbance of the Rhodamine B solution were obtained.

Chapter IV:

Results and discussion

IV. Results and discussion

This chapter presents the results and discussions of the characterization of treated diatomite. and their application to the removal of Rhodamine B. We will show results of the characterization of activated diatomite and present the results of the adsorption of Rhodamine B on diatomite, with the aim of determining the best adsorption conditions by changing the physicochemical parameters (thermal and chemical treatment) and comparing adsorption capacity of Rh B on the studied material (diatomite).

IV.1. Influence of treatments:

a) Thermal treatment:

A temperature effect on diatomite was performed in the range of 75°C to 200°C.

The results are shown in Table IV.1.

Table IV.1: Diatomite mass before and after heat treatment

T (°C)	75	100	150	200
Time(h)	18	18	18	18
Weight befor treatment (g)	10	10	10	10
Weight after treatment (g)	9.89	9.77	9.42	9.34

From these results, we can see that an increase in temperature from 75°C to 200°C is accompanied by a slight decrease in the mass of diatomite.

b) Chemical treatment:

When preparing chemically treated diatomite, we observed gases being released when the acidic solution came into contact with the diatomite.

We calculated the mass loss of chemically treated diatomite after vacuum filtration.

$$\Delta m = \frac{M_i - M_f}{M_i} 100 \ (\%)$$

Where:

M_i: Initial mass of diatomite before chemical treatment (g).

M_f: final mass of diatomite after chemical treatment (g).

Table IV.2: Mass loss of diatomite after chemical treatment

	DIATOMITE (chemical treatment)
M_i (g)	10
M_f(g)	6.34
Δ_m (%)	36.6

From Table IV.2, we can observe the mass loss of chemically treated diatomite after vacuum filtration.

IV.2. Physical and chemical characterization of diatomite:

Knowledge of the physicochemical and structural properties of any material is essential to helping understand the phenomenon of adsorption.

IV.2.1. Characterization of the FRX:

The results of chemical analysis by X-ray fluorescence are shown in Table IV.3:

Note:

- Percentage of elements and oxides in diatomite.
- The viscosity value of each element-ray fluorescence spectroscopy (XRF)

Table IV.3: Geochemical composition of the natural diatomite samples of SIG section

(in Weight (%))

SiO_2	**CaO**	**Fe_2O_3**	**Al_2O_3**	**K2O**	**P2O5**	**MgO**
16,1 KCps	16,4 KCps	10,4 KCps	0,5 KCps	1,0 KCps	0,3 KCps	0,1 KCps
61,1 %	27,5 %	3,88 %	2,56 %	1,48 %	1,14 %	0,586 %

TiO2	**Cl**	**La2O3**	**SrO**	**Sum**	**Compton**
0,2 KCps	0,2 KCps	0,0 KCps	2,7 KCps		11,5 KCps
0,531 %	0,284 %	0,226 %	987 PPM	1,994	37 %

The percentages of the different elements obtained are expressed by X-ray fluorescence, which determines the chemical components of the raw diatomite in the form of oxides, and are given in Table IV.4. The chemical analysis of the raw diatomite shows the predominance of silica (61.1%), calcium oxide and ferric oxide at (27.5%)and (3.88%), and aluminum oxide at (2.56%), while potassium superoxide, phosphorus pentoxide, magnesium peroxide, and other elements were very low.

Table IV.4: Elements of FRX Raw Diatomite

Sum	Compton	Si	Ca	Fe	K	Al
	11,5 KCps	16,1 KCps	16,4 KCps	10,4 KCps	1,0 KCps	0,5 KCps
2,793	13 %	44,4 %	40,5 %	6,67 %	2,39 %	1,98 %

P	Ti	Cl	Mg	La	Sr
0,3 KCps	0,2 KCps	0,2 KCps	0,1 KCps	0,0 KCps	2,7 KCps
0,916 %	0,762 %	0,533 %	0,496 %	0,459 %	0,216 %

The FRX results show that a significant portion of the diatomite consists of several clay minerals.

IV.2.2. Characterization of the DRX:

The results of the mineralogical analysis by X-ray diffractometry of samples are listed in Figure 27:

The XRD spectra do not give an answer on the structure, given the absence of peaks.

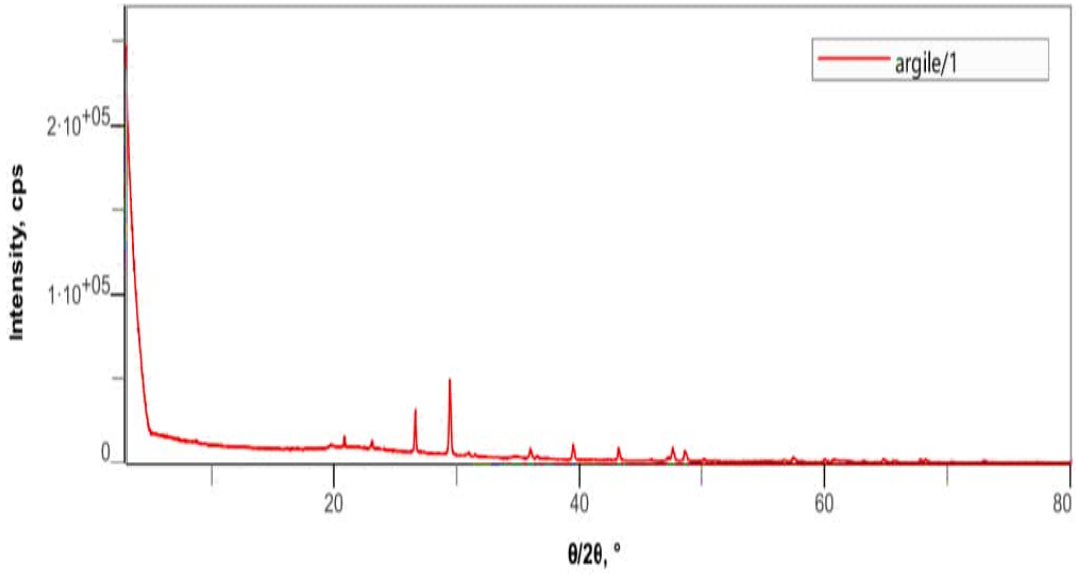


Figure 26 : XRD pattern of the diatomite sample of SIG.

In order to have a fairly complete study of the structure of diatomite and the effects of ionic exchanges with pollutants, it is essential to carry out XRD characterization before and after various thermal and chemical treatments on the one hand and before and after exchange with solutions containing pollutants on the other. As it happens, we only have the XRDs of the untreated diatomite. It is impossible to deduce any information from our XRD spectra. The comparative study will be carried out at a later date.

IV.2.3. Study of Rh B adsorption on treated diatomite:

Selecting the best diatomite for Rhodamine B adsorption in order to identify the best-treated diatomite, it was obtained in the the conditions shown in Table IV.5.
We calculated the mass loss of a chemical and thermal treated diatomite during preparation and tested its ability to adsorb Rhodamine B in the aqueous phase .

$$\Delta m = \frac{M_i - M_f}{M_i} 100\ (\%)$$

Where:

M_i: Initial mass of treated diatomite before adsorption (g).
M_f: Final mass of treated diatomite after adsorption (g).

Table IV.5: Mass loss after adsorption of Rhodamine B treated diatomite

	DIATOMITE							
	Chemical treatment				**Thermal treatment**			
Diluted solutions (Rhodamine B)	Twice	3 times	4 times	5 times	Twice	3 times	4 times	5 times
M_i(g)	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M_f(g)	0.49	0.46	0.495	0.479	0.393	0.425	0.420	0.391
Δ_m (%)	2	8	1	4.2	21.4	15	16	21.8

Note:

We observed the diatomite changing color from beige to purple, indicating the adsorption of Rhodamine B.

Figure 27 : Diatomite color before and after adsorption.

IV.2.4. Analysis by UV-Visible Spectrophotometer:

The concentration of the dyes is determined by a spectro-photometric assay using Beer-Lambert's law.[76]

$$\boldsymbol{A = \varepsilon . C . L}$$

With:

A: The absorbance (dimensionless)

ε: The molar attenuation coefficient or molar absorptivity ($L.mol^{-1}.cm^{-1}$)

L: The path length of the sample (cm)

C: The concentration of the absorbing species ($mol.\ L^{-1}$)

IV.2.4. 1. Determination of λmax:

λ_{max} is determined after scanning wavelengths between 400 and 700 nm, on a sample of dye solution with a concentration of 10 mg/L at different values of pH (acidic, basic, and free).

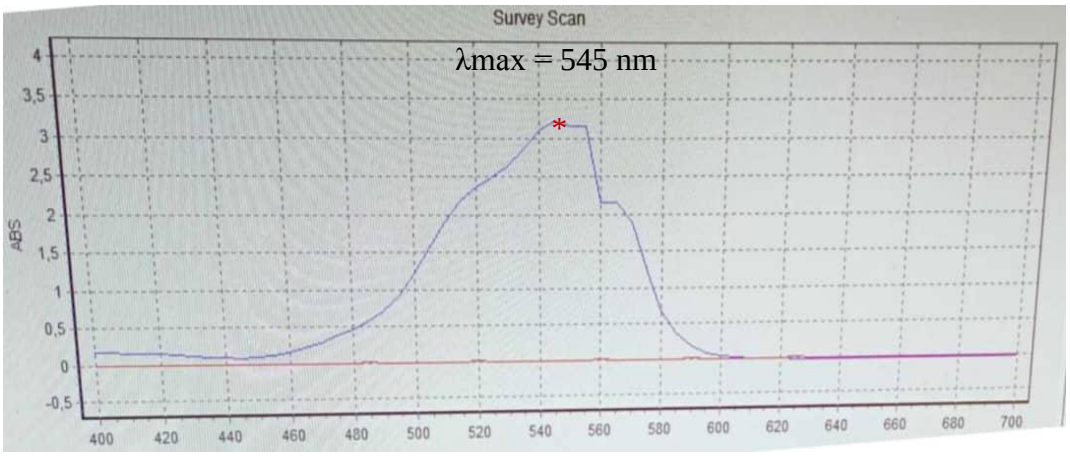


Figure 28: UV-visible spectrum of Rh B at different pH values.

Extrapolation of the results obtained gives us an absorption band at 545 nm, which is λ_{max}, for which the absorbance is maximum.

- absorbance does not depend on pH.

IV.2.4.2. Creating a calibration curve:

We created a calibration curve in the concentration range of 1.5 to 3.5PPM, prepared by diluting the stock's solution several times at free PH and room temperature and analyzing at maximum wavelength (λmax = 545 nm).The results are shown in Figure 30.

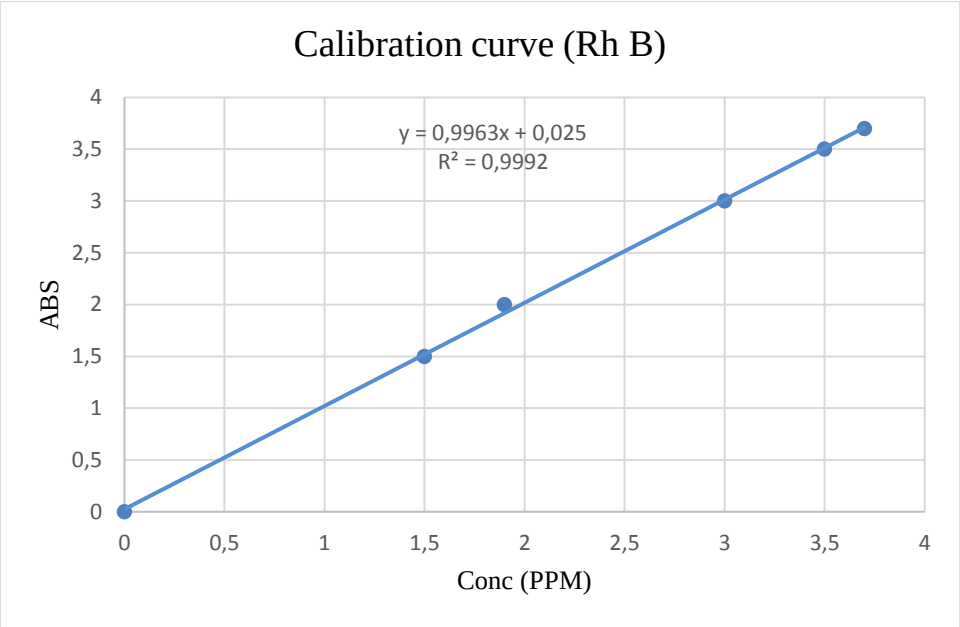


Figure 29: The calibration curve.

The curve obtained is a straight line, the equation of the line is: y=0,9963x+0,025 with a correlation coefficient of R^2 = 0.9992, which is considered a good linear fit.

The results obtained show that the Beer-Lambert law is respected up to the 3,5PPM dye concentration (a straight line is obtained).

IV.2.4.3. Results of UV-vis analyses after adsorption:

The absorbance of the Rhodamine B solution was measured after adsorption on diatomite at a maximum absorption wavelength of 545 nm. This method allows measuring the concentrations of Rhodamine B adsorbed on diatomite, and the results are shown in the following figure 31 and table IV.6 :

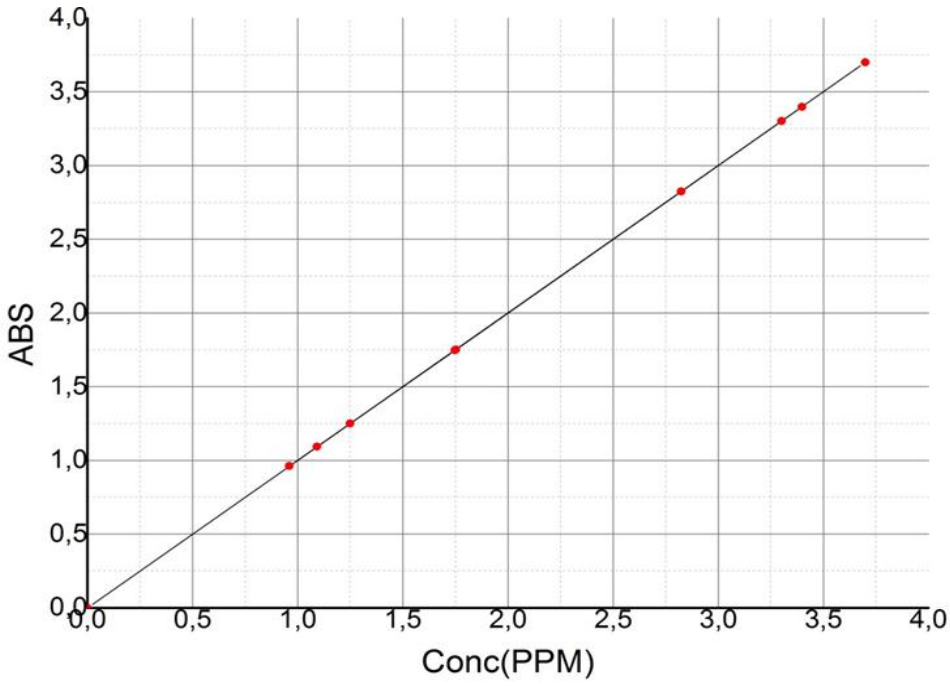


Figure 30 : Calibration curve after adsorption.

Table IV.6: Results of different concentrations and absorbance after adsorption

	Tube (B)	Twice	3 Times	4 Times	5 Times	Twice	3 Times	4 Times	5 Times	Fother solution
Abs	0	3.301	2.824	1.752	1.092	3.398	1.747	1.250	0.961	3.699
C(PPM)	0	3.301	2.824	1.752	1.092	3.398	1.747	1.250	0.961	3.699

Distilled water

Diluted solution (thermal treatment in 200°C)

Diluted solution (chemical treatment)

- The curve obtained is a straight line, the equation of the line is: y=x with a correlation coefficient of $R^2 = 1$, which is considered a good linear fit.
- We observe in a (Table IV.6), when we dilute two times, the results are similar for chemical and thermal treatment, but as we dilute the stock solution to 3 and more, we notice that the chemical solution has lower absorbance results than the thermal one, because the solution with chemically treated diatomite contains additional ingredients such as added acids, so the absorbance is lower.

IV.2.5. Characterization of the (FTIR):

The presence of the diatomite's functional groups both before and after they were used as dye adsorbent was verified using the FTIR technique. This is illustrated in the following figures:

- Analysis of these spectra shows the main bands of vibrational modes for the different functional groups in thermal-treated diatomite (200 °C) before and after adsorption of Rhodamine B.

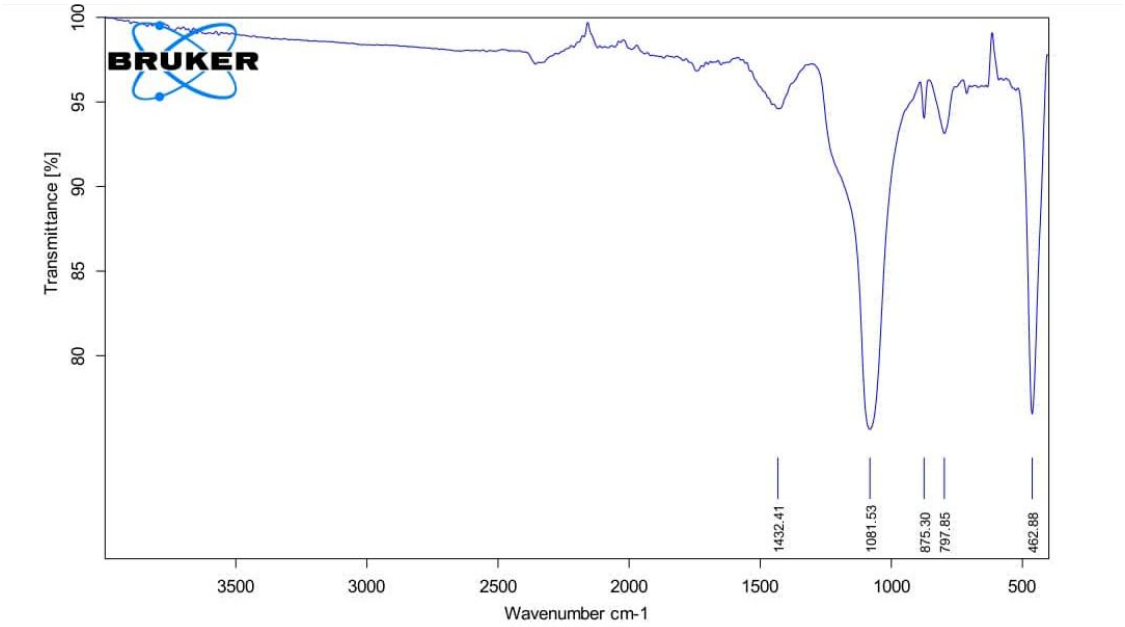


Figure 31 : FTIR spectrum of thermal-treated diatomite before adsorption of Rhodamine B.

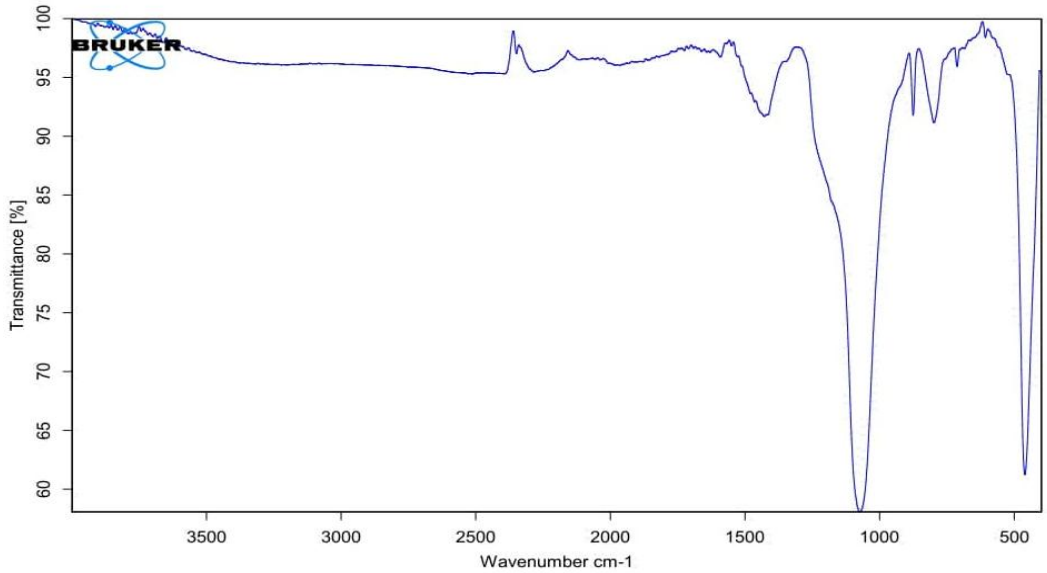


Figure 32 : FTIR spectrum of thermal-treated diatomite after adsorption of Rhodamine B.

- Analysis of these spectra shows the main ranges of vibrational modes for different functional groups in diatomite chemically treated with (HCl and H_3PO_4) before and after adsorption of Rhodamine B.

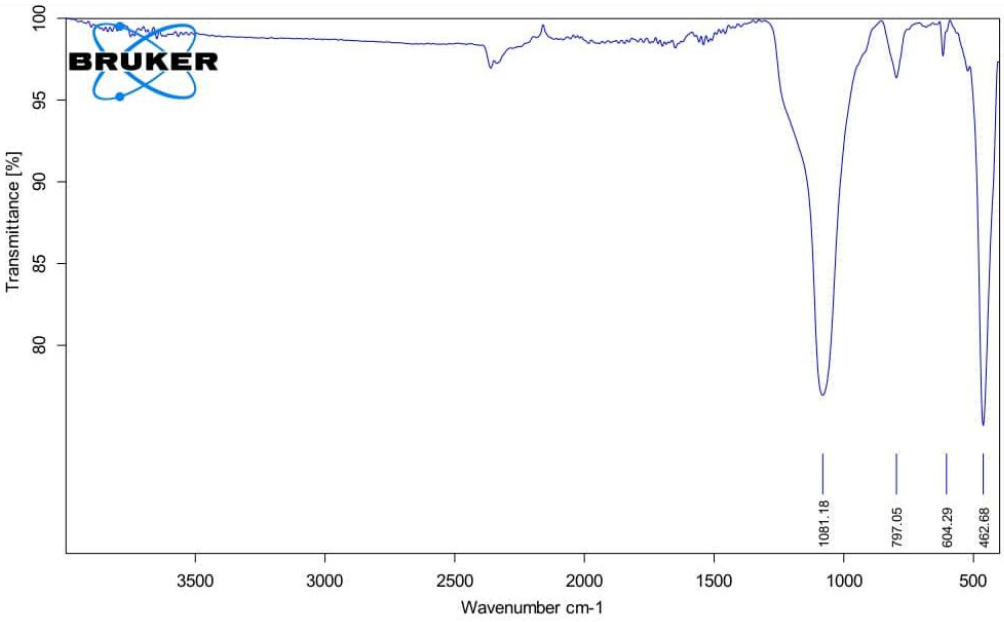


Figure 33:FTIR spectrum of chemically treated diatomite before adsorption of Rhodamine B.

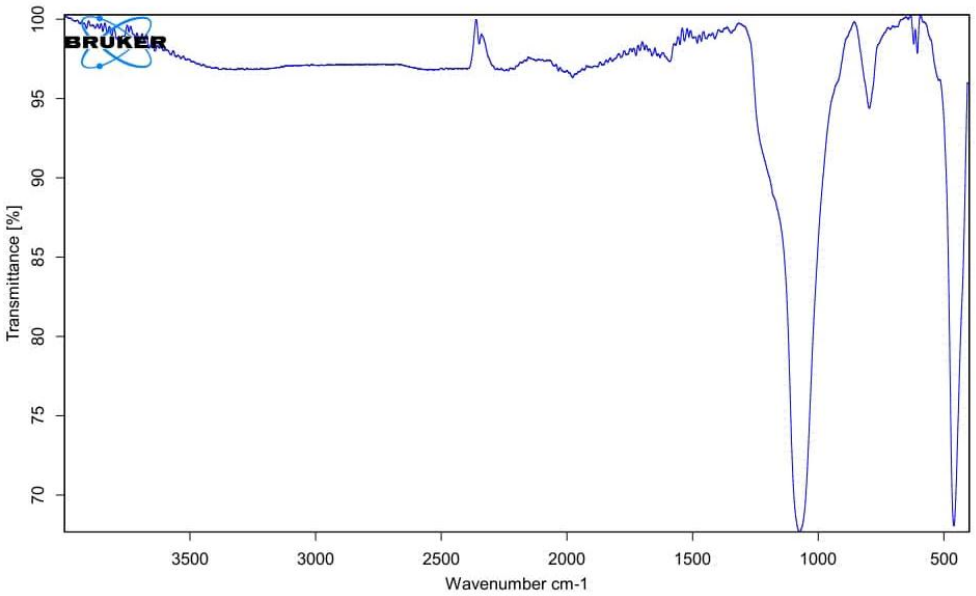


Figure 34 : FTIR spectrum of chemically treated diatomite after adsorption of Rhodamine B

The fundamental characteristic band's locations don't alter all that much. After going over the analysis data, it is evident that the diatomite characteristic peaks are located at 1432.41 cm^{-1}, 1081.53 cm^{-1}, (600-890 cm^{-1}), and 462.88 cm^{-1}.

- The carbonates IR band appears at 1432.41 cm^{-1}
- The rocking and asymmetric stretching vibration band of siloxane (–Si–O–Si–) in diatomite appears at wave numbers 1081.53 cm^{-1}.
- Other bands at (600-890 cm^{-1}) and 462.88 cm^{-1} are also characteristic of silica; the first one may be related to the stretching vibration of Al–O–Si (600-890 cm^{-1}) , but it can be also attributed to O–H deformation or the free silica and/or symmetric stretching in SiO–H, whereas the second band is assigned to the bending vibrations of Si–O–Si.
- At bands (1800-2500 cm^{-1}) are due to stretching vibration of the hydroxyl groups in physically adsorbed water molecules (silanol group SiO–H), and this group is responsible for the adsorption process.

Note:

Looking at these graphical analyses obtained for the diatomite before and after adsorption, we noticed some differences in the size and the transmitance of the peaks, meaning an increase in absorbent elements, indicating that the two treatments contributed significantly to catalyzing the diatomite surface for good adsorption of Rhodamine B dye.

General conclusion

The main objective of this study was to increase the effectiveness of a local product, Diatomite from SIG, Mascara, for the adsorption of a hazardous pollutant (Rhodamine B) that has harmful effects on human health and the environment. The diatomite was thermally and chemically treated and characterized by X-ray fuorescence spectroscopy (FXR), X-ray diffraction (XRD), and Fourier infrared transform (FTIR), and Ultraviolet (UV/Visible) spectrophotometry.
The treatments we used had a positive impact on our results.

- Results show that silica (SiO_2) constitutes the major component of the diatomite, along with a significant amount of carbonate (CaO) beside other minor constituents.
- When applied as an adsorbent for the Rhodamine B (RhB) dye removal study, treated diatomite samples displayed good adsorption ability, evidencing good interactions. We observed the diatomite changing color from beige to purple Rhodamine B.
- In the result of FTIR observe some differences in the size and the transmittance of the peaks for the diatomite before and after adsorption, indicate the two treatments contributed significantly to catalyzing the diatomite surface for good adsorption of Rhodamine B dye.
- The kinetic study fits perfectly with the second-order kinetic model with an excellent correlation coefficient of R^2.
- As for the results of the UV analysis of Rhodamine adsorption showed that the thermal treatment was more effective in the adsorption process than the chemical treatment due to the fact that the chemically treated diatomite was in addition to other components, namely acids, which affected the surface of the diatomite, which reduced the adsorption efficiency, unlike the thermal treatment, which only involved the intervention of heat

This study confirms the practical and economic feasibility of using this material for adsorption, as it is low-cost and environmentally friendly. It is recommended to treat it before use to increase its efficiency.

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