Ministry of Education-The world-And the sea-The science-YMinistry of Higher Education and Scientific Research

University of KasdiMerbah-Ouargla

Faculty of Mathematics and Sciences of matter

Chemistry Departement

Thesis submitted within the completion of requirements for Master's Academic Degree in chemistry
Specialization chemistry of Matter

Prepared by: ARAB Khaoula

Unitled

Development of an alternative to a specific zeolite for the filtration of petroleum filtration of petroleum derivatives

Publicly discussed before the Discussion Committee

On 03/06/2025

BECHKI Lazhar	**UKMO**	**President**
BELFAR Mohammed Lakhdar	**UKMO**	**Discussing**
ZENKHRI Louiza	**UKMO**	**Supervisor**
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HAMADA Djamila	**UKMO**	
DJARI Lebna	**UKMO**	**Economic partner representative**
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Dedication

I dedicate this work to the soul of my beloved mother, and to my dear father who has always been my support and strength. This thesis is the fruit of your continuous encouragement and efforts.

To my aunt **Nadjah Ihsini**, *and my companion throughout this journey – thank you for your love and unwavering support during every step of this path. You were always by my side, encouraging me even in the most difficult moments when I felt like giving up. I couldn't have completed this work without you.*

To my dear family – my brothers and sisters: **Manam, Arwa, Fodil, and Aicha**, *and to those dearest to my heart, my friends:* **Radhia, Aqila, Mariam, Rayane, and Nassira** *– you are the foundation that supports my life, the source of my strength and inspiration. I thank God every day for having you in my life.*

To my dear professor and supervisor, **Mrs. Louiza ZENKHRI**, *who believed in me even when I had lost faith in myself. Without your guidance and continuous efforts, this work would not have been completed.*

And to my dear professor, **Mrs. Manal Bassa**, *my companion during the practical stage of this journey – thank you for your support and motivation, even in the most difficult moments. I couldn't have completed this work without you.*

Finally, to my dear classmates from the **Materials Chemistry Department**, *each and every one of you – thank you for your sincere support. You add a special color to my life, and I'm grateful for every moment we shared.*

With all my love and gratitude,
Khawla Ararabe

Acknowldgment

All praise is due to Allah, who perfected His blessings upon me and helped me overcome difficulties. To Him alone be all praise, first and last, outwardly and inwardly.

With the completion of this scientific work, I can only express my sincere gratitude to everyone who contributed to its accomplishment, whether directly or indirectly, and to everyone who extended a helping hand in my research journey, be it scientifically, practically, or morally.

I extend my deepest thanks and appreciation to my esteemed professor, **Professor Zenkhri Louiza**, who was an excellent supporter and guide. With her warm humanity, open-mindedness, and academic wisdom, she was able to guide me and instill in me the confidence to continue this path to its end. All gratitude for her precise guidance, valuable feedback, and continuous accompaniment.

I would also like to especially thank **Doctor Manal Bassa**, the dedicated scientific supervisor, who carefully and diligently oversaw this project and dedicated much of her time and effort to its success. May Allah reward her abundantly.

I would like to express my sincere gratitude to the esteemed members of my thesis defense jury for their invaluable time, expertise, and insightful feedback. Your presence and contributions have significantly enriched this experience. A special thank you to: Pr. **BECHKI Lazhar**, President of the jury, for overseeing the defense. Pr. **BELFAR Mohammed Lakhdar**, for his diligent discussion and engagement. Pr. **HAMADA Djamila**, for her participation as a distinguished member of the jury. Dr. **DJARI Lebna**, the Economic Partner Representative, for providing valuable insights from an industry perspective. Dr. **SAAdi Sadia**, the Incubator Representative, for contributing her expertise related to innovation and practical application.

I must also express my deep appreciation to all my professors in the Department of Chemistry, who illuminated the paths of knowledge for me and opened up horizons of understanding during my university studies. To you, I extend all respect and appreciation.

I sincerely express my profound gratitude to everyone who facilitated the practical and technical aspects of this work. The staff of the Faculty of Chemistry Lab and the Valorization of Desert Resources Lab (VPRS), in coordination with the CRAPC Lab, played a pivotal role in providing suitable conditions and necessary equipment for conducting experiments. I also want to express

my sincere thanks to those in charge of the Scanning Electron Microscope Lab and the UV-Vis Spectrometry Analysis Lab for their technical support and effective contributions.

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I would also like to express my special thanks and appreciation to the staff of the Sebaa Adrar - Sonatrach Company Lab, who welcomed me warmly and provided all means of cooperation and support. I express my deep gratitude to Ms. Moulay Fawzia, Engineer Chami Mohamed, Engineer Nikili Aida, Ms. Naili Rabie, Supervisor Qoumari Abdelhamid, Mr. Ben Amrani Abdelmadjid, and Engineer Sheikh Yekna Najem for their efforts and for the moral and technical support that had a profound impact on completing this work to the fullest.

At this juncture, I can only offer the highest expressions of thanks and gratitude to my dear family, who have been and continue to be my greatest supporters, providing material and moral support, patience, and constant encouragement. To you, I extend all my love and appreciation.

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Finally, I specifically thank myself for my patience, perseverance, and determination in facing all challenges, and for my ability to overcome difficulties, believing that the end of this road is merely a new beginning for a bigger dream and broader ambition.

Praise be to Allah for what I have accomplished, what I aspire to accomplish, and what I will achieve, God willing.

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General introduction

مقدمة

يُعدّ قطاع تكرير البترول، إلى جانب معالجة الملوثات الصناعية، ركيزتين أساسيتين في عجلة التنمية الاقتصادية لأي دولة، وتتطلب هذه القطاعات الحيوية استخدام مواد كيميائية متخصصة ذات كفاءة عالية، لعل أبرزها الزيوليت الذي يلعب دورًا محوريًا في عمليات الامتزاز والتحفيز. وتواجه العديد من الدول، بما في ذلك الجزائر، تحديًا كبيرًا يتمثل في الاعتماد على استيراد هذه المواد الحيوية من الخارج بالعملة الصعبة، ما يُثقل كاهل الميزانية ويهدد استقلالية القطاعات الصناعية الاستراتيجية.

انطلاقًا من هذا الواقع، جاء اختيارنا لموضوع هذه المذكرة ليُجسّد رؤية طموحة نحو تحقيق الاكتفاء الذاتي وتعزيز الابتكار المحلي. تهدف هذه الدراسة إلى تصنيع بديل للزيوليت ذي كفاءة عالية، لا يقتصر استخدامه على دعم عمليات تكرير البترول فحسب، بل يمتد ليشمل إزالة الملوثات العضوية مثل صبغة الميثيل البرتقالي، التي تُعدّ أحد التحديات البيئية الكبرى.

لقد توّجت جهودنا البحثية المضنية، بفضل الله، بإنتاج مادة بديلة واعدة أظهرت كفاءة مقبولة في التطبيقات المستهدفة. ولم يقتصر الأمر على ذلك، بل امتد ليشمل تطبيق عملي لهذه المادة في إحدى الشركات الوطنية الرائدة في قطاع البترول، حيث أثبتت نتائج مبهرة ورائعة، تُبشّر بآفاق واسعة لدمجها في العمليات الصناعية على نطاق أوسع. إن هذا الإنجاز ليس مجرد نتيجة بحثية، بل هو خطوة عملية نحو تحقيق قيمة مضافة للاقتصاد الوطني، وتقليل فاتورة الاستيراد، وفتح الباب أمام صناعة محلية للمواد المتقدمة.

تتوزع هذه المذكرة على ثلاثة فصول رئيسية:

يتناول الفصل الأول عموميات حول الدراسة، حيث يتم استعراض الخلفية العلمية وأهمية الزيوليت وتطبيقاته، بالإضافة إلى استعراض الدراسات السابقة ذات الصلة.

أما الفصل الثاني، فيُخصّص لعرض المواد والطرق المستخدمة في تصنيع المادة البديلة، بما في ذلك تفاصيل التركيب الكيميائي والخصائص الفيزيائية للمادة.

وأخيرًا، يقدم الفصل الثالث تحليلًا وتفسيرًا مفصلًا للنتائج التي تم الحصول عليها من التجارب المخبرية والتطبيق العملي في الشركة الوطنية للبترول، مع مناقشة كفاءة المادة البديلة وآفاقها المستقبلية.

General introduction

The petroleum refining sector, alongside industrial pollutant treatment, stands as a cornerstone of economic development for any nation. These vital industries necessitate the use of highly efficient specialized chemical materials, with zeolites being paramount due to their crucial role in adsorption and catalytic processes. Many countries, including Algeria, face a significant challenge in relying on the import of these essential materials from abroad using hard currency. This not only burdens the national budget but also threatens the autonomy of strategic industrial sectors.

Stemming from this reality, our choice of subject for this thesis embodies an ambitious vision towards achieving self-sufficiency and fostering local innovation. This study aims **to** synthesize a zeolite substitute with high efficiency, whose application is not limited to supporting petroleum refining operations but extends to include the removal of organic pollutants such as methyl orange dye, which represents a major environmental challenge.

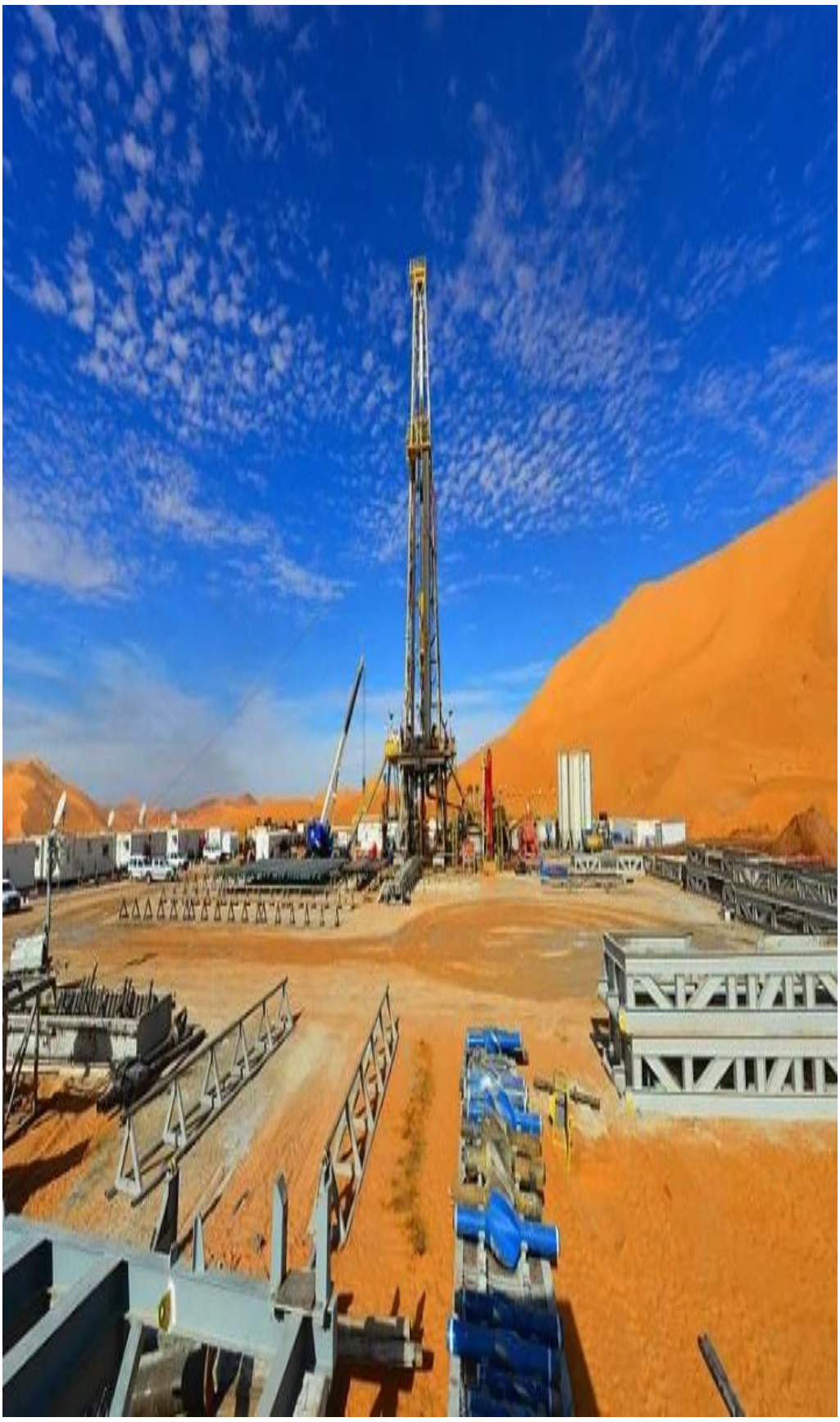
Our diligent research efforts have, by the grace of God, culminated in the production of a promising alternative material that has demonstrated acceptable efficiency in the targeted applications. Furthermore, its practical application was extended to include testing within a leading national petroleum company, where it yielded impressive and excellent results, paving the way for its broader integration into industrial processes. This achievement is not merely a research outcome; it is a practical step towards adding value to the national economy, reducing import costs, and opening doors for a local advanced materials industry.

This thesis is divided into three main chapters:

Chapter One provides a general overview of the study, reviewing the scientific background, the importance of zeolites and their applications, as well as relevant previous studies.

Chapter Two is dedicated to presenting the materials and methods used in synthesizing the alternative material, including details of its chemical composition and physical properties. Finally,

Chapter Three offers a detailed analysis and interpretation of the results obtained from laboratory experiments and the practical application in the national petroleum company, along with a discussion of the alternative material's efficiency and future prospects.



Chapter one

Generalities and previous studies

I-1 Definition of Zeolite

Natural and synthetic zeolite is a mineral found in powder or granular form, characterized by its white color, which can change if the positive ion is replaced by a transition element [1]. It belongs to the family of three-dimensional tetrahedral structures, forming symmetrical sheets characteristic of each zeolite type. These tetrahedra contain aluminum and silicon atoms at their center, with each tetrahedron carrying four oxygen atoms. Like other tetrahedra, each one carries an additional negative charge. The arrangement of tetrahedra in space forms small and large cavities interconnected by narrow channels called **windows** or **pores**, through which external molecules penetrate [2]. Zeolites are widely used in petroleum refining, petrochemical production, and the organic synthesis of important chemicals [3].

I-2 Zeolite Formula and Structure

Zeolite is a microporous crystalline aluminosilicate resulting from a regular three-dimensional sequence of TO4 tetrahedra (where T represents aluminum and silicon elements) connected by oxygen atoms. The general formula is [4]:

$$[M_x/\square(AlO_2)_x(SiO_2)_\gamma . zH_2O]$$

Where:

- **M**: represents an exchangeable cation.
- **n**: represents the valence of cation M.
- **x + y**: the total number of tetrahedra per unit cell.
- **y/x**: is the Al/Si ratio, which in all cases is greater than 1 because two aluminum atoms cannot be directly adjacent (Loewenstein's rule) and can change infinitely to a pure siliceous material (silicalite).
- **z**: the number of water molecules per unit cell.

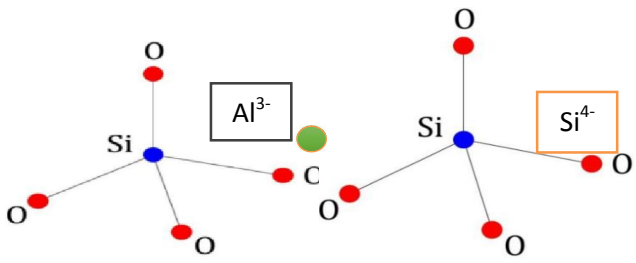


Figure 1-I: Basic building units of zeolite [5]

I-3 Zeolite History

Zeolite was first discovered in the 18th century by the Swedish scientist Axel Fredrik Cronstedt in 1756. Cronstedt observed that when a natural mineral was heated, it released a significant amount of steam, which led him to name it "zeolite" [6]. This Latin word is composed of two segments, "zeo" and "lites," meaning "boiling stone" [7]. Research continued to discover new types of natural zeolite. By 2018, 253 zeolite crystal frameworks had been identified, and over 40 natural types discovered [8, 9].

I-4 Types of Zeolite

I-4-1 Natural Zeolite

Natural zeolite forms as a result of the interaction between volcanic ash and alkaline waters over thousands of years. It's found in volcanic rocks and sediments, having formed under the influence of hot mineral waters [10]. Currently, over 40 types of natural zeolite have been discovered, including mordenite, clinoptilolite, analcime, heulandite, and others. Natural zeolite is used when a process requires high quality, but it cannot be relied upon to meet the massive demands of industry [11]. Natural zeolites are also characterized by their freedom from harmful synthetic materials [12].

Figure 2.I: The first natural zeolite, Stilbite [13]

I-4-2 Synthetic Zeolite

Due to the scarcity of natural zeolites, scientists have tried to create zeolites with similar properties [2]. Currently, over 150 types of synthetic zeolite have been manufactured, compared

to only 40 found in nature [10]. These synthetic versions are more widely used in industry; some have natural counterparts, while others possess unique structures [2]. Synthetic zeolites are known for their high purity and uniform pore structure compared to natural zeolites. They also offer the flexibility to synthesize new pore structures as needed, and their production primarily requires silicon and alumina, which are among the most abundant mineral components on Earth [14].

I-5 Zeolite Classifications

I-5-1 Zeolite Classification According to Their Chemical Composition

Smith categorized zeolites based on their different Secondary Building Units (SBUs), as presented in the table below [15, 16]:

Table I-1: Zeolite Classification According to Their Chemical Composition

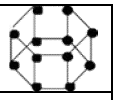
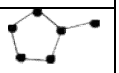
Zeolithe type	Al/Si	Exemple
Zeolithe low selica	Si /Al=1-1 ,5	A, X
Zeolithe midle silica	2,0-5,0=Al /S	,Erionte, chabazite, mordenite, X, Y,
Zeolithe high selica	Si/ Al=5-500	MFI, FER, BEA
Zeolithe under selica	∞=Al /S	Si-MFI (Silicalite-1) Si-MEL (silicalite-2, Si-ZSM-48, Si-UTD

I-5-2 Morphological Classification

Zeolites are classified according to their morphological shapes, as illustrated in the table below [17]

Table I-2: Morphological Classification of Zeolite

مثال	رقم المجموعة	عدد من رباعيالسطوح	الرمز	وحدات البناء الثانوية
Phillipsite	1	4	S4R	
Erionite	2	6	S6R	
NaA	3	8	D4R	

Faujasite	4	12	D6R	
Natrolite	5	5	T5O10 4 - 1	
Mordénite	6	6	T8O16 5 - 1	
Clinoptilolite	7	9	T10O20 4 - 4 - 1	

I-5-3 Zeolite Classification by Pore Diameter

Table (3-1) illustrates the classification of zeolites based on their pore diameter [18]

Table I-3: Zeolite Classification by Pore Diameter

التصنيف	عدد ذرات	عدد ذرات	القياسات(nm)	مثال
المسام الصغيرة	الأكسجين	Al/Si	من0.3 الى 0.45	Linde A ،Bikitaite ،TMA-E
المسام المتوسطة	8	8	من 0.45 الى 0.6	ZSM-22 ، ZSM39،Stilbite
المسام الكبيرة	10	10	من 0.6 الى 0.8	Mordentite ، Linde ZSM-12 Y ،X ،

I-6 Structural Properties of Zeolite

Zeolites possess the following key characteristics [19, 20]:

1. **Ion Exchange**

Ion exchange is a process that allows zeolites to exhibit their catalytic and adsorptive properties. It involves the replacement of positive ions within the zeolite structure with other positive ions of different valencies. Ion exchange can be achieved through several methods: contact with an aqueous or non-aqueous solution, exchange with molten salts, exchange via gaseous compounds, and ion exchange through a heat-based chemical process without a solution (a new technique for ion exchange with zeolite).

2. **Porosity and Surface Selectivity**

The porosity within the zeolite's structural framework enables it to separate mixture components based on differences in molecular size and shape. It also has a selective property, adsorbing certain substances. Thus, zeolite acts as a molecular sieve, filtering, selecting, and separating

materials from other molecules. It allows linear compounds to pass through while blocking branched compounds.

3. **Surface Acidity**

Zeolites are acidic materials (containing acidic sites within their structure) and are considered solid acids. They contain acid sites ranging from "1 to 3" milliequivalents per gram.

I-7 Petroleum Refining Processes

Crude oil is one of the most vital non-renewable natural resources, playing a strategic role in supporting the global economy due to most industrial and commercial sectors relying on it as a primary source of energy and raw materials. Crude oil consists of a complex mixture of hydrocarbon compounds, in addition to varying proportions of inorganic compounds such as sulfur, nitrogen, oxygen, and water. Given that crude oil is not suitable for direct use, there is a clear need for a series of advanced industrial operations known as **Petroleum Refining** processes. These processes aim to separate different components and convert them into usable products, such as light petroleum derivatives (gasoline, kerosene), middle distillates (diesel), and heavy products (oils and waxes). These operations rely on multiple techniques, including fractional distillation, cracking (thermal and catalytic), chemical treatment, and hydrogenation, to improve the quality of the final products and ensure their compliance with environmental and consumer standards. The refining sector is a pivotal link in the oil industry chain, playing a crucial role in meeting the increasing demand for energy and petrochemical materials in global markets [21].

I-8 Types of Zeolite Used in Petrochemical Refineries

Zeolite is primarily used as a catalyst in petroleum refining processes within refineries, especially in **Fluid Catalytic Cracking (FCC)** units. FCC is one of the most important refining operations for producing gasoline, diesel, and other high-value products from crude oil [22].

Petroleum refining organizations typically use different types of zeolite. The variety in zeolite crystal structures leads to differences in pore sizes and shapes. Among the common crystal structures are :

- **Zeolite Y:** Commonly used in hydrocarbon cracking (Figure I-3-a).

- **Zeolite ZSM-5:** Used in hydrocarbon conversion processes and the production of gasoline and diesel (Figure I-4-b).
- **Beta Zeolite:** Used in a variety of catalytic processes (Figure I-5-c).

Each structure possesses unique properties that make it suitable for specific applications in petroleum refining.

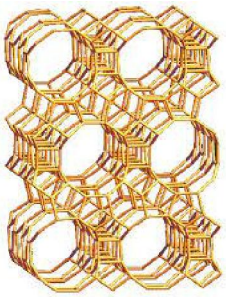


Figure I-3-a: Zeolithe Y [25]

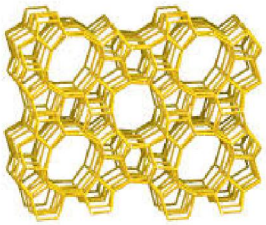


Figure I-4-b: Zeolithe ZSM_5 [24]

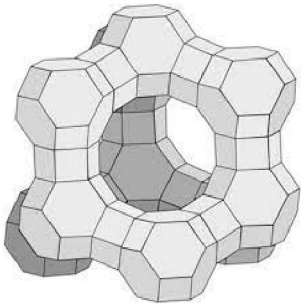


Figure I-5-c: Zeolithe Y [23]

I-9 Crude Oil Composition

Crude oil consists of a complex mixture of hydrocarbon compounds, with alkanes, alkenes, and aromatics making up about 90% of its composition. The remaining portion comprises other compounds containing sulfur, nitrogen, oxygen, and some metals. The compounds making up crude oil are divided into three categories [27]:

1. Hydrocarbon Organic Compounds
2. Non-Hydrocarbon Organic Compounds (Dissolved Impurities)
3. Insoluble Impurities (Water, Salts, and Sediment)

I-10 Crude Oil Refining Processes

Petroleum refining is an essential industrial process aimed at transforming crude oil, which is not directly usable, into a range of valuable products such as gasoline, kerosene, gas, and various oils. These operations are carried out within refineries using techniques that combine physical transformation and chemical treatment.

The petroleum refining process goes through several key stages, the most prominent of which include:

- **Dehydration and Desalting:** To remove inorganic impurities.
- **Atmospheric Distillation:** To separate components based on their boiling points.
- **Vacuum Distillation:** To extract heavy distillates.
- **Conversion Processes:** Such as cracking, especially catalytic cracking, which improves the yield of light products by using efficient catalysts like zeolite.
- **Chemical Treatment:** Including desulfurization and denitrogenation using the same catalysts, which enhances fuel quality and reduces harmful emissions.
- **Blending and Compounding:** To obtain final products with precise specifications.

These stages are crucial for meeting increasing market demands and achieving higher efficiency in utilizing petroleum resources. Furthermore, catalysts, particularly zeolite, play a pivotal role in enhancing the industrial and environmental performance of refineries [28].

I-11 Applications of Zeolite in Petrochemical Processes

Zeolite applications in petrochemical processes are extensive and diverse, owing to its unique properties such as high porosity, large surface area, and molecular selectivity. Zeolite is used as a fundamental catalyst in several industrial processes in oil refineries and petrochemicals [29].

Among its most important applications in petrochemical processes are:

I-11-1 Fluid Catalytic Cracking (FCC)

The Fluid Catalytic Cracking (FCC) unit is one of the most vital units in a refinery. It is widely used to convert large molecular weight hydrocarbon molecules into smaller ones using various catalysts, most notably Zeolite [30]. It functions to:

- Convert heavy distillates into light, high-value products such as gasoline and liquefied petroleum gas [31].
- Accelerate reactions and increase selectivity towards desired compounds [6, 31].

I-11-2 Desulfurization and Denitrogenation during Petrochemical Refining

The removal of sulfur (S) and nitrogen (N) containing compounds is a fundamental step in crude oil refining, especially for improving fuel quality and reducing polluting emissions. These processes are known as:

- **Hydrodesulfurization (HDS)**
- **Hydrodenitrogenation (HDN)**

Although traditional HDS and HDN catalysts often consist of Mo/Co or Ni/Mo on an Al_2O_3 support, zeolite has been increasingly used in these processes, particularly due to its finely porous crystalline structure, which allows it to sort molecules based on size and shape, enhancing reaction selectivity and increasing surface area.

Zeolite is not always used as a direct catalyst; it is often employed as a **support** for active metals like Ni and Mo. The zeolite support increases the selectivity and effectiveness of removing aromatic compounds containing S and N, which are difficult to crack by traditional means [7].

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Chapter two

Experimental Materials and Methods

Introduction

The objective of this chapter is to delineate the foundational chemical reagents (reactants), instrumentation, and laboratory apparatus employed in the synthesis of zeolite. Furthermore, it will elucidate the established characterization methodologies utilized to investigate the chemical and physical attributes of the subject material. The application of these methodologies enabled the interpretation and analysis of the obtained results, serving as a necessary precursor to the subsequent evaluation of the efficacy of the laboratory-synthesized zeolite in petroleum refining processes.

II.1. Chemical Materials Used (Reagent):

Table 1 provides a comprehensive overview of the reactant species utilized in the material synthesis process."

Table II-1: List of chemical reagents used in the zeolite synthesis

Reagent Name	**Molar Mass (g/mol)**	**Vendor**
NaOH	40	FISHER SCIENTHFIC
ZnO	81,38	Eisen-Golden laboratories
$CuSO_4$	159,61	HIMEDIA
$FeSO_4$	278,01	Eisen-Golden laboratories
$C_{14}H_{14}N_3NaO_3S$	327.34	HIMEDIA
Petrolum		SONATRACH

II-2 Natural ReactantMaterials

The primary sample utilized in this study consisted of clay, procured in January 2022 from the OuedEnsa region (geographical coordinates: 34°32' N, 22°20' E), situated at an elevation of 129.49 meters within the El Hadjira district of the Touggourt Province, Algeria.

We have previously familiarized ourselves with clay through a prior theoretical study in a memorandum. This clay is used in filtering turbid water, and in that study, we analyzed its physical and chemical properties. Furthermore, we examined its basic components in addition to understanding the correct method of preparing it for pure and impurity-free use

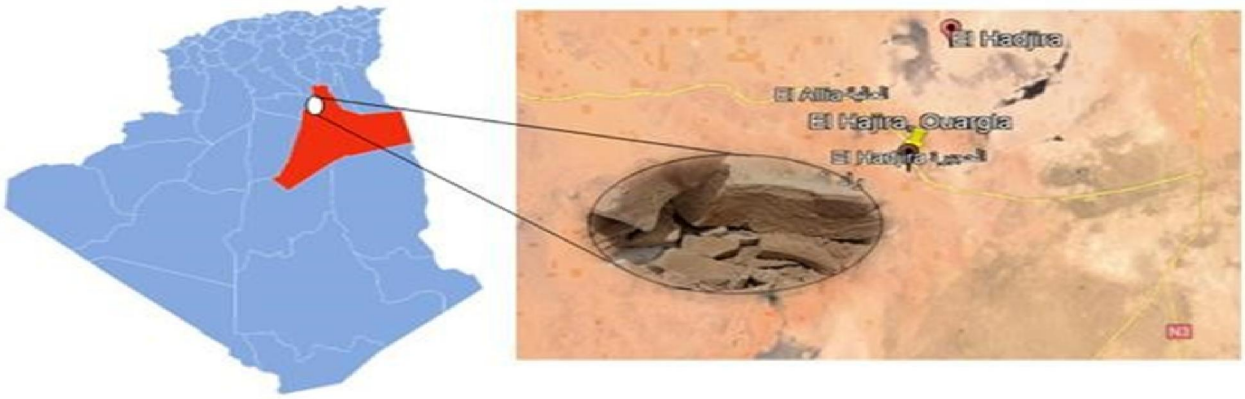

Figure II-1 : illustration of the image of the clay's location

II-3 Solvents Used in Preparation

This table provides a comprehensive list of the solvents utilized during the preparation stages of this study. For each solvent, the table details its name, chemical formula, molar mass, boiling point, and density at standard conditions. This information is crucial for understanding the chemical environment and physical parameters involved in the experimental procedures

Table II-2: Solvents Employed in the Preparation Process

Solvent Name	Chemical Formula	Molar Mass (g/mol)	Boiling Point (°C)	Density (kg/m³)
Distilled water	H_2O	18,01	100	999,9

II-4 Equipment and Apparatus

For the laboratory preparation of the sample under investigation, the subsequent equipment and apparatus were employed:

II-4-1 Laboratory Glassware

- A series of beakers of varying capacities
- Filtration funnel
- Erlenmeyer flask
- Watch glass
- Graduatedcylinder
- Volumetric pipette with bulb
- Magneticstir bar
- Filterpaper

- Laboratory flask (likely a round-bottom or Florence flask, depending on the specific use)

Figure II-2 : Laboratory Glassware Utilized in Chemical Experiments

II-4-2 Equipment

Magnetic stirrer

A magnetic stirrer was employed during the activation and extraction phases within the pedagogical laboratory of organic chemistry, situated at the Faculty of Materials Science and Mathematics, University of Ouargla.Analytical balance

Analytical balance

An analytical balance was utilized across all experimental procedures within the pedagogical laboratory of organic chemistry, Faculty of Materials Science and Mathematics.

Calcination furnace

A calcination furnace was employed for the calcination process within the pedagogical laboratory of Earth Sciences at the Faculty of Biology, El KotbEddakhil campus, University of Ouargla.

Drying oven

A drying oven was used during the activation and extraction phases within the pedagogical laboratory of organic chemistry, Faculty of Materials Science and Mathematics.

Broyeur device (likely a grinder/pulverizer)

A Broyeur device was employed for the grinding of the clay and is located in the scientific research laboratory of CRAPC, University of Ouargla.

Figure II-3: used laboratory equipment.

II-5 Physicochemical characterization techniques

Physicochemical characterization techniques represent indispensable methodologies within scientific research and industrial applications. These descriptive physical and chemical analysis techniques are fundamental for the identification of material properties and the elucidation of their behavior at the atomic and molecular scales. Through the application of these methods, a comprehensive understanding of the structural composition, physical attributes, and chemical characteristics of samples can be achieved. [1].

II-5-1 Ultraviolet (UV) absorbance or **UV absorption**.UV-visible

In this study, the UV-visible absorption spectrophotometer at Ouargla University's Scientific Research Laboratory (CRAPC) was utilized to assess the adsorption capacity of the synthesized sample for methyl orange under both light and dark conditions, in comparison to a control. This technique enabled us to determine the absorption efficiency of the prepared material. The UV-visible absorption spectrophotometer operates by preparing test solutions for analysis.

II-5-2 Fourier Transform Infrared Spectroscopy (FTIR) instrument

Fourier Transform Infrared (FTIR) spectroscopy Figure II-4 , belonging to the University of Ouargla and located in the scientific research laboratory of the Chemistry Department (VPRS)Laboratory for the Valorization and Promotion of Saharan Resources, was employed in this study for the analysis of the synthesized samples. This technique enabled us to identify the chemical bonds and functional groups present in the prepared compound.

The Fourier Transform Infrared spectrometer operates by measuring the interaction between infrared radiation and the analyzed materials. This is achieved by generating infrared radiation using a source such as a halogen lamp or a laser. These radiations are then directed towards the

sample, passing through it. At this point, some of the radiation is absorbed based on the chemical and structural properties of the sample [2].

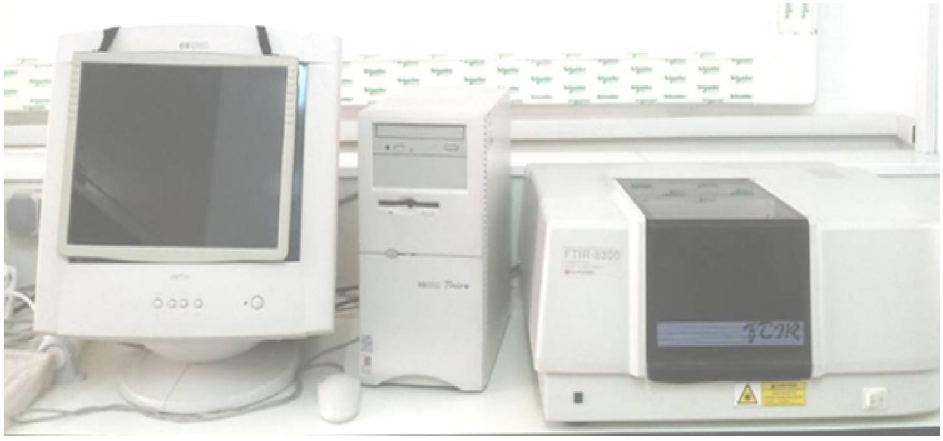

Figure II-4: **Fourier Transform Infrared Spectroscopy (FTIR) instrument**

Sample Preparation

The prepared samples were taken for analysis as follows: The initial step involved ensuring the sample was clean, dry, and free from any contaminants that could interfere with the analysis. Subsequently, the sample was placed on the sample holder. A baseline measurement was conducted using an empty sample holder to account for any background signals. Finally, appropriate measurement parameters such as the wavelength range and resolution were set, and the FTIR analysis was performed by exposing the sample to infrared radiation and recording the resulting absorption spectrum.

II-5-3 Scanning Electron Microscope (SEM)

Scanning Electron Microscopy (SEM) analysis, conducted using the instrument at the scientific research laboratory (CRAPC) of the University of Ouargla on the powder samples studied in this work Figure II-5 , provided detailed information regarding particle morphology, such as their size and shape, as well as insights into the surface's topographical characteristics, including pores, agglomerations, and crystalline structures. This allowed us to understand the material's properties and stability.

Energy-Dispersive X-ray Spectroscopy (EDS) enabled the qualitative identification of the elements present in the samples by analyzing the characteristic X-ray spectra emitted from the sample during electron beam excitation. It also provided quantitative information about the

elemental composition of the sample, determining the relative proportions of the different elements in the samples we examined.

The WEISS EVO 15 instrument is capable of capturing up to 4 individual image detectors simultaneously with a resolution of up to 32000 × 24000 pixels. It is equipped with an advanced SmartSEM control panel with a C2DX (VP, EP) SE1 detector and an (HV) SE Everhart-Thornley detector, which minimizes spurious SE3 signals and reduces charging. Furthermore, a door-mounted color navigation camera is used for navigation monitoring to guide the scanning electron microscope to the correct sample and region of interest, along with an infrared camera [3].

Figure II-5: Scanning Electron Microscope (SEM) Instrument

Sample Preparation

To ensure homogeneity and avoid bias, the sample was carefully spread on a carbon adhesive tape to guarantee a uniform distribution without excessive clumping or aggregation. Subsequently, it was coated with a thin layer of a conductive material (platinum) to dissipate charge during operation, using a Metallizer Quorum Technologies.

II-5-4 X-ray Diffraction (XRD) instrument

X-ray Fluorescence (XRF) analysis, conducted at the geology laboratory of the scientific research center at the University of Ouargla, demonstrated the remarkable capability of this

advanced technique in precisely analyzing the chemical composition of the synthesized samples. Furthermore, it enabled the identification of chemical elements and the estimation of their concentration ratios within the sample, allowing us to study composite and complex materials without altering their physical and chemical structures.

The instrument's operating principle relies on directing a focused beam of X-rays towards the sample under investigation. This interaction causes the X-ray photons to interact with the atoms constituting the material, resulting in the emission of secondary radiation known as fluorescent X-rays. Notably, each element possesses a unique energy spectrum. These emitted radiations are captured by a sensitive detector, and the resulting spectra are analyzed using advanced electronic processing systems. [4]

Figure II-6 : Depicts an X-ray spectrometer.

HighScore Plus software

"HighScore Plus is spectral data analysis software employed in X-ray Diffraction (XRD) analysis. It utilizes an extensive reference database to compare results with the chemical composition of materials. The software offers advanced tools for data analysis and refinement, including background correction and peak analysis, thereby facilitating the precise identification of chemical components.[5].

Flowchart

The flowchart outlines the sequential steps involved in the synthesis and subsequent characterization of the studied material. The process begins with a calcination step, followed by

different treatment conditions denoted by 400, 600, 800, and SEC. Each of these conditions leads to an intermediate stage labeled "Activation". Following this activation, samples are treated with varying molar concentrations (3M, 1.5M, and 4M). All treated samples then undergo a metallization process before the final characterization stage, which involves analysis using FTIR, SEM, and XRD techniques.

The Role of Catalyst Activity Analysis in RFCC

Core Purpose: This analysis is a vital laboratory procedure within oil refining, specifically in petrochemical laboratories. Its main goal is to evaluate the effectiveness of catalysts used in the **catalytic cracking process**.

Process Overview: Catalytic cracking is essential for breaking down heavy hydrocarbons (like those found in crude oil) into lighter, more valuable products such as **diesel and gasoline**. The RFCC unit is designed to handle heavier feedstocks, making the catalyst's performance even more crucial.

Regenerated Catalyst Focus: The emphasis on "regenerated" catalysts highlights that catalysts in RFCC units undergo deactivation during the cracking process (due to coke deposition, metal contamination, etc.). They are then regenerated (e.g., by burning off coke) to restore their activity. Analyzing their activity *after* regeneration is key to ensuring their continued efficiency and making informed decisions about catalyst replacement or rejuvenation.

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Microactivity Test (MAT) for Catalyst Analysis

The text refers to Figure (III-) as showing the Microactivity Test (MAT) apparatus. This is a standard laboratory test used in the refining industry to simulate the catalytic cracking process on a small scale.

Here's why MAT is crucial:

- **Simulates Real-World Conditions:** MAT units allow researchers to test catalyst performance under controlled conditions that mimic those found in commercial catalytic cracking units, though on a much smaller scale.
- **Evaluates Catalyst Activity:** It provides quick and reliable data on a catalyst's activity, selectivity, and stability. This is done by measuring the conversion of a hydrocarbon feedstock into various products over a specific time.
- **Ideal for Research & Development:** MAT is particularly useful for screening new catalysts, optimizing catalyst formulations, and assessing the impact of different operating parameters on catalyst performance.

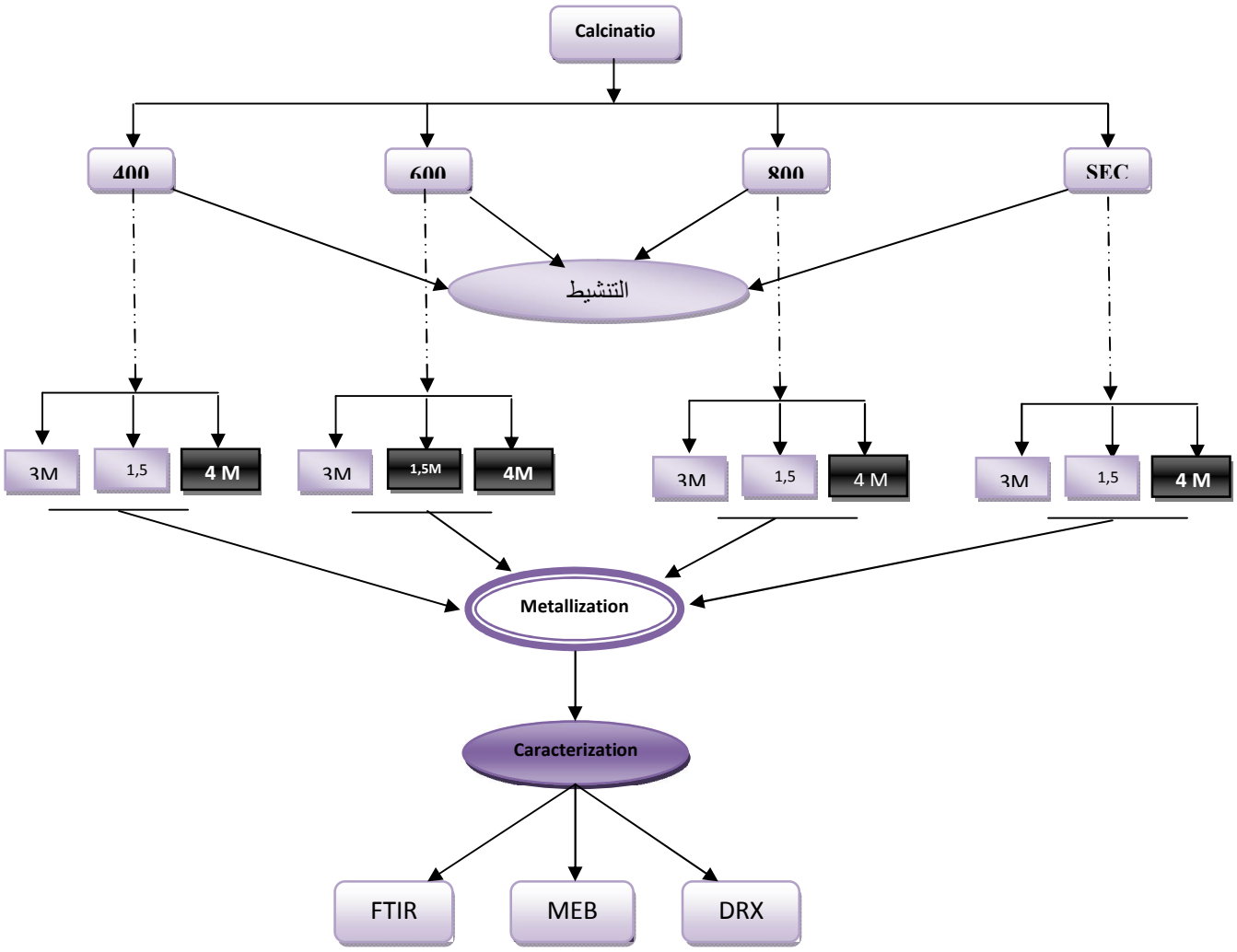
Ultraviolet Fluorescence (UVF) for Sulfur and Nitrogen Detection

The study specifically employed **Ultraviolet Fluorescence (UVF) analysis**, provided by Sonatrach's Adrar facility. This technique was used to assess the catalyst's effectiveness by monitoring its activity under controlled operating conditions and precisely tracking removal performance.

Here's how UVF spectroscopy works in this context:

- **Sensitive Analytical Technique:** UVF is a highly sensitive analytical method used to detect compounds containing **sulfur and nitrogen**. These elements are often present as impurities in hydrocarbon feedstocks and can negatively impact fuel quality and catalyst performance.
- **Fluorescent Signals:** The technique works by exposing the sample to specific UV wavelengths. If sulfur or nitrogen-containing compounds are present, they emit fluorescent signals, which are then detected and measured. The intensity of these signals is directly related to the concentration of these compounds.
- **Tracking Removal Efficiency:** In this study, UVF measurements were taken **before and after treatment with the catalyst sample**. By comparing the fluorescent signals, researchers could accurately track the **efficiency of removing sulfur and nitrogen** impurities. This is a critical indicator of the catalyst's effectiveness in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) processes, which are essential for producing clean fuels.

Ultraviolet Fluorescence (UVF)(III-)الشكل



Flowchart Illustrating the Experimental Methodology for Material Synthesis and Characterization

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Chapter three

Results and discussion

Characterization of the Raw Sample

Characterization of the Raw Sample

Introduction to Experimental Results

This chapter presents the experimental results related to the laboratory preparation of a zeolite substitute. This substitute was synthesized from a natural raw material, clay from the Oued N'sa region of Touggourt (Figure II-1). The study focused on examining the structural and morphological properties of this crystalline material, which possesses a porous structure and has diverse applications, including ion exchange, adsorption, and catalysis.

The chapter provides a detailed description of the adopted preparation methodology, along with an analysis of the results obtained using various laboratory analytical characterization techniques. These techniques included studying the crystalline chemical composition, surface structure, and essential chemical functions of the synthesized material. The discussion also addresses the extent to which these properties align with the known reference characteristics of zeolite.

Characterization of the Raw Sample

We used SEM-EDX to examine the sample's physical microstructure and elemental composition. Scanning Electron Microscopy (SEM) images (Figure III-1) clearly showed the sample consists of individual grains and possesses noticeable porosity, with pore sizes between 1 µm and 2.5 µm (at x5.00 magnification).

Further elemental analysis via Energy-Dispersive X-ray Spectroscopy (EDX) (Table III-1) revealed that silicon (Si), aluminum (Al), and sodium (Na) are the primary elements. Minor elements detected included potassium (K), calcium (Ca), magnesium (Mg), and iron (Fe). The high concentrations of silicon and aluminum indicate these are the main constituents of the clay minerals. While iron is also found in some clays, elements like potassium, calcium, magnesium, and manganese are typically present in smaller amounts, which is consistent with the characteristics of clay mineral compositions.

In short, our analysis confirms a porous clay material predominantly made of silicon and aluminum, along with smaller quantities of other elements—a typical fingerprint of clay minerals.

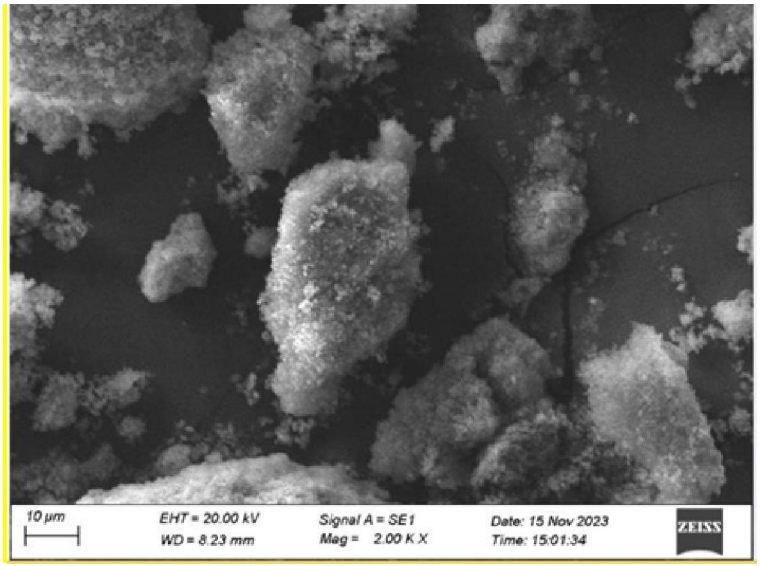


Figure III-1 : Scanning electron microscopic images of clay materials

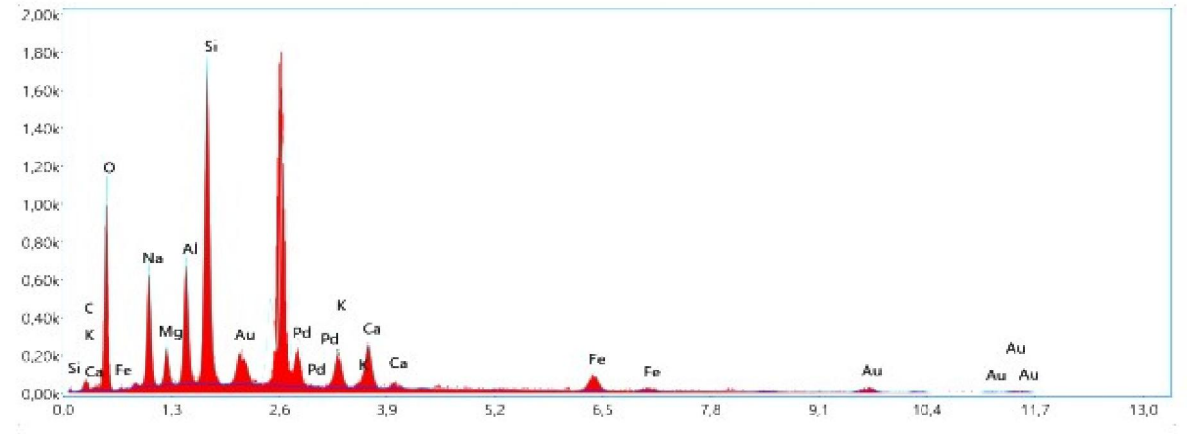


Figure III-2 : Scanning electron microscopic images of clay materials

Table III-1 : Quantitafs result of clay EDX

element	% of mass	% atomic	Intensity total
C K	0.37	0.83	0.41
O K	27.20	46.35	73.64
NaK	11.51	13.65	48.30
MgK	2.65	2.98	16.28
AlK	7.53	7.61	56.17
SiK	17.78	17.26	152.75
PdL	7.94	2.03	26.54
K K	2.86	1.99	17.15
CaK	5.17	3.52	27.21
FeK	4.06	1.98	13.69
AuL	12.92	1.79	6.02

Clay identification using FT-IR

The absorption at roughly 1650 cm^{-1}, which corresponds to the H–O–H angular deformation, confirms the presence of H_2O. The presence of this peak indicates that the clay minerals in the sample have a large surface area and are capable of adsorption of water. The vibrational band at 1950 cm^{-1} is attributed to the CO stretching, which confirms the presence of calcite. The vibration bands of valence at 3400 - 3600 cm^{-1} are characteristic of the vibration of the hydroxyl function of the water of hydration of the clay. As, we can found in the same interval vibrations of the bonding of an atom of aluminum and a magnesium atom (3582 cm^{-1}) or two aluminum atoms (3431 cm^{-1}. The bands between 800 and 750 cm^{-1} , from the Si–O–Al bond, also give way to a band around 778.4 cm^{-1} . The bands observed at 798 cm^{-1} are attributable to the Si–O–Al stretching vibrations and the hydroxyls perpendicular to the surface (translational OH). The band at 660 cm^{-1} is characteristic of the deformation vibrations of hydroxyls in trioctaedric clay minerals in general. Nevertheless, the absorption bands at 797 and 779 cm^{-1} can correspond to Quartz. The Si-O group band, intense at around 1100, 550 cm^{-1} are ascribed to binding valence vibration in clay minerals.

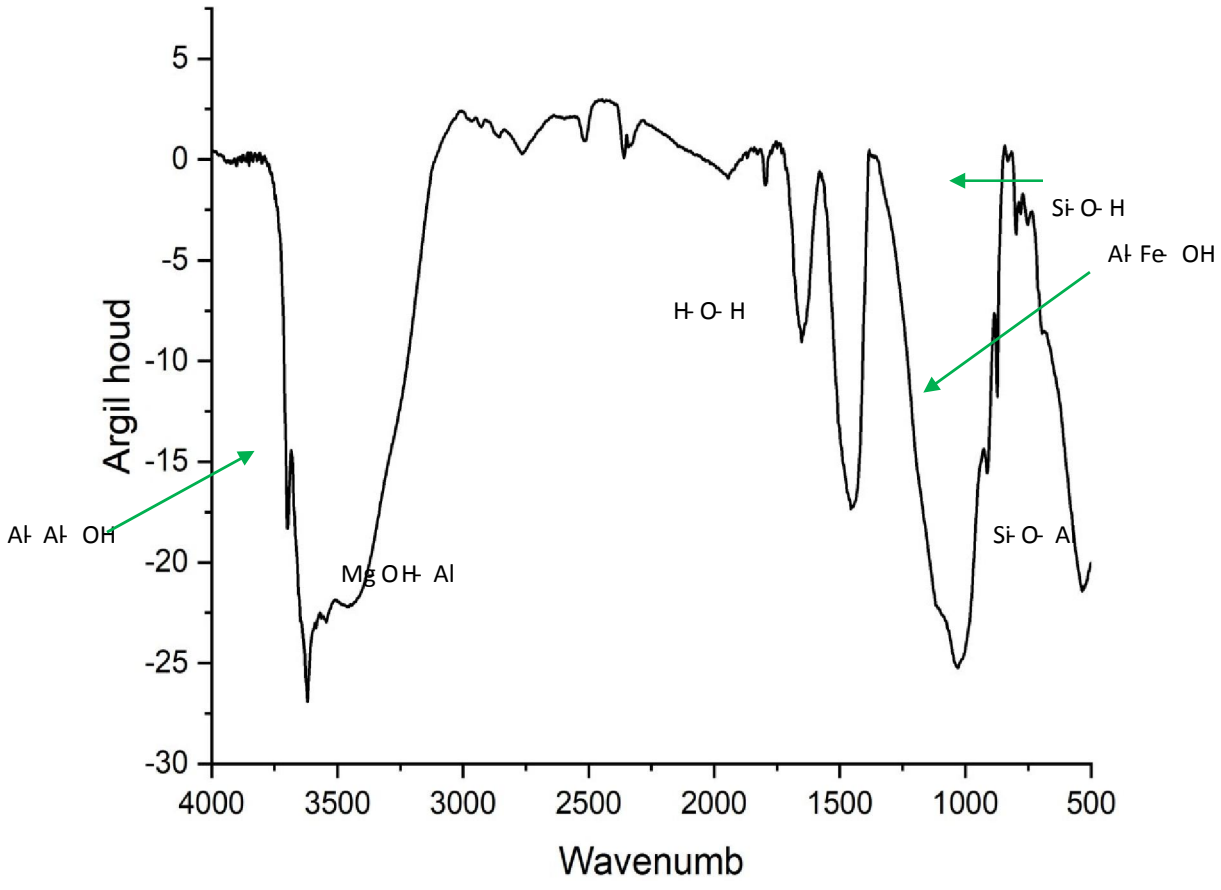


Figure III-3 : FTIR spectrum of clay sample

X-Rays Analysis

X-Ray Diffraction Analysis of Raw Clay

Figure III-3 displays the X-ray diffractogram of the raw clay sample. This analysis, performed with the PDXL2 Program, indicates that the clay is relatively impure, containing several other minerals beyond typical clay phases.

The primary mineral identified is Kornerupine ($Mg_3Al_6(Si_8Al_2)_5O_{21}(OH)$), which is the most abundant phase with a figure of merit of 3.340. Less abundant minerals include Enstatite ($MgSiO_3$) and quartz (silica), with figures of merit of 3.340 and 3.207 respectively, as detailed in Table III-4 (Quantitative Analysis of Clay). The prominent peak at approximately 2θ = 26.6° specifically confirms the presence of quartz, a common mineral often found alongside clay minerals.

The discovery of enstatite and quartz suggests the clay may have been exposed to high-temperature conditions. Enstatite, a high-temperature mineral, typically forms in igneous and metamorphic rocks, while quartz can originate in various geological environments.

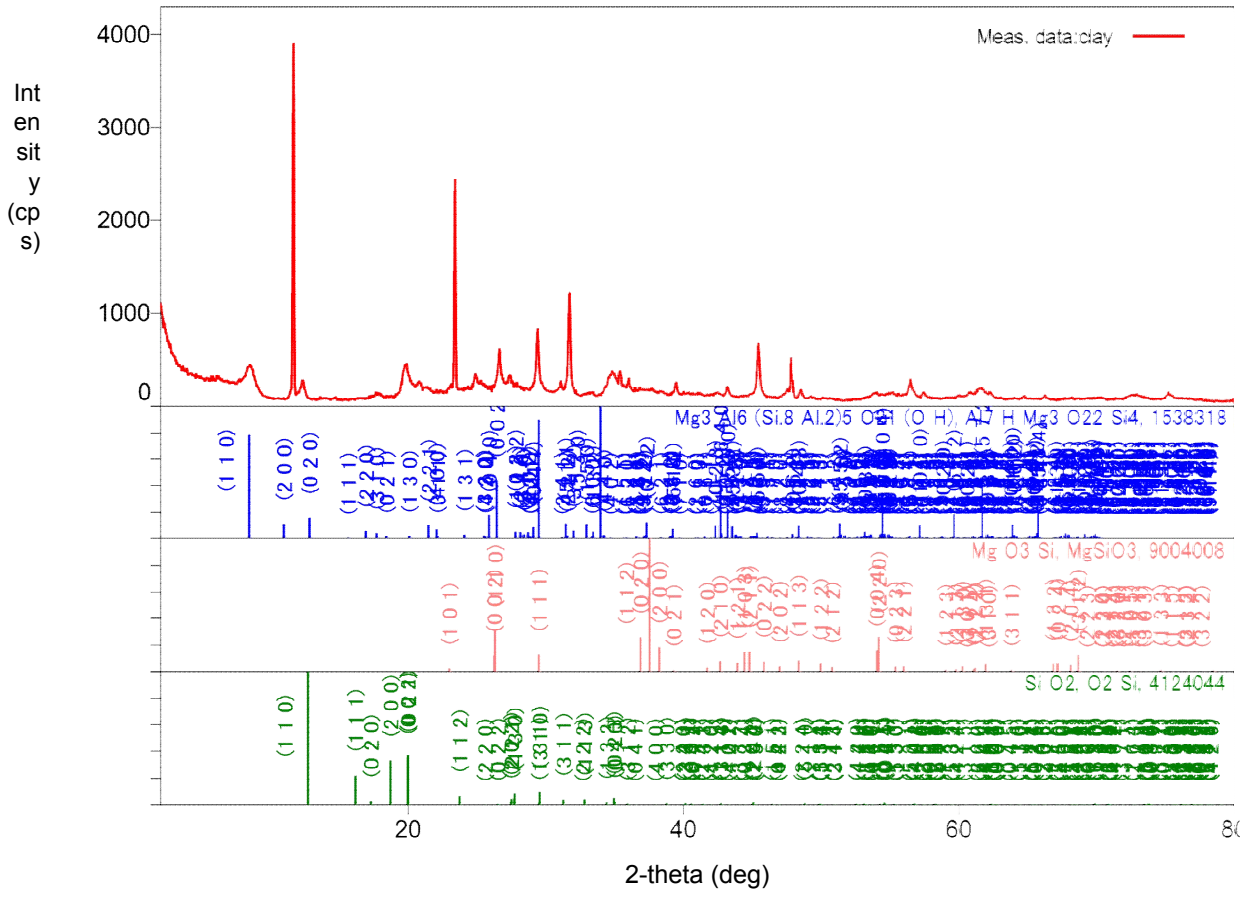


Figure III-4 : Xrays patter of the clay

Table III-2: Qualitative analysis results of the clay

Phase name	Formula	Figure of merit	Phase reg. detail	DB card N°	Space group
Mg3 Al6 (Si.8 Al.2)5 O21 (O H)	Al7 H Mg3 O22 Si4	3.340	User (COD)	1538318	63 : Cmcm
Mg O3 Si	MgSiO3	3.340	User (COD)	9004008	62 : Pbnm
Si O2	O2 Si	3.207	User (COD)	4124044	63 : Cmcm

Table III-3: Cell parameters of the clay phases

Phase name	a(A)	b(A)
Mg3 Al6 (Si.8 Al.2)5 O21 (O H)	15.631615	14.109(
	16.1	13.76
Mg O3 Si	4.618691	4.9093(
	4.701	4.87
Si O2	9.768989	10.312(
	9.475	10.244

VII-3-3-1 Crystallite size and lattice strain

Crystallite size and lattice strain, As previously presented are calculed using Williamson-Hall method. Table III-4 repportthe calculated crystallite sizes and the slopes of the regression lines indicate the lattice strain for each phase.

Table III-4 : Crystallite size and lattice strain

Phase name	Crystallite size(A)	Strain(%)
Mg3Al6 (Si.8 Al.2)5 O21 (O H)	206.59(6)	0.22(3)
MgO3Si	9486(171)	0.3803(10)
SiO2	440.54(4)	0.111(4)

Enstatite has the largest crystallite size, followed by kornerupine and then quartz. This order may be related to the formation conditions of the minerals, with enstatite potentially forming in higher temperature environments compared to the other two.

Kornerupinehas the highest lattice strain, followed by enstatite and then quartz. This suggests that the Kornerupinelattice is more distorted compared to the other two minerals. This could be due to various factors, such as substitutions within the crystal structure or internal defects.

Quantitative analysis result

The quantitative analysis in table III-5 provides information about the relative abundances of the different phases.

Table III-5 : abundances of the different phases in the clay sample

Phase name	Content (%)
Mg3 Al6 (Si.8 Al.2)5 O21	94(19)
Mg O3 Si	2(2)
Si O2	4(2)

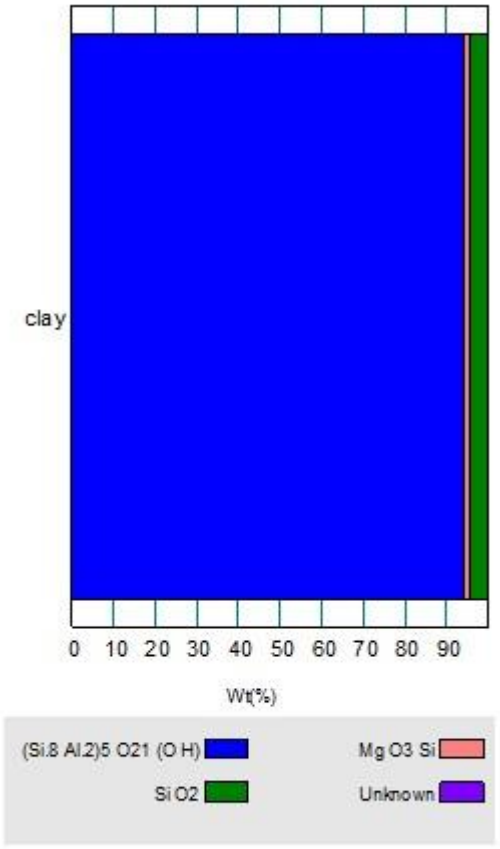


Figure III-4 : Quantitative analysis of the clay

Since kornerupine is the chemical phase that is most prevalent in the sample, we will present his crystal structure based on earlier research because he will be accountable for this sort of clay's efficacy. In order to comprehend the crystal structural structure's content. Clay assymetric unit .

VII-4 Crystal structure description

First, using mercury programm, we visualis the asymetric unit and the molecule (figure III-5), then the package to show the lattice (figure III-6).

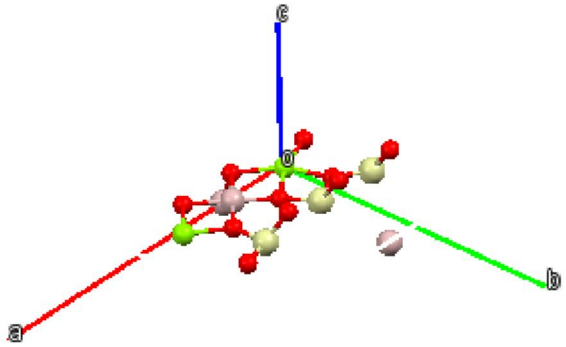


Figure III-5 : asymetric unit

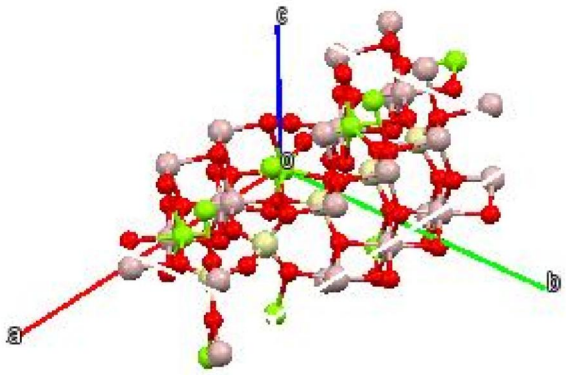


Figure III-6 : the molecule

The crystal structure consists of chains of alternating Mg-O and Al-O octahedra bonded to the walls by further edge-sharing to form dense slabs, and walls made of Al-O edge- and corner-sharing octahedra. Corner-sharing tetrahedral pairs [Si2O7] and corner-sharing tetrahedral triplets [(Al,Si)2SiO10] hold these slabs together.

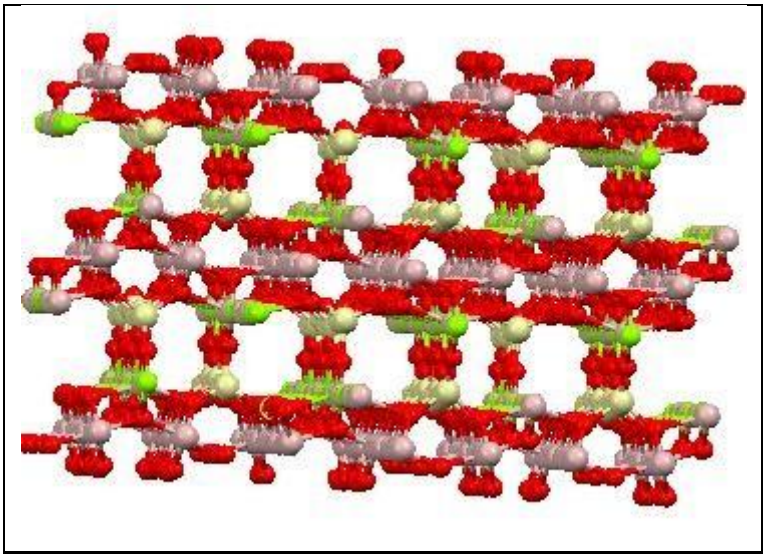


Figure III-7 : arrangement in kornerupine lattice

Description of the retrieved sample

MEB Analysis

Through Scanning Electron Microscopy (SEM) analysis, we aim to investigate the quantitative and qualitative composition of the samplein its as-received state, during the purification process, and after its completion, to understand its structural changes

Sample analysis in its as-received state

Figure III-8 shows an SEM image of zeolite particles, revealing their irregular morphology, agglomeration, and varied size distribution (scale bar: 50µm). The rough, uneven surface texture indicates a porous structure with high surface area, typical of zeolites used in petroleum refining for nitrate and sulfur removal. These characteristics are consistent with zeolites, which are known for their porous structure and high surface area, properties that are crucial for their application in adsorption and catalysis processes, such as the purification of petroleum.

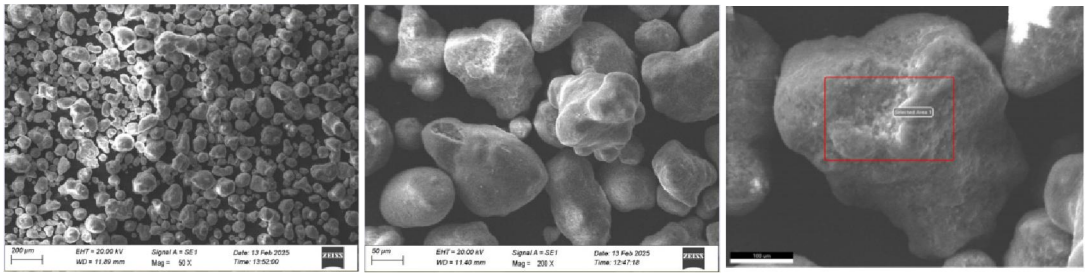


Figure III-8: Morphology of Zeolite Catalyst for Nitrate and Sulfur Removal

The graph in figure III-9 and the table III-6 represents the EDS spectrum of the zeolite sample, illustrating the elemental composition. The peaks in the spectrum correspond to the presence of specific elements within the sample.Noticeablepeaks confirming the presence of Oxygen,Silicon and aluminum, essential element in zeolites. However, Cobalt, Iron, Copper, Titanium, Lanthanum, Terbium, Tm Thulium: Smaller peaks suggesting the presence of these elements in trace amounts.The presence of elements like cobalt, iron, copper, titanium, lanthanum, terbium, and thulium may indicate impurities or dopants within the zeolite.The carbon presence could be from adesif.

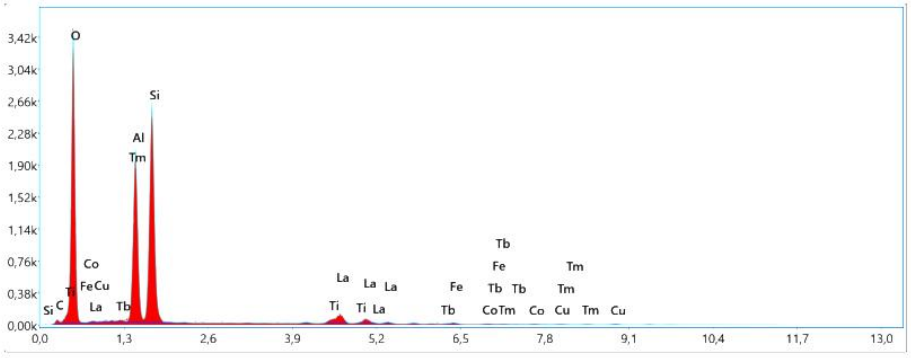


Figure III-9: Energy Dispersive X-ray Spectroscopy (EDS) Spectrum of Zeolite Sample.

Table III-6: qualitative and quantitative composition of the sample before traitment

Elément	% de masse	% atomique
C K	3.11	5.38
O K	48.99	63.65
AlK	15.76	12.14
SiK	22.94	16.98
TiK	0.89	0.39
LaL	6.14	0.92
TbL	0.39	0.05
FeK	0.60	0.22
CoK	0.31	0.11
TmL	0.61	0.08
CuK	0.27	0.09

Sample before, during, and after the petroleum refining process.

MEB Analysis

Figure III-10 presente the sample within the raffinment process with Scanning electron microscopic images of clay materials in figure III-11 and table III-7 of qualitative and quantitative composition of the sample within traitment

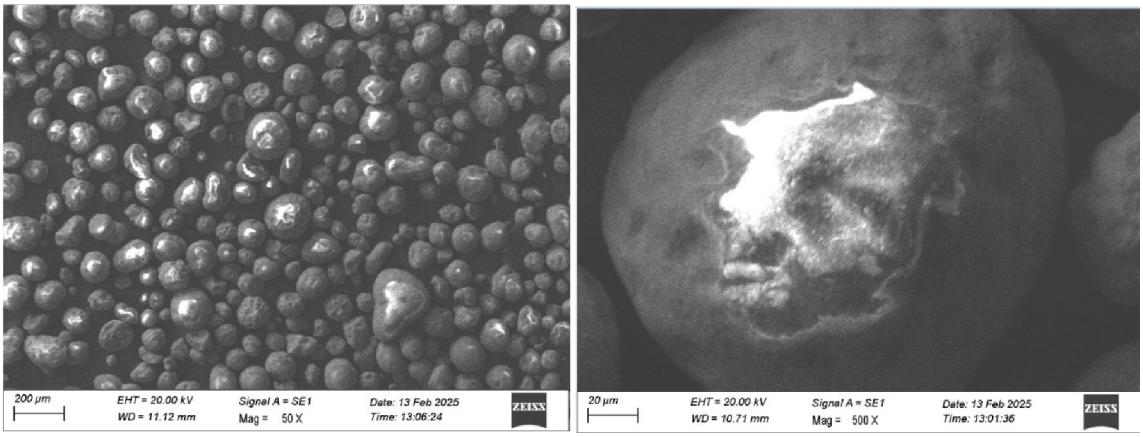


Figure III-10 : Scanning electron microscopic images of clay materials

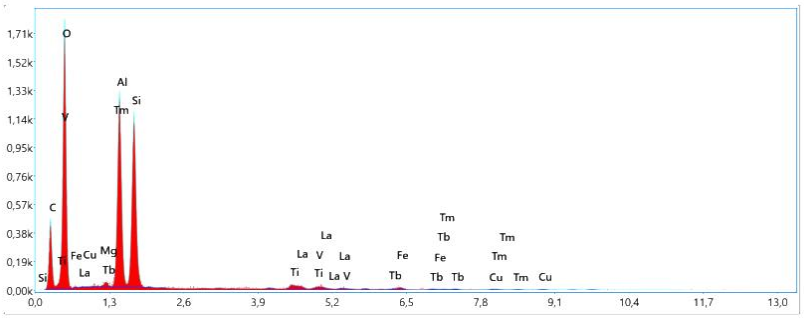


Figure III-11 : Scanning electron microscopic images of clay materials

Table III-7: qualitative and quantitative composition of the sample within traitment

Elément	% de masse	% atomique
C K	24.77	35.09
O K	45.85	48.77
MgK	0.30	0.21
AlK	12.14	7.66
SiK	12.05	7.30
TiK	0.64	0.23
LaL	1.63	0.20
V K	0.32	0.11
TbL	0.68	0.07
FeK	0.65	0.20
TmL	0.57	0.06
CuK	0.38	0.10

Figure III-12 presente the sample after the raffinment process with Scanning electron microscopic images of clay materials in figure III-13 and table III-8 of qualitative and quantitative composition of the sample after traitment

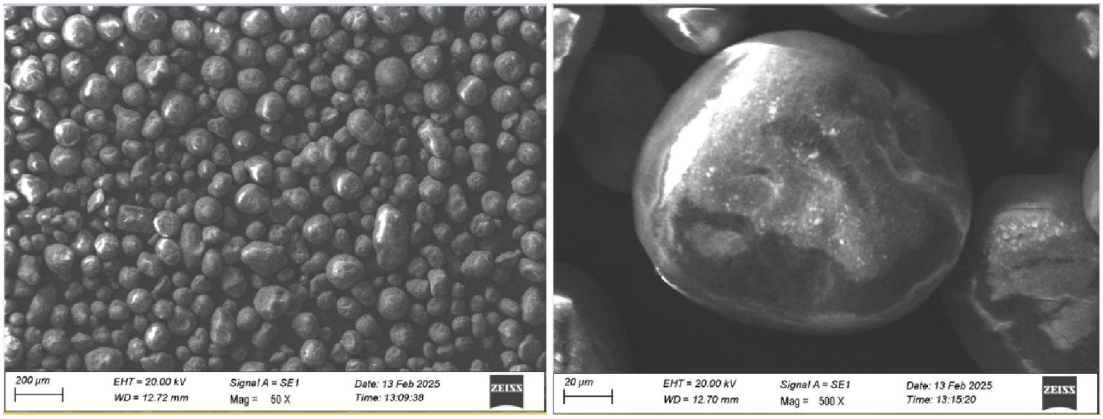


Figure III-12 : Scanning electron microscopic images of clay materials

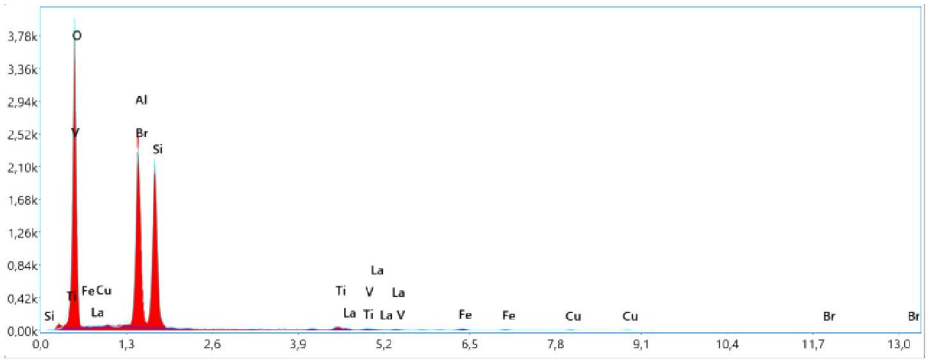


Figure III-13 : Scanning electron microscopic images of clay materials

Table III-8: qualitative and quantitative composition of the sample after traitment

Elément	% de masse	% atomique
O K	54.53	71.93
BrL	10.50	2.77
AlK	12.11	9.47
SiK	19.75	14.84
TiK	0.67	0.29
LaL	0.95	0.14
V K	0.21	0.09
FeK	0.75	0.28
CuK	0.54	0.18

Zeolithe identification using FT-IR

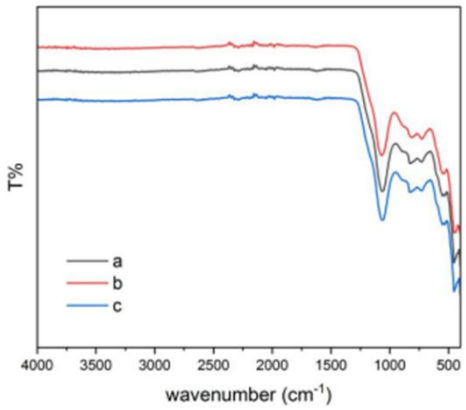


Figure III-14 : Scanning electron microscopic images of clay materials

Zeolithe identification using XDR

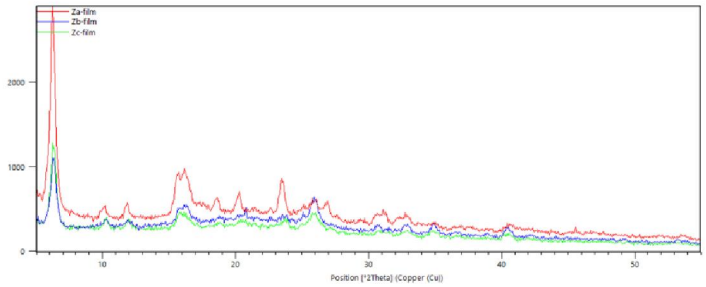


Figure III-15 : Scanning electron microscopic images of clay materials

Development of the alternative to the specific zeolite

For the Zeolite Alternative Compound (Z)

We prepare the zeolite alternative through the basic heat treatment of a natural clay sample obtained from the Oued Ennssa region. This process begins with the calcination of the clay at various temperatures to compare the effect of temperature on the compound's crystal structure, as well as using different basic concentrations.

Preparation Method:

Stage One:

The clay was purified from impurities and undesirable materials such as stones and organic particles. Afterwards, it was ground (Figure 1-III) using a grinding machine (Broyeur) (Figure 2-III) to achieve a fine and homogeneous structure.

1-III 2-III

Figure III-16: Scanning electron microscopic images of clay materials

Stage Two: Calcination

After thorough processing, the clay undergoes calcination at varying temperatures **(**400°C, 600°C, and 800°C**).** This is done to compare the impact of temperature on the weight and color variations of the clay, as detailed in Table (1-III).

For each calcination run, a specific mass of clay is placed in an electric furnace. The furnace's temperature is then gradually and uniformly raised until it reaches the desired set point. This temperature is maintained for two hours to ensure complete dehydroxylation of the sample. The clay material transforms into. Following calcination, the sample is allowed to cool gradually inside the furnace to prevent thermal stress.

Table (1-III) below illustrates the changes in clay mass recorded before and after calcination.

Temperatures (°C)	Weight after Calcination (g)	Weight before Calcination (g)
400	32,86	35
600	31,31	35
800	21,28	35

.Figure (III-3): Color Changes of Clay After Calcination

Figure (III-4): Calcination Apparatus

Stage Three: Activation and Basic Treatment

In this stage, we prepare various basic solutions by dissolving different quantities of sodium hydroxide (NaOH) in 100 mL of distilled water, as detailed in Table (III-2).

A specific amount of the previously treated clay (8g) is then added to a beaker containing one of these solutions. The mixture is stirred using a mechanical stirrer at a speed of 5 rpm for 4 hours, under varying temperatures ranging from 100°C to 200°C (Figure III-5). This process yields 12 samples, as further explained in the diagram.

Table (III-2): NaOH Concentrations Relative to Masses

19,2	14,4	6,4	كتلNaOH(g)
4	3	1,5	التراكيز(mol/l)

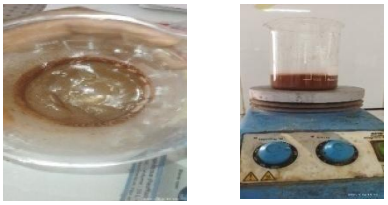


Figure (III-5): Represents an Image of Clay Activation

Stage Four: Washing and Filtration

The treated solution is repeatedly washed with distilled water while continuously monitoring the pH using pH indicator strips (Figure III-6). The washing and filtration (Figure III-7) process is repeated until a pH of **7** is reached, indicating the complete removal of hydroxide residues.

Afterward, the sample is dried in an oven at 105°C for 12 hours to ensure all moisture is completely removed.

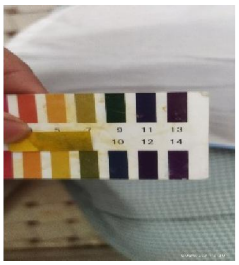


Figure (III-20): Represents an Image of pH Measurement Using Indicator Paper

Figure (III-19): Represents an Image of the Filtration and Washing Process

Stage Five: Mineralization

In this stage, we select five samples (ZA, ZB, ZC, ZD, ZE) out of the original 12.

For each selected sample, we weigh out 2g of the treated clay and add it to 60 mL of distilled water in a beaker. The mixture is stirred for 5 minutes.

Simultaneously, we prepare separate aqueous solutions for each of the mineral salts: $FeSO_4$, $CuSO_4$, and ZnO, each at a concentration of 1 M with a volume of 60 mL.

These mineral solutions are then added separately to the clay in the beakers, as detailed in Table

5	4	3	2	1	رقم التجربة
ZE	ZD	ZC	ZB	ZA	العينة
4 M	4 M	4 M	4 M	1.5 M	التركيز
SEC	400	800	600	600	درجة الحرارة
$CuSO_4$,ZnO	$CuSO_4$,ZnO	$FeSO_4$,$CuSO_4$,ZnO	$CuSO_4$,ZnO	$CuSO_4$,ZnO	تعدين بمحلول من

.

The mixture is left under continuous stirring for one hour (Figure III-8). Then, a 0.4 mol/L NaOH solution is gradually added until the pH is adjusted to 10.

After adjustment, stirring continues for an additional 15 minutes. The precipitate is then separated by washing and filtration (Figure III-9), and dried in an oven at 373 K (100 °C) for 12 hours (Figure III-10).

Figure (III-22): Illustrates the Washing and Filtration Process in the Mineralization Stage

Figure (III-21): Represents an Image of the Shaking Apparatus in the Mineralization Stage

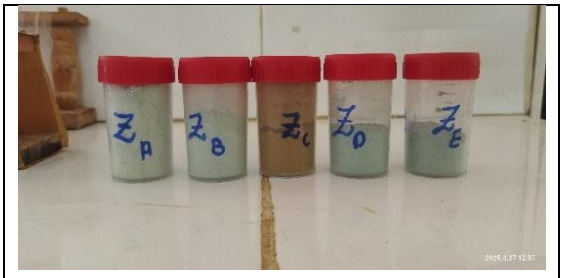


Figure (III-23): Represents the Final Image of the Sample After Drying

Characterization of Zeolite Alternative (Z)

Morphological Shape

The microscopic images in Figure (III-[*Please insert figure number here*]) reveal that the raw clay exhibits a clear granular structure with a relatively rough surface. It was also observed that the particles' color is darker compared to the morphological appearance of the synthesized sample (Z), which showed distinct variations in both shape and color regarding its surface composition.

Specifically, sample ZA appeared more luminous than samples ZB, ZC, ZD, and ZE. As for the shape, samples ZA, ZB, and ZE displayed a very fine fibrous (hair-like) structure, while ZC and ZD appeared granular and entirely different from the raw material's morphology.

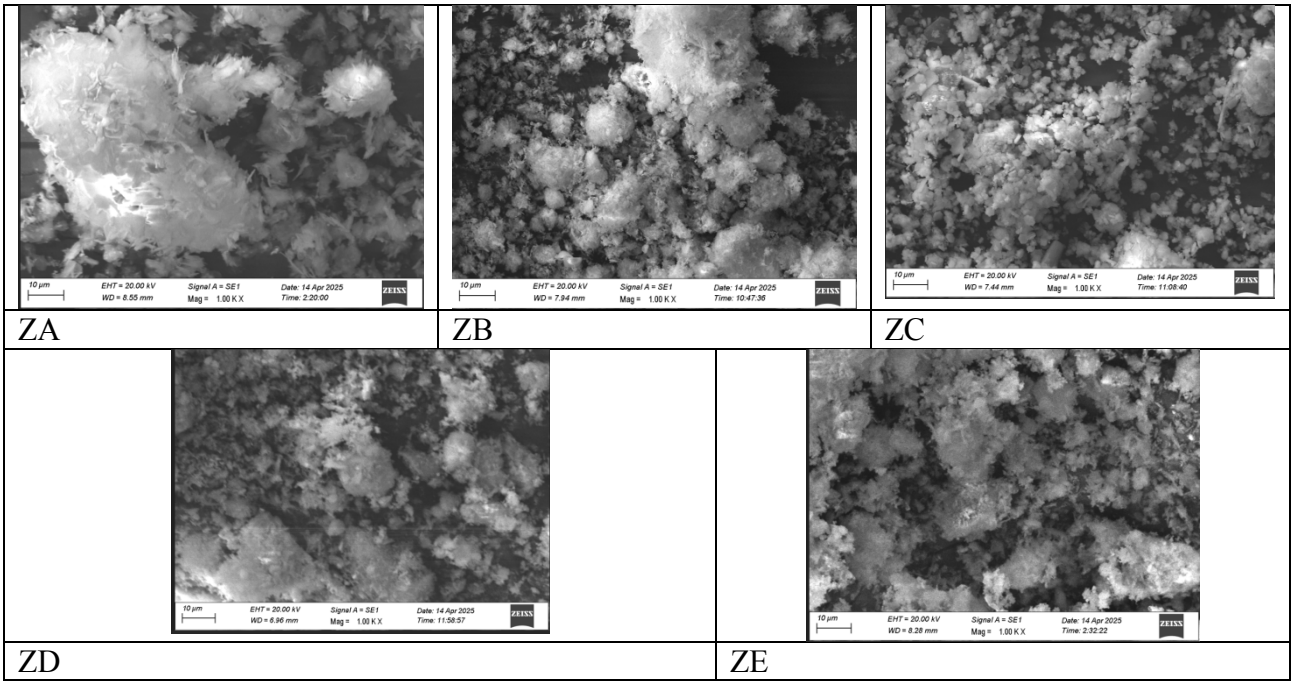
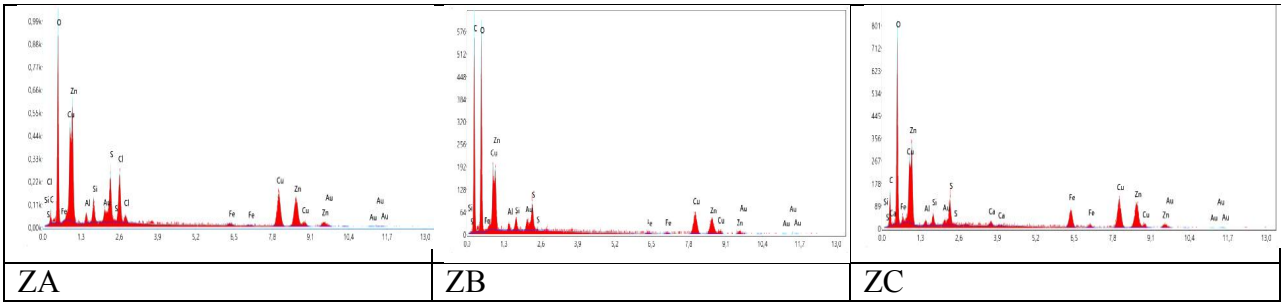
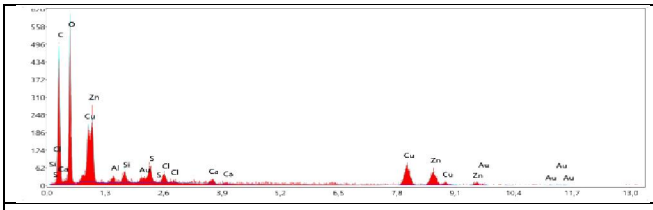
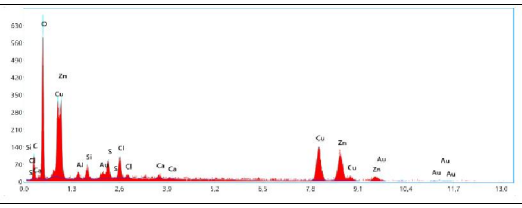


Figure III-24 : Scanning electron microscopic images of clay materials





ZD



ZE

Figure III-25 : Scanning electron microscopic images of clay materials

Elément	% de masse	% atomique
C K	9.59	19.52
O K	38.09	58.17
ZnL	24.12	9.02
AlK	0.90	0.81
SiK	1.83	1.59
S K	3.40	2.59
ClK	3.74	2.58
FeK	0.83	0.36
CuK	12.22	4.70
AuL	5.27	0.65

ZA

Elément	% de masse	% atomique
C K	38.69	56.56
O K	32.46	35.63
AlK	0.57	0.37
SiK	0.88	0.55
S K	1.97	1.08
FeK	1.01	0.32
CuK	9.30	2.57
ZnK	8.84	2.38
AuL	6.30	0.56

ZB

Elément	% de masse	% atomique
C K	12.33	26.59
O K	30.84	49.95
AlK	0.59	0.56
SiK	1.22	1.13
S K	2.87	2.32
CaK	0.85	0.55
FeK	6.43	2.99
CuK	17.37	7.08
ZnK	19.69	7.80
AuL	7.80	1.03

ZC

Elément	% de masse	% atomique
C K	34.85	52.53
O K	33.86	38.32
AlK	0.61	0.41
SiK	1.01	0.65
S K	1.55	0.88
ClK	1.02	0.52
CaK	0.84	0.38
CuK	11.27	3.21
ZnK	9.34	2.59
AuL	5.64	0.52

ZD

Elément	% de masse	% atomique
C K	16.41	30.45
O K	38.29	53.33
AlK	0.72	0.60
SiK	1.20	0.95
S K	1.50	1.04
ClK	1.95	1.22
CaK	0.67	0.37
CuK	15.62	5.48
ZnK	17.03	5.81
AuL	6.61	0.75

ZE

Figure III-26 : Scanning electron microscopic images of clay materials

Quantitative and Qualitative Composition: Exchangeable Cations

Sample ZA

Using X-ray diffraction (XRD) coupled with an electron microscope to identify and quantify the elements present in the sample, a comparison between the raw material and the synthesized material (Z) revealed qualitative and quantitative changes in the composition of synthesized sample ZA. This included an increase in elements like Zn and CuS in quantities shown in Figure

[Please insert figure number here] compared to the raw material, and the loss of some elements such (K, Na, Mg, Pd, Ca, Al). This clearly indicates that cation exchange occurred between the soluble cations in water on one hand, and the interstitial cations in the raw clay on the other.

Sample ZB

For sample ZB, the same elemental exchange was observed but with different mass percentages**.** The presence of Zn and CuS was in lower proportions than those recorded in sample ZA. This explains why ZA appeared with greater intensity than ZB.

Sample ZC

Regarding sample ZC, the same elemental exchange occurred, but with mass percentages greater than ZB and less than ZA. Additionally, the calcium (Ca) element appeared, indicating its non-removal.

Sample ZD

The same elemental exchange was observed in sample ZD, but in smaller quantities than ZA**.**

Sample ZE

By considering sample ZR (raw clay after initial processing and not subjected to any mineralization) as a reference, and noting that the four samples (ZB-ZE) were mineralized at the same concentration but varying temperatures (unlike ZA, which had a different concentration), the mass percentages for these four samples showed a decrease in the presence of Zn and Cu after mineralization. These elements replaced the outgoing cations, each according to its state.

In contrast, sample ZA, which was treated at a lower concentration (1.5 M) compared to the four samples (4 M), exhibited significantly higher mass percentages of Zn and Cu. This is further supported by the electron microscope images, which showed greater luminosity for ZA compared to the other samples**.** This led us to focus on sample ZA for pollutant removal studies. The study of sample ZE was due to the similarity of its results to ZA.

element	% of mass	ZA	ZB	ZC	ZD	ZE
C K	0.37	9,59	38,69	12,33	34,85	16,41

O K	27.20	38,09	32,46	30,48	33,86	38,29
NaK	11.51					
MgK	2.65					
AlK	7.53	0,90	0,57	0,59	0,61	0,72
SiK	17.78	1,83	0,88	1,22	1,01	1,20
PdL	7.94					
K K	2.86					
CaK	5.17			0,85	0,84	0,67
FeK	4.06	0,83	1,01	6,43		
Zn	-	24,12	8,84	19,69	9,34	17,03
S		3,40	1,97	2,87	1,55	1,50
Cu		12,86	9,30	17,37	11,27	15,62
AuL	12.92	5,27	6,30	7,80	5,64	6,61

Characterization Technique: X-ray Diffractometry (XRD)

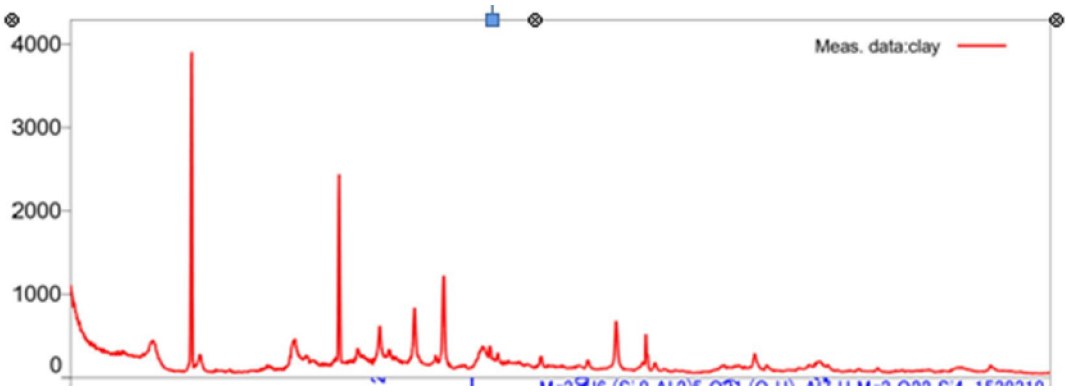


Figure III-27 : Scanning electron microscopic images of clay materials

Figure (III-[*Insert Figure Number Here*]): Results of X-ray Diffraction (XRD) Analysis for the Synthesized Material

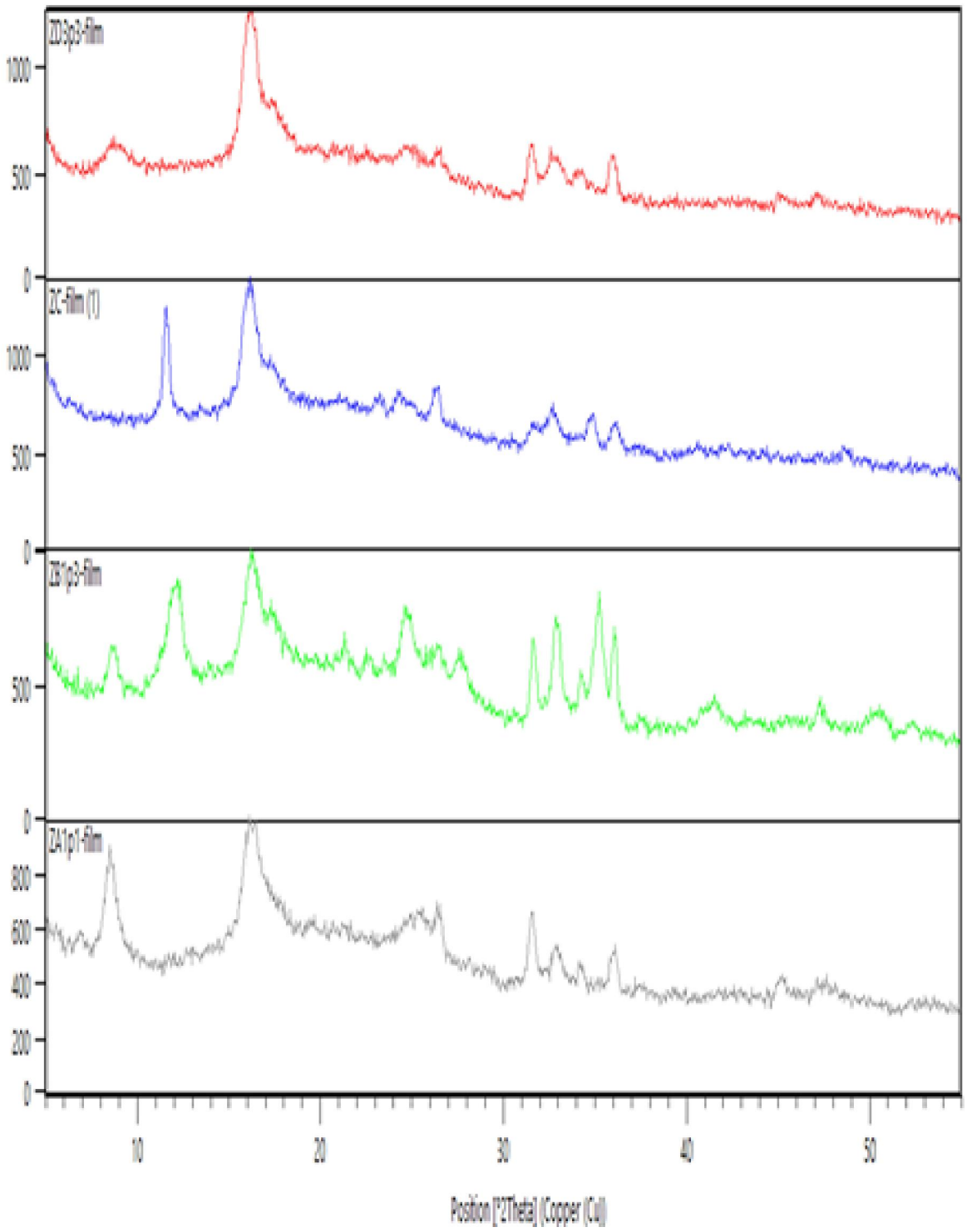


Figure III-28: Scanning electron microscopic images of clay materials

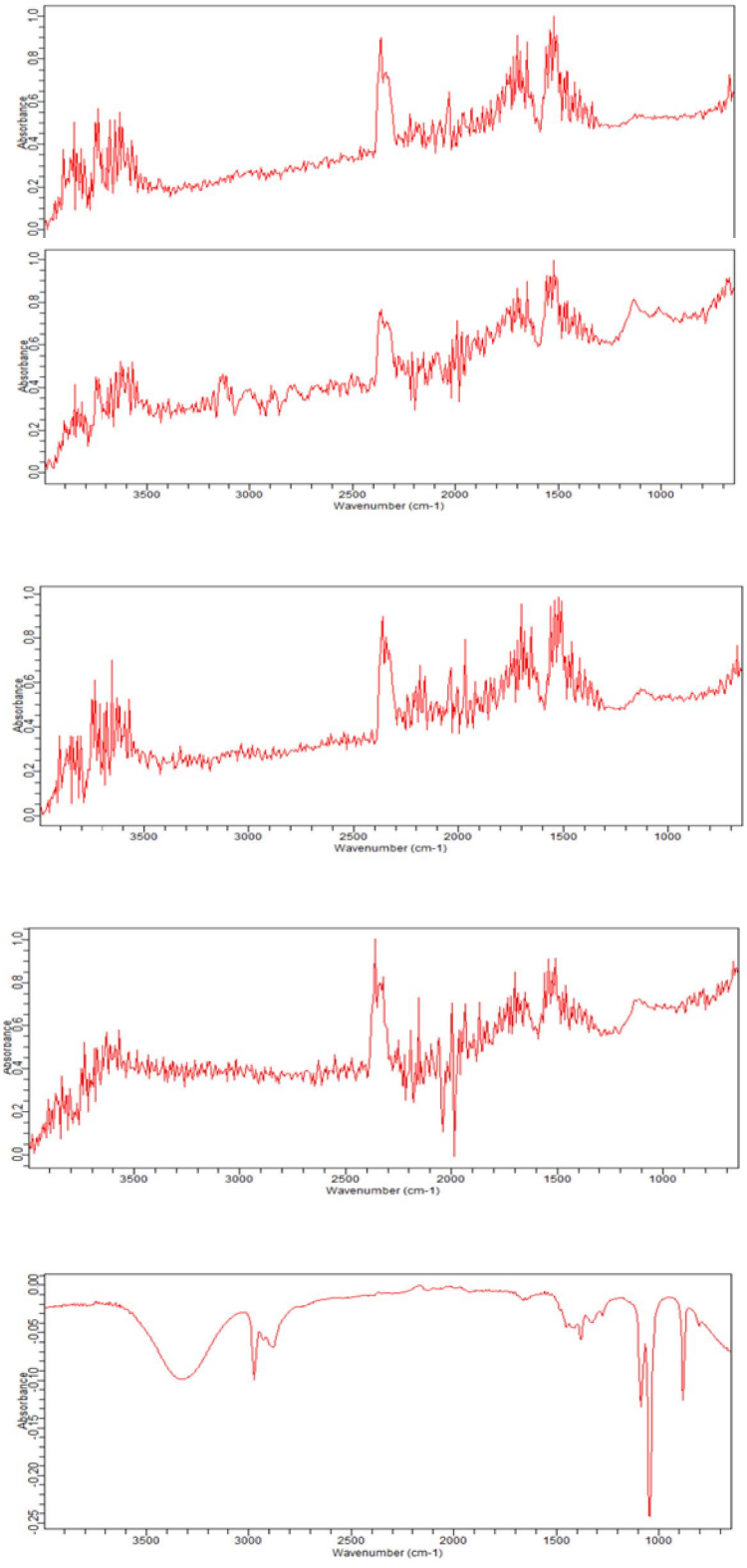


Figure III-29 : Scanning electron microscopic images of clay materials

Microactivity Test (MAT) Analysis

Microactivity Test (MAT) Analysis

The Microactivity Test (MAT) is a vital tool in petroleum refining, especially for evaluating catalyst performance in processes like Fluid Catalytic Cracking (FCC). This test aims to simulate industrial refining unit conditions on a miniature laboratory scale, enabling a rapid and efficient assessment of new or regenerated catalysts.

Importance of Microactivity Test (MAT) Analysis

- Catalyst Performance Evaluation: MAT is primarily used to determine the activity and selectivity of a catalyst for producing desired products (e.g., gasoline, diesel) and minimizing undesirable ones (e.g., coke, gases).
- Simulation of Industrial Conditions: Despite its small scale, the MAT apparatus simulates the thermal and contact conditions found in industrial reactors, providing data relevant to real-world applications.
- Cost and Time Reduction: It allows for numerous experiments with very small quantities of catalyst and feedstock, significantly reducing costs and time compared to larger-scale testing.
- Catalyst Quality Control: It's used to monitor the quality of commercially available catalysts and assess the impact of contaminants (e.g., nickel, vanadium) on their performance.
- New Catalyst Development: Plays a crucial role in the research and development of new catalysts, helping to identify optimal compositions and conditions for best performance.

How a Microactivity Test (MAT) is Conducted

The MAT typically utilizes a fixed-bed reactor compliant with ASTM D3907 specifications. The basic steps involved are:

1. Catalyst Preparation: The catalyst is usually hydrothermally treated (steaming) before testing to simulate changes it undergoes in an industrial unit.
2. Catalyst Loading: A small, precisely measured amount of catalyst (typically a few grams) is loaded into the reactor.
3. Feedstock Introduction: A specific volume of feedstock (often gas oil) is injected onto the catalyst at a defined temperature and pressure.
4. Product Collection: The liquid and gaseous products formed after the reaction are collected.

5. Product Analysis: The collected products are analyzed using techniques like Gas Chromatography (GC) to determine the feedstock conversion rates and the proportions of different products (e.g., gasoline, diesel, gas, coke).
6. Coke Determination: The amount of coke deposited on the catalyst after the reaction is measured.

We tested the manufactured sample using Microactivity Test (MAT) analysis to determine its effectiveness as a catalyst in refinery catalytic cracking. The application procedure was as follows:

Instructions for Microactivity Catalyst Analysis:

1. Device Startup:
    - Turn on the device and wait until the furnace temperature reaches the operating value of 460°C.
2. Chromatography System Preparation:
    - Turn on the chromatograph device, press the "SYSTEM" button, ignite the flame, and allow it to stabilize.
3. Standard Gas Oil (Feedstock) Verification:
    - Ensure the feed beaker, filled with standard gas oil, contains a sufficient quantity and that the suction probe is well immersed.
    - Verify the mass of the standard gas oil to be automatically pumped by pressing the "START" button, but *after* weighing and taring the receiving beaker. This mass should be 1.560.02 grams.
4. Reactor Tube Preparation:
    - Clean the reactor tube thoroughly with acetone, then dry it well with air.
    - Insert a piece of compressed glass wool into the bottom of the tube to form a filter, allowing liquid to pass through while preventing catalyst particles from falling out.
    - Add 5 grams of the regenerated catalyst inside the tube.
    - Close the tube tightly using a wrench.
    - Tap the tube several times with a metal rod to compact the catalyst well downwards, ensuring no catalyst leakage from the bottom.
    - Place the reactor tube inside the furnace and allow it to heat for one hour.
5. Preparation of Reaction Product Collection System:
    - This system consists of:

- A small vial (mini-fiole)
- A beaker
- Two special needles with a stopper:
  - The small needle serves as a "chimney" to vent non-condensable gases.
  - The large needle connects the vial to the reaction tube.

- Preparation Steps:
  - Clean all these components with acetone and dry them thoroughly to remove any residues from previous experiments.
  - Weigh the beaker and all its components, then tare them.
  - Assemble the system below the reactor tube, using Teflon in the connections to ensure a tight seal (refer to Figure No. 1).
  - Place the vial inside an ice bath at 0°C.
  - Secure the standard gas oil injection tube at the top of the reactor tube, also using Teflon.
  - Press the "START" button to begin the injection process.
  - Upon completion of the experiment, the device will emit an audible signal.

6. Post-Reaction Procedures:
   - Remove the "chimney" needle.
   - Quickly disconnect the vial from the tube, place a stopper on the large needle, then weigh the vial with the needle and the beaker.
   - The mass obtained represents the mass of the cracking reaction products inside the tube.
7. Results Analysis:
   - If the obtained mass is ≥ 1.2 grams, proceed to chromatographic analysis of the products.
   - If it is less, repeat the experiment.
   - Calculation of Microactivity (MA):

$$MA = 100 - \frac{W1\left(100 - \frac{A1}{A1 + A2} \times 100\right)}{W}$$

Microactivity Test Variables and Sample Analysis

To evaluate the performance of your synthesized catalyst, the following variables are considered in the Microactivity Test (MAT):

- W1: Mass of collected products (g)
- W: Mass of injected gas oil (g)
- A1: Percentage of gasoline according to chromatographic analysis (%)
- A2: Percentage of remaining gas oil according to chromatographic analysis (%)

Analysis of the Lab-Prepared Sample's Activity

The same instructions and protocol for catalytic activity analysis were applied to your lab-prepared sample. This sample serves as an alternative to the commercial zeolite catalyst currently used in the refinery's catalytic cracking unit. The primary objective of this testing is to compare the catalytic effectiveness of the new, synthesized sample with that of the commercial zeolite catalyst currently in use at the refinery.

Results: Mass Changes After Catalytic Activity Analysis

The table below presents the mass changes (gas oil) observed after the catalytic activity analysis for both the prepared catalyst and the commercial zeolite catalyst.

Sample	Mass Before Analysis (g)	Mass After Analysis (g)
Synthesized Alternative	1.56	1.559
Zeolite	1.56	1.53

Figure III-31 : Gas Oil After Analysis Using

Figure III-30 : Gas Oil After Analysis

Zeolite Alternative Using Zeolite

Product Analysis Using a Chromatograph

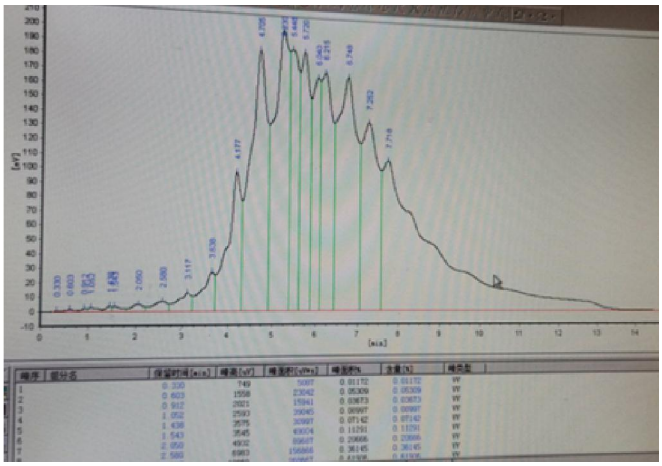


Figure III-32 : Chromatogram Results for the Product Obtained Using the Lab-Prepared

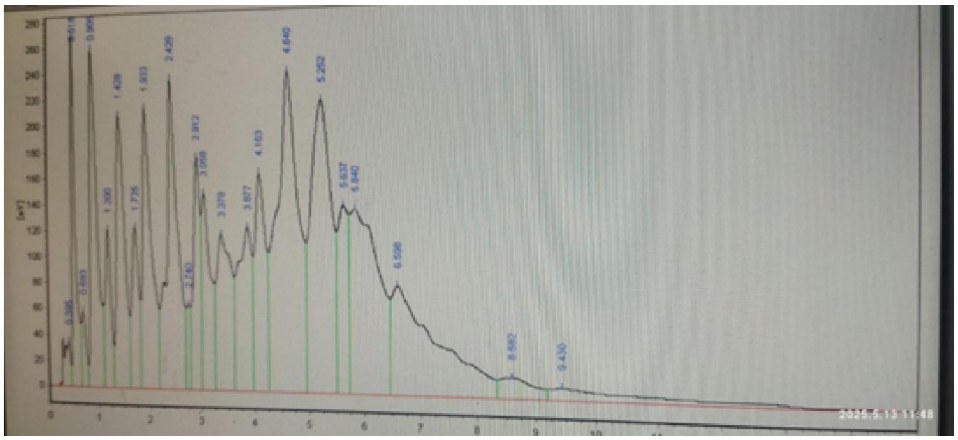


Figure III-31 : Chromatogram Results for the Product Obtained Using Zeolite Catalyst

Discussion of Results: Catalytic Cracking Experiment

After conducting the catalytic cracking experiment using the prepared sample as a zeolite alternative catalyst, the products were analyzed using a Gas Chromatography (GC) system. The aim was to identify the components of the resulting mixture and their respective proportions.

Initial Observations and Mass Comparison

Initial results, observed visually, indicated that no cracking of the gas oil occurred when using the prepared sample. The sample remained in its original state without significant change. This observation was further supported by comparing the mass of the product before and after analysis, referencing the results obtained using the commercial zeolite catalyst.

Chromatographic Analysis

Regarding the chromatogram analysis, the spectra obtained revealed that the resulting extract was identical to the original sample. No lighter compounds or cracking products (such as light alkanes or volatile hydrocarbons like ethane or light ethene) were detected. Instead, gas oil appeared in a large proportion, indicating that the alternative sample was not capable of effectively cracking or separating this type of gas oil.Based on these findings, we conclude that the prepared sample was not effective in the catalytic cracking process for the specific type of gas oil used at the Sabaa refinery.

UV Fluorescence Spectroscopy Analysis

UV Fluorescence Spectroscopy Analysis

We analyzed the synthesized sample using UV fluorescence spectroscopy to test its effectiveness in removing sulfur and nitrogen from petroleum compounds specific to the Sabaa refinery.

Sample Preparation for the ELEMENTAR Instrument:

For each sample:

- Draw a precise volume (e.g., 20 microliters) using a microsyringe.
- Place it in a clean tin capsule.
- Seal the capsule tightly.
- Record the weight (if the analysis is mass-dependent).

Analysis in the Instrument:

- Load the samples into the instrument's autosampler.
- Start the software and enter the data for each sample (name, date, density, volume, etc.).
- Press Start to begin the analysis.
- Record the sulfur and nitrogen content results for each sample.

Results Analysis:

- Calculate the difference between the sulfur (S) and nitrogen (N) content before and after the reaction:
  - $\Delta S = S_{before} - S_{after}$
  - $\Delta N = N_{before} - N_{after}$
- The larger the difference, the higher the catalyst's effectiveness in removing sulfur or nitrogen-containing compounds.

Table: Results of Sulfur and Nitrogen Elemental Analysis in Diesel Samples

ble Pos.	Name	Method	Coefficients	N [µl]	S [µl]	S Area	N Area	S [ppm]	N [ppm]
26	DIESEL Std	TraceSN10µl	RFCC-TANK 2...	10	10	2 005 ...	90 053	504.767	69.98
26	DIESEL Std	TraceSN10µl	RFCC-TANK 2...	10	10	1 997 ...	89 056	502.845	69.22
26	DIESEL Std	TraceSN10µl	RFCC-TANK 2...	10	10	2 000 ...	85 728	503.399	66.67
27	diesl std cr...	TraceSN10µl	RFCC-TANK 2...	10	10	2 150 ...	38 118	538.704	30.08
27	diesl std cr...	TraceSN10µl	RFCC-TANK 2...	10	10	2 148 ...	36 194	538.218	28.61

Uv adsorption

Characterization Technique: UV-Visible Spectroscopy

UV-Visible (UV-Vis) Spectroscopy is a powerful analytical technique used to determine the concentration of substances in a solution by measuring their absorbance of ultraviolet and visible light. In your case, it will be used to assess the effectiveness of your synthesized materials (ZA and ZE) in degrading or removing methyl orange, acting as a model pollutant.

The technique relies on preparing various solutions as follows:

1. Preparation of the Standard (Control):

- Prepare a stock solution of methyl orange by dissolving a mass of m=100 g in 100 mL of distilled water.
- Place the solution on a shaker until the methyl orange is completely dissolved.

2. Preparation of Samples:

- Prepare five beakers, each containing 2.5 mL of the stock solution of methyl orange.
- Dilute each of these solutions with 100 mL of distilled water.
- To two of these beakers, add 40 mg of the synthesized material ZA.
    - One of these two beakers will be shaken under sunlight for 4 hours.
- To two other beakers, add the same quantity of synthesized material ZE (40 mg), following the same procedure as with ZA.
- One beaker containing only the diluted methyl orange solution (without any synthesized material) will be kept as a control for color comparison.

This experimental setup will allow us to compare the degradation of methyl orange in the presence of our synthesized zeolite alternative materials (ZA and ZE) under different conditions with and without sunlight for ZA and ZE against a control solution. UV-Vis spectroscopy will then quantify the remaining methyl orange concentration by measuring changes in its characteristic absorbance peaks.

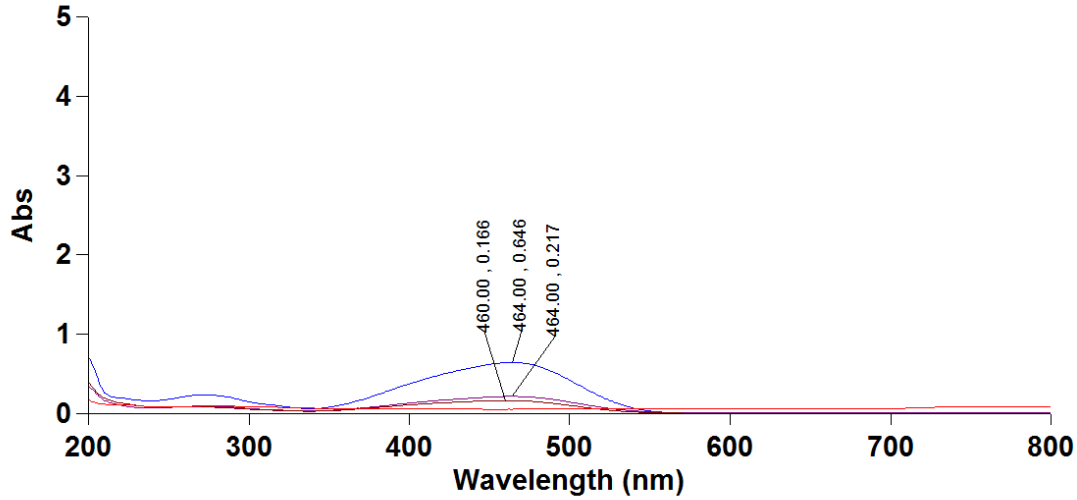


Figure III-32 : Scanning electron microscopic images of clay materials

Here's an interpretation of the provided UV-Vis spectrum and its implications for methyl orange removal:

Methyl orange is an azo dye, and its distinctive orange color in solution is due to its strong absorption of light in the visible region, specifically around 460-470 nm. When methyl orange is degraded or removed from a solution, this absorption peak will decrease in intensity (absorbance). Complete removal would result in the disappearance of the peak.

The graph shows several absorption spectra, likely representing different stages or samples in your experiment. Let's identify the key features based on your description:

1. Blue Spectrum (الشاهد - Control): This is described as. This represents the initial absorption spectrum of the methyl orange solution *without* any treatment. It shows a prominent absorption peak with a maximum absorbance value (around 460 nm) indicating the initial concentration of methyl orange. Looking at the "Peak Table" provided, the peak at 460.00 nm has an absorbance of 0.166. This is likely the absorbance of your control (initial) methyl orange solution.
2. Purple Spectrum - Control): Your description states. This is a bit ambiguous if it's also a "control". However, looking at the graph, the purple line has peaks around 460nm and 464nm with absorbances of 0.646 and 0.217 respectively, which are *higher* than the blue line's 0.166. This suggests it might represent a *different* initial concentration or perhaps an error in labeling. If the "blue spectrum" is truly the initial control, then the purple

spectrum is problematic as it shows higher absorbance, meaning higher concentration, which contradicts the idea of removal. Let's assume the blue line represents the initial concentration of methyl orange at 0.166 Abs at 460 nm.

3. Red Spectrum (Treated Sample): This line shows a significantly lower absorbance across the 400-500 nm range, particularly at the methyl orange peak wavelength. The peak is almost completely diminished, and the line is very close to the x-axis (Abs = 0).

Based on the visual comparison of the spectra, especially if the blue line represents the initial methyl orange concentration (control) and the red line represents the treated sample:

- The significant reduction in the absorbance peak at approximately 460-470 nm in the red spectrum compared to the blue spectrum clearly indicates that methyl orange has been effectively removed or degraded.
- The fact that the red line is very flat and close to zero absorbance in the methyl orange's characteristic absorption range suggests a high efficiency of removal.

The Peak Table shows:

- 460.00 nm: 0.166 Abs (This seems to correspond to your initial/blue spectrum).
- 464.00 nm: 0.646 Abs (This value is notably higher and seems to correspond to the purple line, which might be an anomaly or another higher concentration initial sample if it's also a "control" as per the text. It's crucial to clarify what each line represents.)
- 464.00 nm: 0.217 Abs (This also belongs to the purple line or another sample).

General Conclusion

This thesis embarked on an ambitious journey to address Algeria's reliance on imported specialized chemical materials, particularly zeolites, for the crucial petroleum refining sector and industrial pollutant treatment. Our core objective was to synthesize a high-efficiency zeolite alternative from locally sourced natural clay, aiming for self-sufficiency and fostering local innovation.

Through a meticulously detailed five-stage synthesis process, involving purification, controlled calcination at varying temperatures (400°C, 600°C, 800°C), activation with differing basic concentrations (1.5 M, 3 M, 4 M NaOH), rigorous washing, and targeted mineralization with $FeSO_4$, $CuSO_4$, and ZnO, we successfully prepared a series of alternative clay-based materials (ZA-ZE).

Extensive physicochemical characterization techniques were employed to understand the synthesized materials. Scanning Electron Microscopy (SEM) revealed diverse morphological transformations, including the emergence of fibrous (hair-like) structures in samples like ZA, ZB, and ZE, distinct from the granular raw clay. Energy-Dispersive X-ray Spectroscopy (EDS) confirmed significant qualitative and quantitative elemental changes, particularly highlighting successful cation exchange evidenced by the incorporation of metallic species (Zn and Cu) and the loss of original clay cations (K, Na, Mg, Pd, Ca, Al). Notably, sample ZA, treated at a lower concentration (1.5 M), exhibited a higher uptake of Zn and Cu, a finding supported by its observed luminosity in SEM images, suggesting potentially enhanced structural modification. X-ray Diffraction (XRD) analysis, while not fully detailed in the provided results, is understood to have been crucial for identifying the crystallographic phases and structural changes indicative of zeolite formation or modification.

However, the direct application of the most promising synthesized material (sample ZA) as a catalyst in petroleum refining, specifically for catalytic cracking using the Microactivity Test (MAT), yielded a critical finding. Despite our efforts to create an effective alternative, the prepared sample demonstrated no catalytic cracking activity under the tested conditions at the Sabaa refinery. Gas Chromatography (GC) analysis confirmed that the gas oil remained largely uncracked, indicating that the synthesized material, in its current form, was not effective in simulating the performance of commercial zeolite catalysts for this specific application.

Despite this outcome in catalytic cracking, the successful synthesis and significant modification of local clay, coupled with its demonstrated ability to incorporate pollutant-removing metal species (Zn and Cu) and its intended role in removing organic pollutants like methyl orange dye (though the results for this were not detailed here), underscore the potential of these materials. This research represents a vital initial step towards developing advanced functional materials from abundant local resources.

Perspectives

The findings of this thesis, particularly the divergent results in catalytic activity versus material modification, open several promising avenues for future research and development:

1. **Optimizing Catalyst Activity for Cracking:**

- **Further Characterization:** A deeper understanding of the synthesized material's acidity, pore size distribution (e.g., using BET analysis), and active site accessibility is crucial. The lack of cracking activity suggests insufficient acid sites or inappropriate pore architecture for the tested feedstock.
- **Alternative Synthesis Routes:** Explore different synthesis parameters, such as varying silica-to-alumina ratios, incorporating different templates or structure-directing agents, or employing post-synthesis modifications (e.g., acid treatment, steaming) to enhance acidity and thermal stability for catalytic cracking.
- **Doping Strategies:** Investigate the role of transition metal doping beyond Zn and Cu, as well as rare-earth elements, known to improve zeolite catalytic performance in FCC.
- **Feedstock Specificity:** Test the synthesized materials with different hydrocarbon feedstocks. The current gas oil may be too refractory for the current catalyst design.

2. **Developing Adsorbent Applications:**

- **Pollutant Removal Efficacy:** Systematically quantify the adsorption efficiency of the synthesized materials, especially sample ZA, for methyl orange dye and other organic pollutants, as initially envisioned. This would be a direct validation of their potential in industrial pollutant treatment.
- **Adsorption Mechanism Studies:** Investigate the adsorption kinetics, isotherms, and regeneration capabilities for pollutant removal applications.

- **Industrial Wastewater Treatment:** Explore the feasibility of using these materials for real-world industrial wastewater treatment, potentially as a cost-effective alternative to commercial adsorbents.

3. **Scaling Up and Economic Viability:**

- **Cost-Benefit Analysis:** Conduct a comprehensive economic analysis to compare the production cost of the synthesized alternative with imported zeolites, taking into account raw material availability and local processing costs.
- **Pilot-Scale Production:** If initial lab results are promising for adsorption, undertake pilot-scale synthesis to evaluate production challenges and optimize parameters for larger quantities.

This research, though facing challenges in direct catalytic cracking, has successfully laid the groundwork for leveraging indigenous clay resources. By pivoting to or further refining the successful aspects of material modification and focusing on areas like adsorption where initial promises exist, this work holds significant potential to contribute to Algeria's economic independence and environmental sustainability through local innovation in advanced materials.

الخلاصة العامة

تطرح هذه الرسالة رؤية طموحة لمواجهة اعتماد الجزائر على المواد الكيميائية المتخصصة المستوردة، وخاصة الزيوليت، لقطاع تكرير النفط الحيوي ومعالجة الملوثات الصناعية .كان هدفنا الأساسي هو تصنيع بديل للزيوليت عالي الكفاءة من الطين الطبيعي المتوفر محلياً، سعياً لتحقيق الاكتفاء الذاتي وتعزيز الابتكار المحلي.

من خلال عملية تصنيع دقيقة ومفصلة على خمس مراحل، تضمنت التنقية، التكليس المتحكم به في درجات حرارة مختلفة (400 درجة مئوية، 600 درجة مئوية، 800 درجة مئوية)، التنشيط بتراكيز قاعدية متباينة (1 5.مولار، 3 مولار، 4 مولار من هيدروكسيد الصوديوم)، الغسيل الدقيق، والتمعدن المستهدف باستخدام $FeSO_4$ و $CuSO_4$ وZnO ، نجحنا في تحضير سلسلة من المواد البديلة القائمة على الطين.(ZA-ZE)

تم استخدام تقنيات توصيف فيزيائية وكيميائية شاملة لفهم المواد المُصنّعة .كشف تحليل المجهر الإلكتروني الماسح (SEM) عن تحولات مورفولوجية متنوعة، بما في ذلك ظهور هياكل ليفية (شعرية) في عينات مثل ZA و ZB وZE ، والتي تختلف عن الطين الخام الحبيبي .أكد تحليل مطيافية تشتت الطاقة للأشعة السينية (EDS) حدوث تغييرات نوعية وكمية كبيرة في التركيب العنصري، لا سيما إظهار النجاح في تبادل الكاتيونات من خلال دمج الأنواع المعدنية (الزنك والنحاس) وفقدان كاتيونات الطين الأصلية (البوتاسيوم، الصوديوم، المغنيسيوم، البلاديوم، الكالسيوم، الألومنيوم .(ومن الجدير بالذكر أن العينةZA ، التي عولجت بتركيز أقل (1 5.مولار)، أظهرت امتصاصًا أعلى للزنك والنحاس، وهو ما يدعمه سطوعها الملاحظ في صورSEM ، مما يشير إلى تعديل هيكلي محتمل ومعزز .تحليل حيود الأشعة السينية(XRD) ، على الرغم من عدم تفصيله بالكامل في النتائج المقدمة، كان حاسمًا في تحديد الأطوار البلورية والتغيرات الهيكلية التي تشير إلى تكوين الزيوليت أو تعديله.

ومع ذلك، فإن التطبيق المباشر للمادة المُصنّعة الأكثر واعدة (العينة (ZA كمحفز في عملية تكرير النفط، وتحديداً في عملية التكسير التحفيزي باستخدام اختبار النشاط الدقيق(MAT) ، أسفر عن نتيجة حاسمة . على الرغم من جهودنا لخلق بديل فعال، لم تُظهر العينة المحضرة أي نشاط تكسيري تحفيزي في الظروف المختبرة في مصفاة سابئة .أكد تحليل كروماتوغرافيا الغاز (GC) أن زيت الغاز ظل غير متكسر إلى حد كبير، مما يشير إلى أن المادة المُصنّعة، بشكلها الحالي، لم تكن فعالة في محاكاة أداء محفزات الزيوليت التجارية لهذا التطبيق المحدد.

على الرغم من هذه النتيجة في التكسير التحفيزي، فإن النجاح في تصنيع وتعديل الطين المحلي بشكل كبير، إلى جانب قدرته المثبتة على دمج الأنواع المعدنية المزيلة للملوثات (الزنك والنحاس) ودوره المقصود في إزالة الملوثات العضوية مثل صبغة الميثيل البرتقالي (على الرغم من أن نتائج ذلك لم يتم تفصيلها هنا)، يؤكد الإمكانيات الكبيرة لهذه المواد .يمثل هذا البحث خطوة أولى حيوية نحو تطوير مواد وظيفية متقدمة من الموارد المحلية الوفيرة.

آفاق البحث المستقبلية(Perspectives)

تفتح نتائج هذه الرسالة، وخاصة النتائج المتباينة في النشاط التحفيزي مقابل تعديل المواد، عدة آفاق واعدة للبحث والتطوير المستقبلي:

1. **تحسين النشاط التحفيزي للتكسير:**

- **المزيد من التوصيف :**فهم أعمق لحمضية المادة المُصنّعة وتوزيع حجم المسام (على سبيل المثال، باستخدام تحليل (BET وإمكانية الوصول إلى المواقع النشطة أمر بالغ الأهمية .يشير نقص نشاط التكسير إلى عدم كفاية المواقع الحمضية أو بنية المسام غير المناسبة للمادة الخام المختبرة.
- **طرق تصنيع بديلة :**استكشاف معايير تصنيع مختلفة، مثل تغيير نسب السيليكا إلى الألومينا، أو دمج قوالب أو عوامل توجيه هيكلية مختلفة، أو استخدام تعديلات ما بعد التصنيع (على سبيل المثال، المعالجة بالحمض، المعالجة بالبخار) لتعزيز الحمضية والاستقرار الحراري للتكسير التحفيزي.
- **استراتيجيات التشويب :**دراسة دور تشويب المعادن الانتقالية بخلاف الزنك والنحاس، وكذلك العناصر الأرضية النادرة، والمعروفة بتحسين الأداء التحفيزي للزيوليت في وحدات التكسير التحفيزي السائل.(FCC)
- **خصوصية المادة الخام :**اختبار المواد المُصنّعة بأنواع مختلفة من الهيدروكربونات .قد يكون زيت الغاز الحالي شديد المقاومة لتصميم المحفز الحالي.

2. **تطوير تطبيقات الامتزاز:**

- **فعالية إزالة الملوثات :**تحديد كمية كفاءة الامتزاز للمواد المُصنّعة، وخاصة العينةZA ، لصبغة الميثيل البرتقالي وغيرها من الملوثات العضوية، كما كان متصورًا في البداية .سيكون هذا التحقق المباشر من إمكاناتها في معالجة الملوثات الصناعية.

- **دراسات آلية الامتزاز :**التحقيق في حركية الامتزاز، الأيزوثيرمات، وقدرات التجديد لتطبيقات إزالة الملوثات.
- **معالجة مياه الصرف الصناعي :**استكشاف جدوى استخدام هذه المواد لمعالجة مياه الصرف الصناعي في العالم الحقيقي، ربما كبديل فعال من حيث التكلفة للمواد المازة التجارية.

3. **التوسع والجدوى الاقتصادية:**

- **تحليل التكلفة والفائدة :**إجراء تحليل اقتصادي شامل لمقارنة تكلفة إنتاج البديل المُصنّع مع الزيوليت المستورد، مع الأخذ في الاعتبار توفر المواد الخام وتكاليف المعالجة المحلية.
- **الإنتاج على نطاق تجريبي :**إذا كانت نتائج المختبر الأولية واعدة للامتزاز، فيجب الشروع في تصنيع على نطاق تجريبي لتقييم تحديات الإنتاج وتحسين المعايير لكميات أكبر.

على الرغم من التحديات التي واجهها هذا البحث في التكسير التحفيزي المباشر، فقد وضع أساسًا ناجحًا للاستفادة من موارد الطين المحلية .من خلال التركيز على الجوانب الناجحة لتعديل المواد وتطويرها في مجالات مثل الامتزاز حيث توجد وعود أولية، يحمل هذا العمل إمكانات كبيرة للمساهمة في استقلال الجزائر الاقتصادي والاستدامة البيئية من خلال الابتكار المحلي في المواد المتقدمة.

عنوان المشروع:

تصنيع بديل الزيوليت المستخدم في تصفية البترول

مشروع لنيل شهادة جامعية- مشروعمؤسّسةاقتصادية

(طبقًا لأحكام منشور القرار رقم 008 المعدل و المتمم للقرار 1275 المؤرَّخ في 27 سبتمبر 2022)

صورة العلامة التجارية

الاسم التجاري

ZeOTrust

بطاقة معلومات:

حول فريق الاشراف وفريق العمل

1- فريق الاشراف:

فريق الاشراف	
المشرف الرئيسي:**(01)** زنخري لويزة	التخصص: كيمياء المواد
المشرف المساعد: باسة منال	التخصص: كيمياء المواد

2- فريق العمل:

فريق المشروع	التخصص	الكلية
الطالب: عراب خولة	كيمياء المواد	الرياضيات وعلوم المادة

.1

2. فكرة المشروع (الحل المقترح)

- ✓ يكمن مجال نشاط المشروع ظمن أحد اهم محاور البحث العلمي المسطر من طرف وزارة التعليم العالي وهو الامن الطاقوي لتحيق اهداف في المجال الصناعي تجاري.
- ✓ بدأت فكرة المشروع من خلال فرصة اجراء التربص نهاية الطور المعتاد لنهاية التكوين في اللسانس. اين اكتشفت الاشكال الذي تواجهه شركة مصفاة اسبع ادرار (مجمع تواتي) وتطورت من خلال البرامج الدراسية التي تم تناولها في طور الماستر حيث تعلمنا كيفية تصنيع مركبات كيميائية، توصيفها واستخدامها في مجالات عدة؟
- ✓ في هذا المشروع سوف اقوم بتصنيع مادة تستخدم كمحفز في عملية تكرير البترول بديلة للمادة المستخدمة حاليا والمستورو بالعملة الصعبة. يعني هذه المادة تسهل عملية تسريع تصفية البترول الى مكونات قابلة للتسويق بجزدة عالمية.
- ✓ سيكون ذلك من خلال اجراء تفاعلات كميبائية بين متفاعلات تم التوصل بعد البحث الى تحديد هويتها حيث اهم مكون عبارة عن مادة طبيعية موجودة بكثرة في ةطننا ويمكننا استغلالها بتكلفة اقل من تكلفة استراد هده المادة من الخارج.
- ✓ سأقوم أنا، كطالبة ماستر وصاحبة هذا المشروع، بإنجاز وتطوير هذه الفكرة. ولكن بالنظر الى العمليات و التجهيزات االلازمة لذلك والتي تم معاينتها حين كنت في التربص احتاج في البداية الى مساعدة المشرف ومساعد المشرف.
- ✓ ان انتاج هدا المشروع يحتاج الى دعم والى ورشة عمل

3. القيم المقترحة

يمكن أن تنشأ القيم المقترحة أو المقدمة للزبائن من خلال العناصر التالية:

- الحداثة: تلبي منتوجنا احتياجات جديدة كلياً لم تكن هناك عروض مماثلة لها في السابق لان المادة الموجوة حاليا مستوردة بالعملة الصعبة ونحن سوف نصنع البديل.
- الأداء: يكون أداء المنتج أو مساوي لتوقعات العميلحاليا ونسعى ليكون اعلا مستقبلا..
- التكييف: يمكن في المستقبل بعد تحقيق الهدف الاولي التعديل والتغيير لتكييف المنتج والخدمة تبعا للاحتياجات المحددة للعملاء اخرين.
- إنجاز المهمة: يمكن مساعدة العميل على انجاز مهام محددة.
- التصميم :نعم يمكن جعل التصاميم تتوافق مع رغبات وظروف العميل.
- خفض التكاليف: اكيد يمكن مساعدة العملاء على خفض تكاليفهم وهو الهدف من المشروع.

- الحد من المخاطر: تقليص احتمال تعرض العملاء للمخاطر لدى شرائهم المنتجات أو الخدمات بتقديم ضمانات.
- سهولة الوصول: جعل المنتجات متاحة للعملاء الذين لم يكن بإمكانهم من قبل الوصول إليها عن كطريق الاشهار عنها
- الملاءمة/سهولة الاستخدام: جعل الأشياء سهلة بسيطة الاستخدام.

4. فريق العمل:

- ✓ فريق عملي يتكون من استاذ تعليم عال و دكتورة كلنا من نفس التخصص كيمياء المواد من بين مهاراتهن وأدوارهن في براءة الاختراع هو امتلاكهن المهارة تصنيع المواد الهجينة، والمؤهلات العلمية عبارة تكوين في ميادين مختلفة مثل "الفيزياء، الاعلام الاتي للتسير الاداري ، كيمياء ، بعض برامج التسيير اليومي، بالاظافة الى الدورات التدريبة المتحصل عليها عبر الخط.
- ✓ شركة سوناطراك

5. أهداف المشروع

- انتاج محلي للمواد التحفيزية المستخدمة في المجالات البترولية للحد من التبعية الاقتصادية وباقل تكلفة

6. عرض القطاع السوقي :

- ☐ السوق المحتمل: السوق المحتمل هو مجموعة من المؤسسات الوطنية الاقتصادية البترولية، التي تطلب أو منتجاتنا لإشباع حاجا تهم ورغباته ويتوجدون ظمن خمس وحدات موزعة عبر الوطن.
- ☐ السوق المستهدف (الشريحة): هي المؤسسة البترولية الطاقوية مصفاة سبع ادرار
- ☐ اخترنا هذ السوق بسبب الاحتياج الدائم و المستمر لمتجنا فهي تعتبر المستهلك الاول للمنتج .
- ☐ تحديد إمكانية ابرام عقود شراء مع بعض الزبائن المهمين.

7. قياس شدة المنافسة :

- ☐ المنافسوك المباشرين هم موسسات دولية خارجية
- ☐ والغير مباشرين لا يوجد

- نقاط قوتهم تكمن في احتكار السوق العالمية

8. التكاليف والأعباء :

- تكلفة المادة الاولية
- تكلفة المواد الكيميائية التجارية
- تكلفة سعر الطاقة المستخدمة للاجهزة

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الملحق رقم 04: نموذج

العمل التجاري

✓ شرائح العملاء **-مخابر بحث علمي** **الأرضية التقنية للتحاليل الفزيوكيميائية** **الCRAPC** موسسة بترولية سونطراك	✓ **الميزة غير العادلة** • **تقديم المنتج بطريقة** مختلفة وخاصة بالمنتج الجديد وتقديم منتوج مزدوج العمل	**القيمة المقترحة** **توفير منتج غير موجود وطنيا ونادر عالميا** **تقديم منتج صنع وطني بتكاليف اقل وبكفاءة عالية**	**العلاقة معالعملاء** تواصل رقمي دائم(بريد، منصة، تطبيق) - ندوات وورشات تعريفية وتدريبية .	**الشرائح المستهدفة الشركات البتروكيميائية** سونطراك مصفاة سبع ادرار

	قنوات التوصيل شاحنات كبيرة لح		**الموارد الأساسية** **-مادة ذات مصدر طبيعي** **مواد كيميائية تجارية** **مذيب قطبي ومعادن** **هيدروكسيد الصوديوم**	

✓ **قنوات الربح** ✓ **إيرادات بيع المنتج. ملايير الدولارات**	✓ **هيكلية التكاليف** • **تكاليف تأسيسية: الآلة المختصة ، المعدات المتعلقة بتجهيز المكان والبدء بالعملية ال إنتاجية100000 دولار** • **تكاليف تشغيلية: المواد الخام، مصاريف اخرى 20000 دولار**

الملخص:

تهدف هذه الرسالة إلى تطوير بديل محلي لزيواليت عالي الكفاءة من الطين الطبيعي لتقليل الاعتماد على المواد الكيميائية المستوردة. تم اعتماد خمس مراحل تصنيعية تشمل الكلسنة والترسيب القاعدي باستخدام أملاح مختلفة مثل ZnO و $CuSO_4$و $FeSO_4$. أظهرت التحاليل الفيزيائية والكيميائية (SEM)، EDS، (XRDتغيرات هيكلية وتكوينية تدل على تكون زيواليت. ومع اختبار النشاط التحفيزي(MAT) ، لم تُظهر العينة فعالية في التكسير التحفيزي، مما يدل على أن المادة المصنعة غير مناسبة لتطبيقات زيواليت التكرير حالياً.

الكلمات المفتاحية: الزيوليت، الطين، البترول، المعالجة الحرارية.

ABSTRACT

This thesis aims to develop a locally produced, highly efficient zeolytic alternative from natural clay to reduce reliance on imported chemicals. Five manufacturing stages were adopted, including calcination and basic precipitation, using various salts such as ZnO, $CuSO_4$, and $FeSO_4$. Physical and chemical analyses (SEM, EDS, XRD) revealed structural and compositional changes indicative of zeolytic formation. Catalytic activity testing (MAT) revealed that the sample did not demonstrate catalytic cracking efficiency, indicating that the manufactured material is not suitable for current refining zeolytic applications.

Key Words: zeolite-clay-petroleum-heat treatement.